The Reaction between Diphenylketene and Phenylacetylene[1]

BY LEE IRVIN SMITH AND HARVEY H. HOEHN[2]

In a previous paper[3] it has been shown that the addition product obtained from diphenylketene and cyclopentadiene is a cyclobutanone derivative. Staudinger and Suter[4] added diphenylketene to styrene, and likewise regarded the product as a cyclobutanone derivative, I or II. At first these authors favored structure II with the more hindered carbonyl group, because the substance failed to form a phenylhydrazone or a benzal derivative but later,[5] when it was discovered that the product, on alkaline cleavage, gave α,α,β-triphenylbutyric acid, formula II was abandoned in favor of I. It has been shown recently[6] that formula I is really correct, although the cleavage product is actually β,γ,γ-triphenylbutyric acid, which Staudinger and Rheiner mistook for the α,α,β-acid.

$$C_6H_5CH—CH_2 \qquad C_6H_5CH—CH_2$$
$$(C_6H_5)_2C——C=O \qquad O=C——C(C_6H_5)_2$$
$$\text{I} \qquad\qquad\qquad \text{II}$$
$$C_6H_5C=C—H$$
$$(C_6H_5)_2C—C=O$$
$$\text{III}$$
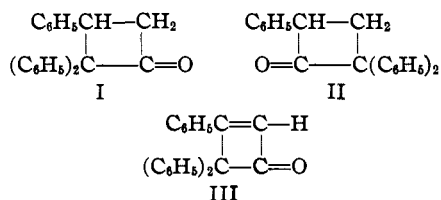
The facile formation of cyclobutanone derivatives is often observed in reactions between ketenes and unsaturated compounds, and in connection with earlier work[3] Agre[7] had sought to obtain further evidence that styrene and diphenylketene reacted to form a cyclobutanone derivative. His plan of attack involved addition of diphenylketene to phenylacetylene; assuming that styrene and phenylacetylene added to the ketene in the same way, then reduction of the adduct III from the acetylenic hydrocarbon should give the adduct II of the ethylenic hydrocarbon.

Contrary to the statement of Staudinger,[8] phenylacetylene and diphenylketene can be made to react with the production in excellent yield of

(1) Presented at the 98th meeting of the American Chemical Society, Boston, Mass., September, 1939.

(2) Abstracted from a thesis by Harvey H. Hoehn, submitted to the Graduate Faculty of the University of Minnesota, in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

(3) Smith, Agre, Leekley and Prichard, THIS JOURNAL, 61, 7 (1939).

(4) Staudinger and Suter, Ber., 53, 1092 (1920).

(5) Staudinger and Rheiner, Helv. Chim. Acta, 7, 8 (1924).

(6) Bergmann and Bergmann, J. Chem. Soc., 727 (1938).

(7) C. L. Agre, Ph.D. Thesis, University of Minnesota, 1937, p. 77.

(8) Staudinger, Ann., 356, 94 (1907).

a crystalline compound melting at 143–144°. Beyond showing that this product had the composition required by formula III and that its chemical properties were quite unusual for a compound of this structure, Agre did no further work upon it.

In the present communication, it is shown that this adduct is not a cyclobutanone derivative at all, but is 3,4-diphenyl-α-naphthol, IV, an isomer of III. Analysis and molecular weight determinations showed the composition to be $C_{22}H_{16}O$. The substance was readily soluble in (methyl) alcoholic potassium hydroxide; it gave a positive phenol reaction (Folin) and in the Grignard machine showed one active hydrogen atom and no addition of the reagent. It formed an acetate (IX) and a methyl ether (X), and it coupled with diazotized sulfanilic acid to give the azo compound XIII.

The adduct (IV) formed a monobromo derivative (V) which was still a phenol for it could be converted into an acetate (XI) or a methyl ether (XII). This bromophenol (V) was readily soluble in aqueous alkali, hence was more strongly acidic than the parent compound IV.

The adduct IV was extremely sensitive to oxidizing agents, even turning brown in air in a few days. It decolorized permanganate instantly, and depending upon the conditions and upon the oxidizing agent used, a variety of products was obtained. Using permanganate or chromic acid under mild conditions, the oxidation led to a product, insoluble in carbonate solution, whose structure has not yet been determined. Using potassium dichromate under vigorous conditions, the products were o-benzoylbenzoic and benzoic acids. The formation of these oxidation products eliminated the possibility that the adduct IV was 1,4-diphenyl-β-naphthol, since the latter compound would have produced o-dibenzoylbenzene on oxidation.

Oxidation of the bromo derivative V by chromic acid in acetic acid or oxidation of the phenol IV by lead tetraacetate produced a bright red solid (VI) having the properties of a 1,2-naphthoquinone. Reduction of VI by zinc and acetic acid or by sodium hydrosulfite gave colorless solutions, which in the air rapidly turned red and de-

DIAGRAM 1

$$(C_6H_5)_2C=C=O + HC\equiv CC_6H_5$$

OH
N=NC$_6$H$_4$SO$_3$Na
C$_6$H$_5$
C$_6$H$_5$
XIII

OH
C$_6$H$_5$
C$_6$H$_5$
IV

Br$_2$ →

OH
Br
C$_6$H$_5$
C$_6$H$_5$
V

→

OR
Br
C$_6$H$_5$
C$_6$H$_5$
XI, R = Ac
XII, R = C$_6$H$_5$

K$_2$Cr$_2$O

COOH
COC$_6$H$_5$
+
COOH

Pb(OAc)$_4$

CrO$_3$

OR
C$_6$H$_5$
C$_6$H$_5$
IX, R = Ac
X, R = CH$_3$

N N
C$_6$H$_5$
C$_6$H$_5$
VIII

O
O
C$_6$H$_5$
C$_6$H$_5$
VI

← →

OAc
OAc
C$_6$H$_5$
C$_6$H$_5$
VII

posited VI when the reducing agent was removed. Reductive acetylation of VI gave a colorless diacetate, VII. Finally, the o-quinone structure of VI was definitely settled by conversion of VI to a phenazine, VIII. That the azo group of XIII occupies the same position as the bromine atom

DIAGRAM 2

O
O
+ 2C$_6$H$_5$MgBr →

C$_6$H$_5$ OH
C$_6$H$_5$ OH
XIV
m. p. 207–208°

Zinc / HOAc →

C$_6$H$_5$
C$_6$H$_5$
XV
m. p. 308°

COOH
COC$_6$H$_5$
+
COOH
Na$_2$Cr$_2$O$_7$ ←
Ac$_2$O | H$_2$SO$_4$

+ red product (VI)
+ yellow product

OAc
C$_6$H$_5$
C$_6$H$_5$
XVI
m. p. 163°

KOH →

OH
C$_6$H$_5$
C$_6$H$_5$
XVII
m. p. 143–144°

of V was shown by the fact that the azo compound on reductive cleavage followed by oxidation of the intermediate amine (not isolated) also gave the red quinone VI.

These transformations, which are shown in dia-

gram 1, are all explained adequately by structure IV, 3,4-diphenyl-α-naphthol, for the product of the reaction between diphenylketene and phenylacetylene.

Although the reactions shown in diagram 1 definitely prove that the adduct IV is a diphenyl naphthol with the two phenyl groups located in positions 3 and 4, these results do not definitely locate the hydroxyl group, for the reactions shown would be just as consistent with the β- as with the α-naphthol structure. In order to locate the hydroxyl group, an independent synthesis of IV was undertaken. Some years ago Franssen[9] studied the addition of phenylmagnesium bromide to 1,4-naphthoquinone; his results, using the structures which he assigned, are summarized in diagram 2.

Franssen's work was of interest in connection with the present work, since the melting points of two of his products, XVI and XVII, coincided with

(9) Franssen, Bull. soc. chim., [4] 37, 902 (1925).

two obtained in this work, those of IX and IV, respectively. That is, Franssen reported a phenol and its acetate which had the same melting points as the phenol IV and its acetate obtained by an entirely different series of reactions. It followed almost certainly that Franssen's compounds and ours were identical, but this could not be the case if the structures assigned by Franssen were correct. Franssen's evidence for structure XIV rested primarily upon the conversion of XIV into 1,4-diphenylnaphthalene, XV. But this compound since has been synthesized by Weiss, Abeles and Knapp[10] and by Allen and Gilman,[11] who report that it melts at 135–137° and 134–136°, respectively, and not at 308° as does Franssen's compound XV. Another serious objection to Franssen's formulations is that the production of o-benzoylbenzoic and benzoic acids by oxidation of XIV and XVI, and the conversion of XIV into XVI, must both involve rearrangements. Crawford[12] showed that phenylmagnesium bromide added to 2,3-dimethyl-1,4-naphthoquinone to give a variety of products, the relative amounts of which depended largely upon the relative amounts of the quinone and Grignard reagent. She showed that when two moles of phenylmagnesium bromide was added to the quinone, the product formed in largest amount was the one resulting from a 1,4-addition to the conjugated system followed by a 1,2-addition to the other carbonyl group. Franssen's products could be reconciled with ours if this same type of reaction were assumed in the case of 1,4-naphthoquinone. To test this point, Franssen's work was repeated. The products which we obtained and their relationships are shown in diagram 3.

When 1,4-naphthoquinone was added to a large excess (5 moles) of phenylmagnesium bromide the addition product XVIII, identical with Franssen's XIV, resulted. That this substance possessed a carbonyl group was shown by the formation of an oxime (XIX). When XVIII was subjected to the action of acetic and sulfuric acids, or to the action of acetic anhydride, it was transformed into the naphthol IV and the acetate IX,

(10) Weiss, Abeles and Knapp, Monatsh., 61, 162 (1932).
(11) Allen and Gilman, THIS JOURNAL, 58, 937 (1936).
(12) Crawford, ibid., 57, 2000 (1935).

DIAGRAM 3

XVIII m. p. 207–208°

XIX m. p. 196–197°

IV m. p. 143–144°

IX m. p. 162–162.5°
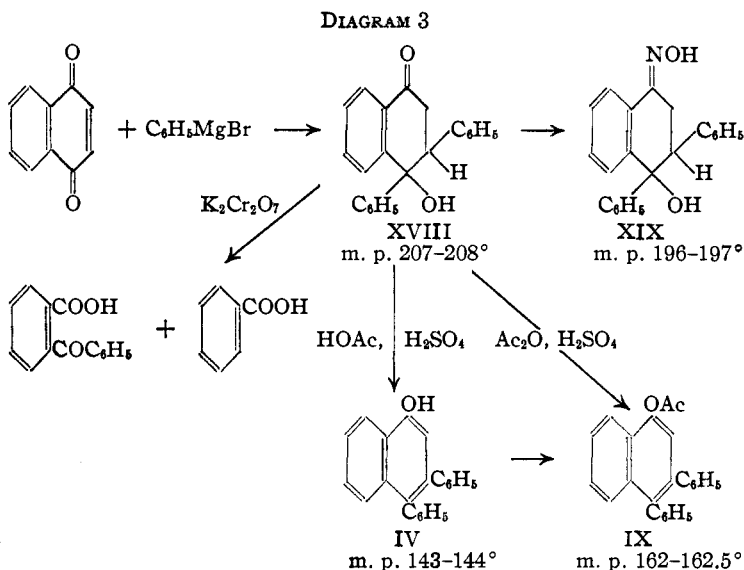
respectively. These transformations can be understood readily on the basis of structure XVIII for the primary product, for the tertiary hydroxyl group in position 4 would be expected to be eliminated readily under the conditions used, giving the naphthol IV directly, or its acetate IX. Structure XVIII also serves to explain the observed oxidation products; Franssen's XIV should give, not the observed oxidation products, but o-dibenzoylbenzene, none of which was obtained by Franssen nor by us. It follows, therefore, that Franssen's formulation of the reaction, and the structure of his products, are incorrect. His XIV must be replaced by XVIII; and his XVI and XVII must be replaced by IX and IV, respectively. What Franssen's hydrocarbon XV can be, it is not possible as yet to say. We have observed similar high melting products when certain of our products are oxidized, but we have not, as yet, been able to establish the structure of any of these. Certainly, however, Franssen's XV is not 1,4-diphenylnaphthalene.

When the results of these two syntheses, and the degradation of the products, are considered and assembled, the proof appears quite definite that diphenylketene reacts with phenylacetylene to produce 3,4-diphenyl-α-naphthol, IV. The reaction between this as well as other ketenes and acetylenic compounds appears to be quite general, and the hydrogen atom in the acetylene is not apparently necessary, for diphenylketene and diphenylacetylene also give a crystalline addition product. Consideration of the limits of

this reaction and also of the mechanism will, however, be reserved for later communications.

Experimental Part[13]

Addition of Diphenylketene to Phenylacetylene; 3,4-Diphenyl-α-naphthol (IV).—Diphenylketene (1.94 g., 0.01 mole) and phenylacetylene (1.02 g., 0.01 mole) were mixed and allowed to stand at room temperature. After about ten hours, the mixture became very viscous and shortly thereafter a yellow solid separated. After standing for three days, the solid was washed with a little petroleum ether (b. p. 28–38°) and then was recrystallized from petroleum ether (b. p. 90–100°). The white needles weighed 2.4 g. and melted at 139–141°. After crystallization twice more, the product melted at 143–144°.

Anal. Calcd. for $C_{22}H_{16}O$: C, 89.19; H, 5.71; mol. wt., 296. Found: C, 89.23; H, 5.80; mol. wt., 296. Calcd. for structure IV: active H, 1.0; carbonyl, 0. Found: active H, 0.97; carbonyl, 0.

The magnesium compound resulting from this determination, on acidification, gave IV, m. p. 143–144°.

The naphthol IV also was produced when a solvent was used, but the reaction was much slower and the yield much less. This undoubtedly was the cause of Staudinger's report that no reaction occurred, for he operated with 0.1 molar solutions. Diphenylketene (17.4 g.), phenylacetylene (9.3 g.) and petroleum ether (18 g., b. p. 57–70°) were allowed to stand for one week in an atmosphere of carbon dioxide. The solid was removed and crystallized from a mixture of petroleum ether and benzene. It weighed 13 g. (50%) and melted at 143–144°.

Apparently the naphthol IV exists in two forms, one melting at 143–144°, and the other at 154°. In the early experiment it was observed frequently that the substance, after melting at 143–144°, would crystallize as the temperature was raised slowly, and then remelt at 154°. In the later stages of the work, however, this phenomenon, which was observed independently by C. L. Agre and one of us (H. H. H.) could not be duplicated.

3,4-Diphenyl-α-acetoxynaphthalene (IX).—The naphthol (5 g.) was dissolved in acetic anhydride (30 cc.) containing a drop of sulfuric acid and the solution was heated to the boiling point. The product, isolated by pouring the reaction mixture over ice, formed white cubes when recrystallized from ethanol. The yield was 5.5 g., and the melting point was 162–162.5°.

Anal. Calcd. for $C_{24}H_{18}O_2$: C, 85.17; H, 5.37. Found: C, 84.86; H, 5.22.

3,4-Diphenyl-α-methoxynaphthalene (X).—The naphthol (500 mg.) and dimethyl sulfate (1.5 cc.) were dissolved in methanol (5 cc.). The solution was heated and stirred, and to it was slowly added a solution of potassium hydroxide (1 g.) in methanol (10 cc.). After refluxing for thirty minutes, water (75 cc.) was added. The precipitate was washed with Claisen's alkali (10 cc.) and then with water. The substance (400 mg.) was then recrystallized, first from alcohol–acetone and then from alcohol. It formed white cubes melting at 203–203.5°.

Anal. Calcd. for $C_{23}H_{18}O$: C, 88.99; H, 5.85. Found: C, 88.74; H, 5.85.

(13) Microanalyses by J. W. Opie, C. O. Guss and H. H. Hoehn.

3,4-Diphenyl-1-methoxy-2-nitronaphthalene.—Although the naphthol IV could not be nitrated (see below), the methyl ether X (200 mg.) in acetic acid (2 cc.) was nitrated readily by addition of nitric acid (0.08 cc.). The mixture was heated to the boiling point and then cooled. The nitro compound (70 mg.) which separated was removed and crystallized from ethanol. It formed yellow needles which melted at 202°.

Anal. Calcd. for $C_{23}H_{17}O_3N$: C, 77.72; H, 4.83. Found: C, 77.99; H, 4.78.

Oxidation of the Naphthol IV. (a) By Lead Tetraacetate.—This is the best preparative method for **3,4-diphenyl-1,2-naphthoquinone, VI.** The naphthol IV (296 mg.) and lead tetraacetate (800 mg.) were refluxed in acetic acid (10 cc.) for five hours. The solution was poured onto ice (100 g.) and most of the acetic acid was neutralized by adding saturated aqueous sodium carbonate. The mixture, containing an orange red precipitate, was extracted with chloroform. The chloroform was removed and the red residue was taken up in hot ethanol and filtered while hot. On cooling, the filtrate deposited orange red needles (130 mg.) which softened at 245° and melted at 247–248°. The melting point was not depressed by addition of a specimen of VI made from the bromonaphthol V; this latter specimen was carefully purified (m. p. 249–250° and was analyzed (see below).

(b) Oxidation by Nitric Acid.—The naphthol IV could not be nitrated; all attempts to do so led only to oxidation, the chief product being the red quinone VI although the yield was poor. The naphthol (1 g.) was dropped into a well-stirred mixture of nitric acid (1 cc.), sulfuric acid (2 cc.) and chloroform (10 cc.). After stirring the mixture for thirty minutes at room temperature, water was added, the chloroform layer was removed and the aqueous layer extracted with chloroform. The combined chloroform solutions were washed with bicarbonate and then with water. Removal of the chloroform left a red residue, which when worked up as described above gave 70 mg. of the quinone VI, m. p. 246–247°. The only other products were uncrystallizable oils.

(c) Oxidation by Dichromate.—The naphthol IV (1 g.) and potassium dichromate (3 g.) were refluxed in acetic acid (30 cc.) for eight hours. The green solution was poured onto ice (100 g.) and some of the excess acetic acid was neutralized with saturated carbonate. The mixture was extracted with benzene; the benzene was then extracted with sodium hydroxide (10%) and the alkaline extract was acidified and steam distilled. From the distillate benzoic acid (100 mg.), m. p. and mixed m. p. 121°, was isolated. From the residue in the distillation flask o-benzoylbenzoic acid (440 mg.) was isolated. This substance was identified as the hydrate after crystallization from water; m. p. and mixed m. p. 95°. From the residual benzene solution there was isolated a small amount (80 mg.) of a yellow solid melting at 280–286° which was not investigated further.

Reduction of the Quinone VI.—The quinone (140 mg.) in acetic acid (10 cc.) and water (1 cc.) was heated with zinc (20 mesh) for an hour. The red color of the quinone disappeared within ten minutes. The mixture was diluted with water, decanted from the zinc, and extracted with ether. The ether solution rapidly turned red, and re-

moval of the ether left red crystals of VI. Practically all of the starting material was recovered. Essentially the same results were obtained when VI was reduced by sodium hydrosulfite.

Reductive Acetylation: 1,2-Diacetoxy-3,4-diphenylnaphthalene (VII).—The quinone (50 mg.) and fused sodium acetate (50 mg.) were dissolved in acetic anhydride (1 cc.), a little zinc dust was added, and the mixture was heated to boiling. The red color faded at once. The zinc was filtered off and the filtrate was diluted with water. The solid (64 mg.) was removed and crystallized from dilute ethanol. It formed white needles which melted at 166–167°.

Anal. Calcd. for $C_{26}H_{20}O_4$: C, 78.76; H, 5.09. Found: C, 78.48; H, 5.15.

Phenazine (VIII).—The quinone VI (95 mg.) and o-phenylenediamine (60 mg.) were heated in alcohol (20 cc.) for thirty minutes on the steam-bath. After about five minutes, yellow crystals of the phenazine began to separate. The solid (110 mg.) was removed from the cooled mixture and recrystallized from alcohol–benzene. It formed yellow needles which melted at 274–275°.

Anal. Calcd. for $C_{28}H_{18}N_2$: C, 87.93; H, 4.75. Found: C, 87.92; H, 4.71.

Coupling Reaction of IV. The Azo Compound XIII.—Sulfanilic acid dihydrate (1.6 g.) was dissolved in sodium carbonate solution (15 cc., 2.5%) and sodium nitrite (0.56 g.) was added. The solution was poured into a mixture of ice (8 g.) and hydrochloric acid (1.5 cc.). To this suspension of the diazonium compound was added a solution of the naphthol IV (2.2 g.) and sodium acetate (0.6 g.) in acetic acid (30 cc.). The mixture was allowed to stand at room temperature for four hours, with occasional shaking. The red solid (2.8 g.) was filtered off and dried. It was not analyzed.

Reductive Cleavage of the Azo Compound: The Quinone VI.—The red compound XIII (1 g.), sodium hydrosulfite (0.4 g.) and sodium hydroxide (0.2 g.) were dissolved in water (20 cc.) and the solution was boiled. More hydrosulfite (0.5 g.) and alkali (0.5 g.) were added. The red color disappeared, and a white solid (the amino naphthol) separated when the solution was cooled. This solid was filtered off as rapidly as possible; the filtrate turned black within a few minutes. The white solid was boiled with aqueous ferric chloride and the mixture was extracted with chloroform. Evaporation of the chloroform left a red residue which, recrystallized from ethanol–ether, melted at 246–247° and showed no depression in melting point when mixed with a specimen of VI made by oxidation of IV or V.

Attempts to purify the intermediate **2-amino-3,4-diphenyl-α-naphthol** by crystallization failed, for solutions of it oxidized in the air very rapidly and turned black.

2-Bromo-3,4-diphenyl-α-naphthol (V).—The naphthol IV (2 g.) in ether (10 cc.) was stirred and brominated by the slow addition of bromine (0.35 cc.) in ether (10 cc.). Stirring was continued for thirty minutes after all of the bromine was added. Water was added, the ether layer was separated, washed with bisulfite and the solvent was evaporated. The residue, when crystallized twice from methanol, formed white needles (2.05 g.) melting at 157–158°.

Anal. Calcd. for $C_{22}H_{15}OBr$: C, 70.39; H, 4.03. Found: C, 70.6; H, 3.82.

2-Bromo-3,4-diphenyl-α-acetoxynaphthalene (XI).—The bromonaphthol V (100 mg.) was acetylated by heating it in acetic anhydride (2 cc.) containing a drop of sulfuric acid. The product (120 mg.), isolated in the usual way and crystallized from ethanol, formed white needles melting at 199–200°.

Anal. Calcd. for $C_{24}H_{17}O_2Br$: C, 69.06; H, 4.11. Found: C, 69.03; H, 4.28.

2-Bromo-3,4-diphenyl-1-methoxynaphthalene (XII).—The bromonaphthol V (750 mg.) was dissolved in sodium methoxide solution (prepared from 60 mg. of sodium and 20 cc. of methanol), and dimethyl sulfate (3 cc.) was added slowly. After stirring the mixture for an hour, sodium hydroxide (4 cc., 40%) was added and the mixture was poured into water and extracted with ether. The ether was evaporated and the residue (500 mg.) was crystallized twice from alcohol. The product separated in fine white needles melting at 209–210°.

Anal. Calcd. for $C_{23}H_{17}OBr$: C, 70.95; H, 4.41. Found: C, 70.52; H, 4.45.

Oxidation of the Bromonaphthol: 3,4-Diphenyl-1,2-naphthoquinone (VI).—A solution of the bromonaphthol V (0.5 g.) in acetic acid (10 cc.) was heated on the steam-bath, and to it was added chromic acid (150 mg.). After heating for two hours, the mixture was poured into water. The product was removed and crystallized twice from ethanol. It weighed 150 mg. The m. p. was 249–250°; when mixed with a specimen of VI prepared from the naphthol IV, the substance melted at 247–248°.

Anal. Calcd. for $C_{22}H_{14}O_2$: C, 85.13; H, 4.54. Found: C, 85.24; H, 4.84.

4-Hydroxy-3,4-diphenyl-α-tetralone (XVIII).—1,4-Naphthoquinone (20 g.) suspended in ether (500 cc.) was added slowly (two hours) to a solution of phenylmagnesium bromide prepared in the usual way from magnesium (16 g.), bromobenzene (99 g.) and ether (500 cc.). The color became first wine red and then orange. After adding all of the quinone, the mixture was stirred and refluxed for five hours. The reaction mixture, which contained a brown, sticky precipitate, was poured into ice and hydrochloric acid (150 cc.). The ether layer was separated, and the tetralone suspended in it was filtered off. The aqueous layer was thoroughly extracted with ether, the ether solutions were combined and the solvent was distilled off. The tetralone, separated during removal of the ether, was removed from time to time. The solids were combined and digested with chloroform. Most of the sparingly soluble red impurity was removed by filtering the hot solution. The filtrate was decolorized with charcoal, and the chloroform solution was concentrated and alcohol was added. The cooled solution deposited white plates of the tetralone XVIII (8.1 g.) melting at 207°. This is the same substance reported by Franssen as having structure XIV.

Anal. Calcd. for $C_{22}H_{18}O_2$: C, 84.04; H, 5.78. Found: C, 83.93; H, 5.87.

Oxime XIX.—The tetralone XVIII (400 mg.), hydroxylamine hydrochloride (1 g.), sodium hydroxide (2 cc., 20%), water (6 cc.) and ethanol (20 cc.) were refluxed

for fifteen minutes, giving a clear solution. Most of the alcohol was distilled off and the residual solution, on cooling, deposited white plates of the oxime XIX (500 mg.) melting at 195–196°. Recrystallization from alcohol gave a product melting at 196–197°.

Anal. Calcd. for $C_{22}H_{19}O_2N$: C, 80.20; H, 5.82. Found: C, 80.09; H, 6.21.

Oxidation.—The tetralone XVIII (1 g.) and potassium dichromate (3 g.) were refluxed in acetic acid (30 cc.) for six hours. The green solution was poured into water (100 cc.) and most of the acetic acid was neutralized with sodium carbonate. Some sticky, orange material rose to the top of the solution; this was removed with a spatula. The aqueous solution was extracted with benzene, and the benzene solution then extracted with sodium hydroxide solution (10%). The alkaline extraction was acidified and steam distilled. From the distillate, benzoic acid (200 mg.), m. p. and mixed m. p. 121°, was isolated. The residue in the distilling flask was extracted with ether; from the ether extract, *o*-benzoylbenzoic acid (hydrate) (520 mg.), m. p. and mixed m. p. 88–90°, was isolated. From the sticky orange solid originally found in the oxidation, a very small amount of the red quinone VI, m. p. and mixed m. p. 245°, was isolated by repeated crystallization from alcohol.

Naphthol IV.—The tetralone XVIII (500 mg.), acetic acid (15 cc.) and sulfuric acid (5 drops) were boiled for thirty minutes and then poured into water. The pinkish solid was removed, dissolved in alcohol and the solution decolorized with charcoal. The alcohol was boiled off and replaced by petroleum ether (b. p. 90–100°). On cooling white needles of 3,4-diphenyl-α-naphthol IV (430 mg.) were deposited. These had a melting point and mixed melting point of 142–143° and showed the phenomenon of solidification after melting with remelting at 153–154° (see above under properties of IV). This is the same substance reported by Franssen as having structure XVII.

Acetate IX.—The tetralone XVIII (1 g.), acetic anhydride (7.5 cc.) and sulfuric acid (1 drop) were boiled for fifteen minutes. The cooled solution was poured onto ice and the pinkish solid (m. p. 160–162°) was removed. The solid was dissolved in chloroform and the solution was decolorized with charcoal. Most of the chloroform was removed, alcohol was added and the solution was cooled. White cubes of the acetate IX (950 mg.), m. p. and mixed m. p. 162–162.5°, were obtained. This is the same substance reported by Franssen as having structure XVI.

Summary

1. Diphenylketene and phenylacetylene react by addition to form, in good yield, 3,4-diphenyl-α-naphthol, IV.

2. The structure of the naphthol was proved by degradation and by an independent synthesis from 1,4-naphthoquinone and phenylmagnesium bromide.

3. The work of Franssen on the addition of phenylmagnesium bromide to 1,4-naphthoquinone has been repeated and his structures for the products have been shown to be incorrect. These have been supplanted by the correct structures.

4. The reaction between diphenylketene and acetylenes appears to be quite general, although no solvent, or quite concentrated solutions, must be used in order to bring about a reaction. As yet the mechanism of this reaction is not known, but observations to be reported later indicate that an acetylenic hydrogen atom is not involved because diphenylacetylene also reacts with the ketene.

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Ortho-quinone Monoxime Inner Complexes

BY HELMUT M. HAENDLER WITH GEORGE McP. SMITH

Recently, Ciusa,[1] in work on phenanthrenequinone, observed that the monoxime behaved as do α-isonitroso ketones in reacting even in extremely dilute solutions with salts of cobalt, nickel, and iron. The divalent cobalt and nickel inner complexes obtained were of regular composition, having the structure
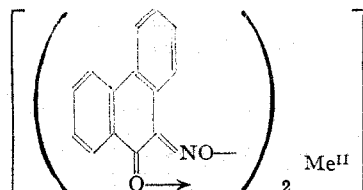
(1) Ciusa, *Gazz. chim. ital.*, **66**, 591 (1936).

In general, cobalt, nickel, and copper form inner complexes more readily than do other metals. To determine, however, the extent to which other inner complexes of this group would form, various metals were tested with phenanthrenequinone monoxime and other oximes possessing the chelating group C, C–NOH, O.[2]

Inner complexes of cadmium, copper, lead, manganese, and uranyl with phenanthrenequinone monoxime were prepared, and complexes of copper, lead, manganese, nickel, and uranyl with chrysenequinone monoxime also were prepared. In all cases except that of the uranyl compounds

(2) Haendler and Geyer, THIS JOURNAL, **60**, 2813 (1938).