Purification by the usual procedure,[2] including chromatoggraphy on silica gel, yielded 37 g. of cycloöctatetraene and 5.0 g. (13%) of the carbinol XI, b.p. 73–75.5° (0.5 mm.), $n^{25}\text{D}$ 1.5370–1.5382. A redistilled analytical sample had b.p. 74.5–75.5° (1.3 mm.), $n^{25}\text{D}$ 1.5370, $d^{25}{}_4$ 1.1024.

Anal. Calcd. for $C_{11}H_{14}O$: C, 81.48; H, 8.64. Found: C, 81.49; H, 8.79.

An authentic sample of the carbinol XI was prepared by adding methyl cycloöctatetraenecarboxylate[3] (1.28 g.) in 10 ml. of dry ether to the methylmagnesium iodide prepared from 0.36 g. of magnesium and 2.27 g. of methyl iodide in 20 ml. of dry ether. The magnesium salts were decomposed with aqueous ammonium chloride and the ether solution was washed with water, dried over magnesium sulfate and concentrated. Distillation of the residue through a semimicro column yielded 0.81 g. of crude XI, b.p. 73–75° (2.5 mm.), $n^{25}\text{D}$ 1.5369–1.5371. The infrared spectrum of the product showed a strong carbonyl band, so it was purified by chromatography on a column containing 25 g. of neutral alumina with activity 3.[10] Elution with 300 ml. of benzene followed by concentration and distillation yielded 0.49 g. of recovered methyl cycloöctatetraenecarboxylate, b.p. 76° (2.3 mm.), $n^{25}\text{D}$ 1.5371, identified by the infrared spectrum. Elution with 300 ml. of ether followed by concentration and distillation through a semimicro column yielded 0.21 g. of XI, b.p. 74.5° (3.0 mm.), $n^{25}\text{D}$ 1.5357, which had an infrared spectrum identical with XI prepared by copolymerization, except for the presence of weak bands at 5.83 and 6.5 μ due to a small amount of impurity.

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(10) H. Brockman and H. Schodder, *Ber.*, **74**, 73 (1945).

Cambridge 39, Mass.

[Contribution from the Baker Laboratory of Chemistry, Cornell University]

Polynuclear Aromatic Hydrocarbons. I. A New Synthesis of Picene

By Donald D. Phillips

Received February 17, 1953

9,10-Dihydrophenanthrene (I) has been found to be a suitable intermediate in a new synthesis of picene. The synthetic scheme, which is considerably shorter than those heretofore reported, depends on the diacylation of I to give the symmetrical diketoester, II, which may be reduced, dehydrogenated and preferentially cyclized to XI, a compound readily convertible to picene, XII. The over-all yield for the synthesis is 7.5%.

Among the dehydrogenation products of pentacyclic triterpenoids are found the substituted picenes. When the structure of these picenes is known, the position of the methyl groups in the extreme rings of the triterpene may usually be determined. An example is the conversion of β-amyrin to 2,9-dimethylpicene.[1] Consequently, it is of some value to devise a synthesis of this ring system which is particularly adaptable to the preparation of picenes encountered in triterpenoid degradations. Such a synthesis forms the basis for the present communication.

The difficulties and potential ambiguities in the recorded preparations of picene derivatives have already been reported by Newman.[2,3] The latter author avoided the use of an intramolecular cyclization catalyzed by aluminum chloride in view of the known lability of alkyl groups under these conditions.[4] However, as many as fifteen steps were still required for the preparation of 2,9-dimethylpicene which resulted in an over-all yield of approximately 0.1%.[3]

It appeared likely that a suitable phenanthrene derivative might serve as a starting material for a shorter synthesis. In this paper we report the successful synthesis of picene (see Charts 1 and 2) from 9,10-dihydrophenanthrene.

It has been found possible to diacylate I by using β-carbomethoxypropionyl chloride and a large excess of aluminum chloride. In this way a 48% yield of diketoester II has been obtained, accompanied by a 36% yield of the expected monoacylated product, VI. Assignment of the second acyl group to the 7-position in II is in accord with the results of Mosettig and Stuart[5] who found that 2-hydroxy-9,10-dihydrophenanthrene gave rise to 7-acyl derivatives when treated with various acid chlorides in the presence of aluminum chloride. These findings are to be expected in view of the well-known tendency of the structurally analogous biphenyl to acylate in the p,p'-positions.[6,7]

Succinoylation of 9,10-dihydrophenanthrene (I) using succinic anhydride in place of the acid chloride gave quantitative yields of the monoacylated product, V, but a large excess of aluminum chloride failed to produce any diacylated compound corresponding to II. Wolff–Kishner reduction of V or VI followed by esterification gave VII and acylation of this ester with β-carbomethoxypropionyl chloride resulted in VIII. Reduction of *either* II *or* VIII gave III.

Although acid III could be dehydrogenated directly to IX by heating with a 10% palladium–charcoal catalyst, much more satisfactory results were obtained by using the ester, IV, followed by hydrolysis to IX.

It was found possible to cyclize acid IX under a variety of conditions, all of which resulted in a mixture of diketones that included XI as the predominant isomer. Yields of ketone XI were highest when polyphosphoric acid[8] was used although stannic chloride gave similar results. A double ring closure of this type has not been previously reported in the phenanthrene series although preferred cyclization as indicated in the conversion of IX to XI could be predicted on the basis of results obtained with monosubstituted phenanthrenes. Thus the acids XIII[9a]

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(1) L. Ruzicka, E. Schellenberg and M. W. Goldberg, *Helv. Chim. Acta*, **20**, 791 (1937).

(2) M. S. Newman, *J. Org. Chem.*, **9**, 518 (1944).

(3) M. S. Newman and W. K. Cline, *ibid.*, **16**, 934 (1951).

(4) C. A. Thomas, "Anhydrous Aluminum Chloride in Organic Chemistry," A. C. S. Monograph No. 87, Reinhold Publ. Corp., New York, N. Y., 1941, pp. 77–94.

(5) E. Mosettig and A. H. Stuart, This Journal, **61**, 1 (1939).

(6) S. L. Silver and A. Lowy, *ibid.*, **56**, 2429 (1934).

(7) L. M. Long and H. R. Henze, *ibid.*, **63**, 1939 (1941).

(8) H. R. Snyder and F. X. Werber, *ibid.*, **72**, 2965 (1950).

(9) (a) W. E. Bachmann and W. S. Struve, *J. Org. Chem.*, **4**, 456 (1939); (b) *ibid.*, **5**, 416 (1940).

CHART 1

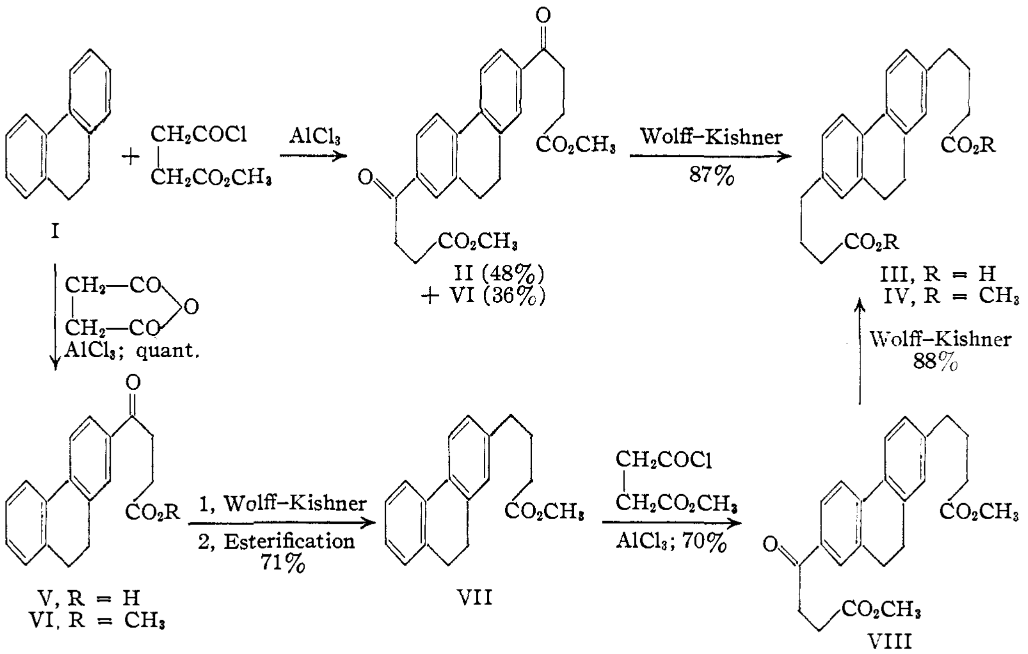
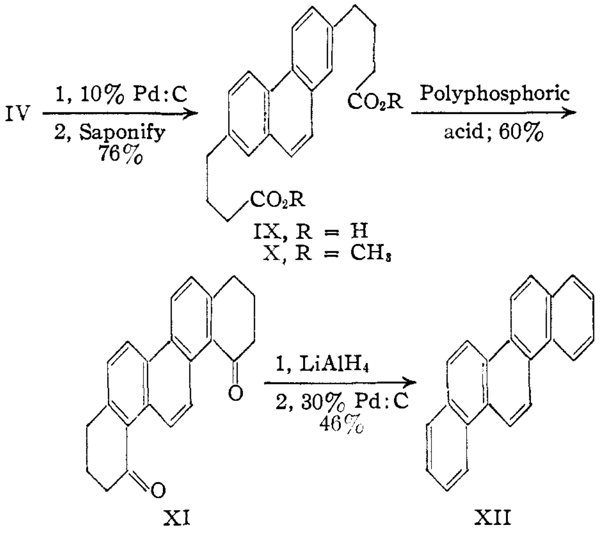
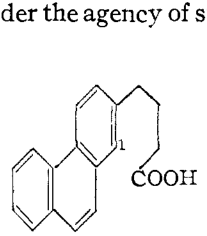
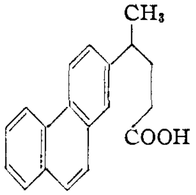


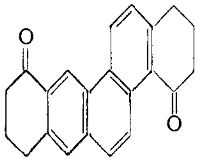
CHART 2

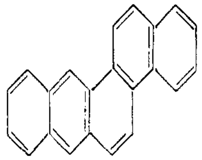


and XIV[9b] cyclized preferentially to the 1-position under the agency of stannic chloride. Consequently, it was suspected that the two butyric acid side chains in IX would act independently of each other and XI would be formed in preference to the two other possible isomers. As mentioned above, such was found to be the case, although a substantial amount (29%) of XV was also obtained as indicated by its conversion to 1,2,6,7-dibenzophenanthrene (XVI). The two diketones were readily separated by chromatography so that the formation of a mixture at this point was no serious deterrent to the ultimate formation of picene (XII).


XIII


XIV


XV


XVI

When XI was reduced according to the modified Wolff–Kishner procedure, *s*-octahydropicene was obtained in crude yields as high as 97%. The dehydrogenation of this compound proved to be extremely difficult, however, and yields of picene never exceeded 30%. When XI was reduced by lithium aluminum hydride and the resultant diol heated to 340° in the presence of 30% palladium–charcoal catalyst, dehydration and dehydrogenation proceeded smoothly to give purified picene in 46% yield.

The application of this synthetic scheme to the preparation of substituted picenes depends on intermediates such as II and XI in which the ketonic functions should be readily replaceable by alkyl groups. For unsymmetrical alkylpicenes, the condensation of substituted succinic anhydrides and acid chlorides is being studied and will form the subject of a later communication.

Acknowledgment.—The author is indebted to Professor James Cason for suggesting the problem and for the many fruitful suggestions while the work was in progress.

Experimental[10]

2,7-Bis-(3-carbomethoxy-1-propanoyl)-9,10-dihydrophenanthrene (II).—A mixture of 39.9 g. (0.22 mole) of 9,10-di-

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[10] Unless indicated otherwise, microanalyses are by Mrs. G. Libowitz, Department of Chemistry, Cornell University. All melting points are corrected and boiling points are uncorrected.

hydrophenanthrene (I)[11–13] and 70 g. (0.47 mole) of β-carbomethoxypropionyl chloride[14] in 500 ml. of carbon disulfide was cooled to 0° and with vigorous stirring, 133 g. (1.0 mole) of anhydrous aluminum chloride was added over 20 minutes. The sticky green-colored complex was stirred at 5° for 5 hours and at room temperature for 48 hours and then poured onto ice and water. The two-phase system was filtered to give 50.3 g. (56%) of crude II, m.p. 90–150°. Trituration with cold methanol gave 43.0 g. (48%) of crude II, m.p. 154–158°, suitable for the Wolff–Kishner reduction. An analytical sample crystallized from acetone as colorless plates, m.p. 162–163°.

Anal. Calcd. for $C_{24}H_{24}O_6$: C, 70.58; H, 5.92. Found: C, 70.52; H, 5.89.

Distillation of the material remaining in the filtrate afforded 24.3 g. (36%) of methyl β-(9,10-dihydro-2-phenanthroyl)-propionate (VI), b.p. 240–250° at 1 mm., m.p. 77–78° (colorless needles from methanol).[15]

2,7-Bis-(3-carboxy-1-propyl)-9,10-dihydrophenanthrene (III).—The modified[16] Wolff–Kishner reduction of 40.8 g. (0.10 mole) of II gave 30.6 g. (87%) of crude acid III, m.p. 185–192°, suitable for esterification. A small sample crystallized from methanol as colorless plates, m.p. 194–197°.

Anal. Calcd. for $C_{22}H_{24}O_4$: C, 74.97; H, 6.86. Found: C, 74.91; H, 6.84.

The **dimethyl ester (IV)**, obtained in 92% yield in the usual manner, crystallized from methanol in colorless needles, m.p. 39.5–41.5°.

Anal. Calcd. for $C_{24}H_{28}O_4$: C, 75.76; H, 7.42. Found: C, 75.66; H, 7.50.

Methyl γ-(9,10-Dihydro-2-phenanthryl)-butyrate (VII).—The modified[16] Wolff–Kishner reduction of 72 g. (0.26 mole) of keto acid V[12] gave 66.5 g. (97%) of crude reduced acid which was not isolated but esterified to yield 49.1 g. (71% based on V) of the methyl ester, VII, obtained as a pale yellow oil, b.p. 205–207° (1.8 mm.).

Anal.[17] Calcd. for $C_{19}H_{20}O_2$: C, 81.38; H, 7.19. Found: C, 81.30; H, 7.30.

2-(3-Carbomethoxy-1-propanoyl)-7-(3-carbomethoxy-1-propyl)-9,10-dihydrophenanthrene (VIII).—To a cooled (0°) mixture of 25.5 g. (0.19 mole) of anhydrous aluminum chloride in 20 ml. of dry nitrobenzene was added over 15 minutes with stirring a solution of 13.4 g. (0.048 mole) of ester VII and 8.3 g. (0.055 mole) of β-carbomethoxypropionyl chloride[14] in 20 ml. of nitrobenzene. The brown complex was stirred at room temperature for 45 hours, decomposed by the addition of ice and water and the nitrobenzene removed by distillation at low pressures (1 mm.). (Excessive decomposition resulted if the nitrobenzene was removed by the usual process of steam distillation.) The red residual oil (16.9 g.) crystallized on standing and finally set to a mass of orange crystals which, when triturated with methanol gave 13.0 g. (70%) of tan microneedles, m.p. 71–75°, suitable for reduction. An analytical sample crystallized from acetone–hexane as tan microneedles, m.p. 78.8–79.6°.

Anal.[17] Calcd. for $C_{24}H_{26}O_5$: C, 73.07; H, 6.64. Found: C, 72.92; H, 6.56.

The modified[16] Wolff–Kishner reduction of 7.8 g. (0.02 mole) of this ester gave 6.8 g. (98%) of crude acid III, m.p. 188–194°. Crystallization from methanol gave 88% of a product, m.p. 193–197°, undepressed on admixture with the acid prepared from II.

2,7-Bis-(3-carbomethoxy-1-propyl)-phenanthrene (X).—Ester IV (23.0 g., 0.06 mole) was intimately mixed with 1 g. of 10% palladium–charcoal catalyst and heated to 270° for 5 hours. The crude melt was chromatographed in benzene solution on a column of "Magnesol"[18] to give 19.0 g. (84%) of ester X, m.p. 85–88°. A sample crystallized from acetone–hexane as beautifully lustrous plates, m.p. 88–89°.

Anal. Calcd. for $C_{24}H_{26}O_4$: C, 76.17; H, 6.93. Found: C, 76.13; H, 6.87.

2,7-Bis-(3-carboxy-1-propyl)-phenanthrene (IX).—Saponification of 19.0 g. (0.05 mole) of ester X gave 15.8 g. (90%) of crude acid IX, m.p. 180–186°, suitable for cyclization. A sample for analysis crystallized from acetone–isoöctane as fine, powdery crystals, m.p. 196–200°.

Anal. Calcd. for $C_{22}H_{22}O_4$: C, 75.40; H, 6.33. Found: C, 75.39; H, 6.31.

1,12-Diketo-1,2,3,4,9,10,11,12-octahydropicene (XI). (a) **Stannic Chloride Cyclization.**—A slurry of 1.28 g. (0.006 mole) of phosphorus pentachloride, 0.96 g. (0.003 mole) of crude acid IX and 12 ml. of benzene was heated under reflux for 3 hours. To the cooled (5°) solution was added 4.5 g. (0.017 mole) of stannic chloride and the red complex was stirred at room temperature for 5 hours, decomposed with ice and ether and the unchanged acid (0.04 g.) extracted with sodium carbonate. Evaporation of the ether left 0.77 g. of a yellow semicrystalline oil which was systematically chromatographed on "Magnesol"[18] to give (eluent in parentheses) 0.23 g. (petroleum ether) of yellow needles, m.p. 170–210°; 0.14 g. (petroleum ether–benzene, 60:40), of colorless plates, m.p. 237–240°; 0.24 g. (petroleum ether–benzene, 40:60), m.p. 235–240°; and 0.11 g. (benzene–ether, 50:50) of an orange oily solid. The second and third fractions (0.38 g., 47%) proved to be the desired ketone as evidenced by the analysis of a recrystallized sample, m.p. 258–261° (dec.) and the subsequent reduction and dehydrogenation to picene (XII). The yield of pure XI was 40%.

Anal. Calcd. for $C_{22}H_{18}O_2$: C, 84.06; H, 5.77. Found: C, 84.20; H, 5.76.

(b) **Polyphosphoric Acid Cyclization.**—A mixture of 1.08 g. (0.003 mole) of dibasic acid IX and 40 g. of warm (40°) polyphosphoric acid[19] was stirred vigorously in the absence of external heating. The resultant orange mixture rose to a temperature of 60° where it was maintained for two days. The cooled solution was then poured into cold water and the crude product collected by suction filtration. The mixture (0.91 g.) was systematically chromatographed on "Magnesol" as described in (a) above to give 0.10 g. of a pale yellow semicrystalline oil, 0.60 g. of XI, m.p. 230–237° and 0.10 g. of recovered acid IX. The yield of purified XI, m.p. 255–259°, based on acid IX consumed, was 60%.

Picene (XII).—To 0.5 g. of lithium aluminum hydride suspended in 25 ml. of tetrahydrofuran was added 0.44 g. (1.4 millimoles) of XI and the mixture was stirred at room temperature for 4 hours. The excess hydride was decomposed with ethyl acetate and water and ether extraction followed by evaporation of the solvent gave a pale yellow oil. This was chromatographed on "Magnesol" to give 0.37 g. of a colorless oil which was dehydrated and dehydrogenated by heating to 340° for 1 hour in the presence of 80 mg. of 30% palladium–charcoal catalyst.[20] The melt was taken up in carbon tetrachloride and chromatographed on alumina to give 0.25 g. of crude picene, m.p. 330–336°. Two recrystallizations from ethyl acetate gave 0.18 g. (46% based on XI) of colorless, fluorescent plates, m.p. 366–367° (sealed tube).

Anal. Calcd. for $C_{22}H_{14}$: C, 94.93; H, 5.07. Found: C, 94.86; H, 5.00.

The sample was identical in all respects with authentic[21] picene, m.p. 366°, as determined by mixed m.p., infrared and ultraviolet absorption spectra analysis.

When XI was reduced according to the modified[16] Wolff–Kishner procedure, there was obtained in 97% crude yield, **1,2,3,4,9,10,11,12-octahydropicene**, m.p. 155–160°. A sample crystallized from petroleum ether in colorless, hair-like needles; m.p. 167–169°, yield 86%.

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[11] A. Burger and E. Mosettig, This Journal, **58**, 1857 (1936).

[12] L. F. Fieser and W. S. Johnson, *ibid.*, **61**, 168 (1939).

[13] J. R. Durland and H. Adkins, *ibid.*, **59**, 135 (1937); **60**, 1501 (1938). A combination of these methods of purification and reduction was necessary for consistent results.

[14] J. Cason and H. Rapoport, "Laboratory Text in Organic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1950, p. 356.

[15] L. F. Fieser and W. S. Johnson, This Journal, **61**, 1647 (1939).

[16] Huang-Minlon, *ibid.*, **68**, 2487 (1946).

[17] Analysis by V. Tashinian, Microanalytical Department, University of California, Berkeley 4, California.

[18] Product of Westvaco Division of Food Machinery and Chemical Corporation.

[19] We are grateful to the Victor Chemical Co., Chicago, for a generous gift of this material.

[20] R. P. Linstead and S. L. S. Thomas, *J. Chem. Soc.*, 1127 (1940).

[21] We are grateful to Dr. M. S. Newman who kindly furnished us with this sample.

Anal. Calcd. for $C_{22}H_{22}$: C, 92.26; H, 7.74. Found: C, 92.04; H, 7.73.

Dehydrogenation of the crude octahydride at 340° in the presence of 30% palladium–charcoal catalyst gave a 30% yield of crude picene, m.p. 304–328°, contaminated with unchanged starting material which was difficult to separate by crystallization or chromatography.

1,2,6,7-Dibenzophenanthrene (XVI).—The first fraction (0.23 g., m.p. 170–210°) obtained in the stannic chloride cyclization of acid IX was reduced with lithium aluminum hydride and dehydrogenated as described above for picene. There was obtained 0.12 g. (60%) of XVI as pale yellow leaflets from benzene, m.p. 292–294°, lit.[22] m.p. 293–294°. The ultraviolet absorption spectrum of this material was very similar to that recorded[23] for authentic XVI.

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(22) N. P. Buu-Hoi, N. Hoan and P. Jacquignon, *J. Chem. Soc.*, 1381 (1951).

(23) E. Clar and D. G. Stewart, THIS JOURNAL, **74**, 6235 (1952).

ITHACA, NEW YORK

[CONTRIBUTION FROM THE LABORATORIES OF THE ISRAELI MINISTRY OF DEFENSE]

Experiments in the 4-Phenyl-2-cycloalkenone Series. Part I. Synthesis of 2,9-Diketo-1,2,3,4,4a,9,10,10a-octahydrophenanthrene

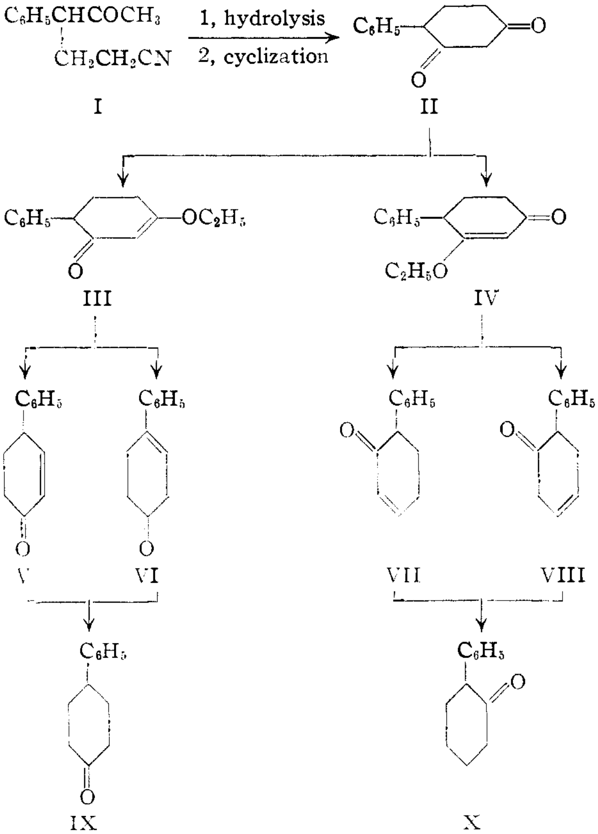
BY ERNST D. BERGMANN AND JACOB SZMUSZKOVICZ

RECEIVED DECEMBER 15, 1952

4-Phenyl-2-cyclohexenone which is obtained together with some isomers in the Dieckmann condensation of methyl γ-phenyl-γ-acetobutyrate, undergoes a Michael condensation with dibenzyl malonate. It can thus be converted into *trans*-4-phenylcyclohexanone-3-acetic acid, which cyclizes to 2,9-diketo-1,2,3,4,4a,9,10,10a-octahydrophenanthrene. In the same way, 2-phenyl-5-cyclohexenone is converted into *trans*-2-phenylcyclohexanone-5-acetic acid.

For certain Michael condensations and Diels–Alder syntheses of polycyclic compounds, 4-phenyl-2-cyclohexenone (V) was required.[1] The method used for its preparation is illustrated in Chart I.

CHART I



Acrylonitrile reacts with phenylacetone—under the conditions employed for the reaction with diethyl malonate[2]—to give γ-phenyl-γ-acetobutyronitrile (I).[3]

The methyl ester of the corresponding acid is cyclized by means of sodium alkoxide to 4-phenylcyclohexane-1,3-dione (II). It was hoped that the carbonyl group in the 1-position would be more prone to form an enol ether III[4,5] which could be converted into the desired 4-phenylcyclohex-2-enone (V) by means of treatment with lithium aluminum hydride and subsequent acid hydrolysis.[4] However, the oily enol ethyl ether which was formed when II was azeotropically distilled with ethanol and benzene in presence of *p*-toluenesulfonic acid, consisted undoubtedly of a mixture of the isomeric compounds III and IV, as the product obtained with lithium aluminum hydride afforded upon hydrogenation a mixture of the known 4- and 2-phenylcyclohexanones (IX, X)[6,7] in a ratio of about 1:1. The two ketones were easily separated by fractional crystallization of their semicarbazones.

The reduction of the two enol ethers (III, IV) with lithium aluminum hydride can be expected to

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(1) Diene syntheses with cyclenones have been reviewed by L. W. Butz and A. W. Rytina, "Organic Reactions," Vol. V, John Wiley and Sons, Inc., New York, N. Y., 1949, p. 153 ff.

(2) L. A. Mikeska, U. S. Patent 2,461,336 (*C. A.*, **43**, 4689 (1949)).

(3) For the reaction of phenylacetone with 2 moles of acrylonitrile, see H. A. Bruson and T. W. Riener, THIS JOURNAL, **64**, 2850 (1942). Alkylation of phenylacetone on the phenyl side, E. M. Schultz, *et al*, *ibid.*, **75**, 1072 (1953).

(4) R. L. Frank and H. K. Hall, Jr., *ibid.*, **72**, 1645 (1950); J. P. Blanchard and H. L. Goering, *ibid.*, **73**, 5863 (1951); H. Conroy, *ibid.*, **74**, 3046 (1952); R. B. Woodward, *et al.*, *ibid.*, **74**, 4223 (1952); M. Bornstein, R. Pappo and J. Szmuszkovicz, unpublished results. See also P. Seifert and H. Schinz, *Helv. Chim. Acta.*, **34**, 728 (1951); **36**, 290 (1953); A. Eschenmoser, *et al.*, *ibid.*, **36**, 482 (1953).

(5) *Cf.* Merling, *Ann.*, **278**, 45 (1894).

(6) (a) L. F. Fieser, M. T. Leffler and co-workers, THIS JOURNAL, **70**, 3186 (1948); (b) J. v. Braun and K. Weissbach, *Ber.*, **64**, 1785 (1931); (c) H. E. Ungnade, *J. Org. Chem.*, **13**, 361 (1948); (d) J. Colonge and L. Pichat, *Bull. soc. chim. France*, **16**, 177 (1949); (e) E. C. Horning, M. G. Horning, M. S. Fish and M. W. Rutenberg, THIS JOURNAL, **74**, 773 (1952).

(7) (a) M. Tiffeneau, B. Tchoubar and S. Le Tellier, *Compt. rend.*, **217**, 588 (1943); (b) M. S. Newmann and M. D. Farbman, THIS JOURNAL, **66**, 1550 (1944); (c) W. E. Bachmann, G. I. Fujiomoto and L. B. Wick, *ibid.*, **72**, 1995 (1950); (d) W. C. Wildman and R. B. Wildman, *J. Org. Chem.*, **17**, 581 (1952).