THE ACTION OF Carbon Monoxide AND 
HYDROGEN ON DEOXYBENZOIN OXIME AND ON 
2-ACETONAPHTHONE OXIME

by

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A THESIS SUBMITTED IN PARTIAL FULFILMENT OF THE 
REQUIREMENTS FOR THE DEGREE OF 

MASTER OF SCIENCE 

in the Department 
of 

Chemistry 

We accept this thesis as conforming to the required standard 

THE UNIVERSITY OF BRITISH COLUMBIA 

May, 1959
ABSTRACT

When deoxybenzoin oxime was reacted with carbon monoxide and hydrogen in the presence of dicobalt octacarbonyl at elevated temperatures and pressures 3-benzylphthalimidine and 3-phenyl-3,4-dihydroisocarbostyryl were produced.

When 2-acetonaphthone oxime was reacted under similar conditions 2-(α-naphthyl)-4-methylbenzo[h]quinoline, 3-methylbenzo[f]phthalimidine and 1-(α-naphthyl)ethylurea were produced. Verification of the structure of 2-(α-naphthyl)-4-methylbenzo[h]quinoline was attained in part through the hydrochloride salt, the methiodide salt, the picrate derivative and the 2-(α-naphthyl)-4-formylbenzo[h]quinoline derivative. 2-(α-Naphthyl)-4-methylbenzo[h]quinoline was also synthesized by reacting 2-acetonaphthone oxime with 2-acetonaphthone at elevated temperatures.

The infrared spectra of the above compounds are described.
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Date April 15, 1959.
ACKNOWLEDGEMENT

I wish to express my sincere thanks to Dr. A. Rosenthal for his patience, advice and encouragement in the direction of this research project.
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I. HISTORICAL

(a) **High Pressure Reactions of Carbon Monoxide with Nitrogen Containing Compounds**

A considerable amount of investigative work has been done on both a purely scientific and a commercial basis on a study of carbon monoxide and hydrogen with olefins. An excellent review of this work has been presented by Wender, Sternberg and Orohin (21).

To the best knowledge of the author there is only one recent paper by other workers (48) on a study of the reactions of carbon monoxide and hydrogen with organic compounds containing the C=N system yielding reduced products but giving no addition with carbon monoxide. However, several workers have recently investigated the carbonylation of a few organic compounds containing the N=N, the C=N and the C-N groupings. In 1949 Buckley and Ray (12) reported that they reacted carbon monoxide with aniline to produce a cross linked polymer containing varying amounts of oxygen in the hydroxyl form and having all its nitrogen in the primary amino form. They also investigated the ability of carbon monoxide to act as a reducing agent (13). Nitrosobenzene and azoxy-
benzene were reduced to azobenzene, N-phenyl-
hydroxylamine was reduced to aniline, and N-phenyl-
benzaldehyoxime was reduced to benzylideneaniline.

Work of a commercial nature has been done in
the preparation of amides from carbon monoxide, olefins,
and amines (49, 51, 52) and formamide has been success­
fully prepared from ammonia and carbon monoxide (41).

Tyson and Shaw in 1952 (68) prepared 3-indole-
carboxaldehyde from carbon monoxide and the potassium
salt of indole. They did not produce any N-formylated
products of indole but in 1956 (63) they produced N-
formylindoline in good yield from both carbon monoxide
and potassium indoline. From this they deduced that
likely the N-formyl form of indole is produced but
that this very readily isomerizes to the 3-carboxal-
dehyde form.

Prichard in 1956 (53) cyclized the aromatic
amide N,N-dibenzoylaniline with carbon monoxide at
325°C. using nickel carbonyl as the catalyst. N-
phenylphthalimidine and benzene were produced.

Similarly an equimolar mixture of benzonitrile and
benzoic acid, which react to form dibenzamide above 250°C. (17), when heated at 325°C. with carbon monoxide and nickel carbonyl gave phthalimide.

In 1955 Murahashi (46) heated benzaldehyde anil in benzene with dicobalt octacarbonyl and 100-200 atmospheres carbon monoxide at 220-230°C. for 5-6 hours. 2-Phenylphthalimididine was obtained in 80% yield. In a similar way p-hydroxybenzaldehyde anil yielded 70% 6-hydroxy-2-phenylphthalimididine.

\[
\begin{align*}
\text{N} & \text{N} \\
\text{C} & \text{C} \\
\text{O} & \text{O}
\end{align*}
\]

\(\approx\)-Naphthaldehyde anil afforded 2-phenylbenzo[\(e\)]-phthalimididine in 96% yield. \(\beta\)-Naphthaldehyde anil yielded 2-phenylbenzo[\(f\)]phthalimididine. The fact that ring closure occurred in the 3-position of the naphthalene moiety is noteworthy since most ring closure reactions of \(\beta\)-substituted naphthalene derivatives

\[
\begin{align*}
\text{N} & \text{N} \\
\text{C} & \text{C} \\
\text{O} & \text{O}
\end{align*}
\]
take place in the 1- or 8-position.

In 1956 Murahashi and Horiie (47) reacted azobenzene with carbon monoxide at 150 atmospheres and 190°C. to form indazoline. At 230°C. an additional mole of carbon monoxide was absorbed per mole of indazoline and the product formed was 3-phenyl-2,4-dioxo-1,2,3,4-tetrahydroquinazoline. That this compound proceeded through indazoline was shown

![Chemical structure](attachment:image.png)

by the fact that the indazoline reacted with carbon monoxide at 230°C. to give 3-phenyl-2,4-dioxo-1,2,3,4-tetrahydroquinazoline in quantitative yield. Similar conversion to the analogues of the above compounds were carried out with 4-chloroaazobenzene and 4-dimethylaminoazobenzene. In the case of the substituted azobenzenes ring closure occurred on the ring containing the substituent.
In 1958, Prichard (54) prepared N-substituted phthalimidines from N-substituted imines of carbocyclic aromatic ketals. For example, he prepared 2-phenylphthalimidine from N-benzylidene aniline and he also prepared the following derivatives of phthalimidine: 6-MeO, 6-Cl, 3-Me, 3-Ph, 6-Me₂N, 2-Me, 2-(1-naphthyl), 2-(p-diethylaminophenyl), and N,N'-ethylenediphthalamidine.

In 1958 Nakamura and Hagihara (48) hydrogenated Schiff bases in the presence of carbon monoxide, hydrogen and dicobalt octacarbonyl at elevated temperatures and pressures. They reduced benzalphenylimine (PhCH=NPh), benzalcylohexylimine (PhCH=NC₆H₁₁), cyclohexanophenylimine (C₆H₁₀=NPh) cyclohexancyclohexylimine (C₆H₁₀=NC₆H₁₁), and cyclohexalcylohexylimine (C₆H₁₁CH=NC₆H₁₁) to secondary amines. The Schiff bases which were the most conjugated were the most easily reduced and formed the lowest amounts of resinous by-products. Nonpolar solvents gave the highest yields with cyclohexane giving higher yields than benzene which, in turn, gave higher yields than did dioxane. Sulphur compounds did not retard the reaction although amines, especially the aliphatics, lowered the yields
considerably.

Although recent work was reported in the study of imines and azo compounds in their reaction with carbon monoxide no work was reported outside that of Rosenthal and Astbury (55) for the reaction of carbon monoxide and hydrogen with oximes. In 1958 they found that benzophenone oxime reacted with carbon monoxide and hydrogen to yield 3-phenylphthalimidine in 80% yield. Cyclization of the oxime with carbon monoxide took place when the ratio of carbon monoxide to hydrogen was large (98:2). O-Benzoylbenzoic acid oxime also gave 3-phenylphthalimidine in almost quantitative yield and, hence, showing that under the conditions of the reaction decarboxylation had taken place.

When acetophenone oxime reacted with carbon monoxide in the presence of hydrogen and dicobalt octacarbonyl a syrup was obtained which was separated into three fractions by alumina chromatography. The first fraction (10%) contained no carbonyl group and was not worked with further. Chemical analysis of
one of the other fractions indicated that two moles of acetophenone oxime had condensed with a mole of hydrogen and a mole of carbon monoxide to yield a dimer which lost a mole of hydroxylamine. This compound failed to give a derivative with 2,4-dinitrophenylhydrazine although it showed a strong carbonyl peak at 1700 cm$^{-1}$ in its infrared spectra. The third fraction recovered from the reaction mixture was identified as 3-methylphthalimidine by comparison with an authentic sample.

(b) Oximes

An aldehyde or ketone with the structure R-TC=O when treated with hydroxylamine gives a single oxime if the radical groups R and T are identical. However, if the two groups R and T are different it turns out in most cases that two isomeric oximes can be detected (1, 7, 27). An explanation put forward by Hantzsch and Werner (29, 30) states in effect that the two isomers were stereoisomers of an ethylenic nature as postulated in formulas I and II. The nitrogen atom

\[
\begin{array}{c}
\text{R-C-T} \\
\text{N-OH} \\
\text{I}
\end{array} \quad \begin{array}{c}
\text{R-C-T} \\
\text{HO-N} \\
\text{II}
\end{array}
\]

like the carbon atom is tetrahedral but differs from
the carbon atom in having an unshared pair of electrons at one of the apices of the tetrahedron rather than an atomic or molecular group (72). That this is the most satisfactory structure explaining the isomerism of the oximes is explained in considerable detail in "Advanced Organic Chemistry" by Wheland (72).

An important reaction for determining the configuration of oximes is the so-called Beckmann rearrangement (4, 5, 6). When a ketone oxime is treated with a reagent such as phosphorus pentachloride, acetyl chloride or sulphuric acid a rearrangement takes place to give a substituted amide. The arrangement is believed to take place in two steps. First, the hydroxyl group exchanges places with one of the radicals joined to the oxime carbon and the resulting lactim form rearranges to the lactam form (72). There is considerable evidence to support a trans rearrangement rather than a cis one (43, 45). The hydroxyl group on the nitrogen exchanges places with the radical anti to it on the oxime carbon.

Due to the stereoisomerism of the oximes it is to be expected that 2-acetonaphthone oxime itself could form two isomers when the oxime is prepared from
the ketone (61). The ratio of the two forms was found by Bachman and Barton (2) to be 99:1 with the naphthyl group anti to the hydroxyl group being the predominant isomer. The oxime was prepared from the ketone with the aid of hydroxylamine hydrochloride in pyridine. A Beckmann rearrangement was carried out on the oxime produced and the resulting amide hydrolysed. Relative proportions of amines and acids present gave the proportion of the oximes originally present.

Little seems to have been done to investigate the isomerism of deoxybenzoin oxime. A Beckmann transformation done by Stephen and Bleloch (64) using thionyl chloride gave for the rearranged product phenylacetanilide. No mention was given that any N-phenylphenylacetamide, which would be the other amide for the other oxime isomer, was found. Hence, the original oxime must have been syn-phenylbenzyl-ketone oxime and the reaction was as follows:

\[
\begin{align*}
\text{CH}_2 - \text{C} \quad &\text{N(OH)} \\
\text{NOH} &\to \quad \text{C} - \text{NHCH}_2 - \text{C}
\end{align*}
\]
(c) Cobalt Complexes of Oximes and other Organic Bases

Glyoximes and alkyl derivatives of glyoximes have been known for a long time to react with metallic salts including cobalt salts. For example, Tschagaeff in 1906 (67) prepared the compound \((HON=CMeCMe=NO)_2\) - \(\text{CoNH}_3\text{Br}\) from dimethyl-glyoxime. Many other salts of glyoximes have been prepared and considerable research has gone into these complexes in order to elucidate their structure and also as agents in the detection and separation of metallic salts. An example of the use of glyoximes is in the detection of nickel salts by the precipitation of the red precipitate of nickel dimethyl-glyoxime (69).

Not only do the glyoximes form metallic salts but other compounds related to them do also. Oximes which form metallic complexes are the benzil monoxime (26,44), monomethyl ether of benzil glyoxime (33), \(o\)-hydroxybenzaldoxime (9), oxime hydrazone of benzil (66), and \(\beta\)-furfuraldoxime (ll). It will be noticed that in all cases the oxime is adjacent to a functional group of some kind. Examples of where this was not the case were offered by Hieber and Leutert (33) who successfully prepared both the nickel and the cobalt salts of acetaldehyde oxime, isobutyraldehyde oxime,
benzaldehyde oxime and cinnamaldehyde oxime. They found that four moles of oxime complexed with one mole of cobalt(II)halide. Less success was shown with ketone oximes (34). Cobalt chloride did not react with acetone oxime in aqueous solutions although suspensions of cobalt chloride in inert solvents became an intense blue when acetone oxime was added. No compound was isolated. When antibenzaldehyde oxime was reacted with cobalt halides the oxime rearranged to the syn form showing that metal salts can have an influence on the geometrical isomerism of the oximes (33, 35).

Up to date there is no published knowledge of any complex which may form between dicobalt octacarbonyl and oximes. However, recent work shows that cobalt carbonyls react with N-bases leading in general to a definite compound of polar structure as follows (36):

\[ 3[\text{Co(CO)}_4]_2 + 12B \rightarrow 2[\text{CoB}_6][\text{Co(CO)}_4]_2 + 8\text{CO} \]

The bases used were \( \alpha \) and \( \beta \) picoline, quinoline, pyrrolidine, morpholine, ethyleneimine, formamide, diacetyl-dianiline (a Schiff base), diethylenetriamine and aromatic amines. Diacetyl-dianiline complexed with the cobalt catalyst in the ratio of 1:2 rather
than 1:4 to give the following structure:

\[
\begin{bmatrix}
\text{C}_6\text{H}_5 & \text{Co} & \text{C}_6\text{H}_5 \\
\vdots & \vdots & \vdots \\
\text{N} = \text{C} - \text{CH}_2 & \text{N} = \text{C} - \text{CH}_2 & 3 \\
\text{C}_6\text{H}_5
\end{bmatrix}
\]

\[\left[\text{Co(CO)}_4\right]_2\]

Diethylenetriamine, on the other hand, complexed with dicobalt octacarbonyl according to the generalized structure \(\text{CoB}_2[\text{Co(CO)}_4]_2\).

The above workers also prepared cobalt carbonyl complexes with oxygen containing bases (37). For example, acetophenone reacted with the metal carbonyl according to the following equation:

\[3[\text{Co(CO)}_4]_2 + \text{C}_6\text{H}_5\text{COCH}_3 \rightarrow \frac{2}{3}[\text{Co(C}_6\text{H}_5\text{COCH}_3\text{)}_2] \left[\text{Co(CO)}_4\right]_2 + 8\text{CO}\]

Benzophenone complexes to give the following structure:

\[3[\text{Co(CO)}_4]_2 + \frac{1}{2}\text{C}_6\text{H}_5\text{COC}_6\text{H}_5 \rightarrow \frac{2}{3}[\text{Co(C}_6\text{H}_5\text{COC}_6\text{H}_5\text{)}_2] \left[\text{Co(CO)}_4\right]_2 + 8\text{CO}\]
II. DISCUSSION

(a) **Reaction of Carbon Monoxide and Hydrogen with Deoxybenzoin Oxime**

When deoxybenzoin oxime was reacted with carbon monoxide and hydrogen (98.5:1.5) in the presence of preformed dicobalt octacarbonyl (71) at 3600 p.s.i. and 250°C, two crystalline products were obtained. The minor crystalline product (16%) was isolated by fractional crystallization of the products with ethanol. The crystalline product so obtained was purified by subsequent recrystallization from ethanol to give colorless needle-like crystals, m. 202-203°C. On the basis of chemical and infrared analysis the product was concluded to be 3,4-dihydro-3-phenylisocarbostyril. The absorption peak at 3250 cm$^{-1}$ is attributed to a bonded N-H stretch frequency for a N-monosubstituted amide (70) and the peak at 1670 cm$^{-1}$ is attributed to a cyclic secondary amide (19).

The major component was obtained by chromatographing the remainder of the product on an alumina column and recrystallizing the chromatographed product from ether-light petroleum ether. A mixed melting point of this sample with 3-benzylphthalimidine (26) gave no melting point depression and, hence, the
product was concluded to be 3-benzylphthalimidine.

The overall equation for the reaction was as follows:

\[
\begin{array}{c}
\text{CH}_2 - C - \text{NOH} \\
\text{CH}_2 - \text{NH} \quad \text{NH} \\
\end{array}
\]

(b) Reaction of Carbon Monoxide and Hydrogen

with 2-Acetonaphthone Oxime

When 2-acetonaphthone oxime was reacted with carbon monoxide and hydrogen in the presence of pre-formed dicobalt octacarbonyl (71) at 4100 p.s.i. and 235°C, three crystalline products were obtained. The major product was the unexpected compound 2-(3-naphthyl)-4-methylbenzo[h]quinoline (A) present in 41% yield. The second compound was the expected (46, 55) 3-methylbenzo[f]phthalimidine (B) present in 17% yield. The third component (19%) appeared to be an unstable one which changed in a short time into the stable crystalline compound C the identity of
which is, at present, still unknown. (See p. 62).

The overall reaction was as follows:

\[ \text{CH}_3 \]

\[ \text{C} \equiv \text{NOH} \]

\[ \text{Co}_2(\text{CO})_6 \]

\[ \text{CO} \]

\[ \text{H}_2 \]

\[ \text{C} \]

Unstable Compound

Compound A was a white crystalline compound and could be recrystallized from either ethanol or ligroin. It fluoresced with an intense blue light in the presence of ultraviolet radiation.

Elemental analysis showed the empirical formula of product A to be C_{24}H_{17}N. Infrared spectra indicated the absence of the N-H bonding system and the presence of an imine linkage conjugated to an aromatic system (Peak at 1623 cm \(^{-1}\)) \((28, 40, 70)\). Ultraviolet spectroscopy indicated that the compound had a phenanthradine type structure. When the ultraviolet spectrum of A was compared with the ultraviolet spectra of phenanthrene and 2,4-dimethylbenzo[h]-quinoline \((39)\) there was a peak at 3450 angstroms for
product A corresponding to peaks of 3460 Å for phenanthrene and 3480 Å for 2,4-dimethylbenzo[h]-quinoline, and also a peak at 3220 Å for product A corresponding to a peak of 3220 Å for phenanthrene (See figure 1; p.25a).

Pyridine and quinoline derivatives form salts with strongly proton donating solvents (20) and product A formed brightly coloured salts with sulphuric acid, formic acid and hydrochloric acid. When the hydrochloride salt was dissolved in aqueous ethanol and titrated against base a molecular weight close to the theoretical value was obtained.

Further verification of a benzoquinoline structure was obtained because of the failure of the compound to reduce in the presence of either magnesium methoxide (73) or lithium aluminum hydride (8). An attempt at oxidation with potassium ferrocyanide (58) failed to affect the molecule. The imine linkage showed great chemical stability in that attempted degradation of the molecule with fused sodium hydroxide (16) at 250°C for six hours gave back most of the unchanged products thus confirming further that the imine linkage was part of a heterocyclic system.

When the compound was subjected to oxidation with chromic acid in acetic acid a bright orange
product was obtained in low yield which proved to have no acidic function and slowly reddened in the presence of sunlight. Treatment with strong base gave rise to immediate blackening. This was the same kind of behaviour as that observed by Johnson and Matthews (39) in their attempt to oxidize 2,4-dimethyl-benzo[g]-quinoline with chromic acid in acetic acid. They also obtained an orange product which they proved to be a quinone and this quinone reddened in the presence of sunlight and gave intractable decomposition products in the presence of strong base. On the basis of the results of the chromic acid oxidation of product A a quinone had been formed and, hence, the original compound was a condensed aromatic or heterocyclic system. That the system was heterocyclic was indicated by the presence of nitrogen in the obtained oxidized product. Any attempts to oxidize product A with chromic acid past the quinone stage met with failure, the failure being consistent with that of Seitz (62) who attempted to oxidize both 2-methylbenzo[g]quinoline and 2-methylbenzo[h]quinoline to pyridine carboxylic acid derivatives using chromic acid without success.

An attempt was made to convert product A into the known compound 2-((β-naphthyl) benzol[h]quinoline (15) by removal of the methyl group by a series of
oxidation steps as follows:

\[
\begin{array}{c}
\text{Np} \\
\text{CH}_2
\end{array}
\quad \xrightarrow{\text{SeO}_2} 
\begin{array}{c}
\text{Np} \\
\text{CHO}
\end{array}
\]

\[
\begin{array}{c}
\text{Np} \\
\text{J}
\end{array}
\quad \triangle 
\begin{array}{c}
\text{Np} \\
\text{COOH}
\end{array}
\]

The product was oxidized at the methyl position with the aid of selenium dioxide (14) to give 2-[(β-naphthyl)-4-formylbenzo[h]quinoline (G). This oxidized product was a bright yellow crystalline solid, m. 139-142.5°C, which by elemental analysis agreed in composition to the postulated structure. It showed the behaviour of an aromatic aldehyde by rapidly reducing Tollens's reagent but not Fehling's and by showing a strong infrared peak at 1700 cm\(^{-1}\), a characteristic frequency of aromatic aldehydes (37, 38). The oxime derivative was prepared melting in the range 170-185°C. without attempt at purification.

Oxidation of the obtained aldehyde was then
attempted with the use of an ammoniacal solution of silver oxide (14) to prepare the known compound 2-(\(\beta\)-naphthyl)-4-carboxybenzo[h]quinoline (H), m. 227-228°C. (15). A compound was obtained melting over the range 220-262°C. without purification.

The 2-(\(\beta\)-naphthyl)-4-carboxybenzo[h]quinoline is easily decarboxylated to 2-(\(\beta\)-naphthyl)-benzo[h]-quinoline (J), m. 117°C., by heating under vacuum. The compound obtained by oxidizing the aldehyde with selenium dioxide was heated under reflux in ethanol and chromatographed to give back some of the original aldehyde plus small amounts of white crystalline product, m. 35-50°C. It is felt that the wanted heterocyclic compound may be present but in an impure form.

An attempt to oxidize the aldehyde with nitric acid was unsuccessful leading only to intractable decomposition products.

On the basis of all the above evidence it was concluded that product A must be 2-(\(\beta\)-naphthyl)-4-methylbenzo[h]quinoline and that it was formed independently of the presence of carbon monoxide as follows:
Since it was postulated that this compound could be produced independently of the presence of carbon monoxide and probably even that of the dicobalt octacarbonyl itself, the two compounds, 2-acetonaphthone and 2-acetonaphthone oxime were mixed in equimolar amounts in benzene and placed in an autoclave which was evacuated and the whole heated at 235°C. for 90 minutes. A colourless crystalline compound was isolated identical to product A on the basis that it gave no melting point depression with product A and that it gave an identical infrared spectrum. Hence, the compound must be 2-(8-naphthyl)-4-methylbenzo[h]quinoline.

On the basis of the above mechanism it follows that 2-acetonaphthone must be produced. Attempts to find this ketone were unsuccessful. However, isolation of a ketone after the subjection of an oxime to the experimental conditions of carbonylation is
known. For example, J. O'Donnell has successfully proved the presence of benzophenone in the reaction mixture recovered after the carbonylation of benzophenone oxime had taken place \( (56) \). That no 2-acetonaphthone was found could be explained on the basis that under the conditions of reaction the ketone would be highly reactive and would immediately condense with 2-acetonaphthone oxime to form product A as soon as it was formed.

It was concluded that product B was the expected 3-methylbenzo[f]phthalimidine. Infrared analysis indicated the presence of the cyclic amide, the characteristic peak for the N-H stretching frequency for an amide at 3280 cm\(^{-1}\) \( (18) \) and the characteristic peak for the carbonyl of the amide at 1638 cm\(^{-1}\) \( (19) \) both being present. The absence of an unsaturated tricyclic system was shown by the absence of absorption in the ultraviolet above 3300 Å \( (39) \). Elemental analysis gives an empirical formula consistent with the proposed structure of compound B (see p. 15).

That the N-H bond was present was further substantiated by the acetylation of product B. That acetylation was successful was apparent due to the disappearance of the infrared peak for the N-H stretching frequency and the shift in the carbonyl frequency to 1695 cm\(^{-1}\). The acetylated product was not successfully crystallized.
Work previously done further substantiates the proposed structure. Since acetophenone oxime formed 3-methylphthalimidine and benzophenone oxime formed 3-phenylphthalimidine in the presence of carbon monoxide, hydrogen and diocobalt octacarbonyl at elevated temperatures and pressures (55), and since Murahashi (46) prepared the linear isomer \( N \)-phenylbenzo[\( f \)]phthalimidine rather than the angular isomer by carbonylating 8-naphthaldehyde anil it was concluded that product B was 3-methylbenzo[\( f \)]phthalimidine.

A syrup F recovered from the reaction mixture appeared to have polarity properties very similar to B on the basis of similar solubility and chromatographic properties but it was concluded that this product was not the angular isomer of B due to the wide differences in carbonyl frequencies in the infrared spectra of both B and F being at 1690 cm\(^{-1}\) for F.

When the original reaction mixture was dissolved in chloroform and the cobalt removed there resulted a dark green solution which upon standing overnight became brown and a white residue was deposited. This residue gave a positive ferric chloride test for a hydroxyl group and it appeared to slowly decompose even under vacuum, at 10\(^{0}\)C., and in the absence of sunlight giving off a putrescent type
of odour. Purification of the resultant degredative product by chromatography gave rise to a white crystalline compound C which appeared to be stable. The crystalline product C gave no ferric chloride test and so it appeared that the hydroxyl function disappeared.

Elemental analysis of product C showed that an extra carbon and an extra nitrogen had been added to the reactant. Infrared showed a strong carbonyl peak at 1650 cm.\(^{-1}\) (19) and a strong N-H peak for an N-substituted amide at 3230 cm.\(^{-1}\) (18) showing that the compound was likely a cyclic amide. Two strong peaks of equal intensity at 3435 cm.\(^{-1}\) and 3350 cm.\(^{-1}\) (42) also appeared which may be attributed to a hydroxyl or a N-H function or probably both. However, the application of the Hinsberg test (59) using benzene-sulfonyl chloride indicated the absence of either a primary or a secondary amine group. Furthermore, the compound behaved indifferently in the presence of strongly proton donating solvents thus confirming the absence of an amino group. That no hydroxylamine group was present was verified on the basis that no result came from the attempt to oxidize C with mercuric oxide (31). When a hydroxylamine compound is oxidized with mercuric oxide a bright blue or green
solution appears due to the nitroso group and mercury metal is also deposited. Ultraviolet analysis indicated that compound C did not contain an unsaturated tricyclic system as shown by compound A.

What has apparently happened is that the reaction of the carbon monoxide on the oxime produced a mixture of compounds, one of which was a nitroso compound (blue-green in colour) which was unstable and in a few days changed into colourless nitrogen rich amide C. No further attempt was made at this stage to elucidate the identity of either the nitroso compound or the product C.

Infrared spectra were taken on the remaining two components of the reaction mixture, D and E, and it was found that a carbonyl frequency of 1710 cm$^{-1}$ (10) existed for E, but that D possessed no carbonyl frequency in its infrared spectrum. The infrared also showed an absence of the N-H function in both components. No further work was done on these two components because of the small amount of each present.

Although oximes undergo a Beckmann rearrangement under the influence of an acid catalyst no evidence was brought forward that a Beckmann rearrangement had occurred in the reaction of 2-acetonaphthone oxime with carbon monoxide and hydrogen in the presence
of diocobalt octacarbonyl.

It was not a simple matter to isolate and purify the components of the reaction. Much painstaking work was required using both column chromatography and fractional crystallization to separate the mixture into its components and to purify the components. The presence of one component affected both the recrystallizing and chromatographic properties of another component making separation and purification a major problem. (See fig. 3, p. 36 for the initial separation of the mixture into its components).

Interesting kinetic results were obtained in following the reaction of carbon monoxide and hydrogen with 2-acetonaphthone oxime at 195° C. At this temperature (see fig. 2, p. 25b ) there was a sudden rise in pressure corresponding to a mole and a half of gas released per mole of substrate. Immediately following this rise there was a drop in pressure taking place at a slower rate equal in magnitude to the rise in pressure. After the bomb had cooled it was noticed that a drop in pressure had taken place and by simple calculation it was found that the drop in pressure was equal in molar magnitude to the changes in pressure that took place at 195° C.
Fig. 1 - Ultraviolet Absorption Spectra of:

1) 2-(\(\beta\)-Naphthyl)-4-methylbenzo[h]quinoline
2) 2,4-Dimethylbenzo[h]quinoline (39)
3) Phenanthrene (39)
Fig. 2 - Plot of Pressure against Time for Reaction of 2-Acetonaphthone Oxime with Carbon Monoxide and Hydrogen at 195°.
III. EXPERIMENTAL

Instrumentation

The high pressure reactions were carried out in an Aminico Superpressure rocker reaction vessel having a void of 280 ml. The infrared spectra were obtained using a Perkin - Elmer model 21 Recording Infrared Spectrophotometer. The ultraviolet absorption spectra were obtained using a Cary Recording Quartz Spectrophotometer. The melting points were determined by means of a polarizing 100 X microscope attached to an electrically heated E. Leitz (Wetzlar) melting point block.

Reagents

Deoxybenzoin and 2-acetonaphthone of reagent grade purchased from Eastman Kodak Company were used. Hydroxylamine hydrochloride of reagent grade was used. Pure thiophene free benzene was prepared by the method of Fieser (25). The carbon monoxide, obtained from The Matheson Co., East Rutherford, N. J., contained 1.5% hydrogen. The hydrogen used was obtained from The Canadian Liquid Air Co. Ltd. of Vancouver, B. C. in 99.7% purity. The aluminum oxide used for the chromatography was procured from the British Drug Houses (Canada) Ltd., Toronto 14.
Chemical analysis

Microanalyses were done by Dr. A. Bernhardt, Mikroanalytisches Laboratorium, im Max-Planck-Institut für Kohlenforschung, Mülheim (Ruhr), Germany. Both elemental analysis and molecular weight determinations (Rast Method) were done.

Preparation of dicobalt octacarbonyl

Dicobalt octacarbonyl was prepared by the method of Wender, Greenfield and Orchin (71). To a glass liner was added 18 g. cobalt(II)carbonate and 60 cc. dry thiophene free benzene. The liner was placed in an autoclave (effective void 280 cc.) and carbon monoxide was run in up to 1660±10 p.s.i. followed by hydrogen up to 3230±10 p.s.i. The autoclave was heated and rocked for 60 minutes at 160°C. where a maximum pressure of 4820±10 p.s.i. was attained. Upon cooling to room temperature the pressure dropped to 2350±10 p.s.i. or a difference in pressure of 860±10 p.s.i. The dark solution was stored at -12°C. in a stoppered container in order to hinder the slow decomposition of the catalyst.
(a) The Reaction of Carbon Monoxide and Hydrogen with Deoxybenzoin Oxime

Preparation of deoxybenzoin oxime

Into 50 ml. water was dissolved 15 g. (0.21 m.) hydroxylamine hydrochloride and the aqueous solution neutralized with 67 ml. 10% aqueous sodium hydroxide. To the solution was added 30 g. (0.135 m.) deoxybenzoin and a homogeneous mixture obtained by the addition of 1050 ml. 95% ethanol. The reaction vessel was allowed to stand at room temperature for six days after which the solution was diluted with 2000 ml. water to bring down a copious white precipitate. The precipitate was filtered and repeatedly washed with water. Recrystallization of the oxime from a water ethanol mixture gave 23.9 g. (75%) of the oxime having a melting point of 97-99°C. Literature m.p. 98°C. (65).

Reaction of carbon monoxide with deoxybenzoin oxime

Deoxybenzoin oxime (15.8 g.; 0.0635 m.) was mixed with 23 ml. [0.02 m. Co₂(CO)₈] catalyst liquor and the whole diluted up to 55 ml. with dry thiophene free benzene in a liner which in turn was placed into the autoclave. Carbon monoxide was run in up to 2000±10 p.s.i. and the whole was heated and rocked for
2 hours at 250°C. whereupon a pressure of 3600±10 p.s.i. was reached. After cooling to room temperature the pressure was 1800±10 p.s.i. or a drop of 200 p.s.i. had occurred.

The product obtained was heated under reduced pressure at 55°C. in order to decompose the catalyst and to remove the solvent. Dissolving the syrup in chloroform and treating with norite to remove the residual cobalt left after evaporating the chloroform 15.9 g. of syrup.

Characterization of the products

Re crystallization of the syrup with the use of 600 ml. anhydrous ethanol at 0°C. for 3 hours led to 2.5 g. of white needlelike crystals (16%). After two more crystallizations from ethanol the compound melted at 202-203°C and was assumed to be 3,4-dihydro-3-phenylisocarbostyryl.

Anal. Calcd. for C_{15}H_{12}NO: C, 80.69; H, 5.87; O, 7.17; N, 6.28. Found: C, 80.32; H, 6.01; O, 7.54; N, 6.19.

Infrared spectrum of 3,4-dihydro-3-phenylisocarbostyryl in Nujol (cm⁻¹): 3250(W), 2920(S), 1670(S), 1600(W), 1528(W), 1450(S), 1375(S), 1245(W), 1150(W), 1070(W), 1028(W), 755(M), 720(M), 695(M).

After removal of the ethanol from the filtrate,
the syrup was triturated with 500 ml. ether to yield a crystalline solid (0.2 g.) which was removed by filtration. Recrystallization of this product from methanol gave a compound melting sharply at 286°C. Because of the low yield of product obtained no further work was done on it.

After removal of the ether by evaporation the syrup was subjected to column chromatography using an alumina column 100 mm. x 38 mm. diameter. A portion of the syrup (0.85 g.) was dissolved in 5 ml. benzene and the solution eluted on the column with benzene. A trace of substance came down and this was discarded. Further elution using benzene-ethanol 99:1 v:v brought down the bulk of the compound in a pale yellow form which when recrystallized from benzene-petroleum ether caused removal of most of the colouration. A further recrystallization from alcohol-water mixture gave a white crystalline compound melting at 135-136°C. A mixed melting point determination with 3-benzylphthalimidine gave no depression (26).
(b) The Reaction of Carbon Monoxide and Hydrogen
with 2-Acetonaphthone Oxime

Preparation of 2-acetonaphthone oxime

Into 150 ml. water was dissolved 40 g. (0.567 m.) hydroxylamine hydrochloride and the aqueous solution neutralized with 150 ml. 10% aqueous sodium hydroxide. To the solution was added 60 g. (0.553 m.) 2-acetonaphthone and a homogeneous mixture obtained by the addition of 950 ml. 95% ethanol. The reaction vessel was allowed to stand at room temperature resulting in the formation of a copious white precipitate in less than three hours. After 15 hours the precipitate was filtered, washed repeatedly with water and recrystallized twice from a water-ethanol mixture to yield 48 g. (73.5%) oxime after drying over phosphorus pentoxide, m. 149-150°C. Literature m.p. 145°C. (3).

Reaction of carbon monoxide with 2-acetonaphthone oxime

2-Acetonaphthone oxime (15.0 g.; 0.08 m.) and 20 ml. catalyst liquor [0.025 moles Co_2(CO)_8] in benzene were added to 40 ml. thiophene free benzene in a liner which was placed in an autoclave. Carbon monoxide was run in up to 2140±10 p.s.i. and the system rocked and heated at 210-235°C. for 50 minutes. After the vessel had cooled the pressure was 1950±10 p.s.i. or a drop of
190 p.s.i. (0.09 moles) had occurred. The benzene solution was heated at 70-80°C. to decompose the catalyst and the solvent was then removed by evaporation. The residual wax was dissolved in chloroform and treated with norite to remove the cobalt after which a dark green solution was obtained. Removal of the chloroform gave 14.1 g. of brown wax.

The above reaction was repeated and pressure readings were recorded and plotted against time at constant temperature (see fig. 2, p. 25b). The autoclave with contents were heated up to 195°C. where a rapid pressure change took place. The readings at 195°C. were as follows:

<table>
<thead>
<tr>
<th>Time</th>
<th>Temperature</th>
<th>Pressure</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 minutes</td>
<td>190°C.</td>
<td>3470 p.s.i.</td>
</tr>
<tr>
<td>1</td>
<td>195°C.</td>
<td>3720</td>
</tr>
<tr>
<td>2</td>
<td>200°C.</td>
<td>3630</td>
</tr>
<tr>
<td>4</td>
<td>198°C.</td>
<td>3650</td>
</tr>
<tr>
<td>5</td>
<td>200°C.</td>
<td>3550</td>
</tr>
<tr>
<td>7</td>
<td>195°C.</td>
<td>3510</td>
</tr>
<tr>
<td>10</td>
<td>195°C.</td>
<td>3470</td>
</tr>
<tr>
<td>11</td>
<td>190°C.</td>
<td>3460</td>
</tr>
</tbody>
</table>

After 20 minutes more heating at 195°C, the
autoclave was allowed to cool. A pressure drop of 190 p.s.i. (0.09 moles) was obtained and 13.8 g. of product removed.

Separation of the Products

After removal of the cobalt from the reaction product obtained at 210-235°C, the product was dissolved in chloroform to give a dark green solution which when allowed to stand overnight at -15°C. turned brown and a white residue C had formed yield 1.6 g., m. 170-205°C, insoluble in benzene, soluble in ethanol.

A portion of the crystalline fraction (0.35 g.) dissolved in 1 ml. pyridine was added to the top of an alumina column (90 mm. x 28 mm. diameter) and developed as follows:

<table>
<thead>
<tr>
<th>Effluent fractions (in millilitres)</th>
<th>Wt. of Fractions (in grams)</th>
</tr>
</thead>
<tbody>
<tr>
<td>700 ml. benzene</td>
<td>Trace of brown oil</td>
</tr>
<tr>
<td>400 ml. 9:1 v:v benzene-ethanol</td>
<td>0.25 g. white crystalline compound C</td>
</tr>
<tr>
<td>600 ml. ethanol</td>
<td>Trace of brown wax</td>
</tr>
</tbody>
</table>

The crystalline product C was further purified by recrystallization from 3-pentanone to give white needle like crystals, m. 204.5-205.5°C.
After removal of the product C from the chloroform solution the chloroform was removed by evaporation and a portion of the residue (7.8 g.) was dissolved in 15 ml. benzene and added to the top of an alumina column (150 mm. x 70 mm. diameter) and developed as follows:

<table>
<thead>
<tr>
<th>Effluent Fractions (in millilitres)</th>
<th>Wt. of Fractions (in grams)</th>
</tr>
</thead>
<tbody>
<tr>
<td>80 ml. Benzene-light pet.ether (1:1 v:v)</td>
<td>0.16 g. pale yellow sweet smelling syrup D</td>
</tr>
<tr>
<td>1000 ml. Benzene-light pet.ether (1:1 v:v)</td>
<td>3.15 g. white crystalline compound A</td>
</tr>
<tr>
<td>1000 ml. Benzene</td>
<td>0.32 g. dark brown wax E</td>
</tr>
<tr>
<td>1700 ml. Benzene - t-BuOH</td>
<td>2.23 g. dark brown wax - mixture (iii) Fig. 3</td>
</tr>
<tr>
<td>900 ml. Benzene-ethanol (1:1 v:v)</td>
<td>1.32 g. pale brown amorphous solid G</td>
</tr>
</tbody>
</table>

Total recovery was 7.2 g. or 92%. It was easy to follow the zones as they were either highly fluorescent in the presence of ultraviolet light or were coloured a yellowish brown or else had both characteristics.

The fourth zone from the column (mixture iii, see fig. 3, p.36) was fractionally crystallized from benzene to yield the white crystalline compound B.
The remaining filtrate (mixture iv, fig. 3) was re-
chromatographed by dissolving 1.64 g. in 7 ml. benzene,
added to the top of an alumina column (140 mm. x 52 mm.
diameter) and developed as follows:

<table>
<thead>
<tr>
<th>Effluent Fractions (in millilitres)</th>
<th>Fractions and weight (in grams)</th>
</tr>
</thead>
<tbody>
<tr>
<td>150 ml. benzene-ether (7:3 vv)</td>
<td>0.10 g. sweet smelling oil</td>
</tr>
<tr>
<td>1000 ml. benzene-ether (7:3 vv)</td>
<td></td>
</tr>
<tr>
<td>900 ml. benzene-ether (7:3 vv)</td>
<td>0.94 g. brown amorphous solid B</td>
</tr>
<tr>
<td>1000 ml. benzene-ether (7:3 vv)</td>
<td>0.08 g. brown amorphous solid F</td>
</tr>
<tr>
<td>1000 ml. benzene-ether-ethanol (69:30:1 vvv)</td>
<td>0.40 g. brown amorphous solid F</td>
</tr>
<tr>
<td>500 ml. ethanol</td>
<td>0.08 g. brown amorphous solid</td>
</tr>
</tbody>
</table>

Again, as above, the zones could be followed
by ultraviolet light. Total yield was 1.60 g. or 97%.

Characterization of 2-(6-naphthyl)-4-methylbenzo[h]-quinoline (Compound A)

2-(6-naphthyl)-4-methylbenzo[h]quinoline came
down as the second chromatographic zone (41%) on an
alumina column and was purified further by recrystall-
ization twice from absolute ethanol to give colourless
Fig. 3 - Separation of the 2-Acetonaphthone Oxime Reaction Products

Mixture (i) and catalyst in benzene

Decomposition of catalyst and removal by aid of chloroform

Mixture (i) in chloroform

Fractional crystallization

Mixture (ii) in chloroform

Chromatography

Zone 5 Zone 4 Zone 3 Zone 2 Zone 1

C-crystalline (7%) C-crystalline (11%)

E-syrup (4%) D-syrup (2%)

A-crystalline (41%)

Mixture (iii)

Fractional Crystallization - benzene

Mixture (iv)

Rechromatography

B-crystalline (3%) B-impure (14%)

F-syrup (5%)
needle-like crystals, m. 123-124°C. Recrystallization could also be done with ligroin giving higher yields than with ethanol but with a lower degree of purity. The compound was soluble in acetone, benzene and chloroform.


Infrared spectrum of A in KBr (cm\(^{-1}\)): 3080-3060(W), 2935(W), 2860-2890(W), 1623(W), 1595(S), 1556(M), 1548(W), 1520-1505(W), 1503(W), 1460(W), 1445(W), 1410(W), 1386(W), 1279(W), 1246(W), 1197(W), 1150(W), 1138(W), 1125(W), 1097(W), 1035(W), 1025(W), 962(W), 922(W), 904(W), 886(W), 867(S), 829(S), 801(S), 776(W), 765(S), 756(S), 741(W), 731(W), 683(W), 645(W).

Ultraviolet spectrum of A in 95% ethanol; angstroms (log molar extinction coefficient \(\epsilon\)): 3620 (4.14); 3450 (4.16); 3220 (4.36); 3160 (4.31); 2870 (4.30); 2780 (4.50); 2430 (4.60); 2120 (4.44).

Attempted reduction of 2-(8-naphthyl)-4-methylbenzo[h]-quinoline with lithium aluminum hydride (8)

To a solution of 5 ml. purified and dried diethyl ether (22) and 0.05 g. lithium aluminum hydride was added dropwise with considerable stirring a solution of 0.2 g. product A in 5 ml. purified and dried ether.
After 30 minutes of refluxing the reaction vessel was cooled in ice water and water was added slowly to destroy any complex and any unreacted lithium aluminum hydride. Ether was added to compensate for any ether lost in the refluxing and was followed by the addition of 3 ml. concentrated sodium potassium tartrate and 2 ml. 10% sodium hydroxide to dissolve the white precipitate. The ether layer was separated from the aqueous layer, dried over calcium chloride, and the ether removed by evaporation to leave behind a white residue which when recrystallized from ethanol gave white needle like crystals m.p. 122-122°C. A mixed melting point with A gave no depression.

**Attempted reduction of 2-(6-naphthyl)-4-methylbenzo-[h]quinoline with magnesium methoxide (73)**

To 40 ml. of almost (2 drops water added) anhydrous methanol was added 0.113 g. product A. About 0.8 g. freshly polished magnesium metal was added and by heating the metal dissolved. After removal of the solvent by evaporation there was left a greenish yellow residue which was treated with ice water and 30% acetic acid to dissolve most of the solid and leave behind a bright yellow residue. Recrystallization from ethanol gave white crystals m.p. 119-112.5°C. which gave a mixed melting point of 119-122.5°C. with product A.
Oxidation of 2-(8-Naphthyl)-4-methylbenzo[h]quinoline (Compound A) by chromic acid (25)

To a solution of 0.1152 g. product A dissolved in 20 ml. acetic acid was added 0.5 ml. chromic acid - acetic acid - water solution (4:3:3 by weight) drop by drop. Precipitation took place and 21 drops concentrated sulphuric acid at 60°C. were required to dissolve the precipitate. The green solution was filtered leaving behind 0.0117 g. of orange precipitate (10% yield). The filtrate was made weakly acid with 10% aqueous sodium hydroxide and concentrated cupric acetate was added. No precipitation took place.

The orange precipitate produced did not recrystallize from ethanol and did not dissolve in ligroin. It started to melt at 125°C. and crystals persisted beyond 360°C. An aqueous alcoholic solution proved neutral to indicator paper and no effervescence was observed when the product was treated with aqueous sodium bicarbonate. Treatment of a small amount of the recovered substance with concentrated aqueous sodium hydroxide caused blackening and tar formation. A nitrogen determination by the sodium fusion method (50) gave a positive test for nitrogen. The product appeared to slowly polymerize in the presence of air.

Attempted Oxidation of 2-(8-Naphthyl)-4-methylbenzo[h]quinoline with potassium ferrocyanide (57)

Into 120 ml. water were added 0.36 g. product A
25 g. potassium ferrocyanide and 4.3 g. potassium hydroxide. The mixture was refluxed with vigorous stirring at 60°C. for 24 hours. At the end of this time 8 g. potassium ferrocyanide and 1.4 g. potassium hydroxide were added and refluxing was continued. At the end of 48 hours 4 g. potassium ferrocyanide and 0.7 g. potassium hydroxide were added and refluxing was continued until a total of 67 hours had passed. The original product was recovered.

Oxidation of 2-(α-naphthyl)-4-methylbenzo[h]quinoline (Compound A) to yield 2-(α-naphthyl)-4-formylbenzo[h]quinoline (Compound G)

To a semimicro three necked flask equipped with a stirrer was added 0.2553 g. product A. The flask was heated to 180°C. with stirring and at this temperature 0.0904 g. of pulverized selenium dioxide was slowly added and the mixture heated for 15 minutes at 180-200°C. The reddish brown viscous syrup produced was repeatedly extracted with diethyl ether to form a bright yellow-orange solution. The ethereal solution was dried over calcium chloride and the ether evaporated off to yield 0.2166 g. of bright yellow product.

Purification of the oxidized product

The product was dissolved in 3 ml. benzene and placed on a 150 mm. x 35 mm. diameter alumina column
prewashed with benzene-petroleum ether (b.p. 30-60°C.) 1:3 v:v mixture. The separation was as follows:

<table>
<thead>
<tr>
<th>Effluent Fractions (in millilitres)</th>
<th>Fractions and Weight (in grams)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. 300 ml. C₆H₅- pet. ether (1:3 v:v)</td>
<td>0.0555 g. colourless crystals</td>
</tr>
<tr>
<td>2. 1250 ml. C₆H₆- pet. ether (1:3 v:v)</td>
<td>0.0102 g. brown crystals</td>
</tr>
<tr>
<td>3. 2300 ml. C₆H₆- pet. ether (1:3 v:v)</td>
<td>0.0476 g. bright yellow crystals</td>
</tr>
<tr>
<td>4. 850 ml. C₆H₆- pet. ether (1:1 v:v)</td>
<td>0.0288 g. orange tarry residue</td>
</tr>
<tr>
<td>5. 500 ml. Ethanol</td>
<td>0.0661 g. brown residue</td>
</tr>
</tbody>
</table>

Total recovery was 0.2022 g. or 93.4%. Zone 1 proved to be the original product A by mixed melting point. Zones 2, 4 or 5 were not worked with.

Characterization of 2-(β-naphthyl)-4-formylbenzo[h]-quinoline (Compound G) (Zone 2)

The product was recrystallized from ligroin (b.p. 100-120°C.) to give bright yellow crystals, m.p. 139-142.5°C.

Anal. calcd. for C₂₄H₁₅NO: C, 86.6; H, 4.51; N, 4.20; O, 4.80; Mol. wt. 333.4. Found: C, 86.26; H, 4.68; N, 4.16; O, 4.7.
Infrared spectrum of G with KBr (cm\(^{-1}\)):

- 2940(S), 2870(M), 1700(S), 1685(W), 1647(W),
- 1585(W), 1560(W), 1547(W), 1525(W), 1510(W), 1460(W),
- 1365(W), 1325(W), 1212(W), 1197(W), 1157(W), 1135(W),
- 1122(W), 1090(W), 1025(W), 928(W), 883(M), 852(M),
- 827(W), 815(M), 798(W), 745(S), 712(W), 707(W).

The yellow product gave a bright yellow solution having a vivid greenish fluorescence. Addition of concentrated alcoholic potassium hydroxide caused the colour to disappear. Acidification or neutralization of the basic solution with glacial acetic acid led to restoration of the yellow colouration. The compound gave a fairly rapid Tollen's test and a negative test with Fehling's solution. Treatment with hydroxylamine hydrochloride caused immediate disappearance of the yellow colouration and the formation of a colourless crystalline oxime melting in the range 170-185\(^{\circ}\)C, without recrystallization.

Oxidation of 2-(\(\beta\)-naphthyl)-4-formylbenzo[h]quinoline (compound G) with silver oxide to yield 2-(\(\beta\)-naphthyl-4-carboxybenzo[h]quinoline (compound H) (14)

To 0.0076 g. of 2-(\(\beta\)-naphthyl)-4-formylbenzo-[h]quinoline dissolved in 10 ml. ethanol was added drop by drop an ammoniacal ethanolic solution of silver oxide (0.022 g. Ag\(_2\)O). Refluxing was carried
out for three hours and the solution allowed to stand overnight. After making the solution basic with potassium hydroxide in alcohol the coagulated silver oxide was filtered to give a pale yellow solution. A silver mirror had formed in the flask. The solution was neutralized with glacial acetic acid, evaporated to dryness and the residue extracted with chloroform. Recrystallization of the residue from isoamyl alcohol was unsuccessful but after removal of the solvent a crystalline residue resulted which melted in the range 220-262°C.

**Attempted decarboxylation of 2-((2-naphthyl)-4-carboxybenzo[h]quinoline**

The 2-((2-naphthyl)-4-carboxybenzo[h]quinoline was recrystallized from ethanol to give a crystalline product melting in the range 125-140°C. (mainly the unoxidized aldehyde). The product after being refluxed in ethanol for 6 hours was freed of solvent and the residue dissolved in 1 ml. benzene and chromatographed on a 110 mm. x 10 mm. diameter alumina column pre-washed with 10 ml. benzene-ligroin (b.p. 30-60°C.) 1:3 v:v mixture. The separation was as follows:
<table>
<thead>
<tr>
<th>Effluent Fractions (in millilitres)</th>
<th>Fractions collected</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. 60 ml. 3:1 light pet. ether-benzene</td>
<td>pale brown oil 1 mg.</td>
</tr>
<tr>
<td>2. 390 ml. 3:1 light pet. ether-benzene 220 ml. benzene</td>
<td>greenish yellow crystals 2 mg.</td>
</tr>
<tr>
<td>3. 120 ml. ethanol</td>
<td>brown wax 1 mg.</td>
</tr>
</tbody>
</table>

The contents of zone 2 proved to be unreacted aldehyde. Attempts to crystallize zone 3 from ethanol were unsuccessful. The product of zone 1 was recrystallized from ethanol to give a mass of white fluffy crystals. This product appeared greasy at room temperature and melted over a range of 25-50°C. The amount of substance isolated was less than a milligram and was not worked with further.

**Sodium Hydroxide fusion of 2-(β-naphthyl)-4-methylbenzo[h]quinoline (A) (16)**

To a thick walled glass test tube was added a mixture of 0.2 g. product A and 2 g. powdered sodium hydroxide. Another 1 g. powdered sodium hydroxide was added on top. A well containing a few drops of water was suspended above the reacting mixture in order to absorb any ammonia which might be produced. The test tube and contents were heated for six hours in a sand bath at 250°C., cooled, and the contents
dissolved in a minimum amount of water and filtered. Neutralization of the solution with 6N sulphuric acid gave a copious white gelatinous precipitate which was repeatedly extracted with ethanol. The remaining residue proved to be inorganic by the flame test. The aqueous solution was evaporated down and also extracted with ethanol. The original residue left after dissolving the solid basic mixture in water was recrystallized to give back product A in 60% yield. The ethanolic extract gave a small amount of intractable decomposition product not worked on.

Behaviour of strongly proton donating solvents with 2-(8-naphthyl)-4-methylbenzo[h]quinoline (Compound A)

Compound A reacted with concentrated hydrochloric acid to give a bright yellow insoluble salt. With concentrated sulphuric acid a bright yellow colouration was imparted to the product and it slowly dissolved. Upon heating the solution the yellow colouration turned to pink. Dilution of the acid with water resulted in the loss of the pink colouration and a greenish-yellow precipitate formed. With formic acid immediate dissolving took place to give a yellow solution. Dilution of this solution with diethyl ether resulted in the loss of colouration and in the precipitation of a colourless compound.
**Reaction of 2-(6-naphthyl)-4-methylbenzo[h]quinoline with dry hydrogen chloride to yield the hydrochloride salt**

The hydrochloride salt of product A was made by passing dry hydrogen chloride through a dry ethereal solution of product A to give an immediate yellow copious precipitate which was filtered, washed repeatedly with dry ether and dried in a vacuum desiccator over phosphorus pentoxide and potassium hydroxide for 48 hours whereupon a bright yellow salt was collected in high yield having a deep greenish fluorescence. Heating the salt at 90-100°C. released the hydrogen chloride and the original product A was recovered.

Ultraviolet spectrum of the HCl salt of A in 95% ethanol; angstroms (log molar extinction coefficient): 3920 (4.23), 3660 (4.14), 3460 (4.04), 3160 (4.47), 2870 (4.49).

Of the dried product a known weight was dissolved in 90% ethanol and aliquot portions were titrated against a standard solution of potassium hydroxide in 90% ethanol using phenolphthalein as indicator. The molecular weight of A was found to be 314.3; Theoretical, 307.4.
Reaction of 2-((6-naphthyl)-4-methylbenzo[h]quinoline with methyl iodide to yield the methiodide salt

The methiodide salt was prepared (24) by dissolving 0.082 g. product A in 3 ml. methyl iodide and adding to a thick walled tube which was sealed. It was heated for 170 hours at 100°C., cooled, wrapped in metal foil, and kept under refrigeration for several days. Black crystals formed which were removed from the tube and washed with dry diethyl ether (40% yield), m. 182-184°C. After evaporation of the methyl iodide solvent there remained pale yellow crystals which after recrystallization from ethanol proved by mixed melting point to be the original product A (0.049 g.).

Anal. calcd. for C_{29}H_{18}NI: C, 63.7; H, 3.92; N, 3.24; I, 29.3. Found: C, 57.12; H, 3.98; N, 3.26; I, 31.26.

Reaction of 2-((6-naphthyl)-4-methylbenzo[h]quinoline with picric acid to yield the picrate derivative (60)

To 3 ml. ethanol was added 0.041 g. picric acid and the picric acid solution was in turn added to 0.052 g. compound A dissolved in 3 ml. ethanol. A copious yellow precipitate formed immediately which was dissolved by diluting the mixture up to 250 cc. with 95% ethanol and refluxing. Refluxing was carried on for five hours after which the ethanolic solution was allowed to stand and cool. The crystallized product
was filtered and recrystallized from 95% ethanol to give 0.068 g. (75%) bright yellow crystals, m. 223-236°G.

Anal. calcd. for C_{30}H_{20}N_{4}O: C, 66.0; H, 3.67; N, 10.22; O, 20.04; Mol. wt. 549.4.
Found: C, 63.63; H, 3.59; N, 9.99.

Attempted reaction of 2-(9-naphthyl)-4-methylbenzo[h]-quinoline with maleic anhydride (39)

To 2 ml. benzene was added 0.23 g. freshly distilled maleic anhydride and 0.0792 g. product A. The solution was refluxed under anhydrous conditions for eight hours. When the reaction had cooled more benzene was added and dry hydrogen chloride passed through. A bright yellow precipitate formed which was separated from the solvent and treated with sodium acetate in boiling acetone to decompose the salt. After filtering off the inorganic salt and evaporating down the solution a yellow oil formed which solidified on cooling, m. 117-124°G. A recrystallization from ethanol yielded a compound m. 122-125°G. A mixed melting point with product A was at 121-124°G.

Characterization of 3-methylbenzo[f]phthalimidine (compound B) (portion collected from chromatography of mixture iv)

Yield 14%. This fraction was triturgated with
successive portions of ligroin, b.p. 65-75°C, to leave behind a trace of dark brown resinous material which was discarded. The pale brown syrup recovered was very soluble in methanol, 3-pentanone, isoamyl alcohol, acetic acid, chloroform and benzene. Attempts at recrystallization from petroleum ether-benzene or petroleum ether-chloroform resulted only in oiling out.

Infrared spectra using a CHCl₃ deposited film on NaCl disc (cm⁻¹): 3310(M), 3050(W), 3005(W), 2960(W), 2905(W), 1628(S), 1598(W), 1560(S), 1508(M), 1452(W), 1375(W), 1272(W), 1245(W), 1217(S), 1177(W), 1127(W), 1017(W), 950(W), 890(W), 855(M), 815(M), 752(S), 665(W).

An acetylation was carried out on B as follows: To 0.023 g. B in 0.70 ml. dry acetic anhydride was added 0.037 g. fused sodium acetate and the mixture was allowed to reflux for six hours. After cooling the contents were poured into ice cold water and vigorously agitated. The water was decanted and the greasy brown residue dissolved in diethyl ether and the ethereal solution washed with water. The ether solution was dried over anhydrous calcium chloride and the ether removed by evaporation to recover 0.0125 g. of product which recrystallized from methanol giving faint white crystals in low yield which presumably
were the acetate derivative as shown by infrared analysis.

Infrared spectra of acetylated B using a \( \text{CHCl}_3 \) deposited film on NaCl disc (cm\(^{-1}\)): 3350(W), 3060(W), 3020(W), 2945(M), 2910(M), 2840(W), 1695(S), 1665(M), 1597(W), 1534(W), 1508(W), 1435(W), 1377(M), 1368(M), 1270(M), 1230(S), 1180(W), 1127(W), 950(W), 890(W), 865(M), 818(M), 750(S), 663(W).

Characterization of 3-methylbenzo[f]phthalimidine (compound B) (portion collected from fractional crystallization of mixture iii, fig. 4)

Yield 3%. This crystalline component was recrystallized from a benzene-ethanol mixture and then from chloroform to give white flake like crystals, m. 218-239°C.

Anal. calcd. for C\(_{15}\)H\(_{11}\)NO: C, 78.8; H, 5.65; N, 7.10. Mol. wt., 197.3. Found: C, 77.90; H, 6.23; N, 6.97.

Infrared spectrum in KBr (cm\(^{-1}\)): 3280(M), 2940(W), 1638(S), 1598(M), 1585(M), 1577(W), 1550(W), 1525(W), 1460(M), 1388(W), 1345(M), 1300(W), 1285(W), 1193(W), 1145(M), 1100(W), 907(W), 870(M), 835(S), 760(S), 687(W).
Ultraviolet spectrum of B in 95% ethanol; angstroms (log molar extinction coefficient):
3500(Sh) (2.598), 3305 (3.100), 3160 (3.064), 2925(Sh) (3.695), 2825 (3.790), 2730(Sh) (3.750), 2370 (4.604), 2280 (4.592).

Characterization of C (portion collected from chromatography of mixture ii, fig. 4)
Yield 13%. The fraction recovered was a dark brown resinous wax. It was dissolved in benzene (1.32 g. in 3 ml.) and added to an alumina column (120 mm. x 52 mm. diameter) and eluted as follows:

<table>
<thead>
<tr>
<th>Effluent Fractions (in millilitres)</th>
<th>Fractions and Weight (in grams)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1700 ml. C₆H₆: t-BuOH (98:2 v:v)</td>
<td>0.33 g. dark brown residue</td>
</tr>
<tr>
<td>200 ml. C₆H₆: EtOH (l:l v:v)</td>
<td>0.82 g. pale brown residue</td>
</tr>
</tbody>
</table>

The first fraction was not worked with further. The second fraction (11% of the total) was very soluble in 3-pentanone, isoamyl alcohol and glacial acetic acid. Recrystallization was accomplished from a chloroform-petroleum ether solvent and then from chloroform to give a white crystalline product, m. 201-207°C.
Anal. calcd. for $C_{12}H_{12}N_{2}O$: C, 70.1; 
H, 6.00; N, 14.00; O, 8.00. Found: C, 71.35; 
H, 6.02; N, 14.12; O, 8.02.

Infrared spectrum in KBr (cm$^{-1}$): 3300(S), 
3210(M), 3040(W), 2950(W), 2910(W), 2850(W), 1660(S), 
1607(S), 1575(W), 1555(W), 1475(W), 1395(M), 1317(W), 
1290(W), 1195(W), 1160(M), 1143(W), 985(W), 970(W), 
925(W), 912(W), 893(W), 875(M), 840(S), 793(W), 
767(S), 678(W).

Sublimation of C at 175°C at about 0.05 mm. 
Hg. gave a white crystalline product, m. 35-60°C. 
The sublimed product failed to give a derivative with 
2,4-dinitrophenylhydrazine.

Characterization of O (portion collected from 
 fractional crystallization of mixture i, fig. 3)

Yield 7%. After three recrystallizations 
from 3-pentanone the compound melted at 204-205.5°C. 
It was soluble in alcohol, insoluble in benzene, 
diethyl ether or ligroin and could be recrystallized 
from chloroform.

Anal. calcd. for $C_{13}H_{14}N_{2}O$: C, 72.8; H, 6.58; 
N, 13.1; O, 7.46; Mol. wt., 214.3. Found: C, 72.6; 
H, 6.62; N, 13.1; O, 7.81; Mol. wt. (Rast) 301. 
The molecular weight determination was likely in error 
as the compound reacted with camphor to give a red 
product.
Infrared spectrum of C in KBr (cm$^{-1}$): 3430(S), 3350(S), 3230(M), 3070(W), 2990(W), 2930(W), 1682(W), 1648(S), 1621(S), 1595(S), 1567(S), 1540(S), 1511(M), 1477(W), 1460(W), 1384(M), 1341(W), 1350(W), 1301(W), 1276(W), 1252(W), 1182(M), 1145(M), 1128(M), 1055(W), 1019(W), 968(W), 954(W), 909(W), 896(W), 878(W), 860(W), 825(S), 775(W), 750(S), 662(M).

Ultraviolet spectrum of C in 95% ethanol; angstroms (log molar extinction coefficient): 3170 (2.310), 3120(Sh) (2.389), 3035 (2.540), 2830(Sh) (3.603), 2730 (3.767), 2650 (3.748), 2240 (4.898).

Some of the original crystalline product collected from the chloroform crystallization gave a positive ferric chloride test and slowly became brown upon standing giving off a putrescent odour even at -10°C. under vacuum and in the absence of light. The oily component produced was easily separated from the crystalline compound C by chromatography on alumina. The degraded compound did not give a ferric chloride test. Prolonged refluxing for six days with mercuric oxide in chloroform (31) gave no apparent change. Compound C behaved indifferently to proton donating solvents although blackening took place in concentrated sulphuric acid.
Characterization of Compound D.

(Yield 2%; a pale yellow sweet smelling syrup). No attempt was made to crystallize this fraction. It was soluble in ethanol and benzene, poorly soluble in ligroin.

Infrared spectrum of D in KBr (cm\(^{-1}\)): 3060(W), 2915(S), 2850(S), 1632(W), 1600(W), 1460(S), 1380(M), 1270(W), 1125(W), 1020(W), 958(W), 947(W), 890(W), 854(M), 817(S), 747(S).

An attempt to prepare the 2,4-dinitrophenyl-hydrazone derivative was unsuccessful.

Characterization of Compound E

The fraction recovered was a dark brown resinous wax, yield 4%. A small crystal was successfully isolated from a ligroin solution b. 100-120\(^{\circ}\)C. after standing several days, m. 206-233\(^{\circ}\)C. The fraction was very soluble in ethanol, isoamyl alcohol, 3-pentanone, acetic acid, chloroform and benzene. It oiled out of ligroin solutions.

Infrared spectrum using a CHCl\(_3\) deposited film on NaCl disc (cm\(^{-1}\)): 3060(W), 3020(M), 2960(S), 2920(S), 2860(M), 1710(S), 1675(M), 1635(W), 1600(W), 1533(M), 1508(M), 1455(M), 1405(W), 1377(W), 1353(M), 1315(W), 1273(W), 1245(W), 1217(S), 1182(W), 1142(W), 1128(W), 1019(W), 953(W), 890(W), 855(W), 820(M), 750(S), 668(M).
A small amount of the fraction was dissolved in ethanol and 2,4-dinitrophenylhydrazine in ethanol was added along with two drops concentrated sulphuric acid and the solution refluxed. After standing overnight a minute amount of red precipitate appeared which melted over a wide range being oily at room temperature and containing crystalline solid at temperatures above 200°C.

Characterization of Compound F

Yield 5%. This fraction was triturated with successive portions of ligroin, b. 65-75°C. to leave behind a trace of dark brown resinous material which was discarded. The pale brown syrup recovered was very soluble in methanol, 3-pentanone, isoamyl alcohol, acetic acid, chloroform and benzene. Attempts at re-crystallization from petroleum ether-benzene or petroleum ether-chloroform resulted only in oiling out.

Infrared spectra using a CHCl₃ deposited film on NaCl disc (cm⁻¹): 3310(W), 3050(W), 3005(W), 2960(W), 2905(W), 1708(M), 1690(S), 1598(W), 1550(W), 1535(W), 1505(W), 1455(W), 1376(W), 1345(W), 1273(W), 1216(S), 1127(W), 1016(W), 950(W), 887(W), 855(W), 817(M), 752(S), 663(W).
(c) **Reaction of 2-acetonaphthone with 2-acetonaphthone oxime to yield 2-((α-naphthyl)-4-methylbenzo[h]quinoline**

Into a glass liner was placed 1.85 g. (0.01 m.) 2-acetonaphthone oxime, 1.70 g. (0.01 m.) 2-acetonaphthone and 10 ml. dry benzene. The liner was placed into an autoclave and the system evacuated to 1.0 mm. Hg pressure. The autoclave was heated and rocked at 235°C. for 90 minutes whereupon the pressure rose to 90±10 p.s.i. When cooled the contents were recovered in the solid state, the benzene solvent having removed itself to outside the liner.

A portion of the recovered solid (0.701 g.) was dissolved in 4 ml. benzene and developed on an alumina column (35 mm. diameter x 120 mm.). Elution was carried out with benzene-ligroin (1:1, v:v) to recover 0.1896 g. of material which fluoresced under ultraviolet radiation and which exhibited identical chromatographic behaviour to that shown by 2-((α-naphthyl-4-methylbenzo[h]quinoline. The remaining zones were discarded.

The recovered compound was dissolved in dry ether and dry hydrogen chloride was passed through the ethereal solution to precipitate a bright yellow salt. Filtration of the yellow salt and removal of the ether
by evaporation left a pale yellow oil 0.1168 g. Hence, 0.0728 g. (11%) of the products were recovered as the hydrochloride salt. The bright yellow salt was decomposed by dissolving in acetone and adding sodium acetate (39) whereupon the yellow colouration disappeared rapidly. The acetone was removed by evaporation and the residue dissolved in one ml. benzene which was placed on an alumina column (10 mm. diameter x 90 mm.). The compound was eluted with benzene-petroleum ether (1:1 v:v). The fraction collected was recrystallized from ethanol to give a white crystalline compound, m. 120-124°C. A mixed melting point with 2-((β-naphthyl)-4-methylbenzo[h]quinoline gave 119-124°C. The infrared spectra of the compound was identical to the infrared spectra of 2-((β-naphthyl)-4-methylbenzo-[h]quinoline.
Fig. 4 - Infrared Absorption Spectra of:

1. 2-(8-Naphthyl)-4-methylbenzo[h]quinoline (in KBr)
2. 3-Methylbenzo[f]phthalimidine (in KBr)
3. 3,4-Dihydro-3-phenylisocarboxystyril (in Nujol on a Perkin-Elmer Intracord Spectrophotometer)
IV. BIBLIOGRAPHY

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V. ADDENDUM

l-(β-Naphthyl)ethylurea from 2-acetonaphthone oxime.

Compound C (see exp. p.51 and disc. p.22) has now been tentatively established to be racemic l-(β-naphthyl)ethylurea on the following bases: the melting point of compound C was found to be 196-198°C, which is in excellent agreement with the literature melting point of 198°C for l-(β-naphthyl)ethylurea (75), elemental analysis (see exp. p.52) is in agreement with the postulated structure as shown below:

\[ \text{CH}_3 \\
\text{CHNHCONH}_2 \\
\text{C (d,l form)} \]

infrared analysis shows peaks at 3450 and 3550 cm\(^{-1}\) which are attributed to the N-H stretching in a primary amide (76). Urea shows peaks at 3434 and 3376 cm\(^{-1}\) (74) and benzylurea shows peaks at 3440 and 3328 cm\(^{-1}\) (56). The peak at 3230 cm\(^{-1}\) for product C can be assigned to the N-H of a secondary amide (76). Furthermore, the peaks at 1648 and 1537 cm\(^{-1}\) are attributed to the amide I and the amide II bands (77).
A suggested mechanism for the formation of 1-(α-naphthyl)ethylurea from 2-acetonaphthone oxime is shown below:

\[
\begin{align*}
\text{C} & \quad \text{CH}_3 \\
\text{C} & \quad \text{NOH} \\
\text{H}_2 & \quad \rightarrow \\
\text{C} & \quad \text{CHNH}_2
\end{align*}
\]

Work in our laboratory (56) has conclusively shown that the oximes undergo hydrolysis under the conditions used to yield some ketone. Furthermore, other workers (48) have shown that unsaturated compounds undergo reduction with hydrogen in the presence of dicobalt octacarboxyl.


77. Ibid.; p. 521-3.