phenols, using an improved procedure employing silver chloride as the oxidizing agent.

The absorptions of the dyes have been determined in four solvents covering a wide range of polarity. The effects of the various substituents on the absorption are explained qualitatively in terms of their effects on the resonance systems involved.

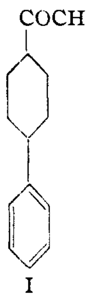
Rochester, New York Received July 8, 1946

[Contribution from the Laboratory of Organic Chemistry of the University of Wisconsin]

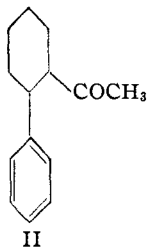
Some Observations on Friedel–Crafts Reactions Involving Unsaturated Ketones. 9-Keto-4b,5,6,7,8,8a,9,10-octahydrophenanthrene

By C. David Gutsche and William S. Johnson

In a previous communication[1] it was shown that the aluminum chloride-catalyzed reaction between acetylcyclohexene (or 2-chlorohexahydroacetophenone) and benzene, which was discovered by Nenitzescu and Gavat,[2] afforded a product which was not homogeneous, but consisted, in large part, of a crystalline form of 4-phenylhexahydroacetophenone, I. The presence of another stereoisomeric form of I was also demonstrated. In a search for other substances in the mixture, we have since submitted the crude reaction product to fractional distillation through an efficient column. Although this work is as yet incomplete it has served to indicate that the mixture is very complex, and has made possible the isolation of a new isomer of I, melting at 80–81°. This substance is shown below to be 2-phenylhexahydroacetophenone, II, and although isolated only in small yield the discovery of its presence has led to a number of interesting experiments and conclusions and to the synthesis of the hitherto unknown 9-keto-4b,5,6,7,8,8a,9,10-octahydrophenanthrene, IX.

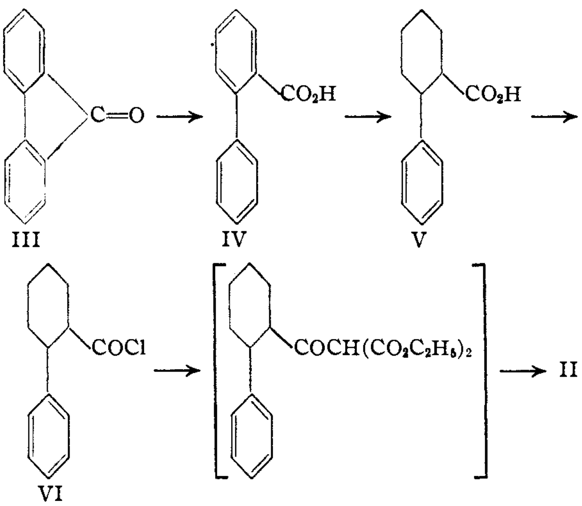


I



II

To prove the identity of the 81° ketone with the previously known 2-phenylhexahydroacetophenone reported to melt at 78–79°,[3] the latter was synthesized for comparison. The method of Kipping and Perkin[3] which involves the condensation of 1-phenyl-1,5-dibromopentane with acetoacetic ester appeared unpromising because of the inaccessibility of starting materials and the poor yields. A new synthesis was therefore developed involving the sequence of reactions indicated in the accompanying flow sheet.



The cleavage of fluorenone, III, with potassium hydroxide by the excellent procedure of Huntress and Seikel[4] gave 2-phenylbenzoic acid, IV, in 93–96% yields. Reduction of IV with sodium and amyl alcohol afforded the previously known[3] stereoisomer of 2-phenylcyclohexanecarboxylic acid, V, in 73% yield. The acid chloride VI was prepared and treated with sodiomalonic ester followed by acid hydrolysis without isolation of the intermediate keto di-ester. The over-all yield of II from V was 84%. The ketone thus obtained proved to be identical with that isolated from the Friedel–Crafts reaction as confirmed by mixed melting point determinations with the ketones and 2,4-dinitrophenylhydrazones.

Cook and Hewett[5] have made attempts to cyclize phenylacetylcyclohexene, VIII, to the keto-octahydrophenanthrene IX, using aluminum chloride or sulfuric acid, but they were able to isolate only recovered starting material. This failure to effect ring closure has since been confirmed by Bergs and Wittfeld,[6] and is indeed surprising in view of the fact that such a cyclization would represent the intramolecular counterpart of the Friedel–Crafts reaction to produce II described above. We have, therefore, reinvestigated this work.

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(1) Johnson and Offenhauer, This Journal, **67**, 1045 (1945).

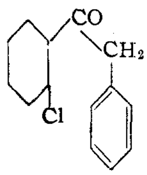
(2) Nenitzescu and Gavat, *Ann.*, **518**, 260 (1935).

(3) Kipping and Perkin, *J. Chem. Soc.*, 304 (1890).

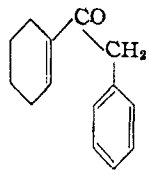
(4) Huntress and Seikel, This Journal, **61**, 816, 1066, 1358 (1939).

(5) Cook and Hewett, *J. Chem. Soc.*, 1098 (1933).

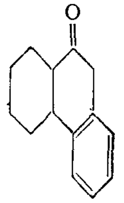
(6) Bergs and Wittfeld, *Ber.*, **67**, 238 (1934).



VII



VIII

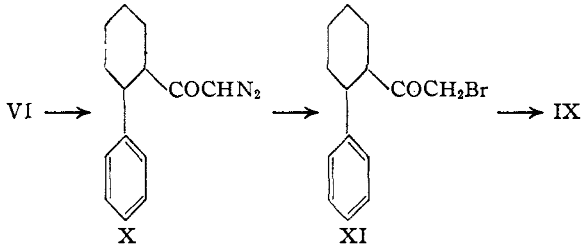


IX

Attempts to cyclize VIII with aluminum chloride under conditions like those described by Cook and Hewett gave, as reported by them, only starting material. However, when the ketone VIII was treated with dry hydrogen chloride and aluminum chloride in refluxing benzene, an oily product was produced which boiled somewhat higher than the starting material and did not solidify. From this material a homogeneous substance was isolated in about 5% yield as the semicarbazone, m. p. 221–222°, which was different from but, as shown by analysis, isomeric with the semicarbazone of VIII (m. p. 170–172°). That this actually was the product of cyclization is shown below. Hydrogen chloride was used in the cyclization because it is known to have a beneficial action on certain intermolecular reactions of a similar type.[7,8] The obvious inference that the chloro ketone VII may possibly be a reactive intermediate suggested that the preparation of the new ketone IX might be carried out in one step from phenylacetyl chloride and cyclohexene with aluminum chloride. This was indeed found to be the case and from the resulting oily product,[9] the 222° semicarbazone was isolated easily in 7–10% yield. Although the yield is low, the method constitutes an easy source of this material.

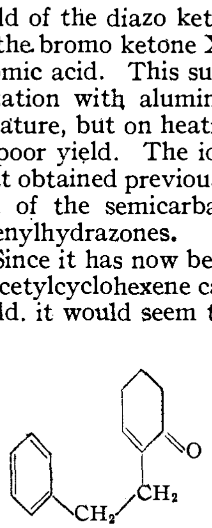
Hydrolysis of the semicarbazone with oxalic acid solution produced a mixture of the *cis* and *trans* forms of IX. One of these was isolated as a colorless crystalline substance melting at 66–66.5° from which the original semicarbazone could be regenerated in practically quantitative yield. The other stereoisomer was not obtained pure but was evidently present in the oily residue. This fraction was convertible to a mixture of semicarbazones from which a small amount of the 222° isomer only could be isolated in a pure state. The ready interconvertibility of the two isomers was demonstrated by the observation that additional solid isomer was obtained from the oily fraction by further treatment with oxalic acid.

The structure of the cyclized ketones was proved by the following series of experiments. The absence of the ethylenic bond was indicated by the fact that no hydrogen was absorbed by either the solid or liquid isomer in the presence of palladium–charcoal catalyst, while under the same conditions phenylacetylcyclohexene rapidly absorbed the calculated amount of hydrogen giving phenylacetylcyclohexane. Moreover, the cyclized ketones decolorized permanganate solution only slowly, whereas VIII reacted rapidly. Both of the cyclized products gave color reactions with alkali characteristic of β-tetralone types. Dehydrogenation over palladium–charcoal at 280–300° gave phenanthrene in 73% yield from the solid ketone and in 70% yield from the liquid ketone. When the reaction was carried out in refluxing *p*-cymene, 9-phenanthrol was obtained in 57 and 43% yields, respectively. These dehydrogenation experiments afford good, but not conclusive, evidence for the structure, because it is possible that cyclization could occur during the dehydrogenation. Indeed, Cook and Hewett[5] found that when the ketone VIII was submitted to Clemmensen reduction followed by dehydrogenation with selenium, phenanthrene was obtained directly. We, therefore, submitted VIII to dehydrogenation over palladium–charcoal and isolated *sym*-diphenylethane along with other unidentified products, but no phenanthrene could be detected.

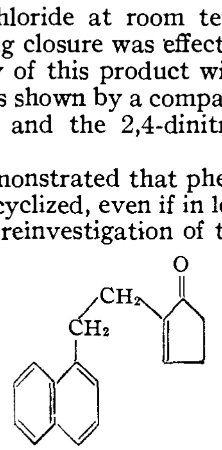


The structure IX was confirmed conclusively by an independent synthesis from the acid chloride VI. Treatment with diazomethane gave a 79% yield of the diazo ketone X which was converted to the bromo ketone XI in 89% yield with hydrobromic acid. This substance was resistant to cyclization with aluminum chloride at room temperature, but on heating ring closure was effected in poor yield. The identity of this product with that obtained previously was shown by a comparison of the semicarbazones and the 2,4-dinitrophenylhydrazones.

Since it has now been demonstrated that phenylacetylcyclohexene can be cyclized, even if in low yield, it would seem that a reinvestigation of the



XII



XIII

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[7] *Cf.* the work of Fuson, *et al.*, see This Journal, 58, 1979 (1936), for references.

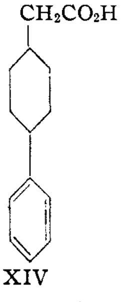
[8] It should be noted that Cook and Cohen, *J. Chem. Soc.*, 1570 (1935), also appreciated this consideration, and accordingly used hydrogen chloride in an attempt to cyclize the unsaturated ketone XIII. Their failure may perhaps be attributable to a failure to employ high enough temperatures.

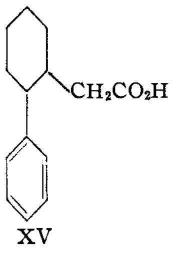
[9] It is interesting to note that the reaction may have been carried to this point by Fulton and Robinson, *J. Chem. Soc.*, 1463 (1933), who were endeavoring to prepare phenylacetylcyclohexene, VIII. They found that with aluminum chloride a non-crystalline product was obtained which had a somewhat higher boiling point than that of VIII.

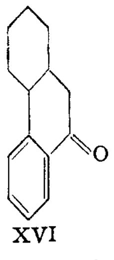
cyclization of the ketones XII and XIII, which has been reported to fail,[8,10] might prove fruitful.

The findings described in this paper help to clarify some of the confusion which is found in the literature regarding the reaction between cyclohexeneacetic acid and benzene in the presence of aluminum chloride. Ghosh[11] describes the reaction as producing 2-phenylcyclohexaneacetic acid, XV, m. p. 69–70° (amide, 196–197°), which on cyclization with sulfuric acid produced the ketoöctahydrophenanthrene, XVI, m. p. 96°. Cook and Goulden[12] and also Nenitzescu and Gavat,[13] on the other hand, obtained only 4-phenylcyclohexaneacetic acid, XIV, by this reaction. The English workers isolated a pure form of XIV, melting at 112.5–113.5° in 7% yield and proved the structure conclusively by degradation to 4-methylbiphenyl. The melting point of the amide (195–196°) corresponded closely with that of Ghosh's amide. The remaining non-crystalline acidic material was treated with sulfuric acid, but none of the ketone XVI was found.

Both stereoisomeric forms of 2-phenylcyclohexaneacetic acid, XV, have since been synthesized by unequivocal methods,[14,15,16] and the isomer (*trans*) which yields the 96° ketone (XVI) on cyclization was found to melt at 114°[16,17] instead of 69–70° as reported by Ghosh. The possibility that he was dealing with a polymorphic form has now been shown to be improbable by the preparation of the hitherto unknown amide of the 114° acid. The latter was obtained by a new synthesis involving the Arndt–Eistert reaction with 2-phenylcyclohexanecarboxylic acid, V. The product thus obtained melted at 114–114.5°, and that this was truly the *trans* acid was shown by cyclization with hydrogen fluoride to the 96° phenanthrone. The amide of this acid was found to melt at 127–128° instead of 196–197° as reported by Ghosh.


XIV


XV


XVI

Since it now appears probable that the product of reaction between cyclohexeneacetic acid and benzene consists of a mixture of position- as well as stereo-isomers, a possible explanation of the results of Ghosh is that the material on which his experiments were conducted was a mixture containing some of the *trans*-2-isomer (giving rise to the 96° ketone) and some of the 4-isomer which yielded the high melting (196°) amide. The failure of Cook and Goulden to find the 2-isomer may be attributed to the likely possibility that the course of such a reaction may be subject to minor variations of conditions as are many Friedel–Crafts type of reactions. The experimental details of Ghosh's work have not been published. This is particularly unfortunate since a similar confusing situation seems to have developed regarding the methylphenylcyclohexaneacetic acids.[18] It is noteworthy that Buu-Hoï and Cagniant[19] have recently described a reaction between ethyl cyclopentene-2-acetate and benzene in which the orientation apparently was of the type observed by Ghosh. The conditions were relatively mild, and the product, after hydrolysis, consisted mainly of one isomer which was most likely 2-phenylcyclopentaneacetic acid as indicated by cyclization experiments.

Fuson and his collaborators[7] have demonstrated that in the presence of hydrogen chloride and aluminum chloride, benzene adds to certain α,β-unsaturated carbonyl compounds like benzalacetophenone by a reversible reaction. The possible mechanism which this would suggest for the reaction between acetylcyclohexene and benzene—namely, a reversible addition to produce the normal product II, and in competition, an irreversible (or a slowly reversible) addition to give abnormal products that would be expected to predominate under more drastic reaction conditions—does not appear to be operating. This was shown by heating 2-phenylhexahydroacetophenone in benzene solution with hydrogen chloride and aluminum chloride. Starting material was recovered in good yield, indicating that under the conditions used the reaction was not reversible; otherwise the ketone II would have been expected to rearrange in part to I.

Experimental Part[20]

The Isolation of 2-Phenylhexahydroacetophenone (II) from the Friedel–Crafts Reaction.—The reaction[21] between acetyl chloride (71 cc.), cyclohexene (102 cc.), aluminum chloride (155 g.) and benzene (600 cc.) was carried out according to the procedure previously described for the preparation of 4-phenylhexahydroacetophenone.[1] Distillation of the reaction product at reduced pressure through a short Vigreux column afforded 124 g. of the crude mixture which was then distilled once through a 10-plate Fenske column packed with glass helices.[22] A

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[10] Cook and Cohen, *J. Chem. Soc.*, 1570 (1935).

[11] Ghosh, *Science and Culture*, **3**, 55 (1937) [*Chem. Zentr.*, **109**, I, 4319 (1938)].

[12] Cook and Goulden, *J. Chem. Soc.*, 1559 (1937).

[13] Nenitzescu and Gavat, *Ber.*, **70**, 1883 (1937).

[14] Cook, Hewett and Lawrence, *J. Chem. Soc.*, 71 (1936).

[15] Blumenfeld, *Ber.*, **74B**, 524 (1941).

[16] Linstead, Whetstone and Levine, This Journal, **64**, 2014 (1942).

[17] The *cis*-isomer melts at 169° and is cyclized to a liquid ketone *cis*-XVI.

[18] See Ghosh, *Science and Culture*, **3**, 120 (1937) [*Chem. Zentr.*, **109**, I, 4319 (1938)] and Chuang, Chu and Kao, *Ber.*, **73B**, 1347 (1940). Note that Ghosh used the lactone while the latter workers employed the unsaturated acid in the Friedel–Crafts reaction.

[19] Buu-Hoï and Cagniant, *Compt. rend.*, **220**, 744 (1945).

[20] All melting points are corrected.

[21] Carried out by Robert D. Offenhauer.

[22] We are indebted to Dr. Thomas P. Carney for conducting this distillation.

total of 38 fractions of approximately equal weight were taken between 155 and 172° (11 mm.) except for the fore-run (fraction 1, 2.7 g.) which boiled at 120–154° (11 mm.). On seeding with the solid isomer of 4-phenylhexahydroacetophenone,[1] the fractions between 13 and 38 all crystallized at least partially, the later fractions (from 22 on) being quite hard. The fractions 1 through 12 remained liquid. After standing several months some crystals were noted in fraction 2. On seeding the remaining liquid fractions with this material, numbers 2 through 6 partially crystallized. Fractions 4 and 5 contained the largest proportion of solid while fraction 6 was mostly liquid. These fractions (2 through 6) were combined and as much of the solid product as possible was isolated. Advantage was taken of the fact that the ketone is volatile with steam, and also can be crystallized from ether–petroleum ether. Thus 1.69 g. of colorless material, m. p. 79–80.5°, and 0.83 g. melting at 66–77.5° was isolated, making the total yield 2.52 g. or about 2% of the total crude product. The purest sample of this material which was obtained by recrystallization melted at 80–81° (reported m. p. 78–79°[3]).

Synthesis of 2-Phenylhexahydroacetophenone (II).—From 10.0 g. of fluorenone (Eastman Kodak Co. grade, m. p. 82–83.5°) there was obtained by the procedure of Huntress and Seikel[4] 10.2–10.6 g. (93–96%) of colorless 2-phenylbenzoic acid, m. p. 110–113°, which was satisfactory for the next step. Thirty grams of powdered potassium hydroxide and 300 cc. of diphenyl ether were used with efficient stirring at 180° for thirty to ninety minutes.

2-Phenylbenzoic acid was reduced by a procedure similar to that recently described for the reduction of 4-(*p*-methoxyphenyl)-benzoic acid.[23]

To a refluxing, stirred mixture of 20 g. of thin slices of sodium freshly added to 50 cc. of isoamyl alcohol, was introduced a hot solution of 10.1 g. of 2-phenylbenzoic acid (m. p. 110–113°) in 500 cc. of isoamyl alcohol over a period of from three to five minutes. The mixture became turbid due to the precipitation of the sodium salt, but became clear after several minutes giving a pale green solution. During the next forty-five minutes a total of 60 g. of sodium and 150 cc. of isoamyl alcohol was added, after which the refluxing viscous solution was stirred for ten minutes and then allowed to cool somewhat. While still warm 1000 cc. of water was added cautiously. After the alcohol was removed by steam distillation, the solution was acidified, steam distilled again to remove volatile acids, and cooled. The yield of crude 2-phenylcyclohexanecarboxylic acid (V), m. p. 92–100°, was 9.8–10.0 g. (94–96%). A single crystallization from petroleum ether (b. p. 60–68°) gave a total of 7.58 g. (73%) of colorless prisms, m. p. 103–105° with slight previous softening. A sample purified by repeated recrystallization had the m. p. 105.5–107° (reported 103–105°,[24] 104–105°,[3] 105–106°,[25] 105–107°[26]). Reductions in which less sodium (45 g. of sodium for 10 g. of acid) was used gave approximately the same yields. The results seemed to be consistently duplicable, and it was never found necessary to re-reduce the product as in a previous instance.[23]

2-Phenylhexahydrobenzoyl chloride (VI) was prepared from 1.20 g. of the acid (m. p. 104–106°) and 3 cc. of purified[27] thionyl chloride in 3 cc. of dry benzene. After forty minutes of refluxing, the solvents were removed under reduced pressure. The last traces of thionyl chloride were removed by twice adding 2–3 cc. of benzene and then removing it under reduced pressure. The process was repeated once using petroleum ether (b. p. 60–68°) and thus 1.26 g. (96% yield) of colorless crystalline acid chloride was obtained; m. p. 80–83° (reported,[28] 85–86°). Material made in this way was used to prepare the methyl ketone according to a procedure developed from that of Wilds and Beck.[29] The acid chloride from 0.78 g. of 2-phenylcyclohexanecarboxylic acid was dissolved in 30 cc. of dry ether and added to a cooled suspension of sodiomalonic ester prepared from 3.0 cc. of diethyl malonate and 0.30 g. of sodium shot in 35 cc. of ether. The solution was stirred for five minutes in the cold (ice-bath), five minutes at room temperature and then allowed to reflux for one hour. The cooled suspension was acidified with cold dilute hydrochloric acid, and the aqueous layer was separated and extracted with ether. The yellow oily keto di-ester which remained on evaporation of the combined ether extracts was boiled for two hours under reflux with 25 cc. of concentrated hydrochloric acid, 25 cc. of acetic acid and 14 cc. of water. Upon steam distillation of the reaction mixture the 2-phenylhexahydroacetophenone was found in the dilute acetic acid distillate from which the colorless ketone crystallized; yield 0.65 g. (84%); m. p. 79–81° Recrystallization from methanol cooled in a Dry Ice-bath gave colorless needles, m. p. 80–81°. No depression of the m. p. was observed on admixture with the material isolated from the Friedel–Crafts reaction described above.

The **2,4-dinitrophenylhydrazone** was prepared in the conventional manner with 2,4-dinitrophenylhydrazine and hydrochloric acid in alcohol. The product crystallized from alcohol in the form of orange needles, m. p. 140–141° (dec.).

Anal. Calcd. for $C_{20}H_{22}O_4N_4$: C, 62.81; H, 5.80. Found: C, 63.01; H, 5.79.

The 2,4-dinitrophenylhydrazone was likewise prepared from the ketone obtained by the Friedel–Crafts reaction. It melted at 140–141° (dec.) alone or on admixture with the authentic sample described above.

Phenylacetylcyclohexene (VIII) was prepared by a modification of previous methods.[5,6,30] The main changes in procedure involved the use of lower temperatures for the Darzens reaction, and the use of collidine for the dehydrohalogenation step.

To a cooled (to −40°) solution of 60 g. of phenylacetyl chloride (b. p. 98–100° at 13 mm.) and 100 g. of anhydrous stannic chloride in 240 cc. of carbon bisulfide was added slowly with stirring 32 g. of cyclohexene (b. p. 82–83° at 740 mm.). During the addition which required one and one-quarter hours, the temperature of the Dry Ice cooling-bath was maintained at −40°. After the addition was complete the temperature was allowed to rise to −15 to −5° and stirring was continued for two hours. The red solution was treated with ice and hydrochloric acid, and the organic layer was washed with dilute hydrochloric acid, saturated sodium bicarbonate solution, water, and finally dried over anhydrous potassium carbonate. Evaporation of the solvent left a red-brown oil which was heated under reflux with 55 g. of γ-collidine for three hours. Ether was added to the cooled solution and the collidine hydrochloride (17.5 g. or 29% of the theoretical) was separated by filtration. The filtrate was washed with dilute hydrochloric acid (to remove unreacted collidine), saturated sodium bicarbonate solution, and dried over anhydrous potassium carbonate. The dark red oil remaining after evaporation of the ether was distilled and the fraction boiling at 128–131° (0.2 mm.) was collected; yield, 33.6 g. (43%) of light yellow oil which crystallized on cooling. The English workers reported 24[5] and 26%[30] yields of comparable material. Bergs and Wittfeld[6] reported a 32% yield of redistilled ketone, m. p. 47°, but did not give many details of procedure. The crude ketone was recrystallized from methanol solution chilled in a Dry Ice-bath. Thus was obtained 22.3 g. (29% yield) of colorless ketone, m. p. 44–46°. A sample recrystallized twice from methanol was obtained in the form of colorless needles, m. p. 47–49°. The reported melting points range from 44.5[30] to 46–48°.[5] The semicarbazone was obtained as colorless crystals from methanol, m. p. 169.5–172° (dec.) (reported 171–172[30] and 168–169°[5]).

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(23) Johnson, Gutsche and Offenhauer, THIS JOURNAL, **68**, 1648 (1946).

(24) Ranedo and Leon, *Añal. soc. españ. fís. quím.*, **23**, 113 (1925) [*Chem. Zentr.*, **96**, I, 2557 (1925)].

(25) Fujise, *Ber.*, **71B**, 2461 (1938).

(26) Cook and Hewett, *J. Chem. Soc.*, 62 (1936).

(27) Fieser, "Experiments in Organic Chemistry," 2nd ed., D. C. Heath and Co., Boston, Mass., 1941, p. 381.

(28) Ranedo and Leon, *Añal. soc. españ. fís. quím.*, **24**, 552 (1926) [*Chem. Zentr.*, **98**, II, 1267 (1927)].

(29) Wilds and Beck, THIS JOURNAL, **66**, 1688 (1944).

(30) Fulton and Robinson, *J. Chem. Soc.*, 1463 (1933).

The **2,4-dinitrophenylhydrazone** prepared by the conventional procedure from 2,4-dinitrophenylhydrazine and hydrochloric acid in alcohol crystallized from alcohol in the form of orange-yellow needles, m. p. 166.5–167.5° (dec.).

Anal. Calcd. for $C_{20}H_{20}O_4N_4$: C, 63.15; H, 5.30. Found: C, 63.50; H, 5.34.

Treatment of the oil remaining after the separation of the phenylacetylcyclohexene with semicarbazide, gave some additional semicarbazone, m. p. 166–170° (dec.). No higher melting derivative could be isolated, thus indicating that little if any cyclization had occurred (see below).

9-Keto-4b,5,6,7,8,8a,9,10-octahydrophenanthrene (IX). (*a*) *Cyclization of Phenylacetylcyclohexene.*—A solution of 4.0 g. of phenylacetylcyclohexene (m. p. 44–46°) in 60 cc. of dry thiophene-free benzene was added slowly with stirring to a refluxing suspension of 9.0 g. of aluminum chloride and 50 cc. of thiophene-free benzene into which dry hydrogen chloride was passed at the rate of about 3 bubbles per second. The addition was complete in one hour, and the treatment was continued for one-half hour longer. The red-brown mixture was then allowed to stir at room temperature for one and one-half hours. After decomposition with ice and hydrochloric acid the organic layer was washed with dilute hydrochloric acid, saturated sodium bicarbonate solution and water. The red oil obtained on evaporation of the benzene was distilled at reduced pressure and separated into two main fractions: (a) 1.06 g., b. p. 135–145° (0.9 mm.), and (b) 1.18 g., b. p. 145–155° (0.9 mm.). Each fraction was treated with semicarbazide hydrochloride and pyridine in methanol, and crude semicarbazones were obtained as follows: from fraction (a) 0.60 g., m. p. over a wide range around 200° and from fraction (b) 0.65 g., m. p. over a wide range around 200°. Treatment of each with boiling methanol gave as insoluble fractions from (a): 0.007 g., m. p. 214–216° (dec.) and from (b): 0.24 g., m. p. 220–221° (dec.). Recrystallization from a large amount of methanol gave colorless plates of the semicarbazone of IX, m. p. 221–222° (dec.). The melting point was not depressed on admixture with the sample prepared as described under *b* below.

When an attempt was made to effect the cyclization at 0° instead of refluxing temperature, 1.43 g. of unchanged starting material was recovered from 1.90 g. The remaining material consisted of high boiling residues. In another attempt, refluxing carbon bisulfide was used in place of refluxing benzene, and from 4.0 g. of phenylacetylcyclohexene 2.90 g. of unchanged starting material was recovered, the remaining material being high boiling. An attempt to effect cyclization with boron trifluoride also failed.

(*b*) *From Phenylacetyl Chloride, Cyclohexene and Aluminum Chloride.*—Out of six experiments, in which the conditions were varied, the best procedure which was found was as follows. A mixture of 60 g. of freshly distilled[31] phenylacetyl chloride (b. p. 98–100° at 13 mm.) and 32 g. of cyclohexene (b. p. 82–83° at 740 mm.) was added dropwise with stirring to a refluxing suspension of 60 g. of aluminum chloride in 240 cc. of carbon bisulfide. After the addition was complete (one hour) the mixture was stirred at refluxing temperature for an additional hour. The cooled mixture was then treated with ice and hydrochloric acid, and the organic layer was washed with dilute hydrochloric acid, saturated sodium bicarbonate solution, water, and finally dried over anhydrous potassium carbonate. Distillation of the residue obtained on evaporation of the solvent gave 35.1 g. of oil, b. p. 143–157° (0.8 mm.). The crude semicarbazone, prepared in methanol with excess semicarbazide hydrochloride and pyridine by refluxing thirty minutes, amounted to 19.6 g. melting over a wide range around 200°. Trituration with boiling methanol (10 cc. per gram of crude semicarbazone) left 10.0 g. (10% yield) of fairly pure semicarbazone, m. p. 217–219° (dec.). No homogeneous semicarbazone was isolated from the solution. A sample of the **semicarbazone of IX** purified by repeated recrystallization either from methanol or from isopropyl alcohol was obtained as colorless plates, m. p. 221.5–222° (dec.).

Anal. Calcd. for $C_{15}H_{19}ON_3$: C, 70.01; H, 7.44. Found: C, 70.12; H, 7.37.

In two experiments the time allowed for addition of the reagents was increased to one and three-fourths hours or to two and one-half hours, and the reaction time after addition was complete was decreased to one-fourth hour and to one-half hour, respectively. The yields of good semicarbazone were 8.7 and 7.6%. In three other experiments the oily reaction product was treated with collidine as in the preparation of phenylacetylcyclohexene described above. The yield of semicarbazone of cyclized material varied from 6.5 to 7.5%. In these instances it was possible to isolate the semicarbazone, m. p. 169–171° (dec.), of phenylacetylcyclohexene from the methanol solution.

The semicarbazone of IX (5.0 g.) was hydrolyzed with a solution of 10 g. of oxalic acid in 100 cc. of water. The suspension was allowed to reflux in an atmosphere of nitrogen for four hours, and the resultant oil was extracted with ether. The combined extracts were washed with dilute hydrochloric acid, saturated sodium bicarbonate solution, water, and dried over anhydrous potassium carbonate. Evaporation of the ether gave 3.72 g. of red oil which was distilled at reduced pressure; yield, 3.20 g. (82%) of colorless oil which partially crystallized on cooling; b. p. 133.5–134° (0.25 mm.), 124–125° (0.01 mm.). A solution of this product in methanol on cooling in a Dry Ice-bath deposited crystals of **α-9-keto-4b,5,6,7,8,8a,9,10-octahydrophenanthrene.** A total of 1.50–1.65 g. of material melting at 59–62° was obtained by repeated concentration of the mother liquors followed by cooling in the freezing mixture. A sample twice recrystallized from methanol by cooling in an ordinary ice-bath, was obtained as colorless needles, m. p. 66–66.5°.

Anal. Calcd. for $C_{14}H_{16}O$: C, 83.96; H, 8.05. Found: C, 83.68; H, 7.94.

Evaporation of the mother liquor remaining after removal of the α-isomer gave a slightly yellow oil, which rapidly darkened on standing, hereafter referred to as the "liquid ketone." When this material was boiled with 2 g. of oxalic acid in 20 cc. of water in an atmosphere of nitrogen for two and one-half hours, and the product worked up as described above for the hydrolysis of the semicarbazone, 0.95 g. of distilled oil was obtained. From this it was possible to separate 0.29 g. of the solid α-isomer, m. p. 56–59°.

Color Reactions of the 9-Keto-4b,5,6,7,8,8a,9,10-octahydrophenanthrenes.—When β-tetralone is treated with alcoholic sodium hydroxide in the presence of air a deep blue color is produced which changes to orange on acidification of the alkaline solution.[32] Although the nature of these transformations is not known, Cornforth, Cornforth and Robinson[33] have observed that both the blue and orange color are extractable by benzene. Similar color changes have been noticed also with various substituted β-tetralones except when one or both of the hydrogen atoms of the reactive methylene group in the 1-position is involved.[33]

In the present work the solid α-isomer of IX was treated with alcoholic potassium hydroxide in the presence of air and was observed to give an orange solution which slowly turned to violet. On acidification the color changed to wine red. Both of the colors were extractable with benzene. The liquid ketone gave an orange-green solution in alkali, turning also to wine red on acidification. It should be noted that phenylacetylcyclohexene did not respond to the above color test.

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[31] In one experiment employing phenylacetyl chloride which had stood for some time and darkened somewhat, a reaction (possibly polymerization) took place when the acid chloride was mixed with the cyclohexene.

[32] Bamberger and Lodter, *Ann.*, **288**, 74 (1895); von Braun, Braunsdorf and Kirschbaum, *Ber.*, **55**, 3648 (1922); Straus and Rohrbacker, *ibid.*, 40 (1921).

[33] Cornforth, Cornforth and Robinson, *J. Chem. Soc.*, 689 (1942).

Formation of Derivatives of the 9-Keto-4b,5,6,7,8,8a,9,10-octahydrophenanthrenes.—The semicarbazone of the α-isomer (0.100 g.) was prepared in 4 cc. of methanol with 0.090 g. of semicarbazide hydrochloride and 0.1 cc. of pyridine by refluxing for five minutes. From the cooled solution there was obtained 0.120 g. (93% yield) of colorless plates, m. p. 215–218° (dec.). A single recrystallization from isopropyl alcohol gave material melting at 221–222° (dec.). The melting point was not depresssed on admixture with a specimen of the semicarbazone obtained from the cyclization experiments.

The semicarbazone of the liquid ketone was prepared in a similar way. From 0.631 g. of ketone there was obtained 0.756 g. (93% yield) of powdery product, m. p. 195–207° (dec.) with previous softening. Attempts to purify the material by trituration with boiling methanol followed by fractional crystallization were not promising. Ultimately a small fraction was isolated which melted at 221–222° (dec.) and was the semicarbazone of the α-isomer since, on admixture of the two samples, no depression of the melting point was observed.

The **2,4-dinitrophenylhydrazone of the α-isomer** was prepared from 0.080 g. of ketone and 0.070 g. of 2,4-dinitrophenylhydrazine in 5 cc. of alcohol. The solution was heated to boiling, 0.1 cc. of concentrated hydrochloric acid was added and refluxing continued for five minutes. On cooling 0.135 g. (89% yield) of product was obtained; m. p. 191–193° (dec.). Several recrystallizations from alcohol gave orange-red blades, m. p. 195.5–198° (dec.).

Anal. Calcd. for $C_{20}H_{20}O_4N_4$: C, 63.15; H, 5.30. Found: C, 62.84; H, 5.19.

The 2,4-dinitrophenylhydrazone from 0.196 g. of the liquid ketone was prepared in a similar manner to give 0.284 g. (76% yield) of an orange-red product, m. p. 165–175° (dec.). Attempts to separate the mixture by fractional crystallization or by chromatographic adsorption were unpromising.

Hydrogenation of Phenylacetylcyclohexene.—A solution of 0.350 g. of the ketone (m. p. 46–48°) in 15 cc. of ethyl acetate was shaken with 0.090 g. of 30% palladium-charcoal catalyst[34] and hydrogen. The calculated amount of gas was absorbed in fifteen minutes. The **2,4-dinitrophenylhydrazone of phenylacetylcyclohexane** was prepared from the oily product. The derivative crystallized from methanol in the form of orange-yellow needles, m. p. 101.5–102.5° (dec.).

Anal. Calcd. for $C_{20}H_{22}O_4N_4$: C, 62.81; H, 5.80. Found: C, 63.01; H, 5.95.

Dehydrogenation of Phenylacetylcyclohexene.—A mixture of 0.200 g. of the ketone and 0.070 g. of 30% palladium-charcoal[34] was heated in an (initial) atmosphere of nitrogen for forty-five minutes at 280–300°. The evolution of hydrogen ceased after about twenty-five minutes, and the total volume amounted to about 20 cc. The ether-soluble material amounted to 0.108 g. of sweet-smelling oil which after standing several days turned to a semicrystalline solid, m. p. about 41–48°. By recrystallization from methanol solution (cooled in Dry Ice) some crystals, m. p. 50–51°, were obtained. On admixture with an authentic specimen of *sym*-diphenylethane (m. p. 51–52°) the melting point was not depressed. Treatment of the mother liquors with picric acid gave no evidence of picrate formation, indicating the absence of phenanthrene.

Dehydrogenation of 9-Keto-4b,5,6,7,8,8a,9,10-octahydrophenanthrene. (*a*) *To Phenanthrene.*—A mixture of 0.100 g. of the α-isomer (m. p. 65–66°) and 0.040 g. of 30% palladium–charcoal[34] was heated in an (initial) atmosphere of nitrogen for forty minutes at 280–300°. About 80% of the calculated amount of hydrogen was evolved. The ether-soluble material amounted to 0.065 g. (73% yield) of crude phenanthrene, m. p. 87–95°. Recrystallization from alcohol gave colorless plates, m. p. 94–98°. A mixture with an authentic specimen of pure phenanthrene (m. p. 99–100°) melted at 96–99°. The picrate had the m. p. 141–143° which showed no depression on admixture with an authentic sample of the picrate (m. p. 143–144°) of phenanthrene.

A 0.050-g. sample of the liquid ketone was dehydrogenated in the same way over 0.020 g. of catalyst. The crude product amounted to 0.031 g. (70% yield), m. p. 88–95°. Recrystallization gave colorless plates, m. p. 96–99°. Mixed melting points with authentic specimens of the hydrocarbon and picrate showed no depression.

(*b*) *To 9-Phenanthrol.*[35]—A solution of 0.200 g. of the α-isomer in 4 cc. of *p*-cymene (twice distilled from sodium) was allowed to reflux with 0.040 g. of 30% palladium–charcoal[34] in an (initial) atmosphere of nitrogen. After twenty-six hours the evolution of hydrogen ceased and amounted to 60% of the calculated volume. After filtering, the solution was evaporated in a stream of air, and the residue was taken up in benzene and extracted with 10% potassium hydroxide solution. The aqueous solutions were acidified, and the precipitate extracted with benzene. Evaporation of the benzene gave 0.110 g. (57% yield) of material, m. p. 138–147°. Two recrystallizations (Norit) from petroleum ether (b. p. 60–68°) gave almost colorless felted needles, m. p. 149–151° (reported for 9-phenanthrol, 151–152°[14]). The neutral fraction consisted of 0.080 g. of a somewhat fragrant oil.

A 0.216-g. sample of the liquid ketone was dehydrogenated in a similar manner. After forty hours 48% of the calculated volume of hydrogen was evolved. The crude phenol amounted to 0.090 g. (43% yield), m. p. 135–145°. The recrystallized material melted at 149–151°.

ω-Diazo-2-phenylhexahydroacetophenone (X).[36]—A solution of the acid chloride VI, prepared as described above from 7.0 g. of 2-phenylcyclohexanecarboxylic acid, in 70 cc. of dry ether was introduced, over a period of ten minutes, into a solution of diazomethane (prepared from 15.0 g. of nitrosomethylurea) in 150 cc. of ether. The solution was shaken during the addition, and then allowed to stand at 0° for thirty minutes, and finally for two hours at room temperature. The pale yellow solution was concentrated at reduced pressure, and allowed to stand in the ice box overnight. The crystals which separated amounted to 4.65 g., m. p. 100–103° (dec.). By further concentration of the mother liquor an additional 1.5 g. of material, m. p. 99–102° (dec.), was obtained making the total yield of material 79%. The residue obtained on evaporation of the mother liquors turned to a sticky solid; weight 1.0 g. A sample of the diazo ketone was purified by repeated recrystallization from ether; very pale yellow blades; m. p. 103.5–104.5° (dec.).

Anal. Calcd. for $C_{14}H_{16}ON_2$: C, 73.65; H, 7.07. Found: C, 73.37; H, 7.24.

ω-Bromo-2-phenylhexahydroacetophenone (XI).—To a solution of 2.0 g. of the above diazo ketone (m. p. 100–103°) in 40 cc. of ether was added slowly with shaking 15 cc. of 48% hydrobromic acid saturated with ether. The mixture was shaken in a separatory funnel until no more gas was evolved. The ether layer was separated, washed with water, saturated sodium bicarbonate solution, again with water and finally dried over anhydrous sodium sulfate. Evaporation of the ether gave 2.2 g. (89% yield) of yellow bromo ketone, m. p. 57–58.5°. A sample repeatedly recrystallized from ether solution (cooled in a Dry Ice-bath) was obtained as colorless needles, m. p. 59.2–59.8°.

Anal. Calcd. for $C_{14}H_{17}OBr$: C, 59.79; H, 6.10. Found: C, 60.13; H, 6.19.

Cyclization of ω-Bromo-2-phenylhexahydroacetophenone.—A solution of 1.0 g. of the bromo ketone (m. p. 57–58.5°) in 20 cc. of dry thiophene-free benzene was allowed to reflux with 1.0 g. of anhydrous aluminum chloride for five hours. After treatment with ice and hydrochloric acid, the benzene layer was separated, washed with 20% hydrochloric acid, saturated sodium bicarbonate solution,

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[34] Linstead and Thomas, *J. Chem. Soc.*, 1127 (1940).

[35] *Cf.* the method of Mosettig and Duvall, This Journal, 59, 367 (1937).

[36] *Cf.* the procedure given by Houben, "Die Methoden der organischen Chemie," 3rd ed., Edwards Brothers, Inc., Ann Arbor, Mich., 1944, Vol. IV, p. 883.

and finally with water. Evaporation gave 0.74 g. of dark red viscous oil which was triturated with methanol. The soluble fraction (0.44 g.) was treated with 0.65 g. of semicarbazide hydrochloride and 0.6 cc. of pyridine. After refluxing for fifteen minutes, and standing several hours a brown precipitate formed. This was separated and washed with hot water followed by ether which removed the color leaving a colorless product, m. p. 211–214° (dec.); yield 0.100 g. or 11%. Recrystallization from methanol gave colorless plates; m. p. 221–222° (dec.), undepressed on admixture with the semicarbazone of 9-keto-4b,5,6,7,8,8a,-9,10-octahydrophenanthrene described above. The 2,4-dinitrophenylhydrazone was prepared directly from the semicarbazone as follows: a suspension of 9 mg. of the latter and 9 mg. of 2,4-dinitrophenylhydrazine in 3 cc. of 65% alcohol containing 50 mg. of oxalic acid was allowed to reflux for fifteen minutes. The alcohol was evaporated in a current of air, water was added, and the crude derivative (5 mg., m. p. 180–190°, dec.) which separated was recrystallized from alcohol as yellow needles, m. p. 189–193° (dec.). A mixture with the 2,4-dinitrophenylhydrazone (m. p. 191–194°, dec.) of the α-isomer described above melted at 190–194° (dec.).

When the cyclization was carried out as described above except that the refluxing period was shortened to one and one-half hours, only a trace of the high melting semicarbazone was isolated. An attempt to effect cyclization at room temperature for eleven hours, gave back 96% of unchanged starting material.

trans-**2-Phenylcyclohexaneacetic acid** (XV) was prepared from ω-diazo-2-phenylhexahydroacetophenone (m. p. 100–103°) according to the general procedure described in Organic Reactions.[37] The diazo ketone (1.00 g.) in 7 cc. of dioxane was added dropwise over a period of twenty minutes to a stirred suspension of 0.13 g. of silver oxide, in a solution of 0.34 g. of anhydrous sodium carbonate and 0.20 g. of sodium thiosulfate in 15 cc. of water. The temperature was held at 50–53° during the addition, and then was gradually raised to 90° during one hour. After cooling, the mixture was acidified with dilute nitric acid and extracted with benzene. The benzene solution was washed with dilute nitric acid, with water, and evaporated to give 0.92 g. of a greenish oil which solidified; m. p. 95–105°. Recrystallization from petroleum ether (b. p. 60–68°) gave 0.536 g. (56% yield) of colorless plates, m. p. 110–112°. Repeated recrystallization finally gave material with the constant melting point 114–114.5°.

A sample of the acid (0.364 g.) was treated for one and one-half hours with anhydrous hydrogen fluoride and worked up according to published procedures.[38] From the neutral fraction was isolated 0.306 g. (92% yield) of crude *trans*-10-keto-4b,5,6,7,8,8a,9,10-octahydrophenanthrene (XVI), m. p. 87–92°. Recrystallization from methanol gave almost colorless plates, m. p. 95–96°.

trans-**2-Phenylcyclohexaneacetamide** was prepared by ammonolysis of the chloride of the acid XV. After repeated recrystallization from dilute methanol, the amide was obtained in the form of colorless microscopic crystals, m. p. 127–128°.

Anal. Calcd. for $C_{14}H_{19}ON$: C, 77.38; H, 8.81. Found: C, 77.55; H, 8.65.

Treatment of 2-Phenylhexahydroacetophenone with Aluminum Chloride.—A solution of 3.0 g. of the ketone (m. p. 79–81°) in 50 cc. of thiophene-free benzene was saturated with hydrogen chloride and then treated with 6.0 g. of aluminum chloride. The suspension, which soon turned dark green, was allowed to reflux for three hours, and was then poured onto a mixture of ice and hydrochloric acid. The product was worked up in the customary manner, the neutral residue finally being submitted to steam-distillation. From the distillate there was isolated by ether extraction, 2.45 g. (82%) of the starting material, m. p. 70–79°. Recrystallization from methanol gave material melting at 77–80°. From the 0.30 g. of residue which did not steam distill, no semicarbazone could be obtained.

Summary

2-Phenylhexahydroacetophenone has been isolated from the product of the aluminum chloride-catalyzed reaction between acetylcyclohexene (or 2-chlorohexahydroacetophenone) and benzene. The structure was proved by comparison with material produced by a new and independent synthesis from fluorenone. The discovery that the 2-isomer is formed as well as the 4-isomer, which was originally thought to be the exclusive product of reaction, has led to a reinvestigation of the (previously unsuccessful) cyclization of 2-phenylacetylcyclohexene, which represents the intramolecular counterpart of the reaction to form 2-phenylhexahydroacetophenone. As a result, conditions were found whereby ring closure was effected to give the hitherto unknown 9-keto-4b,5,6,7,8,8a,9,10-octahydrophenanthrene. This interesting derivative of both β-tetralone and α-decalone has been characterized and the structure conclusively proved by degradation and by synthesis *via* a new and independent route. With the aid of some of the synthetic intermediates it has been possible to prepare some key substances which help to clarify some of the confusion existing in the literature in regard to the course of the aluminum chloride-catalyzed reaction between benzene and cyclohexeneacetic acid.

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[37] Bachman and Struve, "Organic Reactions," **I**, 50 (1942)

[38] Johnson, *ibid.*, **II**, 158 (1944).