scribed for the formation of XVII. Upon refluxing the dark red solution of norbornadiene and tetracyanoethylene in benzene for 0.5 hr. the adduct XIX was obtained in quantitative yield; m.p. 186–188° dec. from benzene. The infrared spectrum of the adduct XIX possessed a weak, sharp band at 4.45 μ and a strong band at 12.30 μ.

Anal. Calcd. for $C_{13}H_8N_4$: C, 70.89; H, 3.66; N, 25.44; mol. wt., 220. Found: C, 71.14; H, 3.88; N, 25.38; mol. wt., 219.

A lower melting form of the adduct, m.p. 158–160°, was obtained in quantitative yield when the addition reaction was carried out at room temperature over a period of 3–4 days. The infrared spectra of the two forms were identical in chloroform solution in the 2–12 μ region and in acetone solution in the 12–15 μ region. The form which had m.p. 158–160° was also analyzed.

Anal. Calcd. for $C_{13}H_8N_4$: C, 70.89; H, 3.66; N, 25.44; mol. wt., 220. Found: C, 71.19; H, 4.05; N, 25.16; mol. wt., 229.

After standing at room temperature for more than a week the lower melting form transformed to the higher melting modification as indicated by m.p. and infrared spectrum in Nujol mull.

Hydrolysis of the Adduct XIX.—The adduct XIX (1.3 g.) was refluxed 24 hr. in a solution of 10 g. of sodium hydroxide in 12 ml. of water and 30 ml. of ethanol. Ammonia was liberated slowly during this period. The reaction mixture was acidified, most of the ethanol removed by distillation, diluted with 10 ml. of water and finally extracted thoroughly with ether. A glassy residue (1.6 g.) was obtained from the ether from which 1.25 g. of the imide XX, 8,9-dicarboxyquadricyclo$[2,2,1,0^{2,6}, 2^{3,5}]$nonane-8,9-dicarboximide, m.p. 205–207° (eff.), was obtained after recrystallization from benzene–ether. This imide XX showed absorption maxima at 5.60 and 5.82 μ (broad) in its infrared spectrum.

Anal. Calcd. for $C_{13}H_{11}O_6N$: C, 56.32; H, 4.00; N, 5.05. Found: C, 56.58; H, 4.10; N, 5.06.

Attempted Reactions of Tetracyanoethylene with Certain Monoölefins.—The olefinic compounds methylene-1,2-cyclopropanedicarboxylic acid (Feist's acid),[20] methylenecyclobutane,[21] methylenecyclononane[22] and norbornene were examined with respect to their behavior when treated with tetracyanoethylene. All tests were run in the same fashion. The olefinic compounds were added to a saturated solution of tetracyanoethylene in benzene. (The mixture was contained in a sealed Pyrex tube if a low boiling olefin was used.) All solutions became orange in color immediately. This color persisted when solutions had been kept at room temperature overnight and subsequently heated at 80–90° for several hours. In all instances starting materials were recovered unchanged.

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(20) We are indebted to D. T. Longone for the sample of Feist's acid.

(21) J. D. Roberts and C. W. Sauer, THIS JOURNAL, **71**, 3927 (1949).

(22) Dr. A. D. Josey very kindly furnished a sample of this compound.

ITHACA, N. Y.

[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY, CORNELL UNIVERSITY]

Many-membered Carbon Rings. XVIII. Synthesis and Acyloin Cyclization of δ,δ-Diphenylazelaic Ester[1]

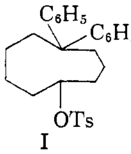
BY A. T. BLOMQUIST AND C. J. BUCK[2]

RECEIVED JULY 15, 1958

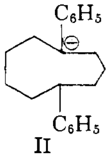
The *gem*-diphenylazeloin, 2-hydroxy-6,6-diphenylcyclononanone, has been obtained in 35% yield by acyloin cyclization of diethyl δ,δ-diphenylazelate. The azelaic ester was synthesized from diphenylmethane in five steps (55% yield) *via* di-alkylation with γ-bromopropyl ethyl ether followed by a suitable bis-homologation of the di-alkylated intermediate.

In recent years there have been numerous exemplifications of transannular hydride migration in medium size rings.[3] Transmigration of alkyl or aryl groups has not, however, been observed to occur. Thus, Prelog and Küng[3i] found that 1,6-dimethyl-1,6-cyclodecanediol did not undergo a transannular pinacol rearrangement to 6,6-dimethylcyclodecanone. Additionally, we observed no products of rearrangement in the acetolysis of 5,5-dimethylcyclononyl tosylate,[4] a solvolysis which proceeded at half the rate observed for the acetolysis of cyclononyl tosylate.[5]

In view of the fact that there have been no reported studies of reactions of medium size carbocycles possessing *aryl* annular substituents, it was of interest to examine the acetolysis of 5,5-diphenylcyclononyl tosylate (I). In this tosylate a phenyl group is well situated conformationally for 1,5-migration while anchimerically assisting, as a bridged phenonium ion,[6] in the rate-determining step of the tosylate ionization. The formation of the tertiary benzyl-type carbonium ion II could provide the driving force for the transmigration.



I



II

Since a convenient route to the tosylate I required the *gem*-diphenylazeloin, 2-hydroxy-6,6-di-

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(1) For the preceding paper in this series see A. T. Blomquist and F. Jaffe, THIS JOURNAL, **81**, 3405 (1959).

(2) This article is an abstract of part of the dissertation presented by C. J. Buck in February, 1958, to the Graduate School of Cornell University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(3) (a) V. Prelog and K. Schenker, *Helv. Chim. Acta*, **35**, 2044 (1952); (b) A. C. Cope, S. W. Fenton and C. F. Spencer, THIS JOURNAL, **74**, 5884 (1952); (c) V. Prelog, K. Schenker and W. Küng, *Helv. Chim. Acta*, **36**, 471 (1953); (d) K. Schenker and V. Prelog, *ibid.*, **36**, 896 (1953); (e) A. C. Cope and W. N. Baxter, THIS JOURNAL, **76**, 279 (1954); (f) V. Prelog, H. J. Urech, A. A. Bothner-By and J. Würsch, *Helv. Chim. Acta*, **38**, 1095 (1955); (g) V. Prelog and V. Boarland, *ibid.*, **38**, 1776 (1955); (h) V. Prelog and M. Speck, *ibid.*, **38**, 1786 (1955); (i) V. Prelog and W. Küng, *ibid.*, **39**, 1394 (1956); (j) A. C. Cope, T. A. Liss and G. Wood, *Chemistry & Industry*, 823 (1956); (k) A. C. Cope, H. E. Johnson and J. S. Stephenson, THIS JOURNAL, **78**, 5599 (1956); (l) H. J. Urech and V. Prelog, *Helv. Chim. Acta*, **40**, 477 (1957); (m) A. C. Cope and G. W. Wood, THIS JOURNAL, **79**, 3885 (1957); (n) A. C. Cope and H. E. Johnson, *ibid.*, **79**, 3889 (1957); (o) A. C. Cope and B. C. Anderson, *ibid.*, **79**, 3892 (1957); (p) A. C. Cope and A. Fournier, Jr., *ibid.*, **79**, 3896 (1957); (q) A. C. Cope, A. H. Keough, P. E. Peterson, H. E. Simmons, Jr., *ibid.*, **79**, 3900 (1957); (r) A. C. Cope, A. Fournier, Jr., and H. E. Simmons, Jr., *ibid.*, **79**, 3905 (1957).

(4) A. T. Blomquist and Y. C. Meinwald, *ibid.*, **80**, 630 (1958).

(5) H. C. Brown and G. Ham, *ibid.*, **78**, 2735 (1956); V. Prelog and R. Heck, *Helv. Chim. Acta*, **38**, 1541 (1955).

(6) For numerous examples and references to the literature see D. J. Cram in M. S. Newman, "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, Chapter 5.

phenylcyclononanone (III), as a starting material, the synthesis and acyloin cyclization of diethyl δ,δ-diphenylazelate (IV) was investigated.

The di-ester IV was obtained from diphenylmethane (V) by the reaction sequence

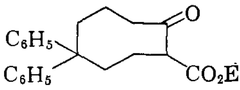
$$\mathrm{V} \xrightarrow[2,\ Br(CH_2)_3OEt]{1,\ KNH_2,\ NH_3} \underset{\mathrm{VI}}{(C_6H_5)_2CH(CH_2)_3OEt} \xrightarrow[2,\ Br(CH_2)_3OEt]{1,\ KNH_2,\ NH_3}$$

$$\underset{\mathrm{VII}}{(C_6H_5)_2C(CH_2CH_2CH_2OEt)_2} \xrightarrow[2,\ KCN]{1,\ NaI,\ H_3PO_4}$$

$$\underset{\mathrm{IX}}{(C_6H_5)_2C(CH_2CH_2CH_2CN)_2} \xrightarrow[H_2SO_4]{EtOH}$$

$$\underset{\mathrm{IV}}{(C_6H_5)_2C(CH_2CH_2CH_2CO_2Et)_2}$$

Alkylation of the monopotassium derivative of V with γ-bromopropyl ethyl ether[7] gave 1-ethoxy-4,4-diphenylbutane (VI) in 80% yield together with some 1,1,5,5-tetraphenylpentane (X).[8] Similarly, alkylation of the ether VI afforded 1,7-diethoxy-4,4-diphenylheptane (VII) in 80–83% yield.[9] Upon refluxing the di-ether VII with sodium iodide in 95% orthophosphoric acid,[10] 1,7-diiodo-4,4-diphenylheptane (VIII) was obtained in 77–84% yield. Conversion of the diiodide VIII to δ,δ-diphenylazelonitrile (IX), m.p. 91.5–92.5°, was quantitative. Ethanolysis of the dinitrile IX in concentrated sulfuric acid gave the liquid di-ester IV (73–80%) together with 4–6% of crystalline δ,δ-diphenylazelaic acid (XI), m.p. 214°.[11]


XIII

Prior to the development of the synthesis outlined above a number of other alkylations of the hydrocarbon V were examined. The objective of these studies was, of course, to obtain intermediates suitable for conversion to the desired di-ester IV. The results are summarized briefly. Alkylation of potassium diphenylmethide with an equimolar quantity of trimethylene chlorobromide afforded only the hydrocarbon X in 73% yield (26% conversion).[12] Alkylation of the di-potassium derivative of the hydrocarbon V with two molar equivalents of ethyl γ-iodobutyrate gave ethyl cyclopropanecarboxylate and ethyl δ,δ-diphenylvalerate. Finally, an attempted di-alkylation of V with γ-chlorobutyronitrile gave cyclopropanecarbonitrile and a high boiling product which resisted characterization.

Acyloin cyclization of the di-ester IV afforded a 35% yield of the diphenylazeloin III contaminated with some of the related diketone, 6,6-diphenylcyclononane-1,2-dione (XII), as a pale yellow extremely viscous liquid, b.p. 202–208° (0.8 mm.). Chromatography of this product on neutral alumina gave crystalline cyclic acyloin III, m.p. 149–150°, and crystalline diketone XII, m.p. 115–116°, identical with XII of m.p. 119.5° obtained by bismuth oxide oxidation of III. The acyloin III was characterized as its acetate, m.p. 139–141°. The diketone XII formed crystalline dioxime and quinoxaline derivatives which showed m.p.'s 191–192° and 174.5–175°, respectively.

A subsequent article will present the results obtained in the acetolysis of the tosylate I obtained from the diphenylazeloin III.

Experimental Part[14]

Materials.—Trimethylene glycol monoethyl ether was prepared according to the procedure of Smith and Sprung.[15] γ-Bromopropyl ethyl ether, b.p. 68–71° (48 mm.), $n^{25}D$ 1.4464–1.4481, was synthesized by minor modifications of known procedures.[16] Trimethylene chlorobromide (Matheson Coleman and Bell) was converted to γ-chlorobutyronitrile by the method of Marvel and Gauerke.[17] Alcoholysis of γ-chlorobutyronitrile to ethyl γ-chlorobutyrate, b.p. 72.5–74° (9.5–10 mm.), $n^{25}D$ 1.4285, was effected under reflux with excess ethanol in concentrated sulfuric acid. Ethyl γ-iodobutyrate, b.p. 77–79° (3 mm.), $n^{25}D$ 1.4950, was prepared from ethyl γ-chlorobutyrate and sodium iodide in acetone.

1-Ethoxy-4,4-Diphenylbutane (VI).—A suspension of potassium diphenylmethide in liquid ammonia was prepared in the usual manner by the addition of a solution of 185 g. (1.10 moles) of V in 500 ml. of anhydrous ether to a solution of potassium amide in 1 liter of liquid ammonia, prepared from 39.1 g. (1.0 g. atom) of potassium metal. The ammonia was evaporated from the ether–ammonia solution by replacing the Dry Ice condensers with water-cooled condensers and allowing the suspension to stir for 12 hr. An additional 1-liter of anhydrous ether was added followed by the addition over one hour of 167 g. (1.00 mole) of γ-bromopropyl ethyl ether. The mixture was stirred for 8 hr. and the active potassium salts were decomposed by the addition of excess ammonium chloride. Sufficient water was added to dissolve the inorganic salts, and the ether layer was separated, washed with water and dried. The liquid residue obtained after removal of the solvent was distilled *in vacuo* to give three principal fractions: (a) recovered γ-bromopropyl ethyl ether (19.8 g., 0.262 mole); (b) recovered V (44 g., 0.262 mole); (c) the ether VI (172 g., 0.677 mole) in 80.7% yield or 67.7% conversion which showed b.p. 127–130° (0.4 mm.), $n^{25}D$ 1.5420–1.5422. A redistilled sample of VI showed b.p. 128°

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[7] Alkylation procedures were based on the methods developed by N. Sperber, M. Sherlock and D. Papa, THIS JOURNAL, **75**, 1122 (1953). β-Bromoethyl ethyl ether was used by these workers as an alkylating agent for the preparation of 1-ethoxy-3,3-diphenylpropane and 1,5-diethoxy-3,3-diphenylpentane from diphenylmethane.

[8] The hydrocarbon X was identical with that obtained in the reaction of potassium diphenylmethide and trimethylene chlorobromide. It must have arisen from displacement of ethoxide in VI by the diphenylmethide ion: $(C_6H_5)_2CH^- + (C_6H_5)_2CH(CH_2)_3OEt \rightarrow X + OEt^-$.

[9] Realization of VII in good yield required the use of excess potassium amide in the preparation of the potassium derivative of VI. When stoichiometric quantities of reagents were used, substantial amounts of starting ether VI and γ-bromopropyl ethyl ether were recovered unchanged.

[10] H. Stone and H. Shecter, *J. Org. Chem.*, **15**, 491 (1950).

[11] The residue obtained in the distillation of the di-ester IV crystallized when triturated with ether. Elemental analysis together with the infrared and ultraviolet absorption spectra of this solid, m.p. 106–110°, indicated it to be 2-carbethoxy-5,5-diphenylcyclooctanone (XIII) (see Experimental Part).

[12] In this alkylation none of the desired 1-chloro-4,4-diphenylbutane was obtained. This indicated that there was no selectivity of bromide displacement over chloride in the reaction. This synthesis of X has been realized in better yield and in more direct fashion than that reported previously.[13]

[13] G. Wittig and B. Obermann, *Ber.*, **67B**, 2053 (1934); **68B**, 2214 (1935).

[14] All melting points and boiling points are uncorrected. Infrared absorption spectra were determined with a Perkin–Elmer double beam infrared spectrophotometer, model 21.

[15] L. I. Smith and J. A. Sprung, THIS JOURNAL, **65**, 1279 (1943).

[16] (a) R. F. Brown and N. M. van Gulick, *ibid.*, **77**, 1079 (1955); (b) R. L. Frank, P. V. Smith and F. E. Woodward, *J. Polymer Sci.*, **3**, 39 (1948); (c) E. P. Anderson, J. V. Crawford and M. L. Sherrill, THIS JOURNAL, **68**, 1294 (1946).

[17] "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc. New York, N. Y., 1941, p. 156.

(0.4 mm.), n^{25}_{D} 1.5415, d^{25}_{4} 0.9965, MR_{D} 80.65 (80.34 *via* Vogel[18]). The infrared absorption spectrum (KBr) of VI showed bands at 3.34, 3.44, 3.53, 6.19, 6.31, 6.70, 6.90, 7.27, 9.00, 13.15, 13.40, 13.60 and 14.25 μ.

Anal. Calcd. for $C_{18}H_{22}O$: C, 84.99; H, 8.72. Found: C, 85.46; H, 8.38.

The viscous, orange-colored, distillation pot residue (14.5 g.) crystallized on cooling. After several recrystallizations from ethanol it had m.p. 75.5–76° and proved to be identical with the hydrocarbon X obtained in the alkylation of V with trimethylene chlorobromide. This was indicated by a mixed m.p. determination and comparison of the infrared absorption spectra.

Anal. Calcd. for $C_{29}H_{28}$: C, 92.50; H, 7.50. Found: C, 92.19; H, 7.53.

1,7-Diethoxy-4,4-diphenylheptane (VII).—A solution of 183.5 g. (0.722 mole) of the ether VI in 250 ml. of anhydrous ether was added, over one hr., to a solution of potassium amide in 1 liter of liquid ammonia prepared from 36 g. (0.922 g.-atom) of potassium metal. The bright red suspension of the potassium salt of VI was stirred for 15 min., the Dry Ice condensers replaced with water-cooled condensers, and a solution of 125 g. (0.748 mole) of γ-bromopropyl ethyl ether in 250 ml. of anhydrous ether added over 1.5 hr. Additional ether (300 ml.) was added, and the gray-colored suspension was stirred for 8 hr. The suspended inorganic salts were dissolved by the addition of 500 ml. of water. The ether layer was separated, washed several times with water and dried over magnesium sulfate. The ether was removed on a steam-bath, and the colorless liquid residue was distilled through a short Vigreux column. After a small forerun and several fractions containing recovered VI (17.0 g.) were collected, the di-ether VII (190 g., 0.599 mole, 77.5% conversion) was collected at b.p. 160–167° (0.7 mm.), n^{25}_{D} 1.5308–1.5310. An analytical sample of VII showed b.p. 158° (0.08 mm.), n^{25}_{D} 1.5303. The infrared absorption spectrum of VII (liquid film) showed characteristic bands at 3.23, 3.27, 3.36, 3.45, 3.54, 6.24, 6.32, 6.68, 7.24, 9.00, 13.25 and 14.26 μ.

Anal. Calcd. for $C_{23}H_{32}O_2$: C, 81.13; H, 9.47. Found: C, 81.30; H, 9.17.

1,7-Diiodo-4,4-diphenylheptane (VIII).—The excellent procedure developed by Stone and Shechter was used.[10] To 590 g. of 85% orthophosphoric acid was added 125 g. of phosphoric anhydride. After the solution had cooled to room temperature, 680 g. (4.53 moles) of sodium iodide and 219 g. (0.644 mole) of VII was added. The reaction mixture was stirred under reflux for 30 hr., cooled to room temperature and diluted with 800 ml. of water and 250 ml. of ether. Stirring was maintained until solution of the inorganic salts was complete. The lower aqueous layer was separated, extracted several times with 250-ml. portions of ether, and the combined ether extracts were washed with successive portions of water, sodium thiosulfate (10%) and sodium chloride (saturated solution). The diiodo compound VIII, which was quite insoluble in ether, crystallized in part from the slightly moist ether extract as large, white, granular crystals. Gradual concentration of the extract afforded additional crops of product which were collected by suction-filtration and washed with ether. The yield of VIII, m.p. 91–93°, by this concentration procedure was 257 g. An additional 15 g., m.p. 92–93°, was obtained on recrystallization (from methanol) of the residue obtained on concentration of the ethereal mother liquors to dryness. The total yield of the di-iodide VIII was 272 g. (83.8%). Three recrystallizations from methanol afforded the analytical sample of VIII showing m.p. 95.5–96°. The infrared absorption spectrum of VIII (KBr) exhibited bands at 3.30, 3.37, 3.51, 6.15, 6.27, 13.04, 13.15 and 14.30 μ.

Anal Calcd. for $C_{19}H_{22}I_2$: C, 45.26; H, 4.40. Found: C, 45.06; H, 4.41.

4,4-Diphenylheptane.—Reduction of 5.8 g. (0.0115 mole) of the di-iodide VIII with lithium aluminum hydride (1.0 g., 0.0263 mole) in refluxing (24 hr.) dry ether gave after the usual work-up 2.3 g. (79%) of crude 4,4-diphenylheptane as a pale yellow liquid. The crude hydrocarbon was distilled *in vacuo*, b.p. 120–122° (0.9 mm.), and recrystallized from methanol at −80° to give the pure hydrocarbon, m.p. 44°. The infrared absorption spectrum of this hydrocarbon (liquid film) exhibited characteristic bands at 3.29, 3.33, 3.42, 3.49, 6.25, 6.33, 6.70, 7.28, 12.89, 13.26, 13.48 and 14.34 μ.

Anal. Calcd. for $C_{19}H_{24}$: C, 90.38; H. 9.62. Found: C, 90.58; H, 9.37.

δ,δ-**Diphenylazelonitrile (IX).**—A solution of 272 g. (0.540 mole) of VIII and 120 g. of potassium cyanide in 250 ml. of water and 500 ml. of acetone was stirred under reflux for 34 hr. The acetone solvent was removed under reduced pressure on a steam-bath, whereupon the dinitrile separated as a viscous upper liquid layer which soon crystallized on cooling. The white, granular, crystalline product was collected by suction-filtration, triturated thoroughly with large volumes of water (to remove potassium cyanide), and dried at room temperature. The yield of dinitrile IX, m.p. 87–90°, was 163 g. (0.540 mole; quantitative yield). An analytical sample of IX showed m.p. 91.5–92.5° after several recrystallizations from ether–heptane. The infrared absorption spectrum of IX (liquid film) showed bands at 3.29, 3.34, 3.43, 3.50, 4.50, 6.29, 6.37, 6.72, 13.24–13.40 and 14.30 μ.

Anal. Calcd. for $C_{21}H_{22}N_2$: C, 83.40; H, 7.33; N, 9.27. Found: C, 83.76; H, 7.06; N, 9.21.

Diethyl δ,δ-**Diphenylazelate (IV).**—A solution of 163 g. (0.540 mole) of the dinitrile IV in 120 ml. of concentrated sulfuric acid and 900 ml. of 95% ethanol was stirred under reflux for 70 hr., cooled to room temperature, poured into 1500 ml. of ice-water and the solution extracted several times with ether. The extract was washed thoroughly with water. On washing with sodium carbonate (10%), there separated a middle oily layer which was separated from the ether and aqueous layers. The ether layer was washed further with sodium chloride (saturated), dried over magnesium sulfate, and the ether removed on a steam-bath to yield 190 g. (0.479 mole, 88.8%) of the diethyl ester IV as a pale yellow, viscous liquid. Distillation of the latter through a short Vigreux column gave, after a small forerun, 171.5 g. (0.433 mole, 80.2%) of pure ester IV, b.p. 204–206° (0.7 mm.), n^{25}_{D} 1.5330–1.5342. An analytical sample of IV showed b.p. 195–196° (0.2 mm.), n^{25}_{D} 1.5308, after repeated distillation. The infrared absorption spectrum (liquid film) of IV showed absorptions at 3.25, 3.37, 3.46, 3.53, 5.76, 6.23, 6.30, 6.67, 7.27, 8.45, 8.70, 12.84, 13.20 and 14.26 μ.

Anal. Calcd. for $C_{25}H_{32}O_4$: C, 75.73; H, 8.14. Found: C, 76.27; H, 7.95.

The middle oily layer from the extraction work-up was dissolved in 250 ml. of water, acidified to *p*H 2 with hydrochloric acid, and the oily upper layer extracted into ether. The ether extract was washed with water, and the carboxylic acid extracted from the ether solution with potassium hydroxide (10%). The alkaline extract was washed once with ether (discarded), acidified to *p*H 2 with hydrochloric acid, and the precipitated product was collected by filtration, washed with water, and recrystallized from glacial acetic acid. The yield of the dicarboxylic acid XI, m.p. 214–216°, was 7.6 g. (0.0224 mole, 4.2%).

The dicarboxylic acid XI was identical in all respects with that obtained by alkaline hydrolysis of the ester IV. The infrared absorption spectrum (KBr) of XI showed bands at 3.28, 3.32, 3.45, 3.81, 3.90, 5.84, 6.24, 6.68, 7.07, 7.79, 8.19, 10.76, 11.10, 12.86, 12.99, 13.25, 14.02 and 14.17 μ.

Anal. Calcd. for $C_{21}H_{24}O_4$: C, 74.09; H, 7.11; neut. equiv., 170.2. Found: C, 74.29; H, 6.76; neut. equiv., 169.8.

The pot residue from the distillation of IV crystallized as a white, amorphous powder when triturated with ether. Several recrystallizations from heptane afforded 3.0 g. of product (XIII), m.p. 106–110°. The infrared absorption spectrum of this product (KBr) showed characteristic bands at 3.28, 3.40, 5.80, 5.90, 6.27, 6.33, 6.70, 8.47, 9.64, 12.91, 13.23 and 14.29 μ. The ultraviolet spectrum was essentially identical with that of 1,1-diphenylethane.

Anal. Calcd. for $C_{23}H_{26}O_3$: C, 78.82; H, 7.48. Found: C, 78.62; H, 7.34.

2-Hydroxy-6,6-diphenylcyclononanone (III).—The procedure used for the acyloin ring closure has been described.[19] The reaction mixture was blanketed with an atmosphere of dry, oxygen-free nitrogen during the entire experiment.

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[18] A. I. Vogel, "Practical Organic Chemistry," Longmans, Green and Co., London, 1951, p. 900.

[19] (a) A. T. Blomquist, R. E. Burge and A. C. Sucsy, THIS JOURNAL, **74**, 3636 (1952); (b) *Org. Syntheses*, **36**, 79 (1956).

To a rapidly stirred (*ca.* 1000 r.p.m.) dispersion of 10.1 g. (0.440 g.-atom) of sodium metal in 1800 ml. of refluxing anhydrous xylene was added, over 9 hr., a solution of 39.6 g. (0.100 mole) of the ester IV in 200 ml. of anhydrous xylene. Stirring was continued for an additional 2 hr. under reflux. After standing at room temperature for 8 hr., the solution was cooled to 0° and the excess sodium metal and the disodium enediolate salt of III decomposed by the dropwise addition of 25 ml. of absolute methanol and a solution of 50 ml. of glacial acetic acid in 300 ml. of water. The temperature during the decomposition steps was never allowed to exceed 5°. The aqueous layer was separated from the pale yellow colored xylene layer and extracted several times with ether. The ether and the xylene extracts were combined, washed with several portions of water and saturated sodium chloride solution and dried over magnesium sulfate. The solvents were removed by distillation from a steam-bath *in vacuo*. The residual crude, viscous, yellow-colored, semisolid product weighed 34 g. and gave a positive test for the α-ketol function with bismuth oxide.[20]

Distillation of a 19.7-g. aliquot of the total crude product (34 g.) through a short Vigreux column wrapped with a heating tape afforded 6.2 g. of the acyloin III, b.p. 202–209° (0.8 mm.), as a pale yellow, waxy, semi-solid, which was contaminated with some diketone VII. The polymeric pot residue weighed 8.0 g. The total yield of III was 10.7 g. (0.0347 mole, 34.7%).

The distilled acyloin gave a strong positive test for the acyloin function with bismuth oxide[20] but resisted numerous attempts at crystallization. For analytical sample preparation, an aliquot portion of the distilled acyloin was purified and separated from the contaminating diketone by chromatography on neutral alumina (Woelm, activity grade I). Elution from the column with chloroform and chloroform–ether mixtures afforded pure diketone XII, m.p. 115–116°, after several recrystallizations from benzene–hexane (1:2). This XII was identical with XII obtained by the bismuth oxide oxidation of III, as indicated by mixed m.p. determinations and comparison of infrared spectra.

The acyloin III was best eluted from the column with ether–methanol mixtures. Recrystallization of the yellow, viscous eluent from benzene–hexane (1:2) afforded the pure acyloin III, m.p. 149–150°, a white crystalline product which was slightly hygroscopic and analyzed as its hemihydrate ($C_{21}H_{24}O_2 \cdot {}^1/_2H_2O$) after thorough drying at 55° for 60 hours *in vacuo*. The infrared absorption spectrum (KBr) of III showed characteristic bands at 2.86, 3.27, 3.39, 3.43, 5.90, 6.24, 6.32, 6.67, 9.00, 13.24, 13.56, 14.08 and 14.27 μ.

Anal. Calcd. for $C_{21}H_{24}O_2$: C, 81.78; H, 7.85; mol. wt., 308. Calcd. for $C_{21}H_{24}O_2 \cdot H_2O$: C, 77.27; H, 8.03; mol. wt., 326. Calcd. for $C_{21}H_{24}O_2 \cdot {}^1/_2H_2O$: C, 79.46; H, 7.94; mol. wt., 317. Found: C, 79.51, 79.72, 79.31; H, 8.12, 7.75, 7.67; mol. wt., 275 (micro-Rast).

The acetate derivative of the acyloin III was obtained by heating III (0.4 g.) with 5 ml. of acetic anhydride and 5 ml. of pyridine. The crude gummy acetate obtained by the usual work-up was chromatographed on neutral aluminum. Elution with benzene–chloroform (1:1) afforded 0.15 g. of the acetate of III, m.p. 134–138° (from hexane). After recrystallization this acetate had m.p. 139–140°. The infrared absorption spectrum (KBr) of the acetate showed bands at 2.88, 3.28, 3.39, 3.46, 5.77, 5.82, 6.25, 6.32, 6.67, 7.26, 8.08, 13.20 and 14.27 μ.

Anal. Calcd. for $C_{23}H_{26}O_3$: C, 78.82; H, 7.48. Found: 79.08; H, 7.64.

Numerous attempts to prepare the *p*-nitrobenzoate derivative of III afforded only *p*-nitrobenzoic anhydride, m.p. 192–193° (lit.[21] m.p. 195°), recrystallized from hexane–benzene.

Anal. Calcd. for $C_{14}H_8N_2O_7$: C, 53.17; H, 2.55; N, 8.86. Found: C, 53.70; H, 2.59; N, 8.66.

On standing at room temperature for about one month, both III and XII decomposed to the acid XI.

6,6-Diphenylcyclononane-1,2-dione (XII).—One gram (0.00324 mole) of the acyloin III and 0.61 g. (0.00130 mole) of bismuth oxide was refluxed in 5 ml. of glacial acetic acid for 30 min. The black precipitate of bismuth metal was removed by filtration, and filtrate diluted with an equal volume of water and extracted with hot benzene. The extract was washed with water, saturated sodium chloride, and dried over Drierite. Removal of the benzene afforded 0.8 g. (80.8%) of the diketone as a viscous, yellow oil. Recrystallization from heptane gave pure diketone XII, m.p. 119.5°, as yellow, grannular crystals. The infrared absorption spectrum (KBr) of XII showed bands at 2.94, 3.13, 3.39, 5.87, 5.99, 6.25, 6.32, 6.74, 12.89, 13.09, 13.28 and 14.34 μ.

Anal. Calcd. for $C_{21}H_{22}O_2$: C, 82.32; H, 7.24. Found: C, 82.58; H, 7.36.

The quinoxaline derivative of XII, prepared according to the method of Leonard and Mader,[22] was obtained as straw-colored needles, m.p. 174.5–175°, after several recrystallizations from 95% ethanol.

Anal. Calcd. for $C_{27}H_{26}N_2$: C, 85.67; H, 6.93; N, 7.40. Found: C, 85.83; H, 6.92; N, 7.47.

The dioxime derivative of XII, m.p. 191–192°, recrystallized from benzene–hexane (1:2), was obtained upon refluxing III with hydroxylamine hydrochloride in alcoholic potassium hydroxide for 5 hr. Less vigorous conditions afforded none of the derivative.

Anal. Calcd. for $C_{21}H_{24}N_2O_2$: C, 74.97; H, 7.19; N, 8.33. Found: C, 75.64; H, 7.39; N, 7.96.

Alkylations of Diphenylmethane (V). (A) With Trimethylene Chlorobromide.—A solution of 168 g. (1.0 mole) of V in 100 ml. of anhydrous ether was added over 1 hr. to 1 l. of liquid ammonia in which 39.1 g. (1.00 g.-atom) of potassium had been dissolved (either hydrated ferric nitrate or red ferric oxide was used as catalyst). Dry Ice condensers were replaced with water-cooled condensers, 500 ml. of anhydrous ether was added and then 157.5 g. (1.0 mole) of trimethylene chlorobromide added dropwise in 1 hr. Additional ether (500 ml.) was added and the suspension stirred for *ca.* 8 hr. to evaporate the ammonia. Ammonium chloride (50 g.) was added to the ethereal suspension of salts followed by 500 ml. of water. The soluton was filtered free of the precipitated hydrated iron oxide, the aqueous layer extracted once with ether, and the combined ether solutions were washed with successive portions of water, 2 *N* hydrochloric acid, water, sodium carbonate (10%) and dried over anhydrous magnesium sulfate. Distillation of the crude liquid product remaining on removal of the solvent afforded recovered trimethylene chlorobromide (60.3 g., b.p. 38–45° (21–16 mm.)) and diphenylmethane (47.3 g., b.p. 86° (1.5 mm.) 81° (0.5 mm.)). Crystallization of the distillation pot residue was induced on trituration with heptane. Several additional recrystallizations from methanol afforded 98 g. (0.260 mole, 26% conversion, 72.6% yield) of 1,1,5,5-tetraphenylpentane (X), m.p. 76–77° (lit.[13] m.p.'s 79–80°, 76–77°). This X was identical with X obtained in the preparation of VI as indicated by infrared spectra and mixed m.p. determination.

(B) **With Ethyl γ-Iodobutyrate.**—A solution of 21 g. (0.125 mole) of diphenylmethane dissolved in 250 ml. of anhydrous ether was added, over 20 minutes, to a solution of potassium amide prepared from 9.75 g. (0.25 g.-atom) of potassium metal in 500 ml. of liquid ammonia. The bright-red suspension was stirred for an additional hour and the Dry Ice condensers were replaced with water-cooled condensers. Ethyl γ-iodobutyrate (60.4 g., 0.250 mole) was added over 3 minutes to the rapidly stirred suspension, 200 ml. of anhydrous ether added, and the stirring was continued for about 7 hr. to allow evaporation of the ammonia. Ammonium chloride (10 g.) was added to destroy the active potassium salts remaining in the ethereal suspension. Water was added to dissolve the inorganic salts, and the ether layer was separated and washed with successive portions of water, hydrochloric acid (10%), water, sodium carbonate (10%), water and sodium chloride solution (saturated). The extract was dried over magnesium sulfate, the solvent removed on a steam-bath, and the liquid residue was distilled through an efficient fractionation column to give three main fractions: (1) 5.4 g., b.p. 130–131.5° (740 mm.), n^{25}D 1.4167; (2) 10.6 g., b.p. 100° (2.8 mm.) and 63–70° (0.09–0.2 mm.), n^{25}D 1.5730–1.5739; and (3) 7.4 g., b.p. 133–143° (0.1 mm.), n^{25}D 1.5444.

The properties of fractions 1 and 2 were in good agreement with the properties reported for ethyl cyclopropanecarboxyl-

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[20] W. Rigby, *J. Chem. Soc.*, 793 (1951).

[21] I. Heilbron, "Dictionary of Organic Compounds," Oxford University Press, New York, N. Y., 1953, p. 642.

[22] N. J. Leonard and P. M. Mader, THIS JOURNAL, **72**, 5388 (1950)

ate[23] and diphenylmethane, respectively. Fraction 3 was found to be ethyl δ,δ-diphenylvalerate. An analytical sample of this ester showed b.p. 147–148° (0.1 mm.), n^{25}_{D} 1.5438.

Anal. Calcd. for $C_{19}H_{22}O_2$: C, 80.81; H, 7.85. Found: C, 81.36; H, 7.88.

Hydrolysis of the ester with boiling concentrated hydrochloric acid gave δ,δ-diphenylvaleric acid of m.p. 91.5–92.5° after two recrystallizations from methanol–water (lit.[24] m.p. 92.5–93.5°).

Anal. Calcd. for $C_{17}H_{18}O_2$: C, 80.28; H, 7.14; neut. equiv., 254. Found: C, 80.01; H, 7.23; neut. equiv., 257.

(C) **With γ-Chlorobutyronitrile.**—A solution of sodium amide in 500 ml. of liquid ammonia was prepared in the usual manner from 6.3 g. (0.274 g.-atom) of freshly-cut sodium metal. A solution of 46.3 g. (0.275 mole) of diphenylmethane in 100 ml. of anhydrous ether was added over 30 min. to the well-stirred solution of sodium amide. The brick-red suspension of sodium diphenylmethide was stirred for 10 minutes followed by the addition of a solution of 28.5 g. (0.275 mole) of γ-chlorobutyronitrile in 50 ml. of anhydrous ether over a period of 3 min. The now gray-colored suspension was treated, after 1 hr., with 11.0 g. (0.282 mole) of powdered sodium amide (Farchan). After the red color due to sodium salt formation had appeared (2 min.) the suspension was treated after 25 min. with another 28.5 g. (0.275 mole) of γ-chlorobutyronitrile dissolved in 50 ml. of anhydrous ether. The reaction mixture was stirred for 45 min., anhydrous ether (100 ml.) and 20 g. of ammonium chloride added, the Dry Ice condensers replaced with water-cooled condensers, and stirring continued for 10 hr. to allow evaporation of the ammonia. Water (200 ml.) was added, the solution filtered, and the ether layer was washed with water, hydrochloric acid (10%), water, sodium carbonate (10%), water and sodium chloride (saturated). The yield of crude product on removal of the solvent from the dried extract was 80 g. Distillation gave a forerun fraction consisting of 7.0 g. of cyclopropyl cyanide, b.p. 64° (80 mm.), 59–61° (45 mm.), n^{25}_{D} 1.4204–1.4216 (lit.[25] b.p. 135°, n^{20}_{D} 1.42293). A middle fraction consisted of recovered diphenylmethane (29.0 g.), b.p. 77–80° (0.3 mm.), n^{25}_{D} 1.5707. A high boiling fraction, 13.8 g., b.p. 216–230° (0.8 mm.), was obtained which resisted numerous attempts at characterization. The infrared absorption spectrum (KBr), which differed greatly from that of the expected dinitrile, showed bands characteristic of nitrile, amide, phenyl and methylenic functions.

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(23) "The Merck Index," Merck and Co., Inc., Rahway, N. J., 1952, p. 317.

(24) L. H. Klemm and G. M. Bower, *J. Org. Chem.*, **23**, 344 (1958).

(25) (a) I. Heilbron, "Dictionary of Organic Compounds," Oxford University Press, New York, N. Y., 1953, p. 649; (b) P. Bruylants, *Bull. soc. chim. Belg.*, **38**, 133 (1929).

[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY AT CORNELL UNIVERSITY]

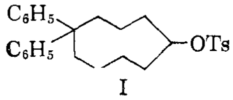
Many-membered Carbon Rings. XIX. Synthesis and Acetolysis of 5,5-Diphenylcyclononanol Tosylate[1,2]

BY A. T. BLOMQUIST AND B. F. HALLAM[3]

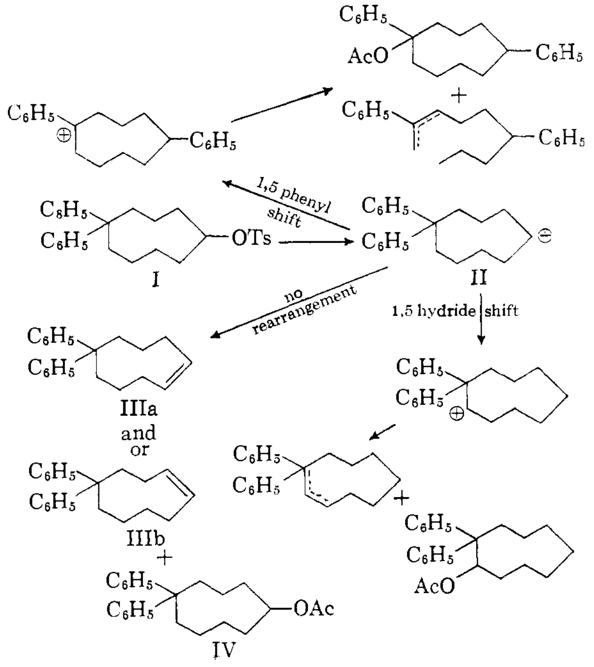
RECEIVED JULY 15, 1958

The *gem*-diphenylazeloin, 2-hydroxy-6,6-diphenylcyclononanone,[1] has been converted by conventional methods to 5,5-diphenylcyclononanol. Acetolysis of the tosylate of this alcohol was studied at 35° and the observed rate was found to be about one-tenth of that observed for cyclononyl tosylate, whilst analysis of the acetolysis products indicated that no transannular migration of phenyl groups had taken place.

The preparation of the *gem*-diphenylazeloin, 2-hydroxy-6,6-diphenylcyclononanone, has recently been carried out.[1] This azeloin was required as an intermediate in the synthesis of 5,5-diphenylcyclononanol tosylate (I). In an attempt to investigate the role of the phenyl groups in reactions of the 9-membered carbocycle, the acetolysis of this tosylate I was undertaken. Although no migration of the methyl groups was observed during the acetolysis of 5,5-dimethylcyclononanol tosylate,[4] many examples of phenyl groups providing anchimeric assistance of ionization have been reported,[5] and it was considered probable that such anchimeric assistance might be observed during the acetolysis of I, leading to a reaction rate appreciably greater than that observed in the case of the unsubstituted cyclononanol tosylate. Any rearrangement of phenyl



I



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(1) For the preceding and closely related paper in this series see A. T. Blomquist and C. J. Buck, THIS JOURNAL, **81**, 672 (1959).

(2) This research was supported by a grant from The Petroleum Research Fund administered by The American Chemical Society. Grateful acknowledgment is hereby made to the donors of this fund.

(3) B. F. H. wishes to thank the U. S. Educational Commission in the United Kingdom for the award of a Fulbright Travel Grant.

(4) A. T. Blomquist and Y. C. Meinwald, THIS JOURNAL, **80**, 630 (1958).

(5) For references see D. J. Cram in M. S. Newman, "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, Chapt. 5.