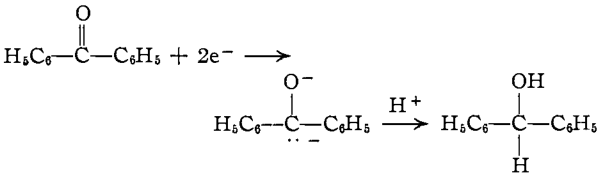
extended electrolysis this color diffused throughout the catholyte, stopping at the glass disc separating the two compartments.

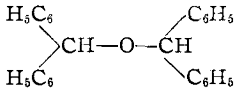
Since electrolytic reduction occurs at the cathode, and since a color is formed resembling that developed in the anolyte, it was anticipated that acid hydrolysis of the catholyte might likewise produce an excellent yield of benzopinacol. In every case, however, hydrolysis of the deep blue-violet catholyte did not produce any detectable amount of this product. Instead, three different products resulting from electrolytic reduction were isolated. By far the major product obtained was benzhydrol (VI), which was isolated in 50–60% current yields. A second neutral product was isolated in variable yield; this substance proved to be dibenzhydryl ether (VII). Formation of this product is not unreasonable, since it is known that benzhydrol can be converted readily to dibenzhydryl ether.[19] A third basic product containing nitrogen proved to be 4,4′-dipyridyl (VIII), which was isolated in only small amounts. This undoubtedly arose by air oxidation of initially formed tetrahydro-4,4′-dipyridyl.

Since no evidence was found in any of the electrolyses for the formation of benzopinacol, it is postulated that the primary reaction occurring in the catholyte is



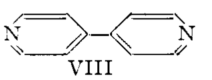
$$H_5C_6-\overset{\overset{\displaystyle O}{\|}}{C}-C_6H_5 + 2e^- \longrightarrow H_5C_6-\overset{\overset{\displaystyle O^-}{|}}{\underset{\cdot\cdot\;-}{C}}-C_6H_5 \xrightarrow{H^+} H_5C_6-\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-C_6H_5$$

V VI



$$(H_5C_6)_2CH-O-CH(C_6H_5)_2$$

VII

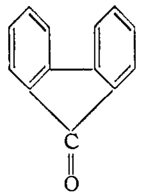


VIII

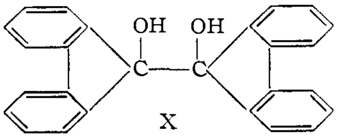
Benzophenone accepts two electrons from the electron-rich cathode and a dinegative benzhydryl anion V is formed; acid hydrolysis of this anion yields benzhydrol (VI). Such an anion as V has been reported to be formed by the action of sodium on benzophenone in ether–benzene solutions.[4,20] This anion has also been reported in the reduction of benzophenone by sodium in liquid ammonia.[21] The solutions formed in these reductions were blue-violet in color.

The small quantity of 4,4′-dipyridyl isolated in several of the electrolyses indicates that solvent pyridine molecules are reduced to only a slight extent in the cathode compartment when benzophenone is present, the latter evidently being preferentially reduced.

Anodic Oxidation of Magnesium in Solutions of Pyridine Containing Sodium Iodide and Fluorenone.—Several electrolyses were carried out in which the organic oxidant present was fluorenone (IX). Again, the V_i was less than two, falling to between 1.60 and 1.80. From the acid-hydrolyzed anolyte small amounts of fluorenopinacol (X) were isolated.



IX



X

Acknowledgment.—The authors are indebted to the Office of Ordnance Research, U. S. Army, for a research grant which has made this investigation possible.

---

[19] G. Oddo, *Gazz. chim. ital.*, **37** (2), 362 (1907); G. Stadnikov, *J. Russ. Phys. Chem. Soc.*, **47**, 1124 (1915); *Ber.*, **57**, 7 (1924).

[20] W. Schlenk and E. Weickel, *Ann.*, **464**, 25 (1928).

[21] C. B. Wooster, THIS JOURNAL, **50**, 1388 (1928).

LAWRENCE, KANSAS

[CONTRIBUTION FROM DANIEL SIEFF RESEARCH INSTITUTE, WEIZMANN INSTITUTE OF SCIENCE]

Studies in the Alicyclic Series. Part II.[1] Synthesis and Reactions of 2-Phenylcyclopent-2-enone

BY YAACOV AMIEL,[2a] ALFRED LÖFFLER AND DAVID GINSBURG[2b]

RECEIVED MARCH 8, 1954

2-Phenylcyclopent-2-enone has been prepared through the nitrosochloride of 1-phenylcyclopentene. The ketone undergoes Michael condensation to yield adducts which may be used for the clarification of certain stereochemical problems.

The value of 2-arylcyclohex-2-enones as intermediates in the synthesis of morphine has been demonstrated,[3] and the use of 2-phenylcyclohept-2-enone in the synthesis of compounds structurally related to colchicine has been reported.[4] In this communication, the synthesis of 2-phenylcyclopent-2-enone (I) through the nitrosochloride of 1-phenylcyclopentene is reported. The ketone has been employed in a number of transformations, permitting clarification of certain stereochemical problems.

The nitrosochloride of 1-phenylcyclopentene was prepared by treatment of the olefin with *n*-amyl nitrite in the presence of hydrochloric acid. The nitrosochloride was a colorless micro-crystalline product which was very unstable, and care must be taken in order to avoid its spontaneous decompo-

---

[1] D. Ginsburg, Part I, *J. Chem. Soc.*, 2361 (1954).

[2] (a) Part of this work forms a portion of a thesis presented by Y. Amiel in partial fulfillment of the requirements of the Ph.D. degree, Hebrew University, Jerusalem. (b) Present address: Israel Institute of Technology, Haifa, Israel. Inquiries should be referred to this author.

[3] D. Ginsburg and R. Pappo, *J. Chem. Soc.*, 516, 938 (1951).

[4] D. Ginsburg and R. Pappo, THIS JOURNAL, **75**, 1094 (1953).

sition. When added moist to pyridine, dehydrochlorination readily occurred, and the oxime of 2-phenylcyclopent-2-enone was obtained. It has been observed that thermal dehydration of oximes of certain 2-arylcyclohexanones, 2-arylcyclohex-2-enones[5] and of 2-phenylcyclohept-2-enone[4] results in the formation of carbazole derivatives. On heating the oxime of 2-phenylcyclopent-2-enone, a very vigorous, almost explosive reaction ensues, with the production of polymeric material. It is thus advisable to obtain the oxime through crystallization rather than to attempt vacuum distillation; crude crops of the oxime were hydrolyzed with acid to the free ketone prior to purification of the latter product by distillation.

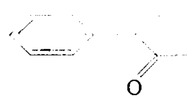
Acid hydrolysis of the oxime afforded 2-phenylcyclopent-2-enone which was purified by high vacuum distillation. The product was identical with the product described by Baker and Jones who obtained it by a more indirect method.[6]

Nunn and Rapson[7] have prepared 4,5-benzazulene by dehydrogenation of 1,2,3,8,9,10-hexahydro-4,5-benzazulene which, in turn, was prepared from 2-phenylcyclopentanepropionic acid (IIIb). This acid was prepared by lengthening the aliphatic chain of the corresponding acetic acid (IIIa) whose stereochemistry was not established.

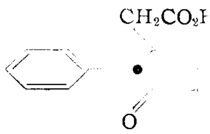
Since it is known[3,4,8] that *trans* adducts are obtained from Michael condensations employing 2-arylcycloalk-2-enones as acceptors, it is reasonable to assume that in the case of 2-phenylcyclopent-2-enone also, the resulting adduct with dibenzyl malonate is the *trans* product. Catalytic hydrogenolysis of the primary adduct followed by decarboxylation yielded *trans*-3-oxo-2-phenylcyclopentaneacetic acid (II). Indeed, this assumption was supported by the results of the treatment of this acid with anhydrous hydrogen fluoride. Hydrogen fluoride cyclization of the corresponding cyclohexanone[3] and cycloheptanone[4] derivatives proceeds in high yield. It would be expected *a priori*, that the cyclopentanone derivative would either remain unchanged or would cyclize in very poor yield, since in the cyclohexanone series a *trans*-α-decalone is formed whereas in the present case a *trans*-α-hydrindanone would be expected. It is known that the stable conformation in the α-decalone series is the *trans* isomer whilst the *cis* isomer is thermodynamically more stable than the *trans* isomer in the α-hydrindanone series. The tricyclic diketone V was, in fact, obtained in low yield by hydrogen fluoride cyclization of 3-oxo-2-phenylcyclopentaneacetic acid, and most of the acid was recovered unchanged even when a very large excess of anhydrous hydrogen fluoride was used or when contact time was prolonged. When the carbonyl group of the acid was removed by the Huang-Minlon procedure, hydrogen fluoride cyclization of 2-phenylcyclopentaneacetic acid proceeded in practically quantitative yield. Since a hydrindane rather than an α-hydrindanone system is present in the tricyclic monoketone VI, this is readily understandable.[9]

No comparison of the properties of *trans*-2-phenylcyclopentaneacetic acid prepared in this investigation could be made with the corresponding products of undetermined stereochemistry prepared by Nunn and Rapson,[7] since both products were oils. However, Arndt–Eistert chain extension of *trans*-2-phenycyclopentaneacetic acid gave the corresponding propionic acid IIIb. Furthermore, intramolecular cyclization of its acid chloride with aluminum chloride in carbon disulfide[7] gave the tricyclic ketone IV. The acid, the ketone and the ketone semicarbazone had properties identical with the corresponding compounds reported by Nunn and Rapson.[7]

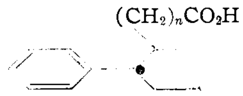
cis-2-Phenylcyclopentaneacetic acid has been prepared recently. The acid was cyclized to *cis*-6-oxo-4,5-benzhydrindane (*cis*-VI).[10] The *cis*-acid was accompanied by a small amount of *trans* isomer IIIa, identical with the product obtained by Nunn and Rapson,[7] and this was cyclized to give VI. The product obtained by the French workers was evidently less pure than that reported in this investigation.



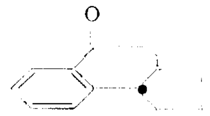
I



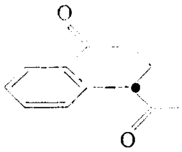
II



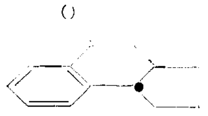
IIIa, $n = 1$
b, $n = 2$



IV



V



VI

Clearly, therefore, Nunn and Rapson[7] were dealing with *trans*-2-phenylcyclopentaneacetic acid and catalytic reduction of 3-phenylcyclopent-2-en-1-one-2-acetic acid[11] over palladium–calcium carbonate affords the *trans* isomer. Clarification of this stereochemical point was of interest in connection with another investigation now in progress in this Laboratory on the relative rates of dehydrogenation of tricyclic systems containing five- and seven-membered rings. Unequivocal proof of the stereochemistry of the tricyclic ketones will be presented at a later date.

Experimental[12]

1-Phenylcyclopentene.—The Grignard reagent was prepared in the usual way from magnesium (90 g.) and bromobenzene (570 g.) in dry ether (2 l.). Cyclopentanone (300 g.) in dry ether (300 ml.) was added dropwise with stirring and ice cooling over a period of 2.5 hr. Hydrolysis was

---

(5) A. Löffler and D. Ginsburg, *Nature*, **172**, 820 (1953).

(6) W. Baker and P. G. Jones, *J. Chem. Soc.*, 787 (1951).

(7) J. R. Nunn and W. S. Rapson, *ibid.*, 1051 (1949).

(8) (a) R. Pappo and D. Ginsburg, *Bull. Res. Council Israel*, **1**, No. 3, 121 (1951). (b) E. D. Bergmann, D. Ginsburg and R. Pappo, "The Michael Condensation," "Organic Reactions," in press.

(9) *Cf.* W. Hückel and H. Friedrich, *Ann.*, **451**, 132 (1926).

(10) M. Mousseron, F. Winternitz and G. Rouzier, *Compt. rend.*, **235**, 660 (1952).

(11) R. Robinson, *J. Chem. Soc.*, 1390 (1938).

(12) Melting points and boiling points are uncorrected.

effected with a saturated solution of ammonium chloride (600 g.). The ether layer was separated and washed, and the solvent was evaporated. The unreacted bromobenzene and cyclopentanone were removed at the water-pump, and the residue (430 g.) was dehydrated using an azeotropic receiver, by means of anhydrous oxalic acid (60 g.) in boiling toluene (1.5 l.). Only 9 ml. of water was obtained showing that most of the 1-phenylcyclopentan-1-ol had dehydrated to a large extent even though mild conditions were used to hydrolyze the Grignard complex. After cooling, water was added, and the toluene layer was separated and washed with water. The toluene was distilled, followed by 1-phenylcyclopentene (415–430 g.), b.p. 133–135° at 25 mm. Baker, *et al.*,[13] report b.p. 78–80° at 2 mm.

2-Phenylcyclopent-2-enone (I). (a) **1-Phenylcyclopentene Nitrosochloride.**—To a vigorously stirred mixture of 1-phenylcyclopentene (117 g.), glacial acetic acid (200 ml.) and *n*-amyl nitrite (178.5 ml.) was added at −10° to −20°, concentrated hydrochloric acid (139 ml.) over a period of 1.5–2 hr. The micro-crystalline nitrosochloride precipitated during the addition, and the mixture was light blue-green in color. Stirring was continued for 2 hr. in a bath maintained at −30°. The mixture was rapidly filtered, using a large diameter büchner funnel. It is necessary to watch for small brown spots in the solid which indicate that spontaneous decomposition is about to take place.

(b) **Oxime.**—The moist nitrosochloride was added to pyridine (160 ml.) in a 3-liter beaker immersed in an ice-bath, and the mixture was cautiously warmed on the steam-bath. An exothermic reaction set in and the temperature was not permitted to rise above 85° (ice cooling). All of the nitrosochloride dissolved to give a brown solution. The solution was diluted with a large volume of water and the oil which precipitated crystallized on scratching. The oxime of 2-phenylcyclopent-2-enone was recrystallized from ethanol, m.p. 158–159°.

Anal. Calcd. for $C_{11}H_{11}NO$: C, 76.27; H, 6.40; N, 8.09. Found: C, 76.23; H, 6.18; N, 8.00.

(c) **Hydrolysis.**—Acid hydrolysis of the oxime as described previously,[4] yielded the ketone. The ketone was extracted with ether, the solvent was evaporated and the residual solid was distilled in vacuum, b.p. 114–120° at 0.5 mm. The light yellow ketone (30 g.) crystallized spontaneously, m.p. 72° (from ethanol). The pure ketone weighed 26 g. (20% yield). Baker and Jones[6] report m.p. 72°; infrared absorption: 1726 cm.$^{-1}$ (—C=C—C=O).

Anal. Calcd. for $C_{11}H_{10}O$: C, 83.51; H, 6.37. Found: C, 83.41; H, 6.41.

A further crop of ketone could be obtained by extracting the aqueous pyridine mixture containing oily oxime with ether. Evaporation of the ether followed by acid hydrolysis of the crude oxime and distillation afforded 12 g. of recrystallized ketone, m.p. 72° (from ethanol); total yield of pure ketone, 30%.

In one case the nitrosochloride decomposed spontaneously in a vigorous exothermic reaction. The resulting dark material was refluxed with 1:1 hydrochloric acid for 5 hr.; the mixture was then extracted with ether and the residue after evaporation of the solvent was subjected to vacuum distillation. Only a very small amount of the desired 2-phenylcyclopent-2-enone was obtained, but two other products were isolated: a neutral product, m.p. 230° (from ethanol) which showed no ketone bands in its infrared spectrum and a ketonic product, m.p. 186–187° (from ethanol) which showed hydroxyl absorption at 3247 cm.$^{-1}$ and carbonyl absorption in the infrared at 1689 cm.$^{-1}$ and gave a 2,4-dinitrophenylhydrazone, m.p. > 340° (from tetrahydrofuran). These products were not investigated further.

Michael Condensation of 2-Phenylcyclopent-2-enone with Dibenzyl Malonate.—The condensation and work-up were carried out exactly as described for 2-phenylcyclohept-2-enone.[4] From 2-phenylcyclopent-2-enone (59 g.), dibenzyl malonate (139 g.) and potassium *t*-butoxide (prepared from 1.62 g. of potassium and 26 ml. of *t*-butyl alcohol) was obtained oily 3-oxo-2-phenylcyclopentanemalonic acid (53 g.). Decarboxylation by heating in an oil-bath at 180–190° for 30 min. gave ***trans*-3-oxo-2-phenylcyclopentaneacetic acid** (II) (44 g.), b.p. 200–210° at 0.6 mm. Trituration with ether gave crystals of the acid, m.p. 109–110° (from ether); infrared absorption: 1715 cm.$^{-1}$ (C=O of COOH); 1752 cm.$^{-1}$ (C=O of ketone).

Anal. Calcd. for $C_{13}H_{14}O_3$: C, 71.54; H, 6.47. Found: C, 71.38; H, 6.36.

***trans*-Methyl 3-oxo-2-phenylcyclopentane Acetate.**—The oily ester was obtained by methylation of the acid in ether solution with diazomethane.

Anal. Calcd. for $C_{14}H_{16}O_3$: C, 72.39; H, 6.94. Found: C, 72.18; H, 6.81.

The brick-red **2,4-dinitrophenylhydrazone** of the ester was prepared in the usual way, m.p. 137–138° (from methanol–ethanol).

Anal. Calcd. for $C_{20}H_{20}N_4O_6$: N, 13.58. Found: N, 13.42.

2-Phenylcyclopentanone.—Since the yield of adduct in the Michael condensation was relatively low, the unreacted 2-phenylcyclopent-2-enone had to be recovered. During the hydrogenolysis of the dibenzyl ester adduct, however, this was reduced to the saturated ketone. The neutral fraction obtained after hydrogenolysis was distilled and 2-phenylcyclopentanone was obtained as an oil, b.p. 115–117° at 1 mm.; infrared absorption: 1745 cm.$^{-1}$ (C=O).

When 2-phenylcyclopentanone remains in contact with air (even in a closed bottle) it is oxidized very readily[14] and γ-benzoylbutyric acid, m.p. 124–126° (from heptane), is obtained. This product is identical with that described by Elad and Ginsburg,[15] and must also have been the product which caused the 2-phenylcyclopentanone obtained by Baker and Jones[6] to become sticky after standing. Furthermore, this acid must have been the product, m.p. 126–127°, reported without analysis by Mitchovitch[16] to be 2-phenylcyclopentanone.

The light orange 2,4-dinitrophenylhydrazone, prepared in the usual way, was obtained in two forms; α, m.p. 124–126° (from ethanol), and the less soluble β, m.p. 142–144° (from ethanol). Baker and Jones[6] report m.p. 146°; light absorption: α, λ_{max} 3670 Å., ϵ_{max} 22,100; β, λ_{max} 3670 Å., ϵ_{max} 25,600.

Anal. Calcd. for $C_{17}H_{16}N_4O_4$: N, 16.46. Found: N, 16.31.

Bromination of 2-Phenylcyclopentanone.—2-Phenylcyclopentanone (7.36 g.) was brominated with bromine in carbon tetrachloride solution using the conditions described for the bromination of 2-phenylcyclohexanone.[17] The dehydrobromination was similarly conducted with 2,6-lutidine to afford after high vacuum distillation of the product, 2-phenylcyclopent-2-enone (4.27 g.), m.p. 72°, identical with the ketone described above.

***trans*-2-Phenylcyclopentaneacetic Acid (IIIa).**—3-Oxo-2-phenylcyclopentaneacetic acid (10 g.) was reduced by the Huang-Minlon procedure[18] to yield ***trans*-2-phenylcyclopentaneacetic acid** (8.5 g.) as an oil; infrared absorption: 1728 cm.$^{-1}$ (COOH).

Anal. Calcd. for $C_{13}H_{16}O_2$: neut. equiv., 204.3. Found: neut. equiv., 199.

***trans*-2-Phenylcyclopentanepropionic Acid (IIIb).**—2-Phenylcyclopentaneacetic acid (9.5 g.) was dissolved in dry benzene (50 ml.) and treated with thionyl chloride (6.7 ml.). After gas evolution was complete (2 hr.), the excess thionyl chloride and benzene was removed (water-pump), dry benzene was added and the solvent was again removed. The residual acid chloride was dissolved in dry benzene (50 ml.) and the solution was added to an ethereal solution of diazomethane (5.86 g.) at 0°. The mixture was allowed to stand overnight at room temperature. The solvents were removed (finally at water-pump) and absolute ethanol (100 ml.) was added. The diazoketone was dissolved by slight warming and freshly precipitated dry silver oxide (10 g.) was added in several small portions. The mixture was refluxed until nitrogen evolution ceased (3–4 hr.). Charcoal (3 g.) was added and refluxing was continued for 30 min. After filtration, potassium hydroxide (15 g.) was added to the

---

(13) W. Baker, F. Glockling and J. F. W. McOmie, *J. Chem. Soc.*, 3357 (1951).

(14) *Cf.* air oxidation of 2-phenylcyclohexanone: W. E. Bachmann, G. I. Fujimoto and L. B. Wick, THIS JOURNAL, **72**, 1997 (1950).

(15) D. Elad and D. Ginsburg, *J. Chem. Soc.*, 4137 (1953).

(16) V. M. Mitchovitch, *Compt. rend.*, **200**, 1601 (1935).

(17) W. E. Bachmann and L. B. Wick, THIS JOURNAL, **72**, 3388 (1950).

(18) Huang-Minlon, *ibid.*, **68**, 2487 (1946).

ethanolic filtrate and the ester was hydrolyzed by refluxing for 4 hr. The ethanol was removed (water pump), water was added and the mixture was extracted with ether to remove unsaponified material. Acidification of the alkaline solution with hydrochloric acid precipitated an oily mixture of acids which was taken up in ether. After drying and distillation of the ether, the residue weighed 8.4 g.

In order to separate unreacted starting material from the desired propionic acid, the crude mixture was subjected to cyclization with anhydrous hydrogen fluoride. Under these conditions the acetic acid is quantitatively cyclized (see below) to give a neutral ketone (0.6 g.), and the propionic acid (7.3 g.) remains unchanged. Thus, the yield of uncyclized recrystallized ***trans*-2-phenylcyclopentanepropionic acid** was 6.7 g., m.p. 77–78° (from petroleum ether). Nunn and Rapson[7] report m.p. 77–78°.

Anal. Calcd. for $C_{14}H_{18}O_2$: neut. equiv., 218.3. Found: neut. equiv., 216.

Cyclization of 2-Phenylcyclopentanepropionic Acid.—2-Phenylcyclopentanepropionic acid (1.92 g.) was dissolved in dry benzene (10 ml.) and thionyl chloride (3 ml.) was added. The acid chloride after removal of the solvents (as above) was taken up in carbon disulfide (25 ml.) and aluminum chloride (1.35 g.) was added in one portion. The mixture was refluxed for 3 hr. and allowed to stand overnight. After decomposition with dilute hydrochloric acid and extraction with ether, the solvents were removed and the residual ketone was evaporatively distilled. The ***trans*-1,2,3,6,7,8,9,10-octahydro-6-oxo-4,5-benzazulene** (IV), crystallized on trituration with petroleum ether, m.p. 66–67° (from petroleum ether) (1.34 g., 75% yield). Nunn and Rapson[7] report m.p. 65.5–67° for this ketone.

Anal. Calcd. for $C_{14}H_{16}O$: C, 83.96; H, 8.05. Found: C, 84.01; H, 8.16.

The semicarbazone was prepared by the pyridine method, m.p. 202–203° (from ethyl acetate). Nunn and Rapson[7] report m.p. 202–204°.

Anal. Calcd. for $C_{15}H_{19}N_3O$: N, 16.33. Found: N, 16.07.

Cyclization of 3-Oxo-2-phenylcyclopentaneacetic Acid.—3-Oxo-2-phenylcyclopentaneacetic acid (10 g.) was dissolved in anhydrous hydrogen fluoride (100 g.) and the solution was allowed to stand for 3 hr. The hydrogen fluoride was removed and potassium carbonate solution was added (foaming!). Ether extraction afforded the neutral tricyclic diketone, ***trans*-3,6-dioxo-4,5-benzhydrindane** (V) (3.5 g.), m.p. 133–134° (from methanol); infrared absorption: 1745 cm.$^{-1}$ (alicyclic C═O), 1686 cm.$^{-1}$ (acetophenone C═O).

Anal. Calcd. for $C_{13}H_{12}O_2$: C, 77.98; H, 6.04. Found: C, 77.26; H, 6.19.

The major portion of the starting material was recovered from the alkaline solution of its potassium salt and could be recycled. However, the yield of ketone was in no case higher than the above even when a large excess of hydrogen fluoride was used, or when a longer contact time was employed.

The dioxime, prepared by the pyridine method formed short colorless needles, m.p. 206° dec. (from methanol).

Anal. Calcd. for $C_{13}H_{14}N_2O_2$: C, 67.81; H, 6.13. Found: C, 67.76; H, 6.06.

The orange-red **2,4-dinitrophenylhydrazone**, was prepared in the usual way, m.p. 187–188° (from ethanol).

Anal. Calcd. for $C_{19}H_{16}N_4O_5$: N, 14.73. Found: N, 15.13.

Cyclization of 2-Phenylcyclopentaneacetic Acid.—The acid (10 g.), cyclized with anhydrous hydrogen fluoride (100 g.) and worked up as above, afforded the tricyclic monoketone, ***trans*-6-oxo-4,5-benzhydrindane** (VI) (8.5 g.), m.p. 87.5–88.5° (from methanol); infrared absorption: 1675 cm.$^{-1}$ (benzoyl C═O).

Anal. Calcd. for $C_{13}H_{14}O$: C, 83.83; H, 7.58. Found: C, 83.29; H, 7.67.

Mousseron, *et al.*,[10] reported m.p. 79–82° for this ketone.

The oxime, prepared by the pyridine method formed colorless prismatic needles, m.p. 181° (from methanol).

Anal. Calcd. for $C_{13}H_{15}NO$: C, 77.58; H, 7.51; N, 6.96. Found: C, 77.91; H, 7.32; N, 6.74.

The orange **2,4-dinitrophenylhydrazone** had m.p. 242–244° (from ethanol). Mousseron, *et al.*,[10] reported m.p. 241–243° for this compound.

Anal. Calcd. for $C_{19}H_{18}N_4O_4$: N, 15.29. Found: N, 15.20.

REHOVOTH, ISRAEL

[CONTRIBUTION FROM CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

Colchicine Studies. II. Synthesis of 2-(2',3',4'-Trimethoxyphenyl)-cyclohept-2-enone

BY DAVID GINSBURG[1]

RECEIVED MARCH 8, 1954

Various routes for the synthesis of 2-(2',3',4'-trimethoxyphenyl)-cyclohept-2-enone are described. As expected, this ketone acts as an acceptor in the Michael condensation.

In view of our interest in the synthesis of colchicine analogs,[2] the synthesis of 2-(2',3',4'-trimethoxyphenyl)-cyclohept-2-enone (IIb) was undertaken.

When cycloheptane-1,2-dione was treated with phenylmagnesium bromide it was possible to isolate 2-hydroxy-2-phenylcycloheptanone (Ia) which was characterized as the highly crystalline semicarbazone. The ketol was dehydrated by treatment with moderately concentrated sulfuric acid and gave the known 2-phenylcyclohept-2-enone (IIa).[2] It is of interest to note that it was not possible to obtain in strongly acid solution, the 2,4-dinitrophenylhydrazone, m.p. 116–117°, previously described although this may be obtained with Brady reagent and an alcoholic solution of the α,β-ethylenic ketone. The low-melting form was convertible to the high-melting form by means of strong acid in ethanolic solution.

Similarly, when cycloheptane-1,2-dione was treated with 2,3,4-trimethoxyphenyllithium, and the resulting mixture was fractionated in a high vacuum, it was possible to isolate 2-hydroxy-2-(2',3',4'-trimethoxyphenyl)-cycloheptanone (Ib) as a viscous oil which showed the presence of an alcoholic function (2.91 μ) and a ketonic function (5.95 μ), in its infrared absorption spectrum. However, it was not possible to dehydrate this ketol to the desired α,β-ethylenic ketone.

The ketone was ultimately obtained by selenium

---

[1] U. S. Public Health Service Postdoctoral Fellow, Harvard University, 1952–1953. On leave of absence from the Weizmann Institute of Science. Present address: Israel Institute of Technology, Haifa, Israel.

[2] D. Ginsburg and R. Pappo, THIS JOURNAL, **75**, 1094 (1953).