

*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  $340^\circ$  in the presence of 30% palladium-charcoal catalyst gave a 30% yield of crude picene, m.p.  $304-328^\circ$ , 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.  $170-210^\circ$ ) 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.  $292-294^\circ$ , lit.<sup>22</sup> m.p.  $293-294^\circ$ . The ultraviolet absorption spectrum of this material was very similar to that recorded<sup>23</sup> for authentic XVI.

(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).

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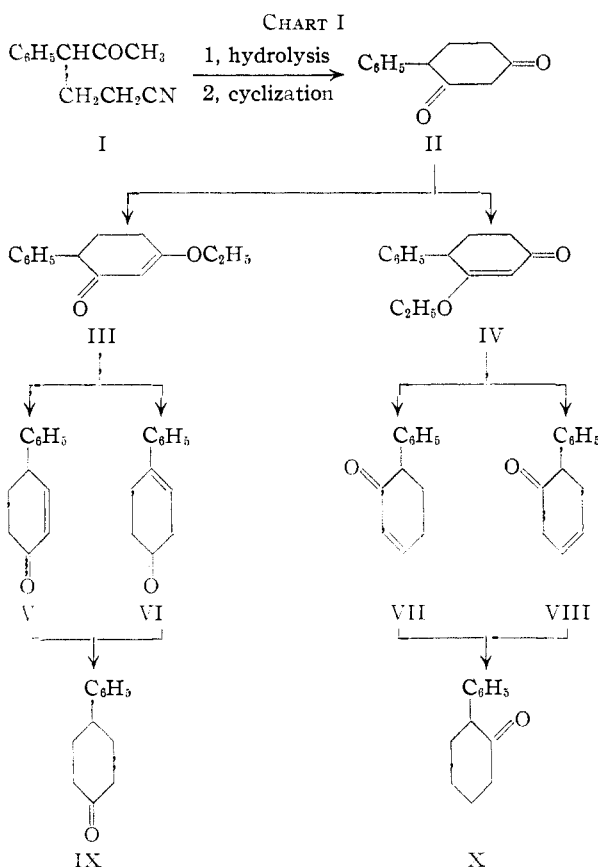
## Experiments in the 4-Phenyl-2-cycloalkenone Series. Part I. Synthesis of 2,9-Diketo-1,2,3,4,4a,9,10,10a-octahydrophenanthrene

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4-Phenyl-2-cyclohexenone which is obtained together with some isomers in the Dieckmann condensation of methyl  $\gamma$ -phenyl- $\gamma$ -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.<sup>1</sup> The method used for its preparation is illustrated in Chart I.



Acrylonitrile reacts with phenylacetone—under the conditions employed for the reaction with di-

(1) Diene syntheses with cyclohexenones 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.

ethyl malonate<sup>2</sup>—to give  $\gamma$ -phenyl- $\gamma$ -acetobutyronitrile (I).<sup>3</sup>

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<sup>4,5</sup> which could be converted into the desired 4-phenylcyclohex-2-enone (V) by means of treatment with lithium aluminum hydride and subsequent acid hydrolysis.<sup>4</sup> 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)<sup>6,7</sup> 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

(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).

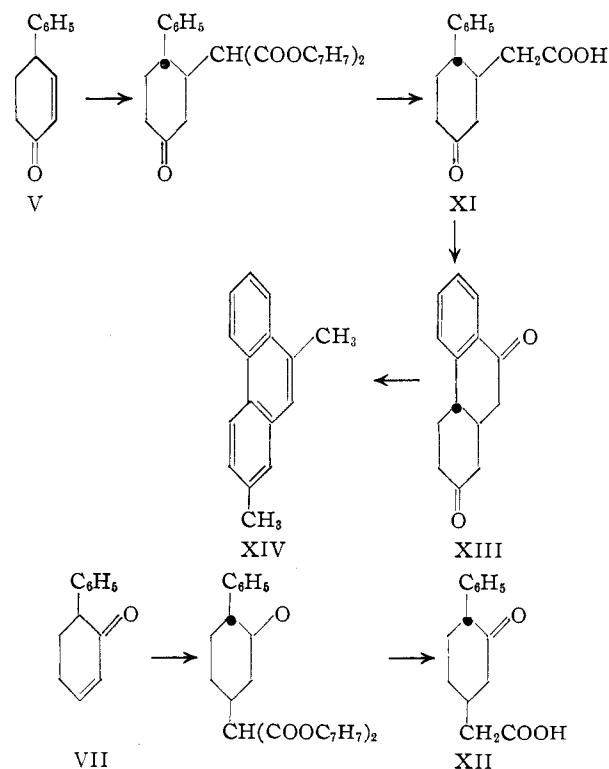
(5) Cf. Merling, *Ann.*, **278**, 45 (1894).

(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. Newman and M. D. Farbmán, *THIS JOURNAL*, **66**, 1550 (1944); (c) W. E. Bachmann, G. I. Fujimoto and L. B. Wick, *ibid.*, **72**, 1995 (1950); (d) W. C. Wildman and R. B. Wildman, *J. Org. Chem.*, **17**, 581 (1952).

lead to four unsaturated ketones (V-VIII).<sup>8</sup> The fact that the product showed a pronounced absorption, but no maximum, can be taken as an indication for the presence of such a complex mixture. Even after treatment of the mixture with ethanolic hydrogen chloride which according to Wildman and Wildman<sup>7d</sup> could convert VIII to VII (see the Experimental Part), all attempts to isolate a defined component of the mixture in preparative quantities, failed.

2-Phenyl-2-cyclohexenones have recently<sup>9</sup> found an interesting application in the synthesis of substituted hydrophenanthrene derivatives. Ketone V can be expected, too, to undergo the Michael condensation with suitable compounds and thus to open a route into the phenanthrene series. Indeed, the mixture of unsaturated ketones reacted smoothly with dibenzyl malonate in presence of potassium *t*-butoxide. Hydrogenolysis and partial decarboxylation gave two well-crystallized acids, which have been identified as 4-phenylcyclohexanone-3-acetic acid (XI) and 2-phenylcyclohexanone-5-acetic acid (XII), respectively. As the following formulae show, this is proof for the presence, in the mixture, of the unsaturated ketones V and VII; it is possible that under the conditions of the Michael reaction, VI and VIII are gradually isomerized into V and VII, respectively. XI is transformed into *trans*-2-phenylcyclohexylacetic acid,<sup>10</sup> by



(8) It is known that VII is more stable than VIII<sup>7d</sup>; whether the same relationship would prevail between V and VI is difficult to predict in view of the observation of D. C. Turner, *THIS JOURNAL*, **73**, 1284, 3017 (1951).

(9) E. C. Horning and R. U. Schock, *ibid.*, **70**, 2941, 2945 (1948); **71**, 1359 (1949); W. E. Bachmann and L. B. Wick, *ibid.*, **72**, 3388 (1950); D. Ginsburg and R. Pappo, *J. Chem. Soc.*, 516, 938 (1951); C. F. Koelsch, *THIS JOURNAL*, **73**, 2951 (1951).

(10) (a) C. D. Gutsche, *ibid.*, **70**, 4150 (1948); (b) W. E. Bachmann and E. J. Fornefeld, *ibid.*, **72**, 5529 (1950).

means of the Huang-Minlon reduction,<sup>11</sup> and XII into *trans*-4-phenylcyclohexylacetic acid.<sup>12</sup>

It is interesting, but in accord with other observations concerning the stereochemistry of the Michael reaction,<sup>13</sup> that the two compounds XI and XII have *trans*-configuration.

XI could be cyclized with sulfuric acid to a diketone, for which the structure of 2,9-diketo 1,2,3,4,4a,9,10,10a-octahydrophenanthrene (XIII) is most likely.<sup>14</sup> The compound gives a well-defined dioxime and shows an absorption spectrum which is typical of an  $\alpha$ -tetralone derivative.<sup>15</sup> For further proof, XIII was converted by successive reaction with methylmagnesium iodide, dehydration and dehydrogenation into the known 2,9-dimethylphenanthrene (XIV).<sup>16</sup>

The reactivity of the two carbonyl groups in XIII is not significantly different. With ethylene glycol in presence of an acidic catalyst, the corresponding *diketal* was formed directly. XIII behaves thus differently from the analogous 4,9-diketo compound.<sup>17</sup>

The further evaluation of the reactions described is now under investigation.

#### Experimental Part<sup>18,19</sup>

$\gamma$ -Phenyl- $\gamma$ -acetobutyronitrile (I).—Sodium (0.276 g., 0.012 mole) was added to 60 g. of phenylacetone (0.45 mole) and the mixture stirred and heated at 95° until the sodium melted. The source of heat was then removed and the reaction allowed to proceed until all the sodium had dissolved (about five minutes). At 80°, 15.9 g. of acrylonitrile (0.3 mole) was added dropwise during 15 minutes to the brown solution (cooling with water). The solution was stirred for another 15 minutes, cooled with ice-water and neutralized with 2 ml. of glacial acetic acid. Ether was added and the solution washed three times with water, dried over sodium sulfate and evaporated. Distillation at 0.1 mm. afforded 17.2 g. of unchanged phenylacetone, b.p. 65–110° (which could be used again without further purification) and 42.5 g. of I, b.p. 124–126°, pale yellow oil,  $n_D^{20}$  1.4250 (80%, based on phenylacetone).

*Anal.* Calcd. for  $C_{12}H_{13}NO$ : N, 7.5. Found: N, 7.2.

Semicarbazone.—With semicarbazide acetate in dilute ethanol; leaflets from dilute ethanol, m.p. 163.5–165.5°.

*Anal.* Calcd. for  $C_{13}H_{16}N_4O$ : C, 63.9; H, 6.6. Found: C, 63.6; H, 6.9.

There remained a residue in the distillation flask which was probably the bis-cyanoethylated product.

(11) Huang-Minlon, *ibid.*, **65**, 2487 (1946).

(12) (a) J. W. Cook and F. Goulden, *J. Chem. Soc.*, **71** (1936);

(b) J. W. Cook, C. L. Hewett and C. A. Lawrence, *ibid.*, 1559 (1937);

(c) C. D. Nenitzescu and J. Gavatt, *Ber.*, **70**, 1883 (1937).

(13) R. Pappo and D. Ginsburg, *Bull. Israeli Res. Council*, **1**, No. 3, 121 (1951). Cf. L. Ruzicka, D. R. Koolhaas and A. H. Wind, *Helv. Chim. Acta*, **14**, 1151 (1931); R. P. Linstead and E. M. Meade, *J. Chem. Soc.*, 935 (1934); J. W. Barrett, A. H. Cook and R. P. Linstead, *ibid.*, 1065 (1935); A. M. Downes, N. S. Gill and F. Lions, *Australian J. Sci.*, **10**, 147 (1948); *THIS JOURNAL*, **72**, 3464 (1950). However, in other cases, *cis* and *trans* configurations have been formed: G. A. R. Kon and M. Qudrat-I-Khuda, *J. Chem. Soc.*, 3071 (1926); L. Ruzicka, *et al.*, mentioned above: W. S. Rapson and R. Robinson, *J. Chem. Soc.*, 1285 (1935); D. A. Peak and R. Robinson, *ibid.*, 1581 (1937); Ch. K. Chuang and Y. L. Tien, *Ber.*, **69**, 25 (1936); E. R. H. Jones and H. P. Koch, *J. Chem. Soc.*, 393 (1942).

(14) It can be assumed that the two hydroaromatic rings in XIII are fused together in *trans*-configuration.

(15) R. A. Friedel and M. Orchin, "Ultraviolet Spectra of Aromatic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1951.

(16) R. D. Haworth, C. R. Mavin and G. Sheldrick, *J. Chem. Soc.*, 454 (1934).

(17) D. Ginsburg and R. Pappo, see ref. 9.

(18) All m.p.'s are uncorrected.

(19) The ultraviolet spectra were measured by Mr. Ch. Eger. Ethanol was used as solvent.

**Methyl  $\gamma$ -Phenyl- $\gamma$ -acetobutyrate.**—I (39 g.) was dissolved in 200 ml. of absolute methanol containing 72 g. of hydrogen chloride and the solution refluxed for two hours. After about five minutes, a heavy precipitate of ammonium chloride appeared and considerable bumping occurred. The mixture was left overnight at room temperature, then cooled in ice, and after addition of water extracted three times with ether. The ethereal solution was washed twice with water, twice with aqueous sodium bicarbonate, once with water and then once with saturated sodium chloride solution. Distillation at 0.1 mm. gave 42 g. (91.8% yield) of a colorless oil; b.p. 112–114°,  $n_D^{25}$  1.5050.

*Anal.* Calcd. for  $C_{13}H_{16}O_3$ : C, 71.0; H, 7.3. Found: C, 71.4; H, 7.6.

**Semicarbazone**, needles from dilute ethanol, m.p. 140.5–141.5°.

*Anal.* Calcd. for  $C_{14}H_{19}N_3O_3$ : C, 60.6; H, 6.9. Found: C, 60.5; H, 7.0.

**2,4-Dinitrophenylhydrazone**, small orange prisms from ethanol, m.p. 100–101°.

*Anal.* Calcd. for  $C_{19}H_{20}N_4O_6$ : N, 14.0. Found: N, 14.0.

**4-Phenylcyclohexane-1,3-dione (II).**—The ketoester (80.5 g.) was added to a solution of sodium (8.45 g.) in 137 ml. of anhydrous methanol and the solution refluxed for two hours with stirring. The resultant brown solution was cooled in ice and 26 ml. of glacial acetic acid was added. The mixture was evaporated *in vacuo* with stirring to a thick paste, water and ether were added and the aqueous layer was extracted three times with ether. The ethereal solution was then extracted with dilute alkali, and the alkaline extract precipitated with dilute sulfuric acid. The resultant oil was taken up in ether, washed with water, dried over sodium sulfate and evaporated to about 150 ml. Upon standing 55.5 g. (80.5%) of a colorless crystalline material was obtained, m.p. 110–113°; after recrystallization from benzene-petroleum ether (40–60°) clusters of rods; m.p. 111–113°,  $\lambda_{max}$  260, 281  $m\mu$ , log *E* 4.20, 4.21.

*Anal.* Calcd. for  $C_{12}H_{12}O_2$ : C, 76.6; H, 6.4. Found: C, 76.6; H, 6.7.

The ethereal mother liquor afforded on standing some more (12.5 g.) of the crude material of m.p. 90–100°.

The diketone II was soluble in hot water and aqueous sodium bicarbonate solution, and gave a violet color reaction with ferric chloride.

**Enol Ethers III and IV.**—A solution of II (36 g.) and of 0.78 g. of *p*-toluenesulfonic acid in 56.5 ml. of absolute ethanol and 420 ml. of benzene was slowly distilled during four hours through a column (29 cm.), packed with stainless steel rings.<sup>20,21</sup> The solution was cooled, washed twice with aqueous sodium bicarbonate and once with water, dried over sodium sulfate and evaporated. Distillation at 0.1 mm. gave 41 g. of product usable in the next step; b.p. 139–141°,  $n_D^{25}$  1.5650,  $\lambda_{max}$  250  $m\mu$ , log *E* 4.53. The product is somewhat unstable, and no satisfactory analyses could be obtained.

*Anal.* Calcd. for  $C_{14}H_{16}O_2$ :  $OC_2H_5$ , 20.8. Found:  $OC_2H_5$ , 19.0.

**Reduction of the Mixture of III and IV.**—The enol ether (41 g.) in 400 ml. of ether was added during five minutes to a solution of lithium aluminum hydride (7.2 g.) in 1 liter of ether with stirring and cooling (ice). The reaction mixture was stirred at room temperature for a further ten minutes and refluxed for 15 minutes, and after 12 hours was decomposed by successive addition of water and 25% sulfuric acid, without external cooling. The ethereal layer was separated and the aqueous solution was extracted with ether. The combined ethereal extracts were washed once with dilute sulfuric acid, and twice with water and dried over sodium sulfate. Distillation at 1 mm. gave 32.0 g. (98% yield) of a mixture of phenylcyclohexenones; b.p. 122–123°,  $n_D^{25}$  1.550.

*Anal.* Calcd. for  $C_{12}H_{12}O$ : C, 83.7; H, 7.0. Found: C, 83.6; H, 7.4.

Ultraviolet spectrum: inflection extending from 220  $m\mu$  (log *E* 4.17) to 234  $m\mu$  (log *E* 4.00).

**Isomerization Experiment.**—Following the directions of Wildman and Wildman,<sup>7d</sup> 5 g. of the phenylcyclohexenone

mixture, 70 ml. of absolute ethanol and 20 ml. of concentrated hydrochloric acid were refluxed for one hour. After about 45 minutes the orange solution became cloudy and an oil appeared. The solution was cooled and diluted with ether, then washed with water, sodium bicarbonate, water and saturated sodium chloride solution and dried over sodium sulfate. Distillation at 0.5 mm. gave 1.7 g., b.p. 105–110° (A) and 2.5 g. of a yellow viscous oil, b.p. 230–240° (B).

*Anal.* of A. Calcd. for  $C_{12}H_{12}O$ : C, 83.7; H, 7.0. Found: C, 83.5; H, 7.2.

The ultraviolet spectrum of A showed an inflection extending from 224  $m\mu$  (log *E* 3.92) to 250  $m\mu$  (log *E* 3.52). A, therefore, appears to be starting material, perhaps isomerized to some extent. The high boiling point of product B indicates that it is dimeric.

*Anal.* of B. Calcd. for  $C_{24}H_{24}O_2$ : C, 83.7; H, 7.0. Found: C, 84.0; H, 7.0.

Ultraviolet spectrum;  $\lambda_{max}$  241  $m\mu$  (4.09). Dimerides of  $\alpha,\beta$ -unsaturated ketones are not unusual. Their structure has been discussed by Alder.<sup>22</sup>

**4- and 2-Phenylcyclohexanone (IX, X).**—The phenylcyclohexenone mixture (3.7 g.) was dissolved in 25 ml. of ethanol and hydrogenated in the presence of 0.1 g. of 10% palladium-charcoal. The theoretical amount of hydrogen was absorbed within ten minutes. From the filtered and concentrated solution, a semicarbazone separated instantaneously when an aqueous solution of 6.5 g. of semicarbazide hydrochloride and 9.5 g. of sodium acetate was added. The crude material (m.p. 170–195°) gave after one crystallization from ethanol 2.3 g. (47% yield) of pure material, melting at 214–215°, which was the derivative of 4-phenylcyclohexanone (IX).

*Anal.* Calcd. for  $C_{13}H_{17}N_3O$ : C, 67.5; H, 7.8. Found: C, 67.8; H, 7.5.

The mixture of this semicarbazone (2 g.), oxalic acid (7 g.) and water (70 ml.) was refluxed for two hours and gave a quantitative yield of 4-phenylcyclohexanone, m.p. 76–78°, from petroleum-ether (40–60°) 76.5–78.5° (reported m.p. 76–77°<sup>6a</sup>); 77–78°<sup>6b</sup>; 77–79°<sup>6c</sup>).<sup>23</sup>

The oxime crystallized from dilute methanol in the form of needles, m.p. 112–113.5° (reported<sup>6c</sup> m.p. 110–111°).

The original mother liquor from the semicarbazone preparation was concentrated and allowed to crystallize at room temperature for three days. A mixture of elongated rods (1.8 g., m.p. 179–181°, 36.0%) and some amorphous material (0.2 g., m.p. 178° with sintering at 167°) was obtained. The rods were separated by hand (1.95 g.) and recrystallized from ethanol; they then melted at 181–183°.

*Anal.* Calcd. for  $C_{13}H_{17}N_3O$ : C, 67.5; H, 7.4. Found: C, 67.6; H, 7.6.

A mixture of this semicarbazone (0.465 g.), oxalic acid (2.5 g.) and 25 ml. of water was refluxed for 1.5 hours. Material melting at 56–58° (0.25 g., 71.5% yield) was obtained after the reaction mixture was cooled in ice. Crystallization from petroleum ether (40–60°) gave 2-phenylcyclohexanone (X) in rods, m.p. 58.5–59.5° (reported m.p. 53–55°<sup>7b</sup>; 58–60°<sup>7c</sup>). The mixed melting point with an authentic sample of 2-phenylcyclohexanone, m.p. 57–58°<sup>24</sup> showed no depression.

Further treatment of the mother liquor of the above two semicarbazones with some semicarbazide acetate yielded 0.540 g. (10.9%) of the semicarbazone of 2-phenylcyclohexanone (X), m.p. 181–183°, bringing the total yield up to 46.9%.

**Preparation of XI, XII and XIII by Michael Condensation of the Phenylcyclohexenone Mixture.**—Dibenzyl malonate<sup>25</sup> (19.5 g.) was added at room temperature to a solution of potassium *t*-butoxide, prepared from 0.17 g. of potassium and 5 ml. of anhydrous *t*-butyl alcohol. Then 5.16 g. of the phenylcyclohexenone mixture was added, while cooling with ice-water. After 64 hours at room temperature, gla-

(22) K. Alder, "Newer Methods of Preparative Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1948, p. 381.

(23) Dr. E. C. Horning has kindly supplied us with a sample of 4-phenylcyclohexanone. The mixed melting point was 77–79°.

(24) The sample was kindly supplied by Dr. W. C. Wildman, see ref. 7d.

(25) B. R. Baker, R. E. Schaub, M. V. Query and J. H. Williams, *J. Org. Chem.*, **17**, 77 (1952).

(20) O. G. Dixon, *J. Soc. Chem. Ind.*, **68**, 88 (1949).

(21) The material was kindly supplied by Dr. I. Dostrovsky, Weizmann Institute of Science.

cial acetic acid (1 ml.) was added, followed by 50 ml. of ethyl acetate (if less ethyl acetate was used, caking of the catalyst occurred), and 0.5 g. of 10% palladium-charcoal. Hydrogenolysis of the benzyl ester groups was carried out under an initial pressure of 54 p.s.i.; two portions of the catalyst of one-half gram each were added, when the reaction slowed down. The theoretical amount of hydrogen was absorbed in about six hours. The solution was filtered and the catalyst washed with ethyl acetate. The solvent was evaporated *in vacuo* and the residue heated at 180–200° for 15 minutes. The product was cooled, dissolved in warm ether and extracted with 5% sodium hydroxide solution. The free acid was taken up in ether and the solution(S) washed with water, and saturated sodium chloride solution, dried over sodium sulfate and evaporated. Five grams of a brown oil was obtained, which started quickly to crystallize. It was worked up in two ways.

(a) Concentrated sulfuric acid (25 ml.) was added and the mixture heated on the steam-bath for ten minutes, then poured on ice and taken up with a mixture of ether and benzene. The organic layer was washed with 5% sodium hydroxide solution, water, and saturated sodium chloride solution, dried over sodium sulfate and concentrated. Two crystallizations of the resulting yellow solid, m.p. 157–160° (2.6 g.), from benzene-petroleum ether (40–60°) afforded clusters of needles of XIII, m.p. 166–168°, which was not raised any further by sublimation under 0.05 mm. pressure. Ultraviolet spectrum, 249  $\mu$  (4.13); 289  $\mu$  (3.30).

*Anal.* Calcd. for  $C_{14}H_{14}O_2$ : C, 78.5; H, 6.5. Found: C, 78.4; H, 6.7.

**Dioxime**, from dilute ethanol, m.p. 210–212° (sinters at 200°).

*Anal.* Calcd. for  $C_{14}H_{16}N_2O_2$ : C, 68.9; H, 6.6. Found: C, 68.6; H, 6.7.

The alkaline extract was acidified with 25% sulfuric acid and taken up with ether. A small quantity of an oily solid was thus obtained which was triturated with benzene and formed then pale yellow plates, m.p. 181–183° (C, 59.3; H, 5.8). The structure of this compound has not been elucidated.

(b) In another experiment in which 15.5 g. of the phenylcyclohexenone mixture was used, and the Michael condensation was run at room temperature for 24 hours, at 80–90° for one half hour and then allowed to stand for two days, the ethereal solution(S), containing the acidic material, was evaporated to about 50 ml. Prisms of 4-phenylcyclohexanone-3-acetic acid (XI), 5.5 g. (m.p. 160–165°) thus crystallized spontaneously. Crystallization from benzene and dilute acetic acid gave colorless plates, m.p. 166.5–168°.

*Anal.* Calcd. for  $C_{14}H_{16}O_3$ : C, 72.4; H, 6.9. Found: C, 72.5; H, 7.0.

Upon further concentration, a crop (5.0 g.) of m.p. 115–125° and a further crop (0.3 g.) of m.p. 126–130° were obtained. Recrystallization from dilute acetic acid afforded plates, m.p. 134.5–135.5°, unchanged on further recrystallization. The substance thus obtained was 2-phenylcyclohexanone-5-acetic acid (XII).

*Anal.* Calcd. for  $C_{14}H_{16}O_3$ : C, 72.4; H, 6.9. Found: C, 72.3; H, 6.8.

**Cyclization of *trans*-4-Phenylcyclohexanone-3-acetic Acid (XI).**—The acid XI (0.5 g.) was heated for ten minutes on the steam-bath with concentrated sulfuric acid (5 ml.).

The reaction product, isolated as described above, melted at 160–165°. From benzene-petroleum ether, 0.3 g. of XIII, m.p. 166–168°, was obtained.

***trans*-2-Phenylcyclohexylacetic Acid. (a).**—The mixture of the keto-acid XI (0.5 g., m.p. 160–165°), 0.5 g. of potassium hydroxide, 3 ml. of hydrazine (64% in water), and 5 ml. of diethylene glycol was refluxed for 1.5 hours. The temperature of the liquid was then raised to 195° and heating continued at that temperature for four hours. The solution was cooled and acidified with 25% sulfuric acid. The solid was extracted with boiling benzene and the solution filtered and evaporated. Crystallization from petroleum ether (40–60°) afforded prisms, m.p. 113.5–114.5° (0.46 g., 95% yield) (reported m.p. 112–112.5°<sup>10b</sup>).

Admixture of an authentic sample of *trans*-2-phenylcyclohexylacetic acid, as prepared below, did not depress the melting point of the product.

(b).—The reduction of *trans*-2-phenyl-3-ketocyclohexylacetic acid<sup>26</sup> was carried out exactly as above. Two crystallizations from petroleum ether (40–60°) afforded prisms, m.p. 111.5–112°.

***trans*-4-Phenylcyclohexylacetic Acid.**—The reduction was carried out as above with 0.055 g. of the keto-acid XII. The crude product was recrystallized twice from methanol and gave needles of m.p. 112–113° (reported m.p. 113–114°<sup>8a</sup>). Mixed melting point with an authentic sample<sup>27</sup> gave no depression.

**2,9-Dimethylphenanthrene (XIV).**—The diketone XIII (0.48 g.), dissolved in 30 ml. of benzene, was added to a Grignard solution prepared from 2.5 g. of magnesium and 14.2 g. of methyl iodide. The mixture was refluxed for four hours. The resultant oil was heated with 0.9 g. of potassium hydrogen sulfate in an atmosphere of nitrogen at 170–180° for 30 minutes, and directly evaporatively distilled at 0.5 mm. pressure (110–120°). A pale yellow oil (0.34 g.) was thus obtained. This was mixed with 0.34 g. of 30% palladium-carbon and heated at 290–295° for 3.5 hours (nitrogen). The oily hydrocarbon so obtained was treated with 0.76 g. of picric acid in ethanol and afforded 0.37 g. of orange needles, m.p. 138–139.5° (reported m.p. 138°<sup>18</sup>). A second crop, 0.110 g. (m.p. 137–138°) was obtained from the mother liquor. The picrate was dissolved in benzene and passed through a short column of alumina using benzene as the eluent. An oil was obtained, which crystallized immediately on cooling; m.p. 56–57°, yield, quantitative. Crystallization from methanol afforded plates, m.p. 57–58° (reported m.p. 56–57°<sup>16</sup>).

**Diethyleneketal of XIII.**—The mixture of 0.35 g. of XIII, 5 ml. of ethylene glycol and 15 ml. of benzene was subjected to azeotropic distillation for 4 hours in the presence of 0.1 g. of *p*-toluenesulfonic acid, and the product washed with bicarbonate and water, and dried over sodium sulfate. Evaporation of the solvent gave an oil which was dissolved in fresh benzene and chromatographed on basic aluminum oxide. Thus prisms were obtained which melted on recrystallization from ethanol at 156.5–158°.

*Anal.* Calcd. for  $C_{18}H_{20}O_4$ : C, 71.5; H, 7.3. Found: C, 71.6; H, 7.1.

TEL-AVIV, ISRAEL

(26) Kindly supplied by Mr. D. Elad of the Weizmann Institute of Science; prepared according to D. Ginsburg and R. Pappo, ref. 9.

(27) Kindly supplied by Dr. H. E. Zaugg of Abbott Laboratories, Chicago, Illinois, through the courtesy of Prof. L. F. Fieser.