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OLUSTEE, FLORIDA

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, RUTGERS UNIVERSITY]

The Acid-catalyzed Conversion of β-Arylketones to Tetrahydroindeno[1.2-a]indenes[1]

BY RODERICK A. BARNES AND BURTON D. BEITCHMAN[2]

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Some reactions of the hydrocarbon which results from the action of acids on 4-methyl-4-(*p*-tolyl)-2-pentanone have indicated it to be a tetrahydroindeno[1.2-a]indene. Although hydrocarbons with this ring system have not been previously described, the synthetic experiments which have been carried out confirm the structural assignment.

Four years ago in our laboratory it was observed that 4-methyl-4-(*p*-tolyl)-2-pentanone (I) was converted by boiling 50% sulfuric acid to a hydrocarbon II of unknown structure.[3] A similar result from the reaction of zinc chloride with 4-methyl-4-phenyl-2-pentanone (III) had been reported previously by Hoffmann.[4]

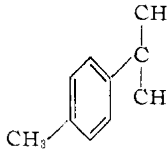
These facts suggested the possibility that an unusual ketone reaction of some generality might be involved. For this reason an investigation of the structure and mechanism of formation of these unknown hydrocarbons was initiated.

On the basis of an analysis and a molecular weight determination by the Rast procedure, Hoffmann assigned to his hydrocarbon IV the molecular formula $C_{24}H_{28}$. This formula would result if two molecules of ketone III reacted with the elimination of two water molecules. A cryoscopically determined molecular weight for our hydrocarbon II and the analysis of nitro and bromo derivatives were in best agreement with the formula $C_{23}H_{28}$; a hydrocarbon of this formula could result from two molecules of ketone I only by elimination of a three-carbon fragment. A similar process would lead to the formula $C_{21}H_{24}$ for Hoffmann's hydrocarbon.

Hydrocarbon II was inert toward potassium permanganate in acetone and reacted with bromine only slowly and with evolution of hydrogen bromide. This evidence for the absence of aliphatic double bonds in II requires the presence of two rings in addition to the two benzene rings. The failure of selenium at 400° to produce a dehydrogenation product suggested that these two rings were probably not six membered.

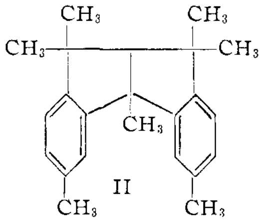
Hydrocarbon IV was not brominated by N-bromosuccinimide nor oxidized by chromic acid; however, both of these reagents attacked hydrocarbon II to yield a dibromide and a dibasic acid, respectively. When the carboxyl groups of the acid were reduced and the resulting glycol treated with phosphorus tribromide, a dibromide identical with that from the N-bromosuccinimide reaction was formed. Lithium aluminum hydride reduction of the dibromide regenerated hydrocarbon II. These transformations furnished definite evidence that except for the two methyl groups in hydrocarbon II *only* quaternary carbons[5] were joined directly to the benzene rings of these compounds.

This situation would result if the C_{10}-fragment (V) from ketone I remained essentially intact during the transformation to the hydrocarbon.



V

If two such fragments are present then only three more carbon atoms are available for constructing a system of two aliphatic rings. Five reasonable structures resulted from such constructions but only one fitted all of the experimental data.



II

The only previous example of a substance having four carbocyclic rings fused in this manner[6] is 9-keto-10-phenyl-9,10-dihydroindeno[1.2-a]indene[7] which was prepared by Kohler.[8]

The synthesis of a simpler homolog of structure II was planned in order to find out if this somewhat strained[9] ring system could be formed by an acid-catalyzed cyclization.

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[1] Presented at the 125th Meeting of the A.C.S., Kansas City, Missouri, March 27, 1954.

[2] Abstracted from a thesis presented by B. D. Beitchman to the Graduate School for the Ph.D. degree, December, 1953.

[3] This observation was made by Dr. G. R. Buckwalter, Ph.D. thesis, Rutgers University, 1950.

[4] A. Hoffmann, THIS JOURNAL, **51**, 2542 (1929).

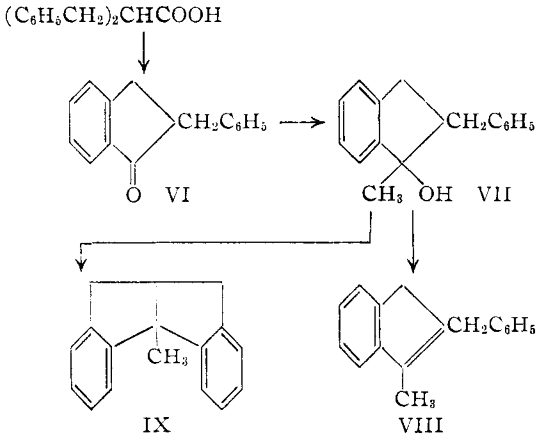
[5] For examples illustrating the fact that N-bromosuccinimide will attack preferentially secondary or tertiary carbon atoms adjacent to a benzene ring rather than a methyl group see R. A. Barnes and G. R. Buckwalter, THIS JOURNAL, **73**, 3959 (1951).

[6] A hydrocarbon, diphensuccindan, having two benzene rings fused in a different manner to the pentalene system was prepared by W. Roser, *Ann.*, **247**, 156 (1888).

[7] The numbering system used is that of A. M. Patterson and L. T. Capell, "The Ring Index," Reinhold Publ. Corp., New York, N. Y., 1940, p. 314.

[8] E. P. Kohler, *Am. Chem. J.*, **37**, 369 (1907).

[9] The five-membered ring of indane itself is distorted because the angle between a substituent group and the benzene ring tends to be near 120°. In structure II two such distorted rings are fused; however, the successful preparation of diphensuccindan, ref. 6, indicates that this kind of structure is possible.



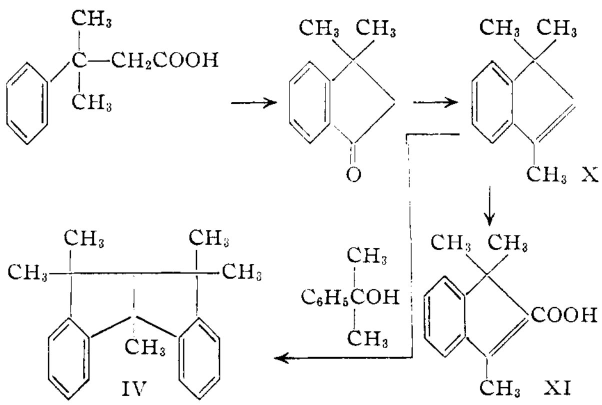
The dehydration of alcohol VII with a mixture of acetic anhydride and acetyl chloride produced indene VIII; the ultraviolet absorption spectrum of this compound was very close to that of similarily substituted indenes. The reaction of alcohol VII with cold 90% sulfuric acid yielded hydrocarbon IX. The ultraviolet spectrum of this product was quite different from that of VIII but was similar to the spectrum of indane and also to that of hydrocarbon IV.

TABLE I

Compound	Maxima, mμ (log ε)
3-Methylindene	252 (3.05)
VIII	260 (4.19)
Indane	260 (3.00), 267 (3.17), 272 (3.28)
IX	261 (3.37), 267 (3.48), 274 (3.47)
IV	260 (3.07), 266 (3.30), 274 (3.36)
II	265 (3.28), 271 (3.46), 273 (3.47), 280 (3.58)

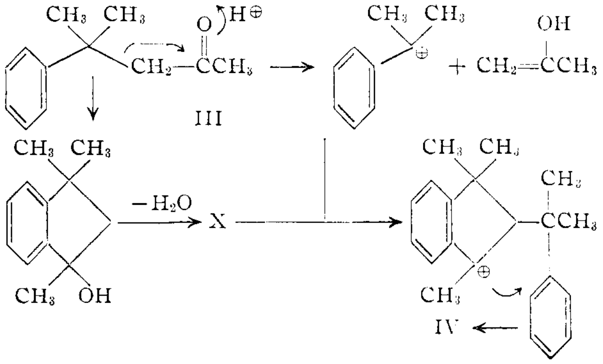
Hydrocarbon II with the two additional methyl groups on the benzene rings absorbs as expected at slightly longer wave lengths; also the central maximum of the other indanes appears as two separate peaks in this example.

After a number of unsuccessful routes were investigated a synthesis for hydrocarbon IV was effected finally by treating a mixture of dimethylphenylcarbinol and 1,1,3-trimethylindene with 90% sulfuric acid at −5°.



An alternate approach was carried as far as the preparation of acid XI, but the next step requiring the aluminum chloride catalyzed addition of benzene to the double bond of acid XI was unsuccessful at moderate temperatures. No attempt was made to use more drastic conditions for this step because the increased possibility for rearrangements would make doubtful any structural deductions.

The successful synthesis of hydrocarbon IV also suggests a reasonable mechanism for its formation from ketone III.



Thus the two intermediates necessary for the formation of IV are both produced in the reaction mixture by the action of acids on III. The acid-catalyzed cleavage of ketones is unlikely except with molecules such as III in which the carbonium ion formed is rather stable. The conversion of ketones similar to III to indenes by various acids is well known.[10]

Attempts to isolate tetrahydroindeno[1.2-a]indenes from acid treatment of a brominated derivative of III, 4-methyl-4-(*p*-bromophenyl)-2-pentanone, and 4,4-diphenyl-2-butanone were unsuccessful. In both of these cases the cleavage to the carbonium ion should be as facile as with ketone III, but the formation of the indene would be expected to be more difficult. In the first ketone the bromine atom would deactivate the benzene ring and in the second the effect of the *gem*-dimethyl group in facilitating the closure of the five-membered ring is lacking.[11]

An attempt to cyclize 3-benzyl-4-phenyl-2-butanone to a tetrahydroindeno[1.2-a]indene with various acids was not successful; this ketone also has no *gem*-dimethyl groups.

Experimental[12]

3,4b,6,9,9,10,10-Heptamethyl-4b,9,9a,10-tetrahydroindeno[1.2-a]indene (II). A.—A mixture of 4-methyl-4-(*p*-tolyl)-2-pentanone[5] and 50% sulfuric acid (600 ml.) was refluxed for eight hours. The cold reaction mixture was extracted with ether, the ether extract was dried and concentrated and finally the residue was vacuum distilled. The fractions (3.7 g.) boiling at 132–178° (8.5 mm.) crystallized on standing and after recrystallization from ethanol *ca.* 2.5 g. (5%) of pure hydrocarbon II was isolated, m.p. 137–138°.

Anal. Calcd. for $C_{23}H_{28}$: C, 90.73; H, 9.26. Found: C, 90.68; H, 9.28.

B.—The preparation of 4-methyl-4-(*p*-tolyl)-2-pentanone (I) was carried out as usual[5] except that the reaction mixture was allowed to stand for 48 hours at room temperature be-

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(10) L. I. Smith and W. W. Pritchard, THIS JOURNAL, **62**, 771 (1940); J. Colonge and G. Weinstein, *Bull. soc. chim. France*, [5] **18**, 961 (1951); J. Koo, THIS JOURNAL, **75**, 1984 (1953).

(11) This effect has been discussed by C. K. Ingold, *J. Chem. Soc.*, **119**, 306 (1921); M. T. Bogert and D. Davidson, THIS JOURNAL, **56**, 185 (1934), have reported examples in the indane series.

(12) All melting points were determined using a Kofler hot-stage; analyses were by W. Manser, Zurich, Switzerland.

fore processing. Besides ketone I a fraction boiling at 160–230° (12 mm.) also was collected. When acetone was added to this fraction and the solution chilled, hydrocarbon II crystallized. There was obtained 22.8 g. (6.4%) of pure II from 225 g. of mesityl oxide.

The molecular weight of II was determined with a Beckmann freezing point apparatus using benzene as a solvent.

Anal. Calcd. for $C_{23}H_{28}$: mol. wt., 304.5. Found: mol. wt., 284, 295.

A dinitration product[13] of II was prepared.[14] This substance melted at 312–314° after several recrystallizations from dilute ethanol.

Anal. Calcd. for $C_{23}H_{26}O_4N_2$: C, 70.03; H, 6.64; N, 7.10. Found: C, 70.20; H, 6.51; N, 7.08.

A dibromo derivative of II was prepared[15] and after recrystallization from glacial acetic acid it melted at 181.5–182.5°.

Anal. Calcd. for $C_{23}H_{26}Br_2$: C, 59.75; H, 5.67; Br, 34.58. Found: C, 59.68; H, 5.52; Br, 34.56.

Oxidation of Hydrocarbon II.—A mixture of II (2.2 g.), acetic acid (60 ml.), water (60 ml.), concd. sulfuric acid (10 ml.) and chromic oxide (14 g.) was refluxed for six hours. The cold reaction mixture was diluted with water and the precipitate was filtered. The crude acid was shaken with a mixture of ether and dilute sodium hydroxide. From the ether layer there was recovered 0.75 g. (34%) of II and from the alkaline solution by acidification there was obtained 0.98 g. (37%) of acid. Subsequent oxidations yielded 47 and 54% of acid. This acid melted with decomposition at *ca.* 340–346°. It was very insoluble and could be recrystallized only from large amounts of glacial acetic acid. A sample prepared in this way apparently retained acetic acid even after the usual vacuum drying.

Anal. Calcd. for $C_{23}H_{24}O_4$: C, 75.80; H, 6.64. Found: C, 74.72; H, 6.69.

The methyl ester of this acid, methyl 4b,9,9,10,10-pentamethyl-4b,9,9a,10-tetrahydroindano[1.2-a]indene-3,6-dicarboxylate (XII), was prepared by adding the acid (7.05 g.) to a solution of diazomethane in ether. After evaporation of the ether the residue was recrystallized from methanol to yield 6.22 g. (81%) of pure ester, m.p. 173.8–174.6°.

Anal. Calcd. for $C_{25}H_{28}O_4$: C, 76.50; H, 7.19. Found: C, 76.90; H, 7.47.

3,6-Dihydroxymethyl-4b,9,9,10,10-pentamethyl-4b,9,9a,10-tetrahydroindeno[1.2-a]indene (XIII).—The dimethyl ester XII (1 g.) was dissolved in ether (27 ml.) and added to a well-stirred solution prepared by refluxing a mixture of lithium aluminum hydride (0.464 g.) and ether for 40 minutes. After decomposition of the reaction mixture the ether layer was separated and concentrated. There was obtained 0.71 g. (82%) of diol XIII which melted at 196.8–197.0° after recrystallization from methanol.

Anal. Calcd. for $C_{23}H_{28}O_2$: C, 82.10; H, 8.39. Found: C, 81.80; H, 8.57.

3,6-Dibromomethyl-4b,9,9,10,10-pentamethyl-4b,9,9a,10-tetrahydroindeno[1.2-a]indene (XIV). A.—A mixture of hydrocarbon II (2.0 g.), N-bromosuccinimide (2.7 g.), benzoyl peroxide (0.08 g.) and carbon tetrachloride (80 ml.) was refluxed for two hours. The cold reaction mixture was washed with water and the organic layer separated, dried and concentrated. The solid residue (2.5 g.) melted at 197.5–199° after recrystallization from acetic acid.

B.—Alcohol XIII (0.5 g.) was added to a solution of phosphorus tribromide (0.1 ml.) in benzene (10 ml.). The reaction mixture was allowed to stand four hours at 0° and 15 hours at room temperature. Water was added and the benzene layer separated. The residue remaining after removal of the solvent was recrystallized from benzene-ligroin to yield bromide XIV which melted at 199–201°.

Anal. Calcd. for $C_{23}H_{26}Br_2$: C, 59.75; H, 5.67. Found: C, 60.16; H, 5.85.

The melting point of a mixture of this dibromide with that prepared in part A was 197–199°. The infrared absorption curves of these two samples were identical.

To a solution of lithium aluminum hydride (0.4 g.) in ether (50 ml.) was added a sample (0.45 g.) of the dibromide prepared by procedure B. The mixture was refluxed for 90 minutes and then processed by addition of dilute sulfuric acid and ether extraction of the product. Evaporation of the solvent left a residue (0.39 g.) of hydrocarbon II which was recrystallized from acetic acid. The melting point was 138–139° alone or when mixed with an authentic sample of II.

Attempted Dehydrogenation of II.—Hydrocarbon II (1 g.) and selenium (1 g.) were heated in a Pyrex tube at 400° for 24 hours. Although some hydrogen selenide was evolved most of the hydrocarbon was recovered unchanged.

2-Benzyl-1-indanone (VI).—The preparation of ethyl α,α-dibenzylacetoacetate was carried out in 53% yield following the procedure of Leuchs, Heller and Hoffmann.[16] The ester melted at 55–57° after recrystallization from ethanol. The crude 2,4-dinitrophenylhydrazone (m.p. 93–116°) prepared from this ester was difficult to purify by recrystallization. However, when this product was chromatographed on acid-washed alumina the main fraction yielded a pure derivative which melted at 129–131.5° after recrystallization from hexane.

Anal. Calcd. for $C_{26}H_{26}O_6N_4$: C, 63.66; H, 5.34; N, 11.42. Found: C, 63.66; H, 5.32; N, 11.31.

The ester (26.7 g.) was boiled for three hours with a solution of potassium hydroxide (14.5 g.) in ethanol (160 ml.). Most of the alcohol was distilled and the residue acidified with 20% hydrochloric acid. The oily acid which separated, solidified on standing and the solid product was filtered and recrystallized from hexane. There was obtained 19.1 g. (79%) of α,α-dibenzylacetic acid which melted at 88–90.5°.

The acid (17.6 g.) was placed in a polyethylene bottle and liquid hydrogen fluoride (334 g.) was added. The reaction mixture was allowed to stand at room temperature for 25 hours. Most of the excess hydrogen fluoride remaining was evaporated by heating the bottle in a water-bath in the hood. Potassium hydroxide solution (50%) was added to the cold reaction mixture until the solution was basic and the product was extracted with ether. The ether was evaporated and the residue distilled to yield 14.8 g. (90%) of VI which boiled at 137–142° (0.10–0.15 mm.), n^{23}D 1.6014.[17]

2-Benzyl-3-methylindene (VIII).—Ketone VI (14.8 g.) dissolved in ether (25 ml.) was added to a cold (−10°) solution of methylmagnesium iodide prepared from magnesium (1.94 g.), methyl iodide (14.9 g.) and dry ether (100 ml.). The reaction mixture was stirred at −10° for an additional hour and finally at room temperature for an hour. Cold ammonium chloride solution was added and the ether layer separated, dried and concentrated to yield crude 2-benzyl-1-methyl-1-indanol (VII).

A solution of crude alcohol VII (1.76 g.) in a 2:1 mixture of acetic anhydride and acetyl chloride (42 ml.) was heated on the steam-bath for six hours. The solvents were removed by distillation and the residue vacuum distilled. There was obtained 1.54 g. (91%) of VIII which boiled at 134–139° (0.02–0.03 mm.). Further purification by evaporative distillation yielded the pure hydrocarbon, n^{25}D 1.6028.

Anal. Calcd. for $C_{17}H_{16}$: C, 92.68; H, 7.32. Found: C, 92.61; H, 7.54.

4b-Methyl-4b,9,9a,10-tetrahydroindeno[1.2-a]indene (IX).—Alcohol VII (2.4 g.) was stirred with 90% sulfuric acid (10 ml.) at −5° for two hours. The cyclized product was extracted from the sulfuric acid with petroleum ether. Evaporation of the petroleum ether left a residue (1.5 g., 67%) of crude product which was purified by evaporative distillation at 120° (0.70 mm.), n^{25}D 1.5948.

Anal. Calcd. for $C_{17}H_{16}$: C, 92.68; H, 7.32. Found: C, 92.62; H, 7.45.

1,1,3-Trimethylindene (X). A.—This hydrocarbon was prepared from 3,3-dimethyl-1-indanone[18] by the addition of methylmagnesium iodide and dehydration of the resulting alcohol, 1,3,3-trimethyl-1-indanol, with anhydrous oxalic

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(13) A consideration of steric and electronic factors leads to the conclusion that electrophilic substitutions in the benzene nuclei of II would take place at the 2- and 7-positions.

(14) R. L. Shriner and R. C. Fuson, "Identification of Organic Compounds," 3rd Edition, John Wiley and Sons, Inc., New York, N. Y., 1948, p. 197.

(15) Reference 14, p. 189.

(16) H. Leuchs, A. Heller and A. Hoffmann, *Ber.*, **62**, 875 (1929).

(17) H. Leuchs, J. Wutke and E. Gieseler, *ibid.*, **46**, 2211 (1913), previously prepared VI using phosphorus pentachloride as the cyclizing agent.

(18) C. F. Koelsch and C. D. LeClare, *J. Org. Chem.*, **6**, 526 (1941).

acid.[19] From the crude indanol (53.0 g.) there was obtained 28 g. (53%) of X which boiled at 52–61° (0.5 mm.), n^{25}D 1.5353 (reported[19] 1.5346). In addition to X there also was obtained 8 g. (8.5%) of an unsaturated hydrocarbon, b.p. 120–124° (0.1 mm.), n^{25}D 1.5637, which may be a di-indene.

B.—When ketone III (11.2 g.) was heated with polyphosphoric acid (84 g.) at 94–108° for 40 minutes there was obtained 0.5 g. of a fraction which boiled at 68–78° (2–3 mm.), n^{27}D 1.5300. This product was almost certainly indene X.

1,1,3-Trimethylindene-2-carboxylic Acid (XI).—Indene X (28.3 g.) was dissolved in carbon tetrachloride (28 ml.) and to this solution at 0° bromine (28.6 g.) was added. The crude dibromide which remained after removing the solvents was treated with a solution of potassium hydroxide (24.4 g.) in ethanol (100 ml.). This mixture was refluxed for ten minutes and then poured into water. The oily product was purified by fractionation to yield 27.8 g. (82%) of material which boiled at 59–71° (0.25–0.35 mm.), n^{25}D 1.5700. A sample was evaporatively distilled for further purification, but analysis indicated that it still contained an unbrominated impurity.

Butyllithium was prepared from butyl bromide (20 g.), lithium (1.8 g.) and dry ether (50 ml.). A solution of the bromoindene (13.6 g.) was added dropwise at room temperature and after 30 minutes of stirring this solution was poured onto powdered Dry Ice. The acidic product was taken up in dilute sodium hydroxide solution. Acidification of this solution yielded 5.4 g. (46.7%) of acid which melted at 162–163° after recrystallization from acetic acid.

Anal. Calcd. for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98. Found: C, 76.92; H, 6.80.

When acid XI (074 g.) dissolved in dry benzene was stirred with anhydrous aluminum chloride (0.98 g.) for three hours either at room temperature or at 50° and the reaction mixture processed, only unchanged acid XI could be isolated.

4b,9,9,10,10-Pentamethyl-4,9a,9,10-tetrahydroindeno[1.2-a]indene (IV). **A.**—Mesityl oxide (200 g.), aluminum chloride (360 g.) and benzene (800 ml.) were allowed to react as in the preparation of hydrocarbon II.

The crude liquid products from this reaction were separated by fractional distillation. The first two fractions (74 g.) were mixtures of 4-methyl-4-phenyl-2-pentanone (III) and indene X (based on infrared spectra and refractive indices). Fraction three (48 g.) was mostly ketone III, but 1.1 g. of hydrocarbon IV could be isolated from it. Fraction four (76 g.), b.p. 134–154° (0.37 mm.), mostly crystallized and after recrystallization from ethanol yielded 26.7 g. (10%) of IV which melted at 131–133°. The pure substance melted at 133–134°.

Anal. Calcd. for $C_{21}H_{24}$: C, 91.25; H, 8.75. Found: C, 91.38; H, 8.59.

This compound was identical with the hydrocarbon prepared from ketone III by the action of zinc chloride at 180°.[4]

The mother liquors remaining after separation of crystalline hydrocarbon IV were concentrated and the residue distilled several times to yield a homogeneous fraction which could be evaporatively distilled at 108–109° (0.05 mm.) n^{25}D 1.5617.

Anal. Calcd. for $C_{21}H_{24}$: C, 91.25; H, 8.75. Found: C, 91.19; H, 8.70.

This product decolorized a solution of potassium permanganate in acetone and is believed to be 1,1,3-trimethyl-2-(α,α-dimethylbenzyl)-indene.

B.—A mixture of indene X (5 g.) and phenyldimethylcarbinol (4.3 g.) was stirred at −5° while 90% sulfuric acid (41.2 ml.) was added dropwise. The mixture was stirred at −5° for two hours and then the product was extracted with petroleum ether. The solvent was removed and the residue distilled to yield 1.75 g. (20%) of crystalline product which melted at 133–134° after recrystallization from ethanol. The melting point of this product and that obtained in part A was also 133–134°. The infrared absorption curves for the two samples were identical.

C.—Polyphosphoric acid (84 g.) at 100° also converted ketone III (11.2 g.) to hydrocarbon IV in 6.8% yield (1.2 g.). Refluxing ketone III (15 g.) with 50% sulfuric acid produced hydrocarbon IV in very low yield (*ca.* 0.1 g.).

Unsuccessful Attempts to Prepare Tetrahydroindeno[1.2-a]indenes. **A.**—4-(*p*-Bromophenyl)-4-methyl-2-pentanone[20] was heated with anhydrous zinc chloride at 180° and at 250°. At the lower temperature most (*ca.* 75%) of the ketone was recovered unchanged. At the higher temperature some reaction had taken place, but only unsaturated non-crystalline oils were obtained.

B.—4,4-Diphenyl-2-butanone[21] was refluxed with 50% sulfuric acid and heated with zinc chloride at 180°. Neither experiment produced any definite products in amounts sufficient for characterization.

C.—3-Benzyl-4-phenyl-2-butanone was prepared by the hydrolysis of α,α-dibenzylacetoacetate with hydriodic acid.[16] It formed a 2,4-dinitrophenylhydrazone which melted at 126–127° after recrystallization from ethanol-water.

Anal. Calcd. for $C_{23}H_{22}O_4N_4$: C, 66.01; H, 5.30; N, 13.39. Found: C, 66.09; H, 5.29; N, 13.56.

This ketone was refluxed with 50% sulfuric acid, heated with zinc chloride at 180° and stirred with 90% sulfuric acid at −5°, but in all these experiments large amounts of the ketone were recovered unchanged and fractional distillation yielded no fractions having the properties of hydrocarbon IX, the expected product.

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[19] J. Colonge and P. Garnier, *Bull. soc. chim. France*, [5] **15**, 436 (1948).

[20] J. Corse and E. Rohrmann, THIS JOURNAL, **70**, 370 (1948).

[21] G. G. Henderson and M. A. Parker, *J. Chem. Soc.*, **71**, 678 (1897).