

aromatic type anhydride, IVc, was obtainable but this product did not yield enough good final hydrocarbon, Vc, to warrant the extra work involved. Accordingly, in the cases of all of the other adducts, III, no further work was done with the crude products. The properties of the purified adducts, III, yields, and their analyses are recorded in Table I.

TABLE I
YIELDS AND PROPERTIES OF INTERMEDIATES

Compound	Yield, %	M.p., b, °C.	Analyses, found	
			Carbon, %	Hydrogen, %
III	61 ^a	314		
III ^a	41 ^a	307	72.1	5.1 ^d
III ^b	55 ^a	330	72.1	4.9 ^d
III ^c	36 ^a	317	71.7	5.0 ^d
III ^d	79 ^a	342	72.1	4.9 ^d
III ^e	45 ^a	328	71.9	4.9 ^d
IV	"			
IV ^a	"	236-238	80.8	3.9 ^f
IV ^b	"	288-290	80.8	3.7 ^f
IV ^c	"	235-236	80.8	3.9 ^f
IV ^d	"	267-269	80.0	3.9 ^f
IV ^e	"	216-217	80.5	3.6 ^f

^a This represents pure compound. Considerably more crude product was obtained but only in the case of the c series was this crude adduct further studied. The yields in the following steps are based on purified adduct except as noted.

^b The melting points represented by a single value are approximate and varied with the rate of heating. ^c Recrystallized from acetone except IIIa which was recrystallized from acetic acid containing 5% of acetic anhydride. ^d Calcd. for C₂₅H₂₀O₆: C, 72.1; H, 4.8. ^e Yields essentially quantitative from pure adduct but not determined from crude adducts. ^f Calcd. for C₂₁H₁₂O₅: C, 80.8; H, 3.9.

Aromatic Anhydrides, IV.—In a typical experiment 205 g. (0.49 mole) of crystalline adduct, IIIc, and 48 g. (1.5 moles) of sulfur were mixed and heated to 230° whereupon the evolution of hydrogen sulfide started. The temperature was raised gradually over one hour to 280° after which the reaction mixture was cooled and triturated with 3 l. of 4% potassium hydroxide solution. The filtered extract was treated with charcoal and acidified. The dark brown solid weighed 162 g. (100%). This material was used without further purification for the decarboxylation. The crude acid was converted into the anhydride by pyrolysis and

vacuum sublimation. Recrystallization from dimethylformamide afforded yellow needles, m.p. 234.8-235.8°. Essentially quantitative yields of aromatic anhydrides, type IV, were obtained in every case. The properties and analyses are listed in Table I. It would surely be possible to obtain more pure aromatic anhydrides, type IV, from the crude adducts, type III, isolated from the mother liquors of crystallization. However, we have not studied this except in the one case mentioned (c series).

Aromatic Hydrocarbons, V.—In a typical run, an intimate mixture of 30 g. of crude IVc (obtained as described above and not recrystallized), 150 g. of anhydrous barium hydroxide, 180 g. of iron filings and 10 g. of copper-bronze was heated under reduced pressure in a flask provided with an efficient all metal stirrer made air tight in a glass bearing by graphite lubrication. The temperature was raised slowly to 170° when all the water was off and was then raised to 350° for 45 minutes. After cooling, the organic matter was extracted with several portions of boiling benzene. On removal of the solvent the residue was distilled to yield crude hydrocarbon which was converted directly to the picrate for purification. The yield of picrate, m.p. 109.5-111.0° after one recrystallization from methanol, was 58%. The pure 4-methylbenzo[c]phenanthrene obtained from this picrate melted at 64.6-65.6°. When the crude adduct, IIIc, obtained from the mother liquors as above described was processed, an over-all yield of only 7.3% of pure V, was obtained. For this reason none of the other crude adducts were processed further.

By similar processes of preparation and purification, the following benzo[c]phenanthrenes were obtained in the following yields from the double Diels-Alder adducts, III: benzo[c]phenanthrene, m.p. 66.4-67.0°, 17 28.5%; 2-methylbenzo[c]phenanthrene (Va), m.p. 80.6-81.4°, 17 36.7%; 3-methylbenzo[c]phenanthrene (Vb), m.p. 54.4-55.4°, 17 40%; 5-methylbenzo[c]phenanthrene (Vd), m.p. 70.6-71.6°, 18 20%; and 6-methylbenzo[c]phenanthrene (Ve), m.p. 76.8-77.6°, 19 31%.

(16) C. L. Hewett, *J. Chem. Soc.*, 1286 (1938).

(17) Compare m.p. with those listed by W. E. Bachmann and R. O. Edgerton, *THIS JOURNAL*, **62**, 2970 (1940).

(18) See M. S. Newman and L. M. Joshel, *ibid.*, **62**, 972 (1940), and C. L. Hewett, *J. Chem. Soc.*, 596 (1936), for other melting points.

(19) When we first prepared Ve, the melting point was 65.1-66.1°. However, this was a polymorphic form inasmuch as it melted at the higher temperature when mixed with a crystal of Ve of the higher melting point kindly sent to us by Dr. Hewett. See C. L. Hewett, *J. Chem. Soc.*, 293 (1940).

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[CONTRIBUTION FROM THE MCPHERSON CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

Synthesis of Hydroaromatic Compounds Containing Angular Methyl Groups. III. 1,2-Cyclopentanonaphthalene Series¹

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Methods which may be suitable for the synthesis of aromatic steroids containing oxygen at positions 11 and 12 are described. Model compounds thus prepared are 4-keto-2-methyl-1,2,3,4-tetrahydro-1,2-cyclopentanonaphthalene (VI) and 3-keto-2-methyl-1,2,3,4-tetrahydro-1,2-cyclopentanonaphthalene (VII). Characteristic infrared absorption bands have been noted for the diazomethyl ketone (-COCHN₂) function.

As early as 1943, experiments designed toward the synthesis of steroids isomeric with estrone and equilenin but containing oxygen in ring C were begun.⁴ Because of certain poorly understood features of this and later work³ publication of results has been postponed. However, we have now discovered the source of the trouble and in this

(1) I and II, *THIS JOURNAL*, **66**, 1550, 1553 (1944).

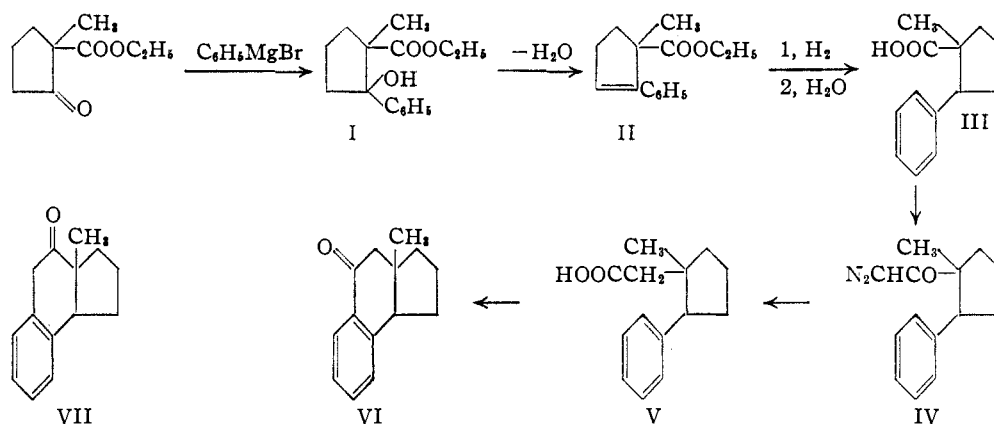
(2) Postdoctoral Fellow, U. S. Public Health Service.

(3) Taken in part from the Ph.D. thesis of H. M. G., Ohio State, 1950.

(4) R. D. Closson, Ph.D. Thesis, Ohio State, 1944.

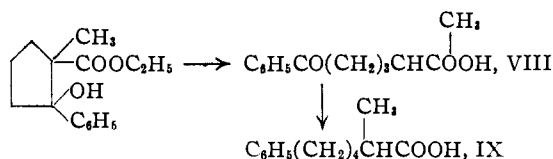
paper is reported the synthesis of one isomer of 4-keto-2-methyl-1,2,3,4-tetrahydro-1,2-cyclopentanonaphthalene (VI) and of 3-keto-2-methyl-1,2,3,4-tetrahydro-1,2-cyclopentanonaphthalene (VII). The stereochemistry of the fusion of the rings bearing the angular methyl group is not known, but is the same for VI and VII. The syntheses are outlined in the chart.

The condensation of phenylmagnesium bromide with 2-carbethoxy-2-methylcyclopentanone yields 2-carbethoxy-2-methyl-1-phenylcyclopentanol (I)



smoothly. The dehydration of I, however, proved to be a very puzzling reaction. In some preparations, dehydration proceeded spontaneously during vacuum distillation; in others, dehydration attempts failed when several common dehydrating systems were employed. Careful analysis of many experiments revealed the fact that dehydration occurred with the most difficulty in those cases where the crude hydroxyester, I, was saponified with alcoholic alkali in order to separate acidic from neutral products of the Grignard reaction. The acid (supposedly of the same structure as I) was then esterified and studied further. It is now known⁵ that during the alkaline hydrolysis of I, cleavage to 6-keto-2-methyl-6-phenylhexanoic acid (VIII) occurred. It is therefore readily understood why the ester of this acid should have resisted attempts at dehydration. The cyclohexyl homolog of I similarly underwent cleavage on alkaline saponification, giving 7-keto-2-methyl-7-phenylhexanoic acid.¹⁵

Such cleavage of cyclic β -hydroxyesters to acyclic keto acids appears to be new, although the cleavage into ketone and acid of acyclic β -hydroxyesters is known to be a troublesome feature in dealing with Reformatsky reaction products.⁶ It is worth noting that in this cleavage a possibly general new route for the extension of a chain by six or seven carbon atoms is at hand.

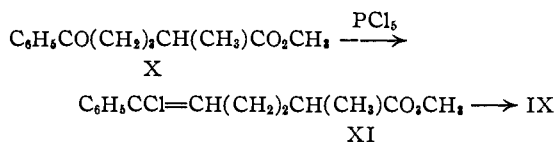


Although irrelevant to the original purpose of this work, some observations on experiments carried out with the ketoacid, VIII, may be of general interest. In an early attempt to obtain reduced acid III from what had been considered to be hydroxyester, I, the supposed methyl ester corresponding to I was treated with phosphorus pentachloride. A compound believed to be the chloride corresponding to I was isolated and reduced to a

(5) Since the events leading to a correct interpretation of this reaction were encountered in another series of similar compounds, the complete account will be delayed until the work in this series is completed.

(6) O. Wallach, *Ann.*, **314**, 147 (1901); J. Von Braun, *ibid.*, **314**, 168 (1901); W. E. Bachmann, W. Cole and A. L. Wilds, *THIS JOURNAL*, **62**, 824, 2086 (1940).

saturated acid, m.p. 31–33°, which was supposed to be the stereoisomer of III, m.p. 73°. However, we now know that the starting methyl ester used was methyl 6-keto-2-methyl-6-phenylhexanoate (X). The chloroester was therefore methyl 6-chloro-2-methyl-6-phenyl-5-hexenoate (XI) and on reduction followed by hydrolysis it was converted into 2-methyl-6-phenylhexanoic acid (IX).



Several attempts to obtain a cyclic ketone from IX by the use of anhydrous hydrofluoric acid or by conversion of IX to the acid chloride followed by treatment with aluminum or stannic chlorides failed. These were carried out at a time when it was believed that IX was III. The results are of interest now because they confirm the fact that it is either extremely difficult or impossible to form an eight-membered ring ketone by an internal Friedel-Crafts reaction.⁷ We were also unable to cyclize the homologous acid, 3-methyl-7-phenylheptanoic (XIII) formed from IX.

In those cases where the ester, I, dehydrated spontaneously (as was generally the case when the entire crude reaction product was distilled) the unsaturated ester, II was obtained. On reduction at 2–3 atmospheres of hydrogen over Raney nickel, the saturated acid, III, was obtained in predominantly one form of unknown stereochemistry.

The acid chloride of III was heat sensitive and rapidly cyclized to 2-methyl-2,3-cyclopentanoindanone (XII) above room temperature. However, if the temperature were kept low during its formation and subsequent treatment, the acid chloride could be converted into the corresponding diazomethyl ketone, IV, which when subjected to the Newman-Beal modification of the Wolff rearrangement⁸ afforded the homoacid, V. Upon

(7) J. Von Braun and H. Deutsch, *Ber.*, **45**, 2171 (1912). See also W. S. Johnson, "Organic Reaction," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1944, Chap. IV.

(8) M. S. Newman and P. F. Beal, *THIS JOURNAL*, **72**, 5163 (1950). Attempts to effect this Wolff rearrangement by conventional procedure (W. E. Bachmann and W. S. Struve, "Organic Reactions," Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1942, pp. 47–53) or by heating with dimethylaniline and benzyl alcohol (A. L. Wilds and A. L. Meader, Jr., *J. Org. Chem.*, **13**, 763 (1948)) failed.

cyclization of V there was obtained the ketone VI which serves as a model compound for the synthesis of aromatic steroids having oxygen at position 11 (steroid system).

Alternately, the diazomethylketone, IV, may be cyclized directly to ketone VII by treatment with acetic acid containing sulfuric acid.⁹ This ketone serves as a model compound for the synthesis of aromatic steroids having oxygen at position 12 (steroid system).

Preliminary work on the cyclohexyl homolog of I, which would have led eventually to the cyclohexyl homologs of VI and VII, is reported here but the investigations have since been discontinued.

Work is now in progress in which 2-methoxy-6-naphthyllithium replaces phenylmagnesium bromide in the above syntheses.

We wish to acknowledge a grant in support of this work from the National Institutes of Health, U. S. Public Health Service.

Experimental¹⁰

5-Carboethoxy-5-methyl-1-phenylcyclopentene (II).—To a solution of 330 g. (1.94 mole) of 2-carboethoxy-2-methylcyclopentanone in 1 l. of ether hold at 0° by ice-salt cooling was added slowly a solution of 1.94 moles of phenylmagnesium bromide in 1.5 l. of ether. After the addition the mixture was stirred four hours, mostly at room temperature, and then hydrolyzed with dilute hydrochloric acid. On vacuum distillation through a short Vigreux column 56 g. (16%) of starting ketoester was recovered. Shortly thereafter, the pressure rose as spontaneous dehydration began in some cases. Subsequently 215 g. (48%) of colorless II, b.p. 107–108.5° at 1.2 mm., n_D^{20} 1.5355, was obtained.

Anal. Calcd. for $C_{15}H_{18}O_2$: C, 78.3; H, 7.8. Found^k: C, 77.4, 77.7; H, 7.5, 7.5.

The free acid obtained therefrom by alkaline hydrolysis melted at 146.6–147.0° after several recrystallizations from petroleum ether, b.p. 60–70°, Skellysolve B₁ and its amide at 146.5–147.5°.

Anal. Calcd. for $C_{15}H_{14}O_2$: C, 77.1; H, 7.0. Found^w: C, 77.2; H, 7.0. Calcd. for $C_{15}H_{16}ON$: C, 77.6; H, 7.5; N, 7.0. Found^c: C, 77.7; H, 7.5; N, 6.8.

6-Keto-2-methyl-6-phenylhexanoic Acid (VIII).—To a well-stirred solution of 148 g. (0.87 mole) of 2-carboethoxy-2-methylcyclopentanone in 330 cc. of dry ether was slowly added 375 cc. of 2.43 M phenylmagnesium bromide (0.91 mole), the temperature being held below 5°. After stirring for 2 hours at 0° and 10 hours at 20–25° the mixture was treated with excess 6 N hydrochloric acid. On vacuum distillation there was obtained 49 g. (33%) of starting ketoester and a higher boiling fraction, b.p. 93–145° at 1 mm. The reason why this fraction could be distilled without appreciable dehydration in some cases whereas in others spontaneous dehydration set in is not known.¹¹ The entire crude distillate was refluxed for 20 minutes in aqueous alcohol containing 80 g. of sodium hydroxide. After removing most of the alcohol by distillation the residual solution was acidified to yield 106 g. (49%) of VIII as colorless crystals, m.p. 79–81.5°. The analytical sample, recrystallized from aqueous alcohol and from benzene, melted at 80.0–81.5°.

Anal. Calcd. for $C_{18}H_{16}O_3$: C, 70.9; H, 7.3. Found^c: C, 70.7, 70.4; H, 7.2, 7.2.

(9) Compare J. W. Cook and R. Schoental, *J. Chem. Soc.*, 288 (1945).

(10) All melting points corrected. Analyses marked c by H. S. Clark Microanalytical Laboratories; marked k by Mrs. E. H. Klotz; marked g by Galbraith Microanalytical Laboratories; marked w by R. L. Warfel, marked v by Joseph Varner, and marked a by Jean Anderson. Infrared absorption measurements were obtained with a Baird infrared recording spectrophotometer, Model B.

(11) A reliable method of dehydration has recently been found. This consists of heating the hydroxyester in benzene with Dowex-50, a sulfonated polystyrene ion exchange resin. Further details will be forthcoming.

The methyl ester, X, a colorless oil, b.p. 159–160° at 3 mm. was prepared in the usual way. Its 2,4-dinitrophenylhydrazone, crystallized from methanol in orange needles, m.p. 144.5–145.0°.

Anal. Calcd. for $C_{14}H_{18}O_4$: C, 71.8; H, 7.7. Found^k: C, 72.0; H, 7.3. Calcd. for $C_{20}H_{22}O_4N_4$: C, 58.0; H, 5.4. Found^w: C, 57.7; H, 5.4.

The infrared spectra of this and similar ketoesters exhibited two distinct strong bands of equal intensity in the carbonyl region, *viz.*, at 5.75 μ (1730 cm^{-1}) and 5.9 μ (1690 cm^{-1}), the latter being attributed to the aromatic carbonyl. The isomeric hydroxy esters (*e.g.*, I) showed typical hydroxyl absorption at 2.85 μ (3500 cm^{-1}) and only the single ester carbonyl band at 5.8 μ (1720 cm^{-1}).

2-Methyl-6-phenylhexanoic Acid (IX).—On heating a solution of 20 g. of X and 17.8 g. of phosphorus pentachloride in 60 cc. of benzene a fairly rapid evolution of hydrogen chloride was noted. After one hour the mixture was rectified to yield 21 g. of an oil, b.p. 140–150° (1–2 mm.) which was slightly impure XI as judged by analysis.

Anal. Calcd. for $C_{14}H_{17}O_2Cl$: C, 66.8; H, 6.8; Cl, 13.8. Found^c: C, 65.4, 65.2; H, 6.8, 6.5; Cl, 12.8, 12.9.

After alkaline saponification of 10 g. of XI, the alcohol was distilled and the residual solution added to 300 cc. of 10% sodium hydroxide solution. While being held at 90° 30 g. of Raney alloy was added in portions over 90 minutes.¹² After refluxing one hour the acid was liberated and purified to yield 5.6 g. (69%) of IX, b.p. 149–154° at 1–2 mm. On standing this material crystallized. Recrystallization from petroleum ether, b.p. 35–40° afforded IX, m.p. 31–33°.

Anal. Calcd. for $C_{13}H_{18}O_2$: C, 75.7; H, 8.8; neut. equiv., 206. Found^c: C, 75.8, 75.6; H, 8.9, 8.8; neut. equiv., 209.

1-Methyl-2-phenylcyclopentanecarboxylic Acid (III).—A solution of 64 g. of II in 100 cc. of absolute alcohol was shaken with 7 g. of Raney nickel catalyst and hydrogen at a starting pressure of 35 p.s.i. After three hours, 97% of the theoretical hydrogen had been absorbed. The ester was saponified by long refluxing (25 hours) with alcoholic potash. The crude acid was recrystallized from petroleum ether (Skellysolve C, b.p. 90–100°) to yield 53 g. (84%) of colorless acid, III, m.p. 72.8–73.3°.

Anal. Calcd. for $C_{13}H_{14}O_2$: C, 76.5; H, 7.8. Found^c: C, 76.7, 76.8; H, 7.8, 7.9.

1-Methyl-2-phenylcyclopentylacetic Acid (V).—The acid, III, was converted into the corresponding diazomethylketone, IV, in the usual way in high yield. The acid chloride of III was quite heat sensitive as it readily cyclized to XII (see below). This acid chloride was made from III using either phosphorus pentachloride or purified thionyl chloride, keeping the temperature below 50° at all times. The diazomethyl ketone, IV, solidified and crystallized in rosettes of fine yellow needles. The infrared absorption curve shows strong peaks at 4.8 μ (2070 cm^{-1}), 6.1 μ (1640 cm^{-1}) and 7.4 μ (1340 cm^{-1}) which appear to be characteristic of the diazomethylketone function, and which are not present in the compounds formed by further reaction of IV. The 4.8 and 6.1 μ bands are probably due to the diazomethyl and carbonyl stretching modes, respectively (*cf.*, the infrared absorption of diazomethane¹³). The 4.8 μ band has proved particularly useful in assessing the completion of reactions of the diazomethyl ketones.^{13a}

In a typical experiment 2.0 g. of IV in 60 cc. of methanol was treated in portions with 1 cc. of a saturated solution of silver benzoate in triethylamine at room temperature.⁸ The theoretical amount of nitrogen was evolved in 25 minutes. A solution of 5 g. of sodium hydroxide in a small amount of water was added and the mixture refluxed for four hours. The acid, V, thus produced was purified by recrystallization from low boiling petroleum ether to yield 1.1 g. (57%) of solid, m.p. 78–79°. A sample of pure ester, obtained from the crude reaction product by elution chromatography on an alumina column using petroleum ether, b.p. 60–70° (Skellysolve B) as eluent, gave on hydrolysis the

(12) D. Papa, E. Schwenk and B. Whitman, *J. Org. Chem.*, 7, 587 (1942).

(13) Ramsay, *J. Chem. Phys.*, 17, 656 (1949).

(13a) Since this paper was submitted, A. K. Bose and P. Yates, *This Journal*, 74, 4703 (1952), have reported similar absorption peaks for a diazomethyl ketone.

pure acid as large transparent prisms, m.p. 80.4–81°, from *n*-heptane.

Anal. Calcd. for $C_{14}H_{18}O_2$: C, 77.1; H, 8.3. Found^o: C, 77.0, 77.2; H, 8.1, 8.2.

In a similar way acid IX was converted into 3-methyl-7-phenylheptanoic acid (XIII), b.p. 172–175° at 3.5 mm. in 73% yield. This acid was converted into a crystalline amide, m.p. 80.1–80.8°.

Anal. Calcd. for $C_{14}H_{21}ON$: C, 76.7; H, 9.6; N, 6.4. Found^o: C, 76.8, 76.9; H, 8.9, 9.1; N, 6.5, 6.5.

Unsuccessful attempts to cyclize XIII included: (1) anhydrous hydrogen fluoride; (2) concd. sulfuric acid for 1 hour at 25°; (3) acid chloride in nitrobenzene with aluminum chloride at 90° for 3 hours; (4) acid chloride, stannic chloride, in benzene at 0° for 35 minutes. From these experiments only tars or recovered XIII were obtained. This provides evidence for the difficulty in cyclization leading to a nine-membered ring ketone.

4-Keto-2-methyl-1,2,3,4-tetrahydro-1,2-cyclopentanaphthalene (VI).—One gram of V was converted into the acid chloride using thionyl chloride and dissolved in 35 cc. of freshly distilled nitrobenzene. On adding 1.3 g. of aluminum chloride the solution turned black. After warming on a steam-bath for 4 hours, the mixture was poured on ice. Distillation of the neutral material under vacuum, followed by redistillation in a micro column¹⁴ afforded 0.6 g. (65%) of VI as an almost colorless oil.

Anal. Calcd. for $C_{14}H_{16}O$: C, 84.0; H, 8.0. Found^o: C, 83.4, 83.5; H, 7.5, 7.6.

The cyclization was also carried out by adding the mixture, obtained by treating the acid with phosphorus pentachloride, directly to a solution of stannic chloride in benzene and allowing to stand for 3 hours. The yield was high but not exactly determined. The ketone, VI, had an absorption peak (infrared) at 5.95μ (1680 cm.^{-1}) and formed a 2,4-dinitrophenylhydrazone which could be obtained in two forms, bright red needles, m.p. 162–164°, from benzene, which after storage turned into orange plates, m.p. 172–173°. Specimens of either exhibited the same infrared absorption (Nujol mull) and the same X-ray powder diagram but it was observed that during the necessary powdering process the lower melting form was fairly rapidly converted into the higher melting modification.

Anal. Calcd. for $C_{20}H_{26}O_4N_4$: C, 63.2; H, 5.3; N, 14.7. Found^o: C, 63.1, 63.1; H, 5.1, 5.1; N, 14.7, 14.9.

3-Keto-2-methyl-1,2,3,4-tetrahydro-1,2-cyclopentanaphthalene (VII).—To 10 cc. of a 10% solution of sulfuric acid in acetic acid was added in one portion 2.0 g. of the diazo-methyl ketone, IV, prepared from III as above described. The mixture heated up and in less than 5 minutes the nitrogen evolution ceased. The mixture was diluted with water and the neutral reaction product was vacuum distilled and redistilled through a micro column.¹⁴ The distillate was arbitrarily separated into two fractions but each had the same properties. The total yield was 1.4 g. (80%) of VII. Only one analysis was run.

Anal. Calcd. for $C_{14}H_{16}O$: C, 84.0; H, 8.0. Found^o: C, 82.8; H, 8.0.

The 2,4-dinitrophenylhydrazone, m.p. 173–174°, was yellow.

Anal. Calcd. for $C_{20}H_{26}O_4N_4$: C, 63.2; H, 5.3; N, 14.7. Found^o: C, 62.7, 62.9; H, 5.0, 5.1; N, 14.6, 14.6.

2-Methyl-2,3-cyclopentanoidanone (XII).—To 100 g. of anhydrous hydrogen fluoride was added with stirring 10 g. of III. After most of the acid had vaporized the remainder was driven off by heating. The neutral product, XII, was obtained as a colorless oil, b.p. 138–141° at 8 mm., in 57% yield.

Anal. Calcd. for $C_{13}H_{14}O$: C, 83.9; H, 7.5. Found^o: C, 84.0, 84.1; H, 7.5, 7.7.

The 2,4-dinitrophenylhydrazone, m.p. 190.1–190.9°, was orange and proved identical with that obtained from the ketone formed when the acid chloride of III was heated.

Anal. Calcd. for $C_{19}H_{18}O_4N_4$: C, 62.3; H, 5.0; N, 15.3. Found^o: C, 62.6, 62.4; H, 5.0, 4.9; N, 14.8, 14.7.

1-Methyl-2-phenylcyclohexene-1-carboxylic¹⁵ Acid.—To a solution of 38.5 g. (0.208 mole) of 2-carbethoxy-2-methylcyclohexanone in 200 cc. of ether held at 0° was added dropwise with stirring over a period of one hour 85 cc. of an ethereal solution of phenylmagnesium bromide (2.46 molar). The reaction mixture was stirred at room temperature for 1.5 hours and then hydrolyzed. Isolation with ether and fractionation gave 36 g. (66%) of 2-carbethoxy 1-phenyl-2-methylcyclohexanol, b.p. 138° at 1.5 mm., n_D^{20} 1.5250.

Alkaline saponification of a small portion resulted in the keto acid, 7-keto-2-methyl-7-phenylheptanoic acid, colorless needles m.p. 87.9–88.1° from benzene-petroleum ether (b.p. 30–40°).

Anal. Calcd. for $C_{14}H_{18}O_3$: C, 71.8; H, 7.7. Found^o: C, 71.6, 71.4; H, 7.8, 7.8.

The acid gave an orange precipitate with 2,4-dinitrophenylhydrazine test solution.

The hydroxy ester (18 g.) was heated with 20 g. of freshly fused potassium hydrogen sulfate under a nitrogen atmosphere for 2 hours at 190–200°. A further addition of 20 g. of potassium hydrogen sulfate was then made and heating continued for 2 hours at the same temperature. Water was added to the cold mixture and the product isolated with ether, and distilled. The distillate was saponified for 30 minutes with 7.5% aqueous potassium hydroxide solution to remove undehydrated ester. The neutral fraction was then twice saponified with 20% methanolic potassium hydroxide for 24 hours under reflux. Isolation of the acid fraction yielded 1-methyl-2-phenylcyclohexene-1-carboxylic acid, 10.4 g., 70%, m.p. 132–134°. An analytical sample crystallized from benzene-petroleum ether (b.p. 30–40°) in colorless needles, m.p. 134–134.4°.

Anal. Calcd. for $C_{14}H_{18}O_2$: C, 77.8; H, 7.5. Found^o: C, 77.7, 77.8; H, 7.7, 7.7.

1-Methyl-2-phenylcyclohexane-1-carboxylic Acid.¹⁵—A solution of 2.2 g. of 1-methyl-2-phenylcyclohexene-1-carboxylic acid in 40 cc. of glacial acetic acid was hydrogenated with platinum catalyst. The absorption was complete in 15 minutes. The acid crystallized in flat needles on removal of the solvent and had m.p. 90–91.5°, raised to 93.4–93.8° after recrystallization from water-methanol.

Anal. Calcd. for $C_{14}H_{18}O_2$: C, 77.0; H, 8.3. Found^o: C, 76.8, 76.7; H, 8.1, 8.1.

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(14) L. E. Craig, *Ind. Eng. Chem., Anal. Ed.*, **9**, 441 (1937).

(15) M. D. Farbman, Ph.D. Thesis, Ohio State, 1943.