THE ACTION OF CARBON MONOXIDE AND DICOBALT OCTACARBONYL

ON SOME AROMATIC OXIMES

by

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Abstract

When syn-benzaldoxime was reacted with carbon monoxide containing about 0.04 volume percent of hydrogen and dicobalt octacarbonyl in benzene solution at elevated temperatures and pressures the following compounds were produced; sym-dibenzylurea (35%), mono-benzylurea (10%) and benzaldehyde (10%). Also isolated were 15% yields of two unidentified components referred to as compounds A and B.

When benzophenone oxime was subjected to the same reaction conditions the major product was 3-phenylphthalimidine (75%). Also isolated was a 5% yield of an unidentified component called compound B. It was demonstrated that under the reaction conditions used considerable amounts of dicobalt octacarbonyl are needed for successful reaction. When the octacarbonyl was present in only catalytic amounts the course of the observed reaction was greatly affected and the major isolated product was benzophenone (70%). Small amounts of 3-phenylphthalimidine and of the original oxime were also isolated.

When the O-methyl ether of benzophenone oxime was reacted the only product isolated was 3-phenylphthalimidine in 75% yield.

Reaction pressures corrected to constant temperature are plotted against reaction time for each substrate and the results discussed.

A new method of synthesizing the O-methyl ether of benzo-phenone oxime (using O-methyl hydroxylamine), and a dichromate-acetic acid oxidation of sym-dibenzylurea giving a high yield of dibenzoylurea are described. A platinum oxide in acetic acid reduction of 3-phenylphthalimidine which reduced both benzene rings but left the lactam group intact is also described.

Infrared spectra are included for all compounds obtained.

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HISTORICAL INTRODUCTION

A. Reactions of Oximes.

The Beckmann rearrangement has been investigated by many workers. Its generality and mechanism are now well established (23), (47). Catalysts for this reaction include concentrated sulphuric acid, phosphorous pentachloride, polyphosphoric acid (35), (27), hydrogen chloride, boron trifluoride and benzenesulphonyl chloride.

Hydrolysis of an oxime will regenerate the parent carbonyl compound. Oximes are generally amphoteric and form well characterised salts of both types. They are reduced by many agents to amines. Aldoximes may be dehydrated to produce nitriles; oximes will form esters with common esterifying agents. This is believed to be the necessary first step in the Beckmann rearrangement (47).

B. Isomerism of Oximes

Three distinct types of isomerism are possible for oximes. First is the geometrical syn and anti type where the hydroxyl can be cis or trans to an identifiable radical attached to carbon. These isomers have been isolated in the aromatic series but similar isolation of pure compounds has not yet been achieved with aliphatic analogs (26). Second is the oxime-nitroso tautomeric equilibrium. Till recently it

has been believed that this equilibrium was almost 100% in favor of the oxime form, for primary and secondary oximes (56). However recent work has shown that large scale preparation of many primary and secondary nitroso compounds is possible (12), (7). The opinion has been expressed (16) that hydroxylic solvents and low concentrations favor formation of the oxime.

Third is the oxime-nitrone equilibrium. Recent information (9) indicates that oximes may normally exist in equilibrium with a small percentage of the nitrone form. Semper and Lichenstadt (45) isolated four different methyl ethers when they treated benzaldoxime with methyl sulphate. O- and N- ethers were formed in approximately equal amounts.

C. Reactions of Carbon Monoxide

The reactions of carbon monoxide have been reviewed recently by Orchin and Wender (33). These authors show carbon monoxide can react as a Lewis base, a Lewis acid, or as a free radical.

As a base it can react with carbonium ions according to the following scheme

$$RCH_2^+ \ + \ \overset{-}{:}C::O^+ \ \longrightarrow \ RCH_2C::O:^+$$

$$\Updownarrow$$

$$RCH_2:C::O:^+$$
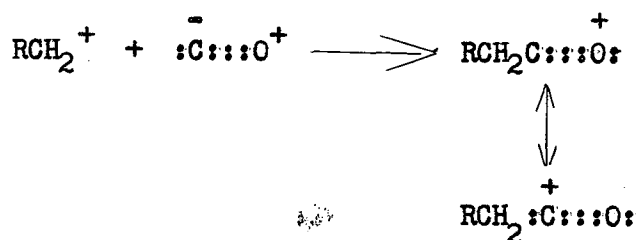
This carbonium ion can now react with nucleophilic reagents present in the system to form esters, acids or anhydrides. Anhydride formation is shown here

$$RCH_2\overset{+}{C}O \quad + \quad R'COOH \quad \longrightarrow \quad \left[R\text{-}CH_2\text{-}\overset{\overset{O}{\|}}{C}:O\text{-}\overset{\overset{H}{|}}{C}\text{-}R' \right]^{+} \quad \longrightarrow$$

$$RCH_2\overset{\overset{O}{\|}}{C}\text{-}O\text{-}\overset{\overset{O}{\|}}{C}\text{-}R' \quad + \quad H^{+}$$
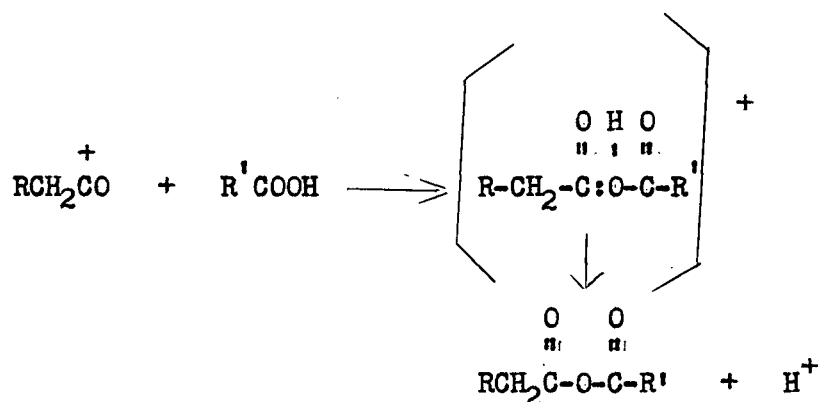
These reactions allow the formation of esters, acids, or anhydrides from olefins, alcohols, ethers and to a limited extent from ketones or aldehydes provided the conditions for formation of the appropriate carbonium ion are present in the system.

Carbon monoxide also acts as an electron acceptor though examples of this are less extensive. The synthesis of sodium formate is an established example

$$C::O: \quad + \quad OH^{-} \quad \longrightarrow \quad \left[HO:C:O: \right]^{-}$$
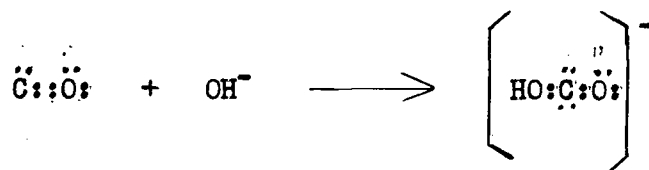
Acid formation from alcohols is known in the presence of alkoxide ion

$$C_2H_5OH \quad + \quad CO \quad \longrightarrow \quad HCOOC_2H_5$$
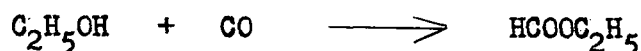
Carbon monoxide reacts with Grignard reagents; for example the reaction with tert-butyl magnesium chloride is shown

$$2(CH_3)_3\text{-}C\text{-}MgCl \;+\; 2CO \;\longrightarrow\; (CH_3)_2\overset{\overset{\text{O}}{\parallel}}{C}\text{-}CHOH\text{-}C(CH_3)_3$$
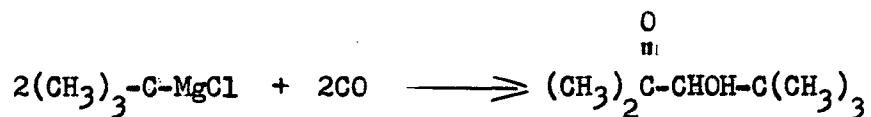
There are isolated examples in which carbon monoxide reacts by a radical mechanism especially when photosensitized. Its reaction with ammonia to produce formamide is believed to proceed by such a mechanism.

$$NH_3 \;+\; CO \;\xrightarrow{h\nu}\; HCONH_2$$
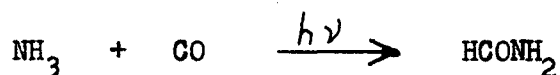
However radicals with a carbonyl group more commonly decompose according to the following scheme

$$RCH_2\dot{C}O \;\longrightarrow\; R\dot{C}H_2 \;+\; CO$$

A radical initiated copolymerization of carbon monoxide and ethylene has recently been reported. Foster et al (14) report formation of such a polymer including such chain transfer agents as ethyl mercaptan, carbon tetrachloride, and alcohols.

An unusual reaction discovered by Buckley and Ray (6) illustrates the reducing action of carbon monoxide. When aniline containing a small amount of aniline hydrochloride reacted at 250° C under 3000

atmospheres pressure carbon dioxide and a brown amorphous solid were obtained. This was shown to be a cross linked polymer of I.

H_2N ⬡ CH_2 ⬡ NH_2
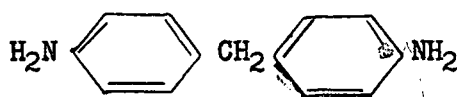
I

It was believed this intermediate was obtained by reduction of II

H_2N ⬡ CH ⬡ NH_2
         OH
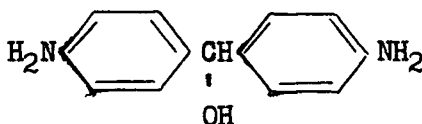
II

which in turn had been formed by condensation and rearrangement of two moles of formanilide. The same authors found many organic compounds were reduced by carbon monoxide at high temperatures and pressures with the formation of carbon dioxide. Without catalyst nitro, nitroso and azoxybenzenes were reduced to azobenzene and phenylhydroxeylamine was reduced to aniline. In the presence of Raney cobalt benzyl alcohol, phenylmethylcarbinol and benzhydrol were reduced to the corresponding hydrocarbons.

Buckley and Ray also discovered a remarkable stepwise reduction to produce III

$$\begin{array}{ccc} N & - & N \\ \| & & \|| \\ HC & & CH \\ \diagdown & N & \diagup \\ & \| & \\ & NH_2 & \end{array}$$
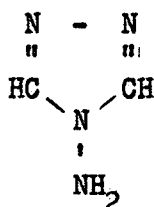
III

from carbon monoxide and hydrazine under extreme conditions.

D. Dicobalt octacarbonyl and related compounds.

I. Formation and properties (ref 53, pp 89 to 106)

The formation of dicobalt octacarbonyl from a cobalt salt may be written in the following manner

$$H_2 \longrightarrow 2H^+ + 2e$$

$$2H^+ + 2e + Co(OAc)_2 \longrightarrow Co + 2HOAc$$

$$2Co + 8CO \longrightarrow Co_2(CO)_8$$
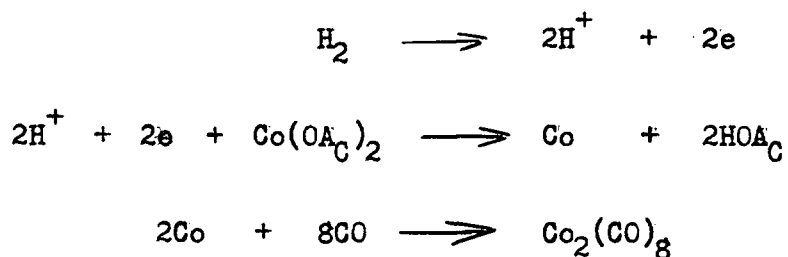
This reaction is carried out at 160° C using a slurry of a cobalt salt with benzene under 3200 p.s.i. of a 1:1 mixture of carbon monoxide and hydrogen. This reaction actually forms cobalt hydrocarbonyl ($H Co(CO)_4$) as has been proven by cooling the reaction vessel to -51° C before releasing the gas pressure. Dicobalt octacarbonyl is formed only on

releasing the pressure at room temperatures.

Under a slight pressure of carbon monoxide the octacarbonyl is stable indefinitely at room temperatures. In the absence of carbon monoxide decomposition takes place according to the following equation

$$2 \ Co_2(CO)_8 \longrightarrow Co_4(CO)_{12} + 4CO$$

The octacarbonyl is readily soluble in hydrocarbon solvents but reacts more or less readily with polar solvents such as alcohols, ketones, amides and amines.

The tetramer, ($Co_4(CO)_{12}$), is pyrophoric but indefinitely stable in an inert solvent.

Cobalt hydrocarbonyl ($HCo(CO)_4$), forms pale yellow crystals stable below their melting point (-26° C). Above this temperature it decomposes rapidly.

$$2 \ HCo(CO)_4 \longrightarrow H_2 + Co_2(CO)_8$$

It is a stable strong acid in oxygen free aqueous solution at 25° C and may be titrated using phenolphthalein as an indicator. The accepted electronic structures for these compounds are shown below: (III, IV)
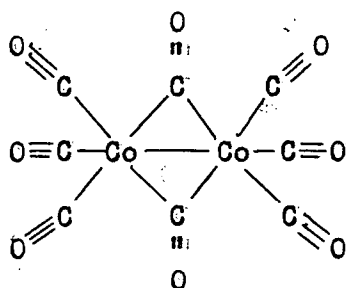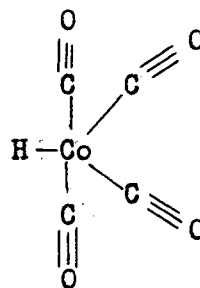
III   IV

II. Reactions

The reactions of dicobalt octacarbonyl may be classified as follows

(a) Homomolecular disproportionation

$$3Co_2(CO)_8 \ + \ xB \longrightarrow 2\left[CoBx\right]^{+} \ \left[Co(CO)_4\right]^{-} \ + \ 8CO$$
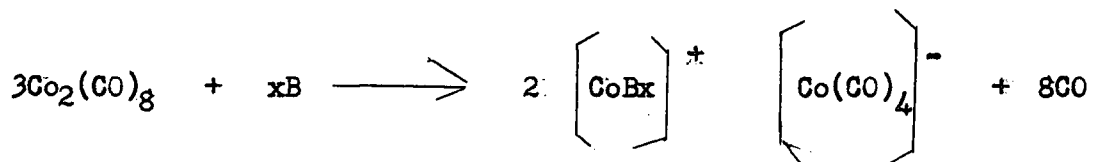
B may be ammonia, water, methanol, ethanol, piperidine or formamide. The group B must be a Lewis base and fulfill geometric requirements. Where B is a primary or secondary aliphatic amine salt formation may take place according to the following equation

$$B \ + \ Co_2(CO)_8 \longrightarrow \left[BCo(CO)_4\right]^{+} \ \left[Co(CO)_4\right]^{-}$$
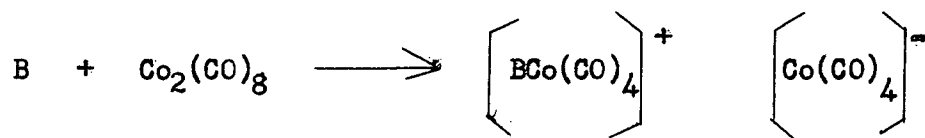
Hieber and Wiesboeck (21) examined the products when many nitrogen bases reacted with dicobalt octacarbonyl. They used picoline, quinoline, pyridine, aniline and others, and arrived at this general equation where B represents a monofunctional nitrogen base.

$$3 \left(Co(CO)_4 \right)_2 \ + \ 12B \ \longrightarrow \ 2 \left[CoB_6 \right]^{+} \left[Co(CO)_4 \right]^{-} \ + \ 8CO$$
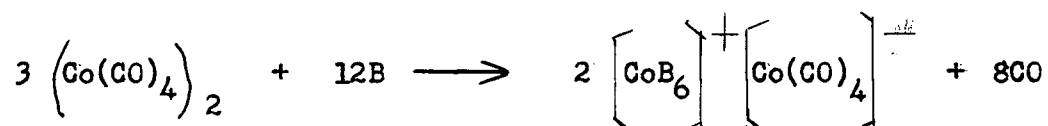
Formamide also formed a compound of analogous composition.

Oxygen bases formed compounds of different composition. Acetophenone for example reacted as follows

$$3 \left(Co(CO)_4 \right)_2 \ + \ ph\text{-}\overset{O}{\overset{\|}{C}}\text{-}CH_3 \ \longrightarrow \ 2 \left[Co(ph\text{-}\overset{O}{\overset{\|}{C}}\text{-}CH_3)_{\frac{1}{2}} \right]^{+}$$

$$\left[Co(CO)_4 \right]^{-} \ + \ 8CO$$
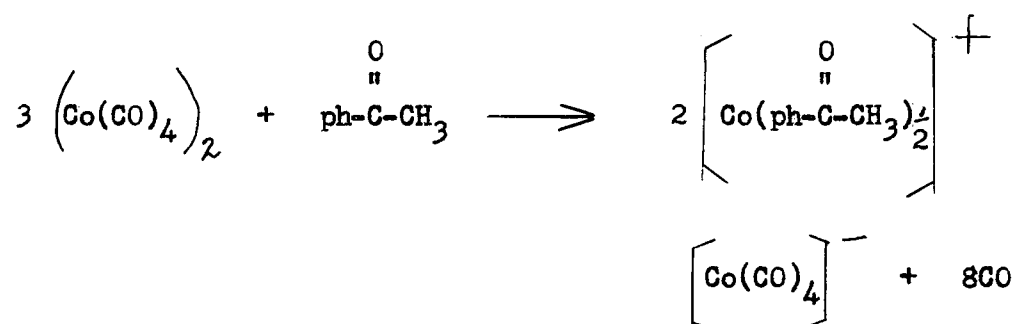
These compounds were generally formed near 5° C and some could be destroyed by refluxing slightly above room temperature in light petroleum ether.

(b) External electron transfer

Dicobalt octacarbonyl will react with metallic sodium or hydroxyl ion according to the following equations.

$$2 \text{ Na} + Co_2(CO)_8 \longrightarrow 2 \text{ NaCo(CO)}_4$$

$$2 \text{ Co(CO)}_8 + 4OH^- \longrightarrow 4 \text{ Co(CO)}_4^- + 2H_2O + O_2$$
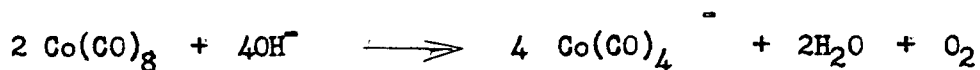
(c) Replacement of the carbonyl group

Isonitriles, the RS group of mercaptans, and acetylene have been shown to replace one or more carbonyl groups. Acetylene for example replaces the two bridge carbonyl groups according to

$$Co_2(CO)_8 + HC \equiv CH \longrightarrow Co_2(CO)_6C_2H_2 + 2CO$$
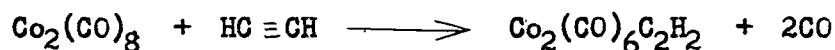
Sly (46) reports a detailed X-ray crystallographic study of diphenyl acetylene dicobalt hexacarbonyl and reports its structure as shown.
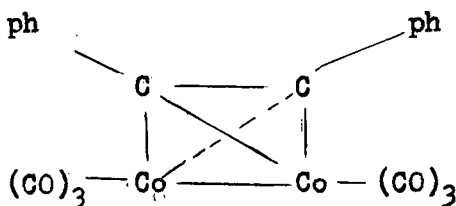
He found that each carbon was bonded to each cobalt and that the plane of the carbon-carbon bond was roughly at 90° to the plane of the

Cobalt-cobalt bond. Sly stated that this structure represents one of the first molecules to be studied which exhibits a multipoint attachment of a single organic molecule to more than one metal atom. He feels this is possibly analogous to the postulated attachment of an organic substrate to a metal surface during heterogeneous catalytic reactions.

E. Hydroformylation - The Oxo Reaction

I. Nature and scope of the reaction

The literature concerning this reaction has been extensively reviewed by Wender et al (53). The overall reaction is most easily visualized as involving the addition of a hydrogen atom and a formyl group across the double bond of an olefin. Conditions for the reaction are approximately 75 to 200° C under 100 to 300 atmospheres of a mixture of carbon monoxide and hydrogen in the presence of a cobalt catalyst. It appears that at least three carbonyls of cobalt are involved in the addition of carbon monoxide and hydrogen to an olefin. These are dicobalt octacarbonyl, cobalt hydrocarbonyl, and the cobalt tricarbonyl tetramer. It is of interest to note that the hydroformylation of an olefin occurs practically to the complete exclusion of its hydrogenation even though the free energy change for the hydrogenation is much greater than that for the hydroformylation reaction. Hydrogenation becomes a competitive reaction when the olefinic linkage is conjugated. Every simple olefin submitted to hydroformylation conditions has been shown to undergo this reaction.

Double bond isomerization occurs readily under hydroformylation conditions. For example the products obtained when 1-pentene and 2-pentene are submitted to the reaction are the same. This is found in spite of the observed fact that isomerization is a slow process compared to hydroformylation (55). The amount of hydrogen present has no particular effect on the rate of isomerization. Isomerization occurs in the absence of hydrogen and is not fast even when large amounts of hydrogen are added (10, 11). These facts lead to the assumption that the structure of the olefin carbonyl complex is the same for both 1 and 2-pentene. Some mechanism must exist for the facile movement of hydrogen in these complexes. In general the straight chain aldehyde is the favoured product.

II. Mechanism

Wender and Sternberg (55) point out that the Fischer-Tropsch synthesis is probably a heterogeneously catalyzed reaction since it takes place at comparatively low pressures below the point where the tendency toward formation of metal carbonyls becomes large. The formation of metal complexes destroy the surface intermediate. In contrast hydroformylation is homogeneously catalyzed. Homogeneous reactions catalyzed by the carbonyls involve formation of soluble metal complexes. They also observe that it is likely that all three reactants, that is, olefin, carbon monoxide and hydrogen are united in one complex at some stage of the reaction. The following mechanism is presented in the

light of this idea and appears to agree with all available data.
Cyclohexene is used in this example.

$$C_6H_{10} \quad + \quad Co_2(CO)_8 \quad \longrightarrow \quad Co_2(CO)_7C_6H_{10} \quad + \quad CO$$
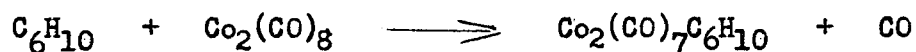
V

V may have the structure shown, by analogy with the proven structure
of acetylene complexes (46).

$$\begin{array}{c}
O \\
\parallel \\
C \\
\diagup \quad \diagdown \\
(CO)_3 \text{—— Co ——— Co —— } (CO)_3 \\
\mid \qquad\qquad \mid \\
R \text{—— C ——————— C —— } R \\
\qquad H \qquad\qquad H \\
\end{array}$$
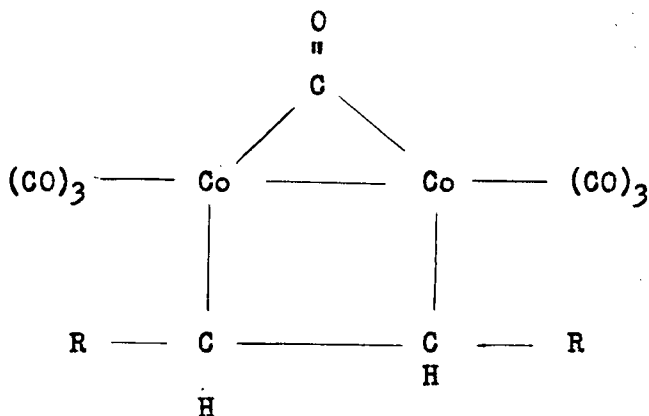
The ease of formation of V is strongly influenced by the steric
requirements of the olefin (ref 53, p. 79).

$$Co_2(CO)_7C_6H_{10} \quad + \quad H_2 \quad \longrightarrow \quad Co_2(CO)_6 \quad + \quad C_6H_{11}CHO$$
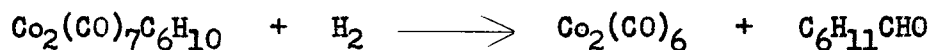
V

This equation is most probably realized in two steps. The complex V
probably splits a hydrogen molecule, as shown, to obtain the complex VI.

```
                    O
                    ‖
                    C
                  /   \
(CO)3    Co — H   H —Co      (CO)3
         |              |
         C ——————————— C
       / |            / \
      R  |           R   H
         H
```
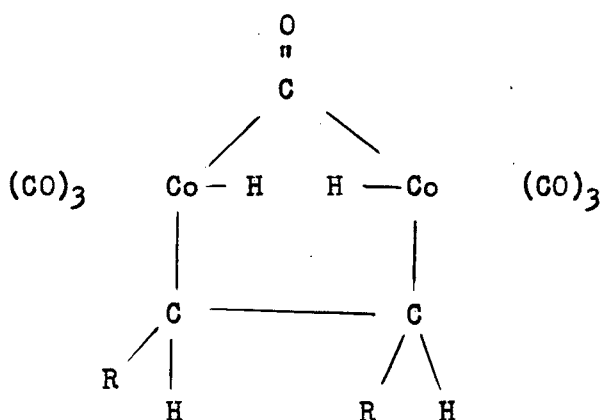
VI

In the next step VI splits to form dicobalt hexacarbonyl and the product aldehyde. Then dicobalt hexacarbonyl reacts with carbon monoxide to reform dicobalt octacarbonyl.

In contrast with the above mechanism Aldridge et al (1) suggest that the hydroformylation reaction may be heterogeneously catalyzed. They report data from which it can be deduced that the rate of hydroformylation of an olefin is not directly dependent upon the amounts of soluble cobalt present under reaction conditions. The insoluble cobalt may provide a fresh highly active metal surface which is constantly being consumed and deposited by carbonyl formation and breakdown. These authors conclude that it appears likely that any direct role in hydroformylation catalysis that cobalt carbonyls or cobalt hydrocarbonyls may play must be carried out in conjunction with a solid cobalt surface.

F. Carbonylation

Relatively little appears in the literature about a system which contains no hydrogen, consisting of the substrate, carbon monoxide

and the metal carbonyl catalyst. A reaction mechanism has been proposed by Tirpak et al (50) for the system where a disubstituted acetylene is allowed to react with carbon monoxide and dicobalt octacarbonyl in the absence of hydrogen. Disubstituted acetylenes form stable compounds by replacing the bridge carbonyls of dicobalt octacarbonyl (see page 10, ref. 46). These have the composition $RC_2R'Co_2(CO)_6$.

Tripak quotes Sternberg et al (48) who have established that a dicobalt nonacarbonyl can be produced under certain conditions. This involves the homolytic fission of the cobalt-cobalt bond to add a third bridge carbonyl to produce the structure VII.
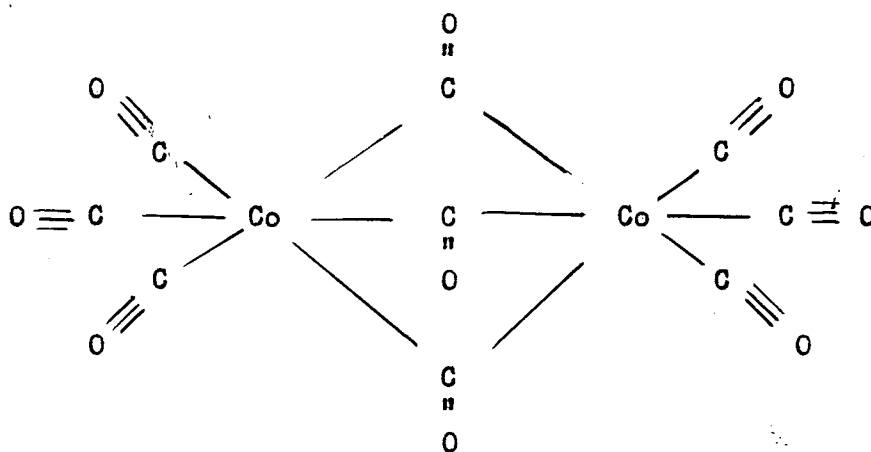
VII

By analogy with this compound he suggests the presence of VIII in the acetylenic reaction.

$$
\begin{array}{c}
O \\
\parallel \\
C \\
\diagup \quad \diagdown \\
(CO)_3 - Co - C - Co - (CO)_3 \\
\diagdown \quad \parallel \quad \diagup \\
\quad O \\
C = C \\
\diagup \quad \diagdown \\
R \quad\quad R
\end{array}
\qquad \text{VIII}
$$
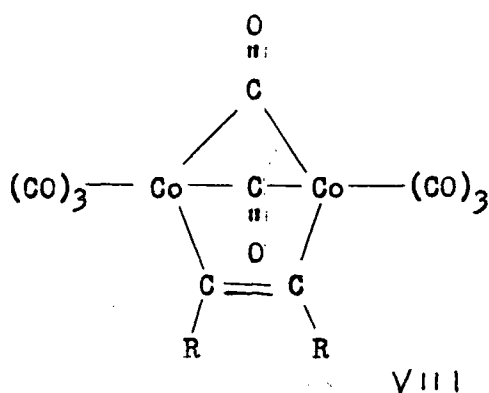
This would be formed in the first step of the reaction followed by decomposition to obtain the more stable structure analogous to that of Sly (46).

G. Reactions Related to Hydroformylation

Lonsbury and Meschke (25) reacted cyclohexene at 800 atm and 300° C with carbon monoxide and hydrogen. They obtained besides the expected hydroformylation products a perhydrofluorenone
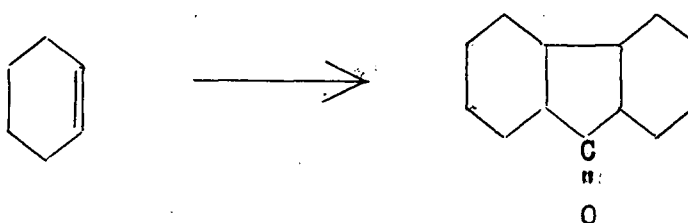
They showed this compound could be produced in the absence of hydrogen or any catalyst. An analogous product could be obtained from cyclopentene but no reaction occurred with a variety of aliphatic olefins. The authors offer no suggestions of a possible mechanism for the reaction.

A 91% conversion of olefins to aldehydes has been reported
(43) using a cobalt, thoria, magnesia, catalyst under hydroformylation
conditions. The product appeared in a greenish black solution con-
taining cobalt carbonyls.

Nakamura (31) reports reduction of Schiff bases under hydro-
formylation conditions. Reaction of benzalcyclohexylimine for 4 hours
at 135° C produced 79% of benzylcyclohexylamine. The authors noted
those Schiff bases which are most conjugated are most easily reduced
and form the lowest amounts of resinous byproducts. They also noted
amines, especially aliphatics, lower the yield considerably. This is
possibly connected with the type of reaction mentioned by Hieber (page
9, ref. 21). Kirch and Orchin (24) showed that complex formation does
take place in a toluene solution of cobalt hydrocarbonyl and 1-hexene.
At 0° C the solution absorbed 2 moles of carbon monoxide. At 25° C
the complex decomposed to form aldehydes. The authors state the complex
has the composition $2HCo(CO)_4RCO$ where R represents olefin.

Rosenthal and Read (41) reported that when 3, 46, tri
O-acetyl-D-galactal was allowed to react under hydroformylation con-
ditions a hydroxymethyl group was added across the double bond. Nuss-
baum et al (32) recently reported a similar addition of a hydroxy
methyl group to a double bond of a steroid nucleus.

H. Reactions of carbon monoxide involving nitrogen compounds.

The work of Buckley and Ray (6) and that of Hieber and Wies-

boeck (21) has already been referred to. Hallwell (19) reported the
formation of dimethylglycine from formaldehyde and dimethyl amine
according to the equation

$$HCHO \quad + \quad (CH_3)_2NH \quad \xrightarrow[CO]{HCl} \quad (CH_3)_2NCH_2COOH$$
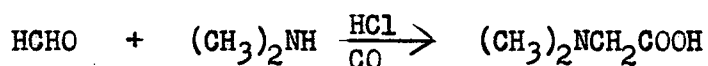
Tyson and Shaw (51) produced the 3 carboxaldehyde derivative
from potassium indole using a dicobalt octacarbonyl catalyst. When
indoline was reacted under similar conditions the N-formyl compound
was isolated. The authors concluded that N-formyl indole isomerized
readily to the 3 derivative under reaction conditions. These authors
obtained no conclusive results when 2 or 3 substituted indoles were
used (52). Steric effects were believed responsible for the failure
of the reaction. Winteler et al (57) reacted primary and secondary
amines with carbon monoxide at 150 atm in the presence of sodium alco-
holate. The overall reaction was

$$R'R''NH \quad \xrightarrow{\hspace{3cm}} \quad R'R''N-\overset{\overset{\displaystyle O}{\overset{\|}{}}}{C}H$$

They noted the rate of reaction increased rapidly with temperature.
They postulated that the first step in the reaction was the addition of
carbon monoxide to the alcoholate

$$RO^- \quad + \quad CO \quad \longrightarrow \quad R-\overset{\overset{\displaystyle O^-}{\diagup}}{C}=O \quad \longrightarrow \quad R-\overset{\overset{\displaystyle O}{\|}}{\underset{\diagdown}{C}}_{OH}$$
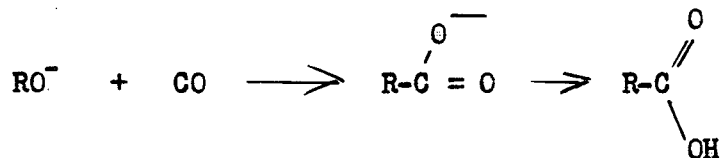
This then reacted with the amine

$$R\text{-}COOH \quad + \quad R_2NH \quad \longrightarrow \quad R_2NCH \quad + \quad ROH$$
$$\overset{\|}{O}$$
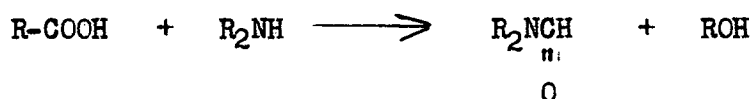
Teter and Olson (49) produced nitriles from olefins and ammonia using a mixture of $CoSO_4$ and $NiSO_4$ as catalyst at $340°$ C and 100 atmospheres; the overall reaction was

$$CH_3\text{-}CH = CH_2 \quad + \quad NH_3 \quad \longrightarrow \quad CH_3\text{-}CH_2\text{-}C\equiv N$$
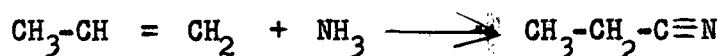
Using extreme conditions Bengelsdorf (3) produced IX from aromatic nitriles

$$3 \ Ar\text{-}C\equiv N \quad \Longrightarrow$$
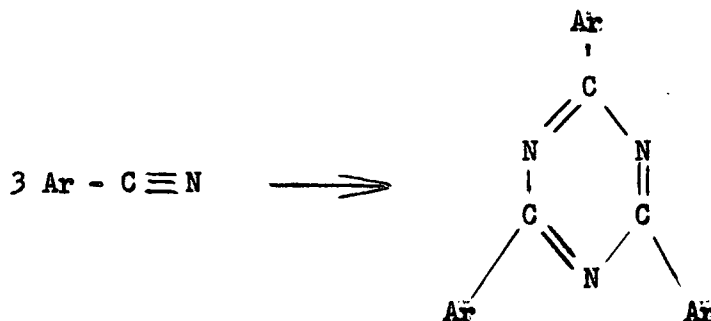
IX

This s-triazine trimer was formed at 50,000 atm and $500°$ C.

Benzamide under these conditions was dehydrated in situ and produced an analogous product. Syn-benzaldoxime, a structural isomer of benzamide, when subjected to these conditions decomposed explosively to produce ammonia and a carbonaceous material resembling amorphous carbon.

When O-tolunitrile was subjected to reaction conditions the analogous product was obtained in poor yield showing steric hindrance is not overcome even at these extreme pressures. Phosphoric acid (85%) however allowed a quantitative yield from O-tolunitrile. Phthalonitrile yielded phthalocyanine.

Sauer et al (44) reacted 3, diethylamino-propyne-1 at 125° C and 500 atmospheres of carbon monoxide to produce 2, 3 dihydro, 3 (NN diethyl formamido), 5 diethyl amino furan, in 44% yield. They reported
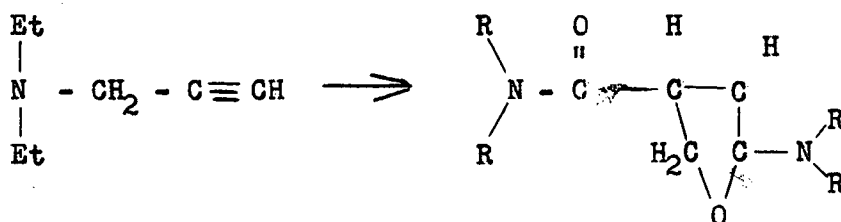
that catalytic amounts of dicobalt octacarbonyl were required for this reaction.

I. Reactions of Carbon Monoxide Involving Ring Formation.

Pritchard (36) cyclized the aromatic amide N,N-dibenzoyl-aniline with carbon monoxide at 325° C using a nickel carbonyl catalyst.
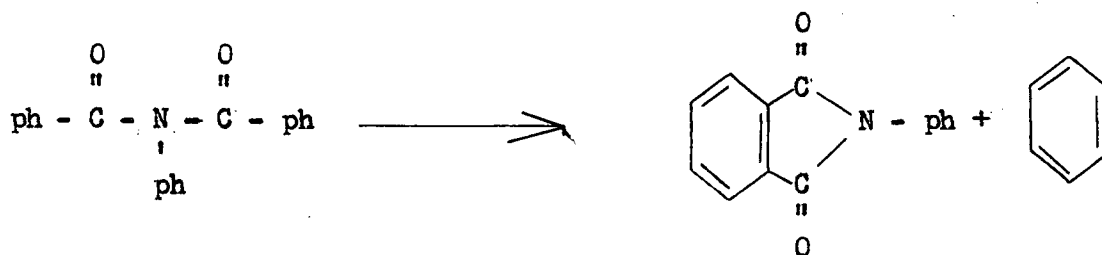
The products were N-phenylphthalimide and benzene. Benzoic anhydride
reacted similarly to produce phthalic anhydride and benzene. Benzonitrile
and benzoic acid apparently reacted above 250° C to give dibenzamide,
which subsequently cyclized to give phthalimide. It is noted here that
no carbon monoxide is used. Its function is not known although the
reactions fail without it.

Pritchard (37) subsequently prepared N-substituted phthali-
midines from N-substituted imines as shown.
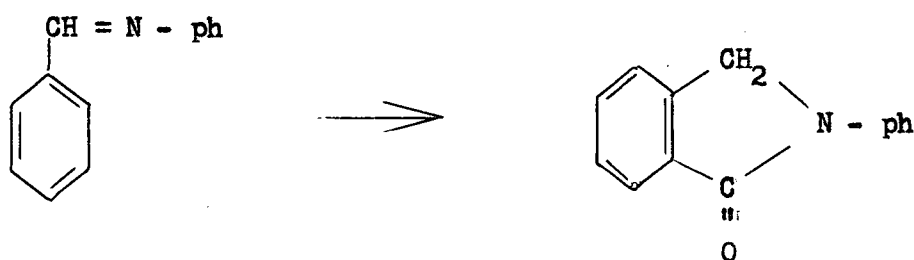
He carried out the reaction with different substituents both
at the 3 position and on the ring on which the ring closure occurred.

Pritchard also submitted phenyl bromide to the reaction
conditions adding alkali carbonates. The products were phthalic an-
hydride and benzene which apparently were obtained through preliminary
formation of benzoic anhydride.

Pritchard (38) further reacted azobenzene with catalytic
amounts of nickel corbonyl at 250° C. The reaction absorbed at least
two moles of carbon monoxide. They isolated 2 phenyl indazolone (X)
from the mixture.
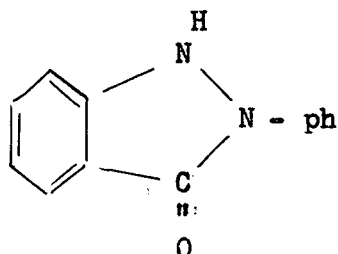
X

Murahashi and Horiie (30) also reported on azobenzene. They showed that at 190° C the chief product was the indazolone X but they reported that at 230° C a second mole of carbon monoxide was absorbed to produce XI
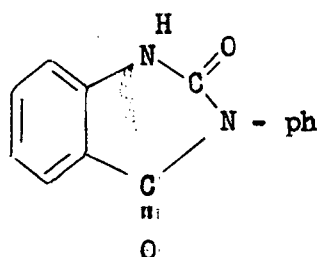
XI

Substituents in the 4 position (chloro or dimethylamino) did not affect the reaction except that ring closure occurred on the ring carrying the substituent. Diphenylurea was obtained in small amounts as a byproduct.

Murahashi (29) reported that the reaction with benzaldehyde anil failed with nickel catalysts but ring closure occurred in 80% yield with dicobalt octacarbonyl present.
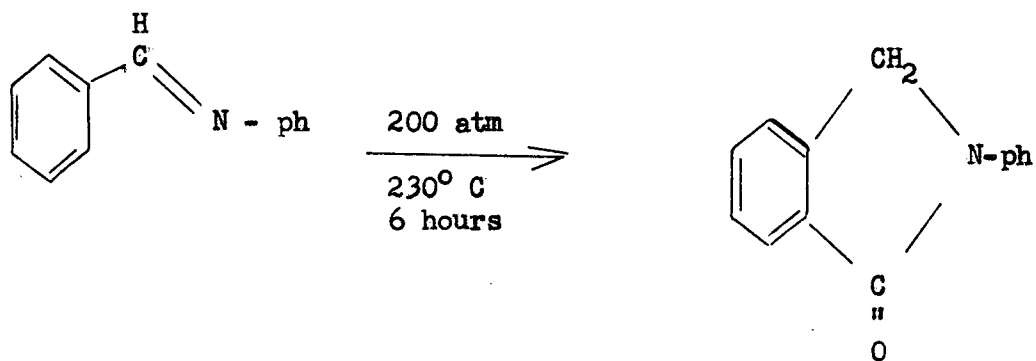
1-Naphaldehyde anil produced an analogous compound. It is worthy of note that ring closure occurred to produce the linear isomer, whereas 2 substituted napthalenes usually substitute further in the 1 position. Rosenthal et al (40) have reported examples of ring closure using aromatic oximes to produce substituted phthalimidines. This reaction has been successful for benzophenone oxime and acetophenone oxime. Benzyl phenyl ketoxime gave both possible products. Cyclization took place to each available ring to produce 3 benzylphthalimidine and 3-phenyl, 3-4-dihydroisocarbostyril.
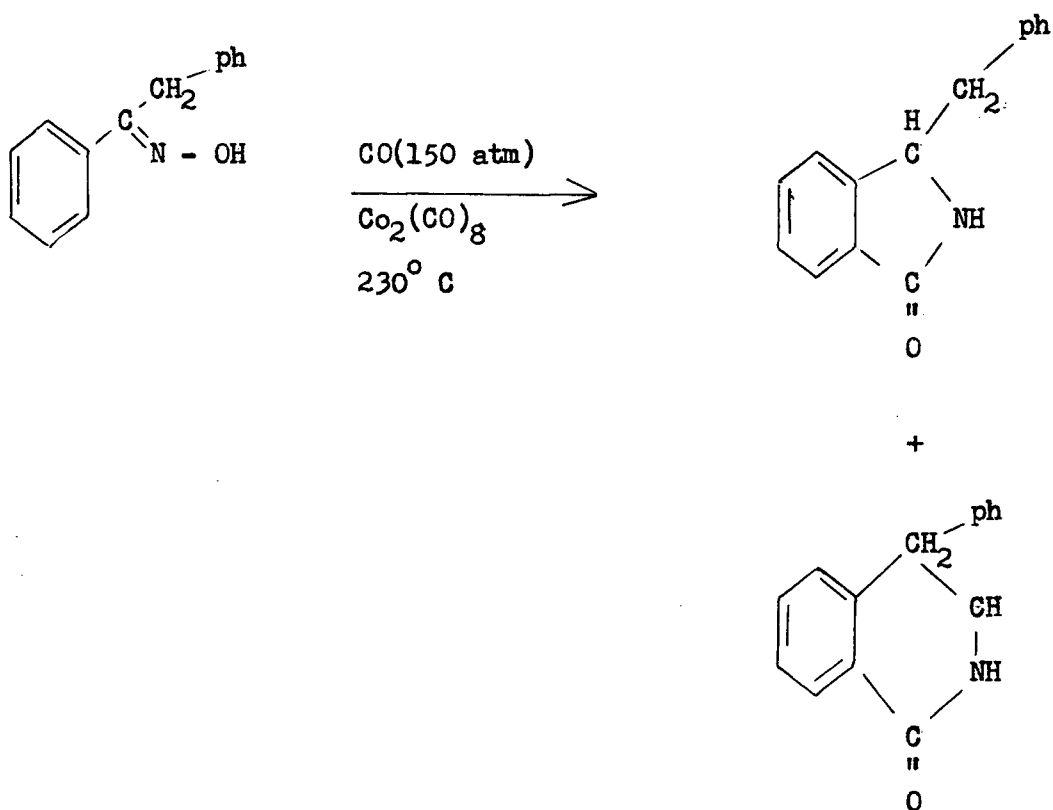
It is notable that the expected product would be the N-hydroxy compound. Apparently the known reducing action of carbon monoxide converts this to the NH compound either before or after cyclization takes place.

DISCUSSION

A. Syn-benzaldoxime

The principal effort of the present work was directed towards establishing the further generality of the reaction reported by Rosenthal et al (40). These authors showed that certain aromatic oximes reacted in the presence of dicobalt octacarbonyl and carbon monoxide at about 4100 p.s.i. and at 200 - 250° C to yield lactams as shown in equation I.
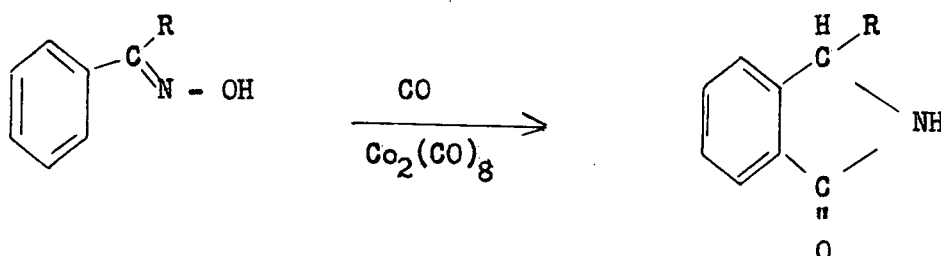
I

This reaction was successful where R was phenyl, methyl or benzyl (See introduction page 23).

In the present work syn-benzaldoxime, benzophenone oxime and the O-methyl ether of benzophenone oxime were allowed to react under the following conditions. The temperature range was 170° to 230° C

and initial pressures were near 2200 p.s.i. Maximum pressure reached under reaction conditions was near 4500 p.s.i. The reactions were carried out in purified benzene solutions in the presence of preformed dicobalt octacarbonyl.

In the case of syn-benzaldoxime the following products were isolated from the reaction mixture; sym-dibenzylurea (35%), mono-benzylurea (10%), benzaldehyde (10%), compound A (15%), compound B (15%).

By analogy with the above described established reaction (40) phthalimidine could be expected as a product of this reaction. It was not found possible to isolate any of this compound.

Total recovery shown above is 85%. It is believed that considerable amounts of organic materials were complexed with degradation products of the catalyst. An example of this is material I (see page 56 experimental section) which contained carbon, hydrogen and nitrogen as well as cobalt. Other examples of ignitable, cobalt containing, materials appear in the experimental section.

No characterization work was done on compounds A and B since their infrared spectra showed no absorption in the carbonyl region and the principal interest lay in the carbonylated compounds. These compounds failed also to show absorption in the OH or NH stretching regions of the infrared.

The presence of benzaldehyde in the reaction mixture seems to indicate that hydrolysis of the oxime has occurred. Care was taken to

use dry solvent and substrate but a small amount of water may have
been present in the carbon monoxide used. However the comparatively
large yield (10%) of benzaldehyde indicates some other method of pro-
ducing this compound is probable. This could have occurred in some
manner such as rearrangement of the oxime while complexed with the
carbonyl catalyst.

$$
\begin{array}{c}
O \\
\| \\
C \\
\diagup \quad \diagdown \\
(OC)_3 - Co \longrightarrow Co - (CO)_3 \\
\mid \qquad\qquad\qquad \mid \\
ph - C \longrightarrow N \\
\mid \qquad\qquad\qquad\quad \diagdown OH \\
H
\end{array}
$$
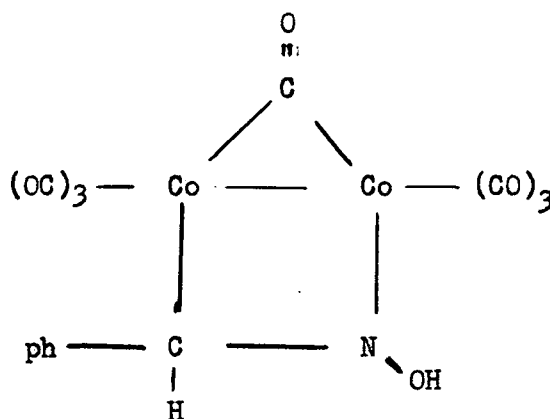
I

Formula I represents a hypothetical intermediate analogous to
those established for alkynes and alkenes (46, 50, 24) (See introduction
page 10). It was pointed out earlier (introduction page 12) that some
mechanism must exist for the facile movement of hydrogen in the com-
plexes suggested for olefin reactions. Some analogous rearrangement
involving the hydroxyl group could produce benzaldehyde.

The behaviour of the first material eluted from the chroma-
tographic separation of the reaction products (see page 44) is similar
to that reported for a complex with dicobalt octacarbonyl by Greenfield

et al (17). These authors listed the following properties for acetylenic dicobalt hexacarbonyls; deep red color, weak intermolecular forces, high volatility, high solubility in organic solvents and easy removal from activated alumina. These properties are consistent with the behaviour of the eluted material mentioned above, since the material from the column first formed a homogeneous red alcohol solution. An attempt to isolate the dissolved material produced a brown solid insoluble in alcohol plus an organic component which has been referred to as Compound A. The brown solid was shown to contain cobalt. Greenfield et al also reported that benzil was a major component in the decomposition of diphenylacetylene dicobalt hexacarbonyl at room temperature. This observation may parallel the isolation of benzaldehyde as a reaction product.

Mono-benzylurea and sym-dibenzylurea were identified by mixed melting point using authentic samples (8). These compounds also possessed infrared spectra identical with those of the authentic samples (pages 49 and 55). Sym-dibenzylurea was oxidized to produce sym-dibenzoylurea.

This writer is unable to postulate a reasonable mechanism for the formation of the observed substituted ureas. It would be sufficient to explain the production of mono-benzylurea since sym-dibenzylurea can be obtained from mono-benzylurea by heating and would be expected under the reaction conditions if mono-benzylurea were present (8).

It may be mentioned that the hydrolysis information reported is consistent with the behaviour of ureas. The alkaline conditions (page 50) should hydrolyze most amides (13) but higher temperatures and/or longer times are needed for ureas (42). It is worthy of note that each organic compound recovered from the chromatographic separation was accompanied by a yellow oily material. At first on recrystallizing these compounds it was felt that an oxidation was taking place. Subsequent isolation of the yellow material, however, always showed the presence of cobalt. It is felt that the amides present may in some manner be complexed with a cobalt compound and the complex decomposes fairly slowly. Hieber (21) indicated amide complexes with dicobalt octacarbonyl may be broken down in refluxing petroleum ether.

In the first run of the syn-benzaldoxime reaction the overall absorption of carbon monoxide was 2.1 moles per mole of substrate. The rerun showed an absorption of 1.25 moles per mole of substrate. The second run was carried out in a new stainless steel bomb without a glass liner whereas the first run used a glass liner. In spite of this difference in carbon monoxide absorption the same organic components could be isolated from both reactions. It was impossible to compare relative yields because of an accident involving shattering of a distilling flask containing the reaction product from run two. In each case the presence of dicobalt octacarbonyl after completion of the reaction was shown.

The carbon monoxide used for the reactions contained 0.04 volume percent of hydrogen according to an analysis supplied by the

manufacturer (Matheson, New Jersey). Vapor phase chromatography carried out in this department obtained a result of 1.5% by volume. Vapor phase chromatography of the product gases showed the absence of hydrogen. The conditions under which the sampling was done do not preclude the possibility that any hydrogen present had united with catalyst molecules rather than with the substrate. The sampling was done at room temperature and high pressure (2000 p.s.i.). Under these conditions cobalt hydro-carbonyl is stable and does not decompose until the pressure is released (33).

It was mentioned above that no phthalimidine could be detected in the product mixture. It is possible that any phthalmidine formed condensed to more complicated products under the severe reaction conditions since two uncharacterized products were present. It is suggested here that subjection of the O-methyl ether of benzaldoxime to the reaction conditions may lead to ring closure since the methyl group may provide hindrance to competing reactions. This statement is made considering the analogous case of the O-methyl ether of benzo-phenone oxime where the only organic product was 3-phenylphthalimidine and the side product found with benzophenone oxime was not present.

B. Benzophenone Oxime.

In the reaction with benzophenone oxime the major product (70%) was 3-phenylphthalimidine. A minor product (approximately 5%)

was the unidentified compound B. 3-Phenylphthalimidine was identified

by direct comparison with an authentic sample (39). A mixed melting

point showed no depression and their infrared spectra were identical.

An acetate derivative was also prepared.

The reaction with benzophenone oxime was run with varying

amounts of catalyst. In one trial 0.07 moles of substrate and 0.02

moles of catalyst were used. In the second case 0.1 moles of substrate

and 0.02 moles of catalyst were used. Case one showed an absorption

corresponding to 1.75 moles of carbon monoxide per mole of substrate.

Case two showed an absorption of 1.80 moles per mole of substrate. The

composition of the recovered organic product did not seem to be affected

by the difference in substrate to catalyst ratio. However in a third

trial the amount of catalyst was reduced to approximately 0.002 moles

and a major difference in the course of reaction was noted (see page 34).

Also present in this reaction was cobaltous carbonate. The results of

the reaction indicate that appreciable amounts of dicobalt octacarbonyl

were not formed from the cobaltous carbonate under the reaction conditions.

In both of the first two cases the recovery of organic

material was near 75% of which roughly 5% was the unidentified component

B. An exact yield for compound B is not available because no complete

separation was carried out. It was noted that compound B was more

soluble in ether than 3-phenylphthalimidine. Therefore ether extractions

of the total organic amount were carried out to obtain a solution con-

taining a larger proportion of compound B. This solution was then

chromatographed to separate B from remaining 3-phenylphthalimidine.
It was not possible to state how quantitative the ether separation
was. It was simple to obtain pure 3-phenylphthalimidine since
recrystallization of the original mixture from ethanol, methanol, or
benzene would produce pure compound. Extensive trials of recrystal-
lication solvents failed to produce pure compound B. The behaviour
of a mixture of B and 3-phenylphthalimidine was unusual when recrys-
tallization from ether was attempted. The first crop of crystals was
largely 3-phenylphthalimidine the second was 60% compound B and 40%
3-phenylphthalimidine. The third was largely 3-phenylphthalimidine.
These results were obtained through alumina chromatography (page 64).

A reduction of compound B was carried out using hydrogen over
platinum oxide in acetic acid solution. The products of this reduction
were compared to the products of a parallel reduction of 3-phenylphthali-
midine. The major product for the reduction of 3-phenylphthalimidine
was 3-cyclohexylhexahydro-phthalimidine (XII) as is shown on page 6 3
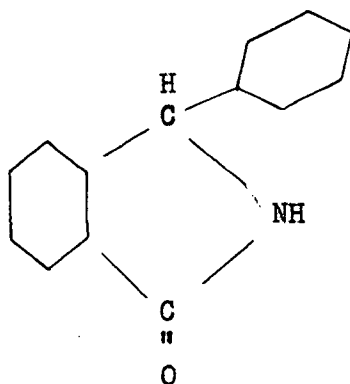
XII

A small sample (5% yield) of an identical compound (mixed melting point and infrared spectra) was secured from the reduction of compound B. This same compound was also obtained by a parallel reduction of an authentic sample of 3-phenylphthalimidine prepared by the method of Rose (39). These experiments provided extra proof of the identity of the 3-phenylphthalimidine produced. However the results are not believed to give an indication of the structure of compound B since the material used for the reduction is not now considered pure. The compound B used was obtained by a recrystallization procedure and melted sharply at 197 - 199° C. The analysis obtained showed an empirical formula corresponding to a dimer of 3-phenylphthalimidine ($C_{28}H_{22}N_2O_2$). However subsequent chromatographic purification failed to change the melting point though it did change the analysis so that the best fit empirical formula became $C_{27}H_{22}N_2O_2$. A possible explanation of the observed phenomena is that the compound B used for the reduction was contaminated with 3-phenylphthalimidine but that sufficient similarity in crystal structure prevented lowering of the melting point.

A summary of the properties of compound B follows: It was soluble in ether, benzene and alcohols. It was insoluble in boiling water, boiling 20% sodium hydroxide, or boiling concentrated hydrochloric acid. Conditions suitable for hydrolysis of all but the most hindered aromatic amides failed to affect compound B. Even though its infrared

spectrum indicated active hydrogen stringent acetylation conditions failed to affect the compound. (Fused sodium acetate refluxed in acetic anhydride for 6 hours).

When the amount of catalyst was reduced to 0.002 moles (trial III) the major product of the reaction was benzophenone which was recovered in 70% yield. Less than a 1% yield of 3-phenylphthalimidine was recovered and no trace of compound B was found. Also recovered from the reaction was 5% of the original oxime. This indicates that conversion of the oxime to benzophenone is a slow process since some original oxime was recovered after 4 hours heating.

C. O-Methyl Ether of Benzophenone Oxime.

The O-methyl ether of benzophenone oxime was subjected to the reaction conditions in an attempt to produce an N-substituted cyclic compound in accordance with equation I

$$C = N-OCH_3 \quad \xrightarrow[\text{Co}_2(\text{CO})_8]{\text{CO}}$$
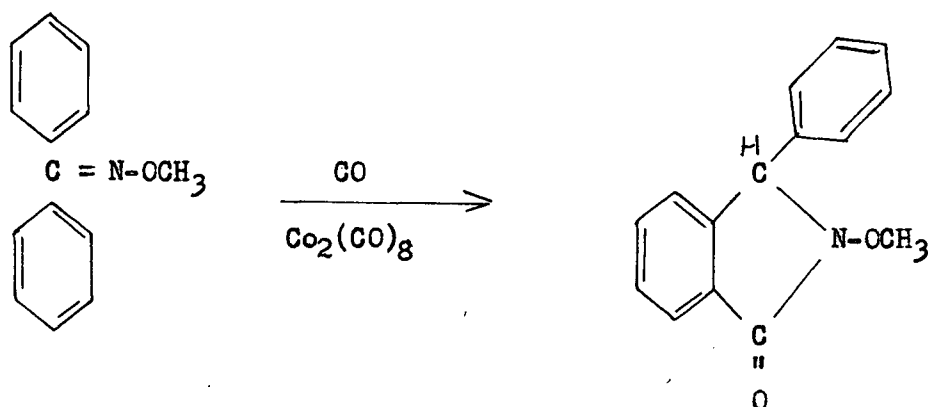
However the resulting product was a 70% yield of 3-phenylphthalimidine. Only a trace of another organic component could be found.

It is of interest that on washing an alumina column with
acetone after elution of the reaction products a light brown oil was
obtained which was obviously (judging from quantity) not a product of
the reaction. This material reacted instantaneously with ice cold 2%
potassium permanganate and with bromine in carbon tetrachloride. The
boiling point of the material was 163 - 166° C (corrected). The liter-
ature value for diacetone alcohol is 164 - 166° C.

D. Discussion of Pressure Plots

Detailed records were kept of the variation of pressure with
time and temperature for all reactions. Plots for each substrate used
are shown on pp 42, 66, 73.

The plots show variation of pressure with reaction time at
constant temperature. All pressures are corrected to 0° C. All pressures
are corrected for the vapor pressure of the benzene solvent. The
assumption is made that the variations in pressure remaining after these
corrections are due to absorption or release of carbon monoxide. It is
realized that the solubility of carbon monoxide in the liquid phase may
change with temperature in the closed system. However this cannot account
for the sudden changes in pressure noted at fairly constant temperature.
Another possibility is that some other gas besides carbon monoxide is
released in the system. This could best be checked by sampling the gases
at the peak of the pressure curve. This procedure is difficult and
dangerous with the present equipment due to the high toxicity of carbon

monoxide and cobalt carbonyls and the high reaction pressures and temperatures. However a reducing valve could be installed for this purpose. Plots of the nature submitted would be of more definite value if the benzene solution containing catalyst could be heated to reaction temperature with carbon monoxide under pressure before injection of the substrate. If the reaction were then carried out at constant temperature any pressure variations could definitely be ascribed to be results of the reaction.

It should be mentioned that carbon monoxide may be treated as an ideal gas throughout the pressure temperature range involved. This was established by use of the reduced pressure reduced temperature approximation.

Comparison of the plots for benzophenone oxime (page 66) and its O-methyl ether (page 73) shows both materials cause a release of carbon monoxide at low temperatures (20 to 55° C), nearly $2\frac{1}{2}$ moles per mole of substrate in the case of the ether, but only 0.6 moles for the oxime itself. Both of these figures are minimums for two reasons. First the carbon monoxide releasing reaction may have taken place partly while the carbon monoxide was being added. The initial pressure could not be measured until all the added gas was present and some time had to be allowed for solubility equilibrium to be reached. Secondly there is little detail on the plots in this area so the actual maximum may not have been recorded. In the case of syn-benzaldoxime no points were recorded in the corresponding area. Since steric hindrance plays an

important part in the rate of formation of complexes (see page 13) it
is felt that the O-methyl ether should form a complex least readily
and therefore part of the initial pressure recorded in the cases of
benzophenone oxime and syn-benzaldoxime may actually have come from the
reaction of the substrate and catalyst. This conjecture could be
checked by equilibrating the reaction mixture at constant temperature
before injection of the substrate.

All the plots show that any gas released is quickly reab-
sorbed. The O-methyl ether plot remains comparatively near the original
pressure value once the temperature reaches 165° C until the heating
element was turned off. After this point it shows an absorption of 1
mole of carbon monoxide per mole of substrate. This phenomenon could
correspond to some reaction absorbing carbon monoxide or to the conden-
sation of some unknown gaseous component. The benzaldoxime shows similar
behaviour if the assumption is made that original complex formation was
very rapid and that the original pressure recorded already includes the
carbon monoxide released by the complexing action.

The benzophenone plot shows remarkable pressure changes from
the point where the temperature reaches 160° C. There is a sudden
evolution of 1 mole of carbon monoxide followed by a sudden absorption
of 2 moles. All this takes place in 5 minutes. No explanation can be
offered for this interesting phenomenon. It is realized the pressure
peak at the 37 minute mark is evidenced by only one point but the

behaviour was obtained on a second trial and the phenomenon also
appears in the work of Hubscher (22).

At least two examples appear in this work of cobalt containing
compounds which were soluble in benzene and lost their solubility in
this solvent after refluxing in light petroleum ether. This behaviour
could be similar to that reported by Hieber (21) and mentioned on page
9.

EXPERIMENTAL

A. General

All infrared spectra reported were obtained using a Perkin-Elmer Model 21 spectrometer in this department except for the spectrum of the reduced product of 3-phenylphthalimidine which was obtained on a Baird-Atomic spectrometer in the Forest Products Laboratory. The vapor phase chromatography was carried out on equipment constructed in this department. All alumina used for chromatography was British Drug Houses chromatographic grade calcined alumina. Elemental analyses were carried out by Dr. A. Bernhardt of the Max Planck Institute, Mulheim, Ruhr, Germany. Melting points were determined using a polarizing microscope on an electrically heated hot stage. Corrected melting points were read directly.

Acknowledgement is hereby expressed to Mr. Harold MacLean of the Forest Products Laboratory and Mrs. Zell of this department for infrared determinations and to Dr. S. Ryce and Mr. S. Ruzicka of this department for vapor phase chromatography.

B. Reaction of Syn-benzaldoxime with Carbon Monoxide
in the Presence of Dicobalt Octacarbonyl.

a. Preparation of reactants

Syn-benzaldoxime was prepared according to the method of
Beckmann (2). The yield obtained was 31% of pure product based on
benzaldehyde. An infrared spectrum in chloroform solution was obtained
as a check on the purity of the aldoxime (34) and for comparison with
reaction products. Dicobalt octacarbonyl was prepared according to the
method of Wender et al (54). The catalyst was not isolated but was used
directly in the benzene solution in which it was obtained. The catalyst
prepared in this manner contains 0.25 gm or 7.3×10^{-4} moles per ml.
Specially dried and purified thiophene-free benzene was used both to
prepare the catalyst and to carry out the reactions. The carbon monoxide
used contained 1.5% by volume of hydrogen as determined by vapor phase
chromatography. An analysis supplied by the Matheson Company from whom
the carbon monoxide was purchased indicated a hydrogen percentage of
0.04% by volume. The analysis here was carried out by comparing the
observed peak height of 100% hydrogen with the hydrogen peak from the
carbon monoxide. A better procedure would have been to use a known
mixture closer in composition to the unknown. This may have given
results closer to the Matheson figure.

b. Reaction procedure.

The reaction was carried out in a glass lined Aminco super-

pressure reaction vessel which was equipped with a rocker mechanism. Temperature control was achieved through a Brown pyrometer using a thermocouple which had been calibrated against a standard thermometer.

An amount of 6.5 gm of syn-benzaldoxime (0.054 mole) was placed in the glass liner with 25 ml of catalyst solution (0.02 mole). A homogeneous solution resulted. Purified benzene was added to make the total volume 60 ml and the liner placed in the reaction vessel (effective void 180 ml). The sealed vessel was flushed twice with carbon monoxide to remove air. Carbon monoxide was run in to a total pressure of 2300 p.s.i. at 12° C (2200 p.s.i. at 0° C). Heating was then commenced. The Thermostat was set at 170° C and the temperature rose to this point in 39 minutes. After 6 minutes at this temperature the lack of variation in the observed pressure indicated no reaction, so the temperature was raised in steps of ten degrees to 220° C. The temperature was held at each ten degree level for 6 to 8 minutes. Finally the temperature was maintained at 220° C for 17 minutes before turning off the heating element. The total elapsed time from start to end of heating was 100 minutes. The reaction vessel was then allowed to cool to room temperature overnight. The final pressure observed was 2070 p.s.i. at 11° C (1990 at 0° C). This is an overall drop of 210 p.s.i. at 0° C and corresponds to 0.115 mole of carbon monoxide which is 2.1 moles per mole of substrate or 5.8 moles per mole of catalyst. A detailed record of pressure time and temperature was kept and the results plotted on page 42.

TOTAL REACTION PRESSURE CORRECTED
to 0°C FOR SYN-BENZALDOXIME

0.054 MOLES SUBSTATE
0.02 MOLES CATALYST

NOTE: CORRECTED FOR
VAPOUR PRESSURE
OF BENZENE

PRESSURE IN PSI

MOLES OF CARBON MONOXIDE
FORMED PER MOLE OF SUBSTRATE

TEMPERATURE IN °C

TIME IN MINUTES

42
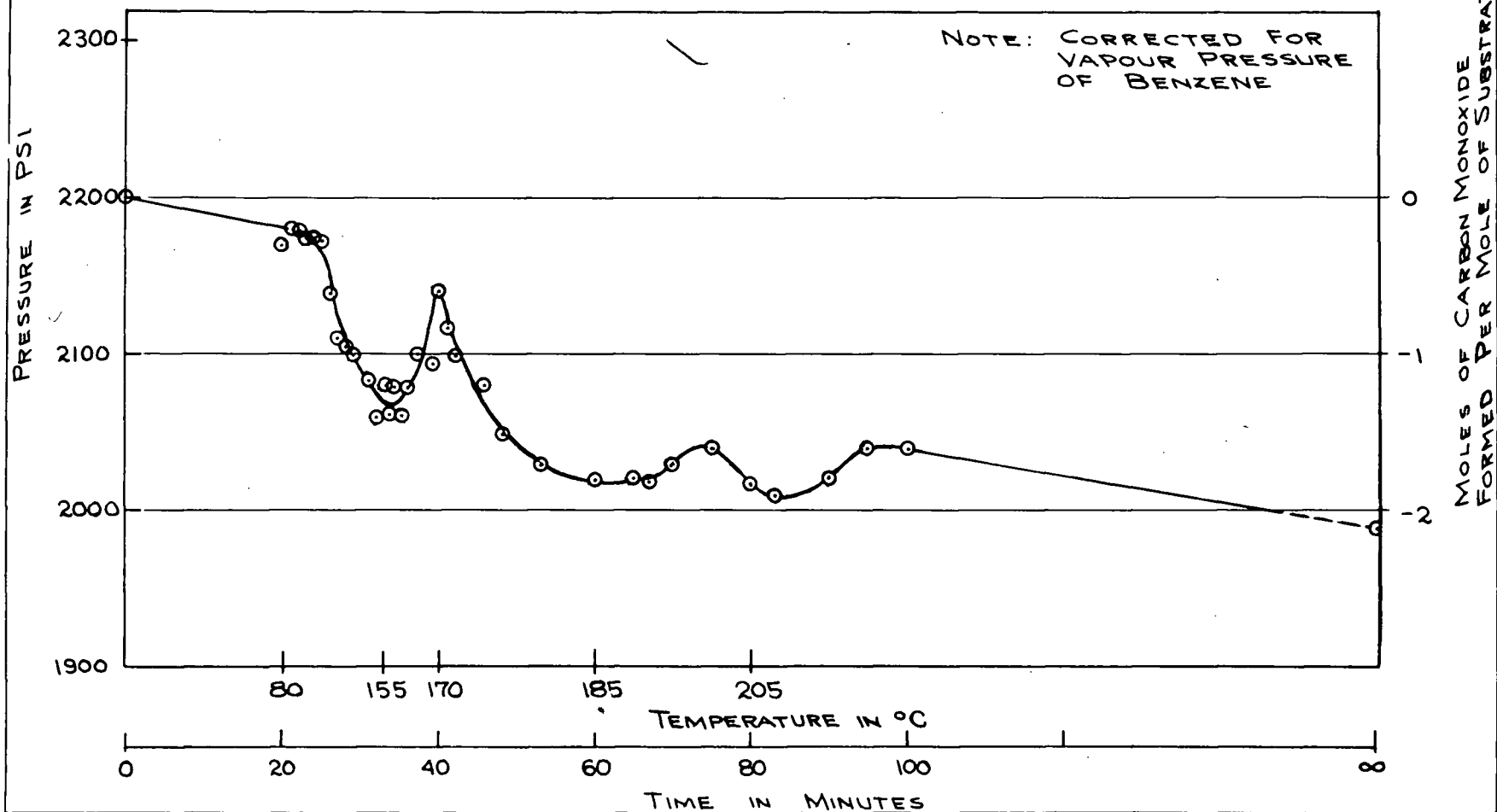
The reaction product was a brown homogeneous solution. This solution was evaporated at 25 - 35° C using a water aspirator to remove any unchanged catalyst and the benzene solvent.

c. Separation and identification of products

The reaction product after removal of the benzene was a green tarry material. It dissolved completely in warm benzene to a solution of 51 ml total volume. A 3 ml aliquot of this solution was placed on an alumina column ($12\frac{1}{2}$ cm x 3 cm diameter) for chromatography. The results for this aliquot (one seventeenth of the total reaction product) are detailed on page 44.

(i) First fraction from chromatogram (compound A)

On commencing elution with benzene a purple band moved quickly down the column and resulted in a red benzene solution. On standing the color of this solution gradually changed to brown. Evaporation of the solvent left a mixture of white and brown solids. Addition of ethanol produced a red colored ethanol solution and left a white crystalline residue. This white material was easily soluble in benzene leaving the brown residue. This brown residue failed to melt at 350° C and left a cobalt-containing residue on ignition. The white material was recrystallized from petroleum ether and melted at 239 - 242° C with some change in crystal structure near 220 - 225° C. The infrared spectrum of this material (compound A) showed no absorption in the

Chromatography of Reaction Product of Syn-benzaldoxime

(Aliquot containing one-seventeenth of reaction product)

Eluent	Amt. used in ml	Product	Description	Weight in mgm
Benzene	0-125	Compound A	purplish oily crystals odor of benzaldehyde	40
Benzene	125-175	Nothing		
Benzene	175-325	Compound B	white crystals	40
Benzene	325-775	Nothing		
Benzene ethanol 99:1	775-875	Nothing		
Benzene ethanol 99:1	875-1075	Compound C	yellow oily material plus white crystals	120
Benzene ethanol 98:2	1075-1225	Nothing		
Benzene ethanol 98:2	1075-1225	Nothing		
Benzene ethanol 98:2	1225-1275	Compound D	yellow oil	27
Benzene ethanol 98:2	1275-1325	Nothing		

Further washings with 200 ml benzene ethanol 50:50, 200 ml of absolute ethanol, and 200 ml of acetone produced nothing.

Apparent organic yield from aliquot   227 mgm

Total apparent yield   3.86 gm

carbonyl region so no further work was done on it. The infrared spectrum (potassium bromide disc) showed the following major absorption peaks: 3050W, 1598sh, 1589W, 1523S, 1369S, 1301W, 1175W, 1069W, 1029W, 843M, 746S, 686S, 648M. The infrared spectrum is reproduced on page 46.

(ii)   Second fraction from chromatogram (Compound B)

This fraction appeared white but picked up a yellow color during evaporation of the solvent (water aspirator less than 35° C). Melting range of the crude material was 100 - 230° C. Light petroleum ether dissolved the yellow material leaving a white residue which melted at 280 - 282° C after two recrystallizations from 30 - 60° C petroleum ether. The infrared spectrum of compound B failed to show absorption in the carbonyl region so no further work was done on it. The infrared (potassium bromide disc) showed the following major absorptions: 3055W, 1601W, 1579W, 1507W, 1492M, 1465M, 1447W, 1414W, 1400W, 1325W, 1204W, 1153W, 1072W, 973W, 917W, 767M, 736M, 714M, 698S.

(iii)   Third fraction from chromatogram (sym-dibenzylurea)

This fraction also consisted of a white material with some yellow. The yellow color was slightly soluble in light petroleum ether and very soluble in ether. White crystals were slightly soluble in either solvent. Crude material was extracted with ether and 30 - 60° C petroleum ether to leave a white material melting at 160 - 167° C

Infrared spectrum (potassium bromide disc)
Compound A

WAVE NUMBERS IN CM⁻¹

4000   3000   2000 19 18 17   16 15 14 13 12 11 1000 9   8   7   600

46

Infrared spectrum (potassium bromide disc)
Compound B

WAVE NUMBERS IN CM⁻¹
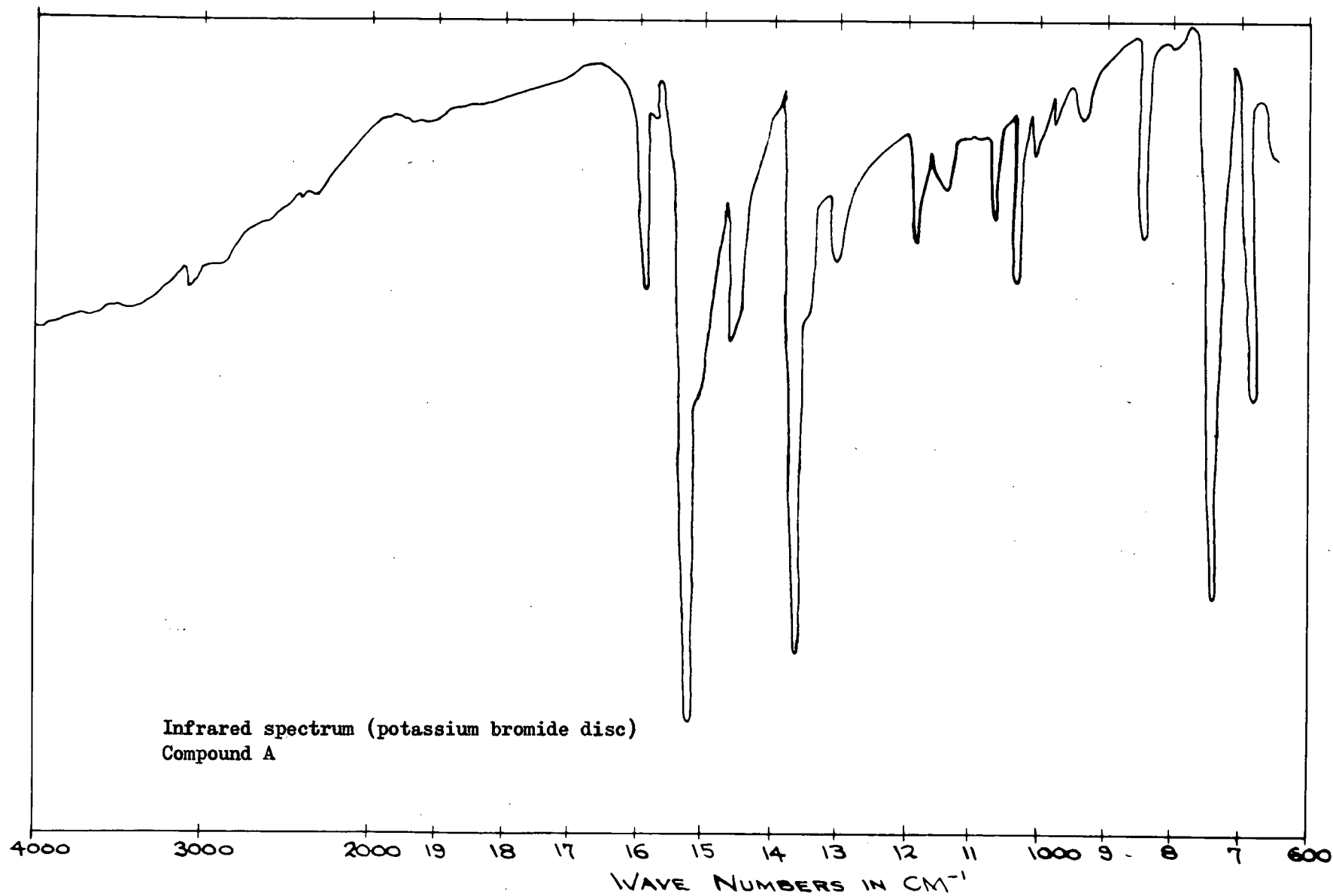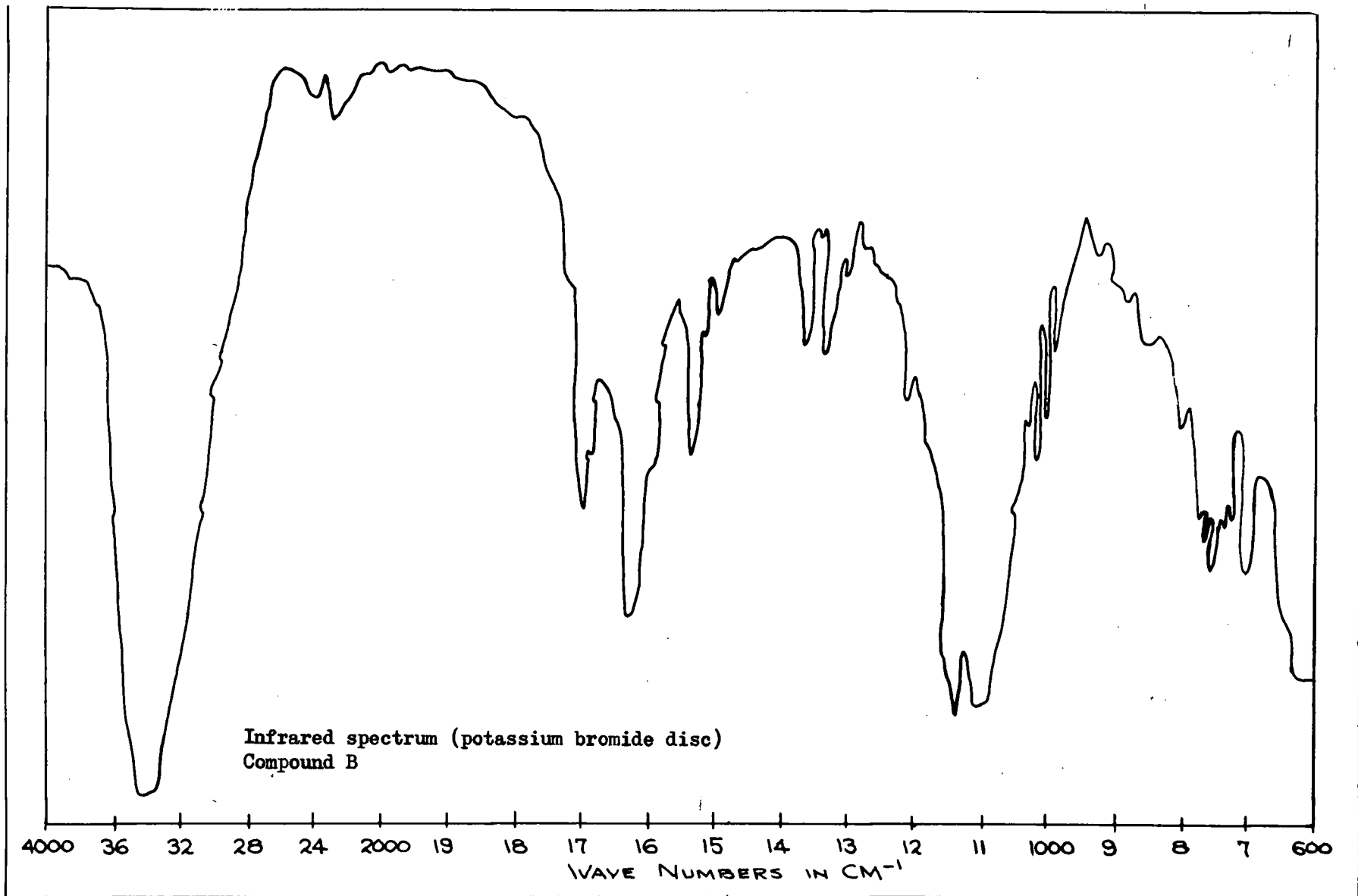
(Compound C).

Compound C dissolved fairly readily in benzene and left a small amount of green residue. This green material contained cobalt and failed to melt at 310° C. It dissolved readily in concentrated hydrochloric acid to a green solution. On dilution and treatment with sodium hydroxide the presence of cobalt was proven.

Compound C was now recrystallized from benzene petroleum ether and melted at $168 - 169\frac{1}{2}^{\circ}$ C. The infrared spectrum (potassium bromide disc) showed the following major absorptions: 3337S, 3043W, 2922W, 1625S, 1591S, 1575S, 1497W, 1475W, 1458M, 1435W, 1369W, (1275 to 1225 broad absorption), 1080S, 1027W, 757W, 733W, 698S. The infrared spectrum is reproduced on page 49.

Compound C was soluble in benzene, alcohol, ether, but very little in light petroleum ether. The compound was insoluble in cold water but dissolved slowly in hot concentrated sodium hydroxide. It was insoluble in cold concentrated hydrochloric acid but slowly dissolved on heating to a light yellow colored solution. No precipitate could be obtained from either the basic or acidic solutions by neutralizing with hydrochloric acid or sodium hydroxide respectively.

Compound C was soluble in concentrated sulphuric acid and no precipitate was obtained on dilution with water.

The acid solutions above were extracted with benzene. The material recovered proved identical with original by mixed melting point.

Infrared spectrum (potassium
bromide disc)
sym-dibenzylurea (————————)
sym-dibenzoylurea (— — — — — —)

WAVE NUMBERS IN CM⁻¹

3600　3000　　2000　19　18　17　16　1500　14　13　12　11　1000　9　8　7　600

67
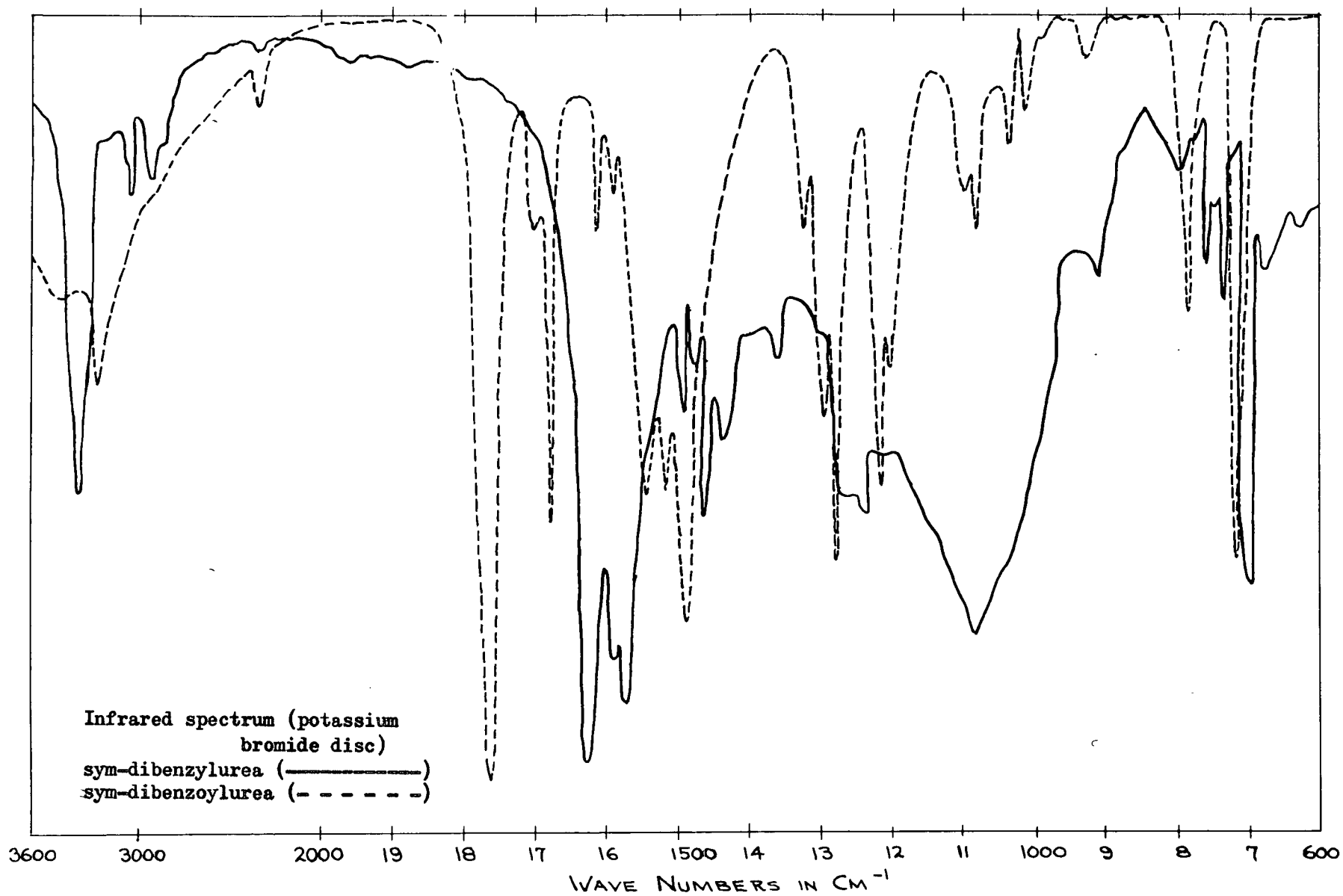
Compound C was now heated at reflux temperature for forty hours in 20% sodium hydroxide in ethanol water. On neutralization with hydrochloric acid crystals were obtained identical to original by mixed melting point.

An attempt to prepare an acetate derivative under the following conditions produced an oil. An amount of 5 mgm of compound C was refluxed for four hours with fused sodium acetate (50 mgm) and 5 ml of acetic anhydride. On pouring the acetylating mixture onto ice a small amount of oil which was insoluble in hot water was obtained. This oil was not crystallizable from the common solvents.

An amount of 50 mgm of compound C was heated on a steam bath in concentrated hydrochloric acid resulting in a lightly yellow colored solution. Aqueous dilution of this acid solution produced a milky appearance with some curdy white material. Ether extraction removed the milky appearance. Evaporation of the ether layer resulted in recovery of the original material. Yellow coloration shows slight hydrolysis. An amount of 10.8 mgm of compound C was now refluxed for 6 hours with concentrated hydrochloric acid. The solution was diluted to 6 normal and allowed to stand overnight. No crystals appeared. An ether extract of this solution contained nothing. The aqueous layer was now neutralized with sodium hydroxide. There was no immediate precipitate but on standing overnight a flocculent precipitate appeared. This material was extracted with chloroform. Again the material isolated was the original.

The aqueous layer remaining after the chloroform extraction was extracted with ether. The ether contained nothing.

Oxidation of phthalimidine was now attempted to develop a suitable oxidation procedure for compound C. The phthalimidine was prepared from phthalimide by the method of Graebe (18). An infrared spectrum of phthalimidine was obtained for comparison with reaction products. An amount of 239 mgm of phthalimidine was dissolved in 50 ml of glacial acetic acid. One gm of solid sodium dichromate was added slowly while the solution was heated strongly on a steam bath. Reflux was carried out for 4 hours after completion of the dichromate addition. The reaction mixture was poured into 50 ml of water resulting in a homogeneous solution. This aqueous solution was extracted with chloroform to yield a residue of an acetic acid solution. Addition of water to the acetic acid produced crystals. These were redissolved in chloroform and the chloroform was washed with water to get rid of most of the acetic acid and again evaporated. Water added now again caused precipitation of crystals which were now recrystallized directly from water. The material dissolved slowly in boiling water and recrystallized rapidly on cooling (m.p. 236 - 238° C with softening at 230° C). This behaviour is exact for phthalimide. A mixed melting point showed no depression. Yield was 79% of recrystallized product.

Sixty-three mgm of compound C were now oxidized under the same conditions using 25 ml of glacial acetic acid and 0.3 gm of sodium dichromate. The oxidizing mixture was extracted directly with chloroform.

Treatment as above yielded 42 mgm of a product melting at 202 - 203° C after two recrystallizations from ethanol water. The infrared spectrum (potassium bromide disc) of this oxidized product is shown on page 49 compared to compound C. The major absorption peaks were measured as follows: 3240W, 1753S, 1670S, 1603W, 1577W, 1534M, 1506M, 1480M, 1288M, 1266S, 1200M, 1192W, 1067W, 771M, 696S. This product did not react with sodium bicarbonate and was not an acid. The product dissolved very readily in acetone but required warming to dissolve in ethanol. It was dissolved by boiling water. The product was small well formed needles.

The aqueous layer from the oxidation reaction remaining after chloroform extraction was now acidified with sulphuric acid since an acid stronger than acetic acid if formed in the reaction would not otherwise be extracted by organic solvents. Now sodium bisulfite was added to destroy excess oxidant. Ether extraction of the resulting green acid solution recovered 5 mgm of an organic acid which was easily soluble in ether, ethanol or benzene, but soluble less readily in light petroleum ether. The acid failed to crystallize from light petroleum ether but recrystallized from water at 0° C. After 2 recrystallizations m.p. was 120 - 122° C. Mixed melting point with an authentic sample of benzoic acid was 120 - 122° C.

Thionyl chloride was added to 3 mgm of dry material from above and refluxed on steam bath for one-half hour. Mixture was poured into 1 ml of cold concentrated ammonium hydroxide. A precipitate separated and was washed with water. The precipitate was dissolved in ethanol and precipitated out with water. Melting point was 126 - 127° C.

Literature for benzamide is 127° C.

Analysis calculated	C, 75.00; H, 6.67; N, 11.67;
for $C_{15}H_{16}N_2O$	Mol. wt. 240
Found	C, 74.87; H, 6.79; N, 11.91;
	Mol. wt. (Rast) 263

The high amount of hydrogen suggests a linear structure and the infrared of the oxidation product demands 2 different carbonyls. Sym-dibenzylurea fits m.p., analysis, infrared, solubility, and hydrolysis information. So an authentic sample was prepared according to the procedure of Davis and Blanchard (8). This authentic sample proved to have an identical infrared spectrum with compound C. No depression was obtained in a mixed melting point determination.

The oxidized product must now be sym-dibenzoylurea whose m.p. is 203° C as reported by Biltz (5). No explanation is offered here for the melting point of 208° C reported by Billeter (4).

(iv) Fourth fraction from chromatogram (mono-benzylurea)

Compound D was also accompanied by a yellow oily material. Repeated recrystallization from benzene - petroleum ether was required to produce a pure sample which melted at 147 - 149° C. The infrared spectrum in a potassium bromide disc showed the following major absorptions; 3440S, 3328S, 3035W, 2922W, 2876W, 1651S, 1601S, 1564S, 1499W, 1471M, 1458M, 1389M, 1338W, 1329W, 1312W, 1209W, 1144M, 1109M,

1079W, 1027W, 758M, 752M, 697S. This spectrum is reproduced on page
55. Since the expected product of the reaction was phthalimidine
(melting point 150° C), by analogy to previous work of Rosenthal et
al (40) immediate comparison was made with an authentic sample of
phthalimidine (18). The infrared spectra were considerably different
and a mixed melting point showed 25° C depression so that compound D
was not phthalimidine. The infrared spectrum of D strongly suggested
the presence of a primary amine or amide since it showed strong ab-
sorption at 3440, 3328, 1601, and 1564. Solubility considerations
ruled out the amino group and presence of an apparent carbonyl function
at 1651 cm^{-1} supported the primary amide. The carbonyl function failed
to react with 2, 4, dinitro-phenylhydrazine thus confirming the amide
hypothesis. Since sym-dibenzylurea may be obtained from mono-benzylurea
by simple heating, a sample of mono-benzylurea was prepared (8). Mixed
melting point and comparison of infrared spectra showed compound D to
be identical with mono-benzylurea.

d. Repeat of reaction between carbon monoxide and

syn-benzaldoxime in the presence of dicobalt octacarbonyl.

Syn-benzaldoxime and dicobalt octacarbonyl were prepared and
reacted as on page 40. A sample of the product gases was analyzed by
vapor phase chromatography. The only gas detected was carbon monoxide
showing any hydrogen originally present had reacted. The pressure drop
observed corresponded to the absorption of 0.075 moles of carbon monoxide.

Infrared spectrum (potassium
bromide disc)
mono-benzylurea

WAVE NUMBERS IN CM⁻¹

55
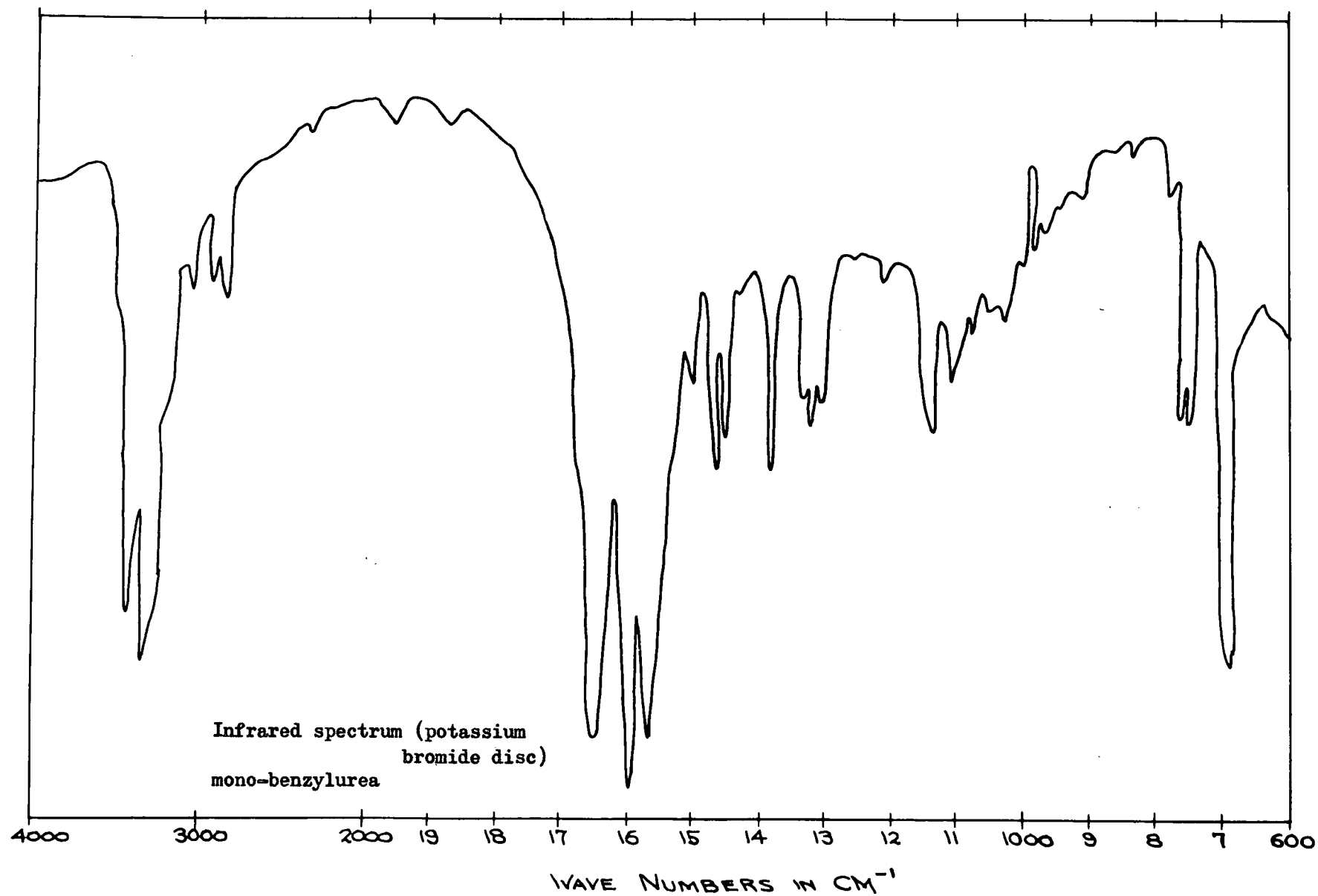
Since 0.06 moles of substrate were used this is 1.25 moles per mole of substrate.

The reaction product was a homogeneous dark brown benzene solution. This solution was evaporated under vacuum (water aspirator) at less than 35° C to remove or decompose any unreacted catalyst and benzene solvent. The distillate was a light yellow benzene solution containing excess catalyst. The solid residue appeared black in color.

The residue was extracted twice with boiling chloroform. This left a dark green (cobalt containing) residue and a brownish green solution. This residue was now extracted with boiling acetone and appeared partly soluble. Filtration of the acetone after crystallization produced a light green solid (material I) (0.4 gm) which ignited in a flame and left a cobalt containing residue. This solid was stable at 350° C on the melting point slide. It dissolved in hydrochloric acid to a bright green solution without effervescence but was insoluble in water. The infrared spectrum of material I was determined and failed to show absorption attributable to the carbonyls of a cobalt carbonyl compound (33). Analysis of material I failed to show any simple relationship between the constituents.

Found: Co, 31.26; C, 12.28;, N, 2.99; H, 2.75.

Further extraction of the residue with refluxing acetone dissolved nothing and left a green insoluble material (material II) (2.3 gm) which was similar in appearance to material I and also ignited

in the flame test leaving a black cobalt residue.

The above chloroform solution containing organic products was evaporated to leave a green residue which was repeatedly extracted with refluxing petroleum ether (30 - 60° C). The petroleum ether was colored wine straw and on cooling became opalescent. The green residue remained unchanged in appearance.

Evaporation of the petroleum ether solution yielded 0.8 gm of a brown viscous liquid whose smell resembled benzaldehyde.

Saturated aqueous sodium bisulphite was added and some insoluble crystals extracted with ether. On addition of the ether a very small amount of cobalt containing violet material separated. This was filtered off and discarded. The ether layer on evaporation produced 5 mgm of a material which melted at 229 - 230° C with a change in crystal structure at 210 - 215° C after recrystallization from alcohol. This was shown identical by mixed melting point with Compound A (page 43).

The aqueous layer was acidified with hydrochloric acid and warmed to destroy the bisulphite. 2, 4-Dinitrophenylhydrazine reagent was added and an immediate yellow precipitate was formed (0.54 gm) m. p. 235 - 237° C. Mixed m.p. with an authentic sample of benzaldehyde 2, 4-dinitrophenylhydrazone was 235 - 237° C.

The green residue from the petroleum ether extraction was now extracted with benzene and a violet solid was found to be insoluble (1.6 gm). The major part of the organic product was now contained in

the benzene solution. On standing 0.4 gm of white crystals precipitated. Chromatography of a small sample of these crystals showed them to be a mixture of compound C and compound D (pages 47 and 53).

The green benzene solution on evaporation yielded 2.26 gm of a brown oil which dissolved completely in 15 ml of cold benzene for chromatography. Chromatography of the above benzene solution on alumina ($7\frac{1}{2}$ x 10 cm) gave the following results.

Eluent	Amount		
Benzene	0 - 400	compound A m.p. 244 - 245° C	130 mgm
Benzene	400 - 800	nothing	
Benzene ether 50:50	0 - 400	nothing	
Benzene ether 50:50	400 - 800	compound B m.p. 287$\frac{1}{2}$ - 289° C	100 mgm
Benzene ether 50:50	800 - 1000	nothing	
Benzene ether 50:50	1000 - 1200	yellow oil	0.2 gm
Benzene ether 50:50	1200 - 1400	nothing	
Ethanol	0 - 500	compound C m.p. 165 - 172° C	0.4 gm
Ethanol	500 - 700	nothing	
Ethanol	700 - 1000	brown oil	1.1 gm

The final fraction from this chromatographic separation was shown by recrystallization to contain cobalt and 0.2 gm of compound D.

Yield from chromatogram was 1.93 gm from 2.3 added. Total overall
yield of organic material from the reaction was 5.2 gm.

C. Action of Carbon Monoxide on Benzophenone Oxime
   in the Presence of Dicobalt Octacarbonyl.

a. Preparation of benzophenone oxime

A mixture of 20 gm of benzophenone, 20 gm of hydroxylamine
hydrochloride, 20 ml of pyridine and 200 ml of ethanol was refluxed
on a steam bath for four hours. The alcohol was then removed by
distillation to leave a syrupy mixture. This mixture was cooled in
an ice bath and 150 ml of water added slowly with stirring. The
resulting crystals were recrystallized twice from ethanol water. Yield
after two recrystallizations was 13.5 gm (62% of theoretical) (m.p.
143 - 145° C). Literature 144° C.

b. Reaction procedure

The catalyst was prepared as on page 40 and reaction was
carried out in essentially the same manner. Thirteen gm (0.07 mole)
of benzophenone oxime and 25 ml of catalyst solution were used (0.02
moles). Original pressure was 2210 p.s.i. corrected to 0° C, final
pressure was 1990 p.s.i. corrected to 0° C. This is an absorption of
0.12 mole of carbon monoxide or 1.75 moles per mole of substrate.

Total heating time was seventy-two minutes.

    c. Separation and identification of the products

The glass liner contained crystalline material and a brown benzene solution. The benzene was evaporated at 25 - 35° C to leave brown crystals. Some unreacted dicobalt octacarbonyl distilled with the benzene to produce an orange colored solution.

Solution of the brown crystals in hot chloroform produced a deep blue solution. Norite was added and the solution filtered hot after a few minutes reflux. The solution retained the blue color. Some pink material remained with the norite. The chloroform solution was cooled and white crystals separated which melted 197 - 210° C (material I). Recrystallization from chloroform failed to change this melting range. All common solvents were used in an attempt to find a suitable recrystallization solvent. Repeated recrystallization of the material from benzene or from ethanol gave crystals melting at 225 - 227° C. Material I was extracted in a Soxhlet apparatus for 4 hours using ether. An ether insoluble residue (20 mgm) melted at 280 - 284° C (compound A).

Evaporation of the ether solution gave crystals melting at 198 - 230° C (Material II).

Material II was white fluffy needles which gave a red color with concentrated sulphuric acid dissolving to a light yellow solution.

Dilution destroyed the color and reprecipitated white material. Concentrated hydrochloric acid showed a green coloration and formic acid produced a red color. It was noted that these same colors can be produced by action of the above reagents on cobaltous salts.

An ether solution of material II was partially evaporated and the resulting crystals separated. These recrystallized from methanol three times still gave above colors with acids. Melting point of this material was 197 - 199° C (compound B). Reaction of the material with acetic anhydride and sodium acetate under anhydrous conditions produced light yellow crystals which melted at 197 - 199° C. Analytical results on compound B were:

C, 80.21; H, 5.35; N, 6.53; Mol. wt. 380

Calculated for $C_{27}H_{22}N_2O_2$:

C, 79.80; H, 5.40; N, 6.89; Mol. wt. 406

Calculated for $C_{28}H_{22}N_2O_2$:

C, 80.38; H, 5.26; N, 6.70; Mol. wt. 418

Repeated recrystallization from methanol of that part of material II which seemed least soluble in ether gave crystals melting at 225 - 227° C (compound C). Compound C was compared with an authentic sample of 3-phenylphthalimidine (39) and found to be identical through infrared spectrum and mixed melting point. The acetate derivative melted at 153 - 154° C; literature m.p. 154° C (39).

Analysis of compound C:

Calculated for   C, 80.38; H, 5.27; N, 6.70;
$C_{14}H_{11}NO$ Mol. wt. 209

Found: C, 80.35; H, 5.56; N, 6.65;
   Mol. wt. (Rast) 226

Compound B was reduced using the following experimental con-
ditions: compound B (63 mgm) (.0015 moles), 17 mgm of platinum oxide
in 25 ml of glacial acetic acid. Hydrogen was added at atmospheric
temperature and pressure (64.4 ml) (.003 moles of hydrogen were absorbed
in $5\frac{1}{2}$ hours). The hydrogen was absorbed rapidly initially and then at
a steady rate. No significant change in the rate of hydrogen absorption
could be detected at any time. The material left after evaporation
of solvents melted at 100 to 210° C. This material was dissolved in
benzene for chromatography using an alumina column ($1\frac{1}{4}$" x 4"). The
first 120 ml of benzene eluent produced nothing. The next 40 ml
produced a yellow oil from which hot ligroin extracted white crystals
(material B 1, m.p. less than 110° C). Further benzene (100 ml) and
benzene containing 2% ethanol (100 ml) produced nothing. Benzene
(100 ml) containing 10% ethanol yielded small needles which grew to
large needles at 175° C and melted at 223 - 224° C (Material B-2).
One hundred per cent ethanol (100 ml) produced crystals melting at
175 - 185° C (material B-3).

Compound C (3-phenylphthalmidine) was reduced using the same
experimental conditions. Chromatography of the reaction product gave

three fractions of melting point; 125 - 150° C (C-1), 169 - 170° C

(C-2) and 223 - 224° C (C-3). These materials were also obtained from

a parallel reduction of 3-phenylphthalimidine prepared by the method

of Rose (39). Material B-2 and C-3 were shown to be identical by com-

parison of infrared spectrum and mixed melting point. The infrared

spectrum of compound C-3 in potassium bromide disc showed the following

major absorptions; 3210S, 2920S, 2830S, 1673S, 1440M (broad), 1383W,

1347W, 1325W, 1275M, 1255M, 1195W, 1172W, 1142W, 982W, 888W, 862W,

752M, 717W.

The spectrum of 3-phenylphthalimidine compared to its re-

duced product is shown on page 64. Detailed comparison of the spectra

of C-3 was made with that of 3-phenylphthalimidine. Bands present in

3-phenylphthalimidine at 1458 cm^{-1}, 1472 cm^{-1}, 1497 cm^{-1}, 1599 cm^{-1} and

1608 cm^{-1} were not present in the reduced product. The 3-phenylphthalmi-

dine band at 3020 cm^{-1} associated with aromatic C-H is not present in

the reduced product. The bands in the 700 cm^{-1} region associated with

ring substitution also are not found in C-3. The 2830 cm^{-1} vibration

associated with tertiary CH is stronger in the reduced product than in

3-phenylphthalimidine. The lactam carbonyl (1677 cm^{-1}) of

3-phenylphthalimidine appears in the reduced product with a slight

change in frequency (1673 cm^{-1}). All of these observations are con-

sistent with the reduction of both benzene rings to produce 3-cyclohexyl

hexahydro-phthalimidine.

Infrared spectrum (potassium bromide disc)
3-phenylphthalimidine (————————)
3-cyclohexylhexahydrophthalimidine (– – –)

WAVE NUMBERS IN CM⁻¹
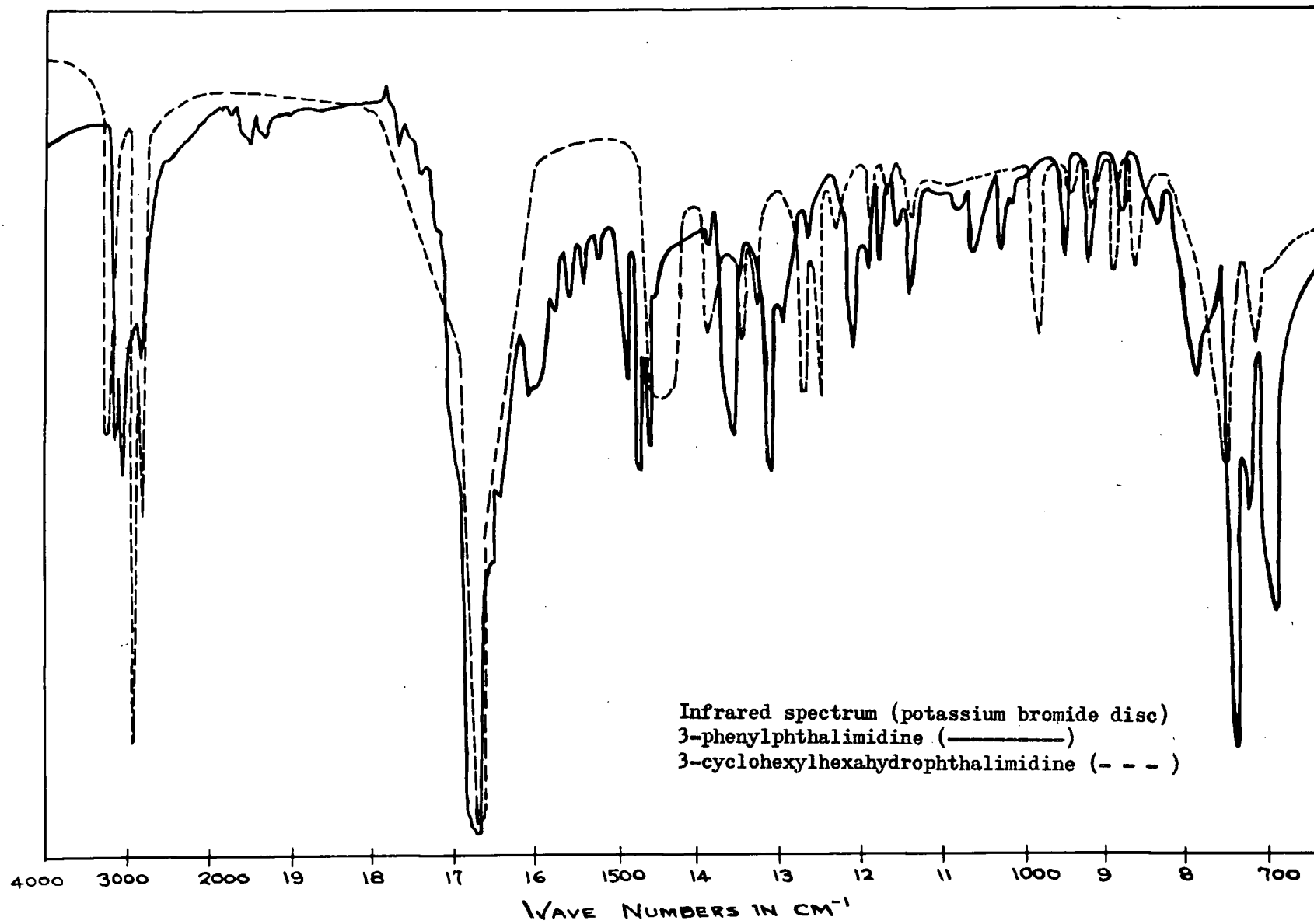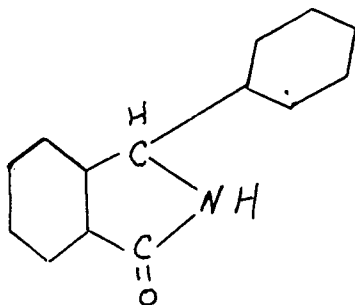
This conclusion is supported by analysis of C-3.

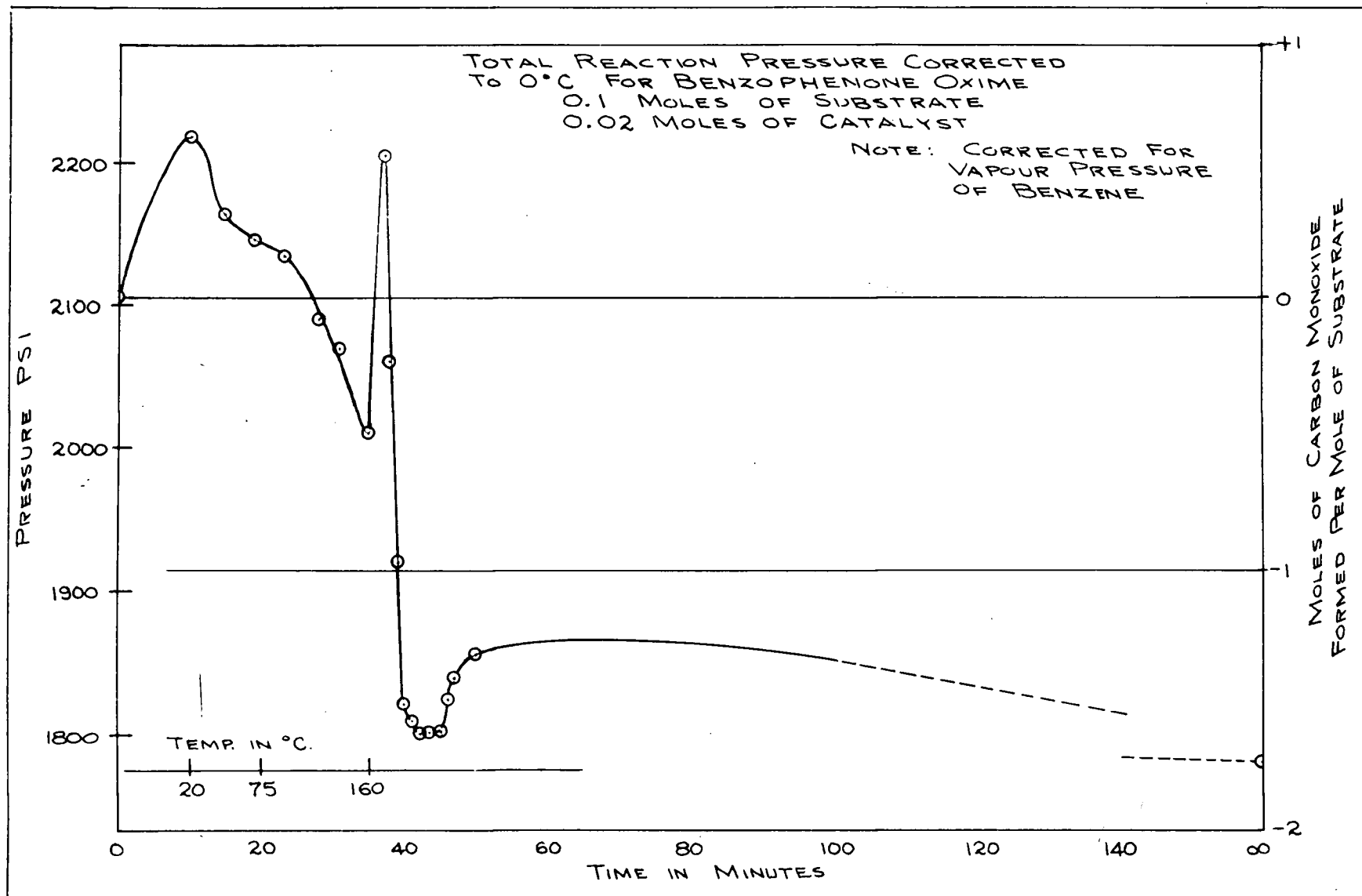Calculated for   C, 76.02; H, 10.41; N, 6.33; m.w. 221
$C_{14}H_{23}NO$:

Found: C, 76.17; H, 10.37; N, 6.15; m.w. 216

d. Repeat of reaction of benzophenone oxime

Benzophenone oxime was reacted with carbon monoxide under the same general conditions as on page 40. Initial pressure of carbon monoxide was 2250 p.s.i. at $18°$ C (2105 p.s.i. at $0°$ C). Benzophenone oxime (19.5 gm) (0.1 mole) was dissolved in 30 ml of catalyst solution (0.02 mole) and the total volume brought to 60 ml with benzene. Details of pressure readings were plotted, and are graphed on page 66. The overall pressure drop was 1.77 moles per mole of substrate, calculated as carbon monoxide.

The material from the bomb was heated for 30 minutes at the temperature of refluxing benzene. Benzene was evaporated to leave brown crystalline material. This material was extracted with hot chloroform and an insoluble residue filtered off (material I). Evaporation of the chloroform yielded a dark brown material which formed a dark brown solution in methanol and left a dark red residue (material II).

TOTAL REACTION PRESSURE CORRECTED
TO 0°C FOR BENZOPHENONE OXIME
0.1 MOLES OF SUBSTRATE
0.02 MOLES OF CATALYST

NOTE: CORRECTED FOR
VAPOUR PRESSURE
OF BENZENE

99

Material II turned green on drying and failed to melt at 350° C. It left a black residue on ignition which tested for cobalt.

White crystals (7 gm) crystallized from the methanol (m.p. 180 - 210° C) (material III). Extensive trials of recrystallization from organic solvents failed to produce a pure compound corresponding to compound B of section I. Pure compound C could be obtained by repeated recrystallizations from benzene or methanol. From the methanol mother liquor, containing catalyst decomposition products, it was possible to isolate 6 gm of organic material making the total yield 13 gm.

An ether extract was made of material III. The resulting crystals (1 gm) melted at 194 - 200° C. These were recrystallized from ether and 3 separate crops were obtained. The first (100 mgm) melted 220 - 230° C; the second (200 mgm) 170 - 195° C; and the third (100 mgm) 220 - 230° C. The middle crop (200 mgms) was dissolved in 3 ml of benzene placed on an alumina column (3½ cm x 8 cm) and eluted with benzene with the following results; the first 250 ml of benzene produced nothing; the next 200 ml produced, after recrystallization, 120 mgm of compound B (m.p. 197 - 199° C).

The infrared spectrum of this material showed the following major absorptions (potassium bromide disc); 3420(broad)S, 2885W, 1704M, 1690W, 1627M, 1535M, 1499W, 1475W, 1463W, 1366W, 1346W, 1329W, 1140M, 1086M, 774W, 765W, 753W, 741W, 731W, 700M. The spectrum is reproduced on page 47.

A further 100 ml of benzene produced nothing. Benzene ethanol 50:50 (100 ml) produced 3-phenylphthalimidine.

The first and third crops were now chromatographed and both yielded only traces quantities of compound B. They consisted almost wholly of 3-phenylphthalimidine.

Compound B failed to react with cold aqueous or alcoholic potassium permanganate. It failed to react with bromine in water or carbon tetrachloride. No reaction was visible with hydrochloric or formic acids. A red color could be detected by pouring concentrated sulphuric acid onto dry crystals which would subsequently dissolve to a pale green solution.

A hydrolysis was attempted using the following conditions. Twenty mgm of compound B and 8 gm of potassium hydroxide were dissolved in 30 ml of ethanol and 20 ml of water. Compound B was insoluble in the cold mixture but dissolved at reflux temperature. Reflux was carried out for 30 hours. The solvent was evaporated under reduced pressure, and allowed to crystallize at 0° C. Crystals recovered were shown identical with compound B by mixed melting point.

Twenty mgm of compound B were heated on the steam bath for one-half hour with concentrated sulphuric acid. The reaction mixture was poured into cold water and crystals recovered proved identical to compound B.

3-Phenyloxindole was prepared by the method of Meisenheimer (28) for comparison with compound B, because of similarity in analysis, solubilities and chemical properties. Mixed melting point produced a marked depression.

A re-analysis of compound B produced the following results:

Calculated for $C_{27}H_{22}N_2O_2$:

C, 79.80; H, 5.42; N, 6.90; Mol. wt. 406

Found:

C, 79.44; H, 5.28; N, 6.86; Mol. wt. 379

e. Reaction of benzophenone oxime in the presence
of small amount of dicobalt octacarbonyl

Reaction between benzophenone oxime and carbon monoxide was carried out in the presence of a small amount of dicobalt octacarbonyl in the following manner. After preparation of the catalyst most of the catalyst solution was poured off leaving the unreacted residue of cobaltous carbonate with approximately 2 ml (0.002 mole) of catalyst solution. A solution of 16 gm (0.088 mole) of benzophenone oxime in benzene was added to this residue and the total volume made exactly 50 ml with benzene. On reaching 200° C it was apparent that the reaction was not proceeding as described in section III. The reaction vessel was allowed to cool and reheated twice on the assumption the reaction might be proceeding slowly. Total heating time was four hours.

The benzene was evaporated off and the product was digested in chloroform to obtain a brown filtrate and a pink residue. This

residue contained no organic material, but did contain cobalt and appeared identical in appearance with cobaltous carbonate. On evaporation of the brown chloroform solution a brown oil was obtained as product (10.5 gm). The brown oil was dissolved in ether and cooled at 0° C. Crystals were obtained and recrystallized from methanol, to yield 90 mgm of 3-phenylphthalimidine. The brown oil was soluble in alcohols, acetone, ether, benzene, chloroform, or carbon tetrachloride. It was stable to the action of hot concentrated hydrochloric acid or hot concentrated sodium hydroxide. It was insoluble in water, hydrochloric acid or sodium hydroxide. Concentrated sulphuric acid produced a green solution. On dilution a colorless colloidal suspension was obtained which would not dissolve on basifying with sodium hydroxide.

The oil boiled at 290° C (uncorrected) $305 - 307^{\circ}$ C (corrected). It distilled without decomposition at atmospheric pressure. Reaction with hydroxylamine hydrochloride in aqueous ethanol yielded white crystals (m.p. $144 - 145^{\circ}$ C). Reaction with 2-4-dinitrophenylhydrazine yielded yellow crystals (m.p. $245 - 247^{\circ}$ C). The literature values for benzophenone oxime and benzophenone, 2-4-dinitrophenylhydrazone are 144° C and 247° C. The literature boiling point for benzophenone is 306° C. These observations identify the major reaction component as benzophenone.

The residue from the distillation of the brown oil was recrystallized from a water-ethanol mixture (m.p. $144 - 145^{\circ}$ C). Mixed

melting point with an authentic sample of benzophenone oxime was 144 - 145° C. The residue reacted with bromine in carbon tetrachloride without evolution of hydrogen bromide. Crystals produced melted at 223 - 224° C.

D. Reaction of O-methyl Ether of Benzophenone Oxime
in the Presence of Dicobalt Octacarbonyl

a. Preparation of the O-methyl ether of
benzophenone oxime

Benzophenone (20 gm) (0.11 mole) and O-methyl hydroxylamine hydrochloride (14 gm) (0.195 mole) were refluxed for 4 hours with 20 ml of pyridine and 200 ml of ethanol. The ethanol was then removed under reduced pressure. Slow addition of water with stirring produced crystals. These were recrystallized twice in the following manner. The crystals were dissolved in minimum quantity of acetone and an equal quantity of methanol was added. Water was added till the cloud point was reached. Crystallization was allowed to proceed at 0° C. The yield was 20.0 gm (0.095 mole) (87% of theoretical). This recrystallization procedure was taken from Hauser and Hoffenberg (20).

b. Reaction procedure

The carbonylation reaction was carried out essentially as in previous sections. An amount of 10.5 gm (0.05 mole) of O-methyl ether

of benzophenone oxime and 35 ml (0.026 mole) of catalyst liquor were

used. The total volume of reaction solution was 50 ml. The thermo-

stat was originally set at 180° C. No reaction was apparent at this

temperature so the temperature was raised in 10 degree steps to 220° C

maintaining the temperature for 6 or 7 minutes at each level. Heating

was continued at 220° C for 71 minutes; after cooling the overall

pressure drop was 120 p.s.i. measured at 0° C. This represents 0.065

mole of carbon monoxide or 1.3 moles per mole of substrate. A detailed

plot of pressure versus time at constant temperature is shown on page

73.

c. Separation and identification of products

The product was a homogeneous benzene solution. The benzene

was removed under reduced pressure to produce a yellow distillate from

which a very few orange crystals separated which had the appearance of

dicobalt octacarbonyl. The residue was a dark tarry material. This

material was sludged with cold chloroform to produce 50 ml of a brown

chloroform solution and a residue which contained organic material and

cobalt. Seven ml of this solution were evaporated and dissolved in

benzene then placed on a column (50% alumina and 50% celite) (3 cm

diameter x 6 cm) for chromatography. The first 100 ml of benzene eluent

produced a brown oil which on warming in light petroleum ether became

insoluble in petroleum ether or benzene. This material failed to melt

and gave a positive test for cobalt. Further elution with benzene pro-

duced nothing. Elution with ethanol produced a similar oil which also

Total Reaction Pressure Corrected To 0°C For O-Methyl Ether of Benzophenone Oxime. 0.05 Moles Substrate — 0.026 Moles Catalyst. Note: Corrected for Vapour Pressure of Benzene.
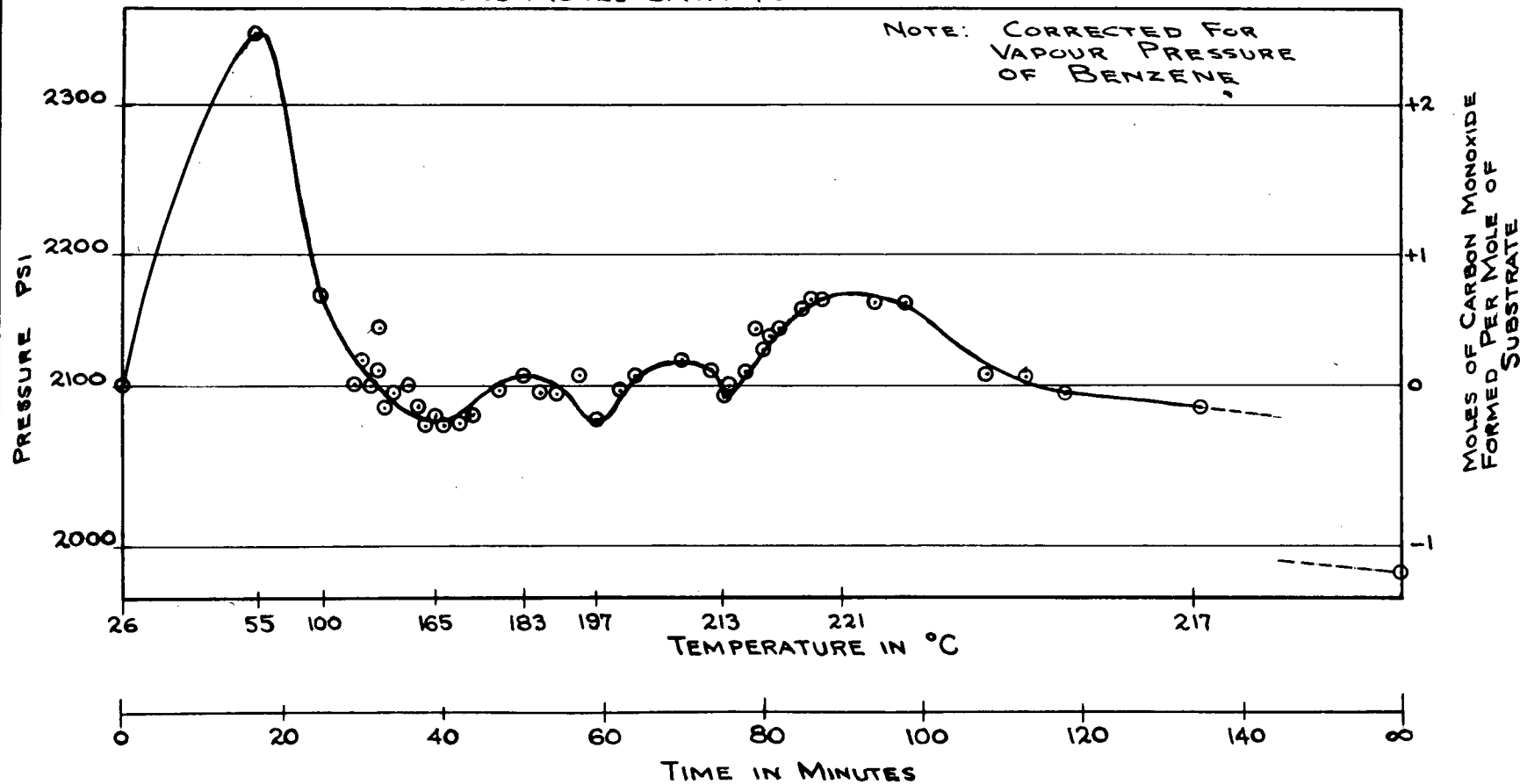
contained cobalt. Material (20 mgm) crystallized from the ethanol
solution of m.p. 220 - 222° C. The residue from the chloroform ex-
traction was treated with cold benzene. A blue solution was obtained
and a violet residue. On evaporation of the solution white crystals
covered with a deep blue oily material resulted. Cold acetone dissolved
the blue color completely leaving some white crystals. The acetone was
evaporated to leave a blue oily material which burned brightly on an
ignition test leaving a black residue. The residue contained cobalt.
The infrared spectrum of this material failed to show a high frequency
absorption which could be associated with the carbonyl stretching
frequency of a cobalt carbonyl compound. This oil was soluble in organic
solvents (acetone, benzene, chloroform, alcohols) and soluble without
effervescence in concentrated hydrochloric acid. An acetone solution
of the oil was allowed to crystallize at 0° C. The crystals which were
produced melted at 217 - 222° C. These were shown identical to
3-phenylphthalimidine after recrystallization.

The residue from the cold benzene extract was now treated with
hot chloroform to give a green solution and a violet residue. The
residue seemed to contain no organic material but did contain cobalt.
The above chloroform and benzene solutions were evaporated to yield
7 gm of light brown organic material m.p. 200 - 217° C. A warm benzene
extraction dissolved 2.7 gm leaving a residue of 4.3 gm. A 10% aliquot
of the benzene solution was chromatographed on an alumina column (9 cm
x 3 cm). The column retained a narrow brown band at the top and pro-
duct appeared very slowly on benzene elution. Each fraction collected

melted in the range 210 - 217° C. These fractions were combined and recrystallized from methanol and benzene. Their m.p. was 222 - 224° C. after recrystallization. Mixed m.p. and preparation of acetate derivative (m.p. 153 - 154° C) proved this compound to be 3-phenylphthalimidine. A total of 0.25 gm was recovered from the column. Ethanol elution produced 150 mgm of a component m.p. 210 - 250° C (material V). The column was then washed with 500 ml of acetone. A light brown fluid (7 gm) was obtained which was obviously not a product of the original reaction. This fluid reacted instantaneously with ice cold 2% aqueous potassium permanganate and with bromine in carbon tetrachloride. The boiling point of this material was 163 - 166° C (corrected). Literature for di-acetone alcohol is 164 - 166° C. All solvents which had been used were evaporated down to try to reproduce this liquid without success.

Material V (150 mgm) (the high melting fraction) was now rechromatographed. Benzene elution produced 140 mgm melting 219 - 222° C. Alcohol elution produced 1 mgm of material melting 218 - 300° C.

This last 1 mgm is apparently the only organic compound present which is not 3-phenylphthalimidine.

IV. BIBLIOGRAPHY

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