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.

---

[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).

ITHACA, N. Y.

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

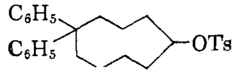
Many-membered Carbon Rings. XIX. Synthesis and Acetolysis of 5,5-Diphenylcyclononanol Tosylate[1,2]

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

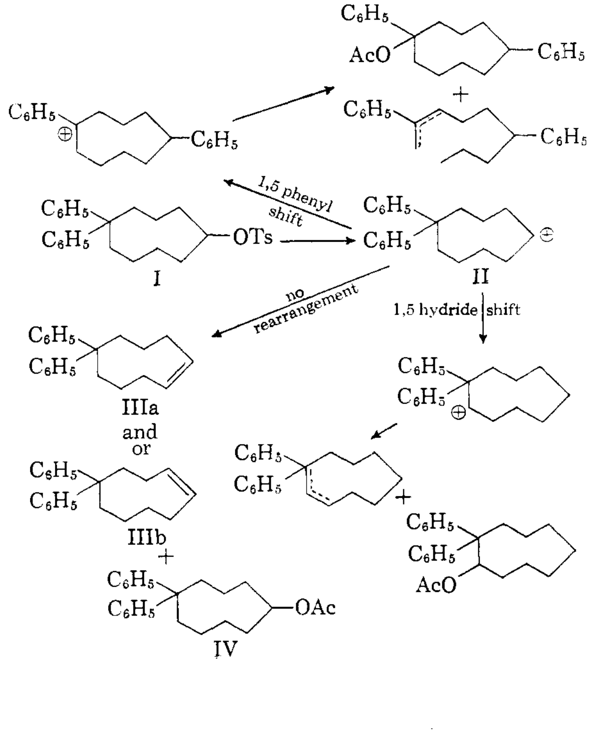
RECEIVED JULY 15, 1958

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



---

[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.

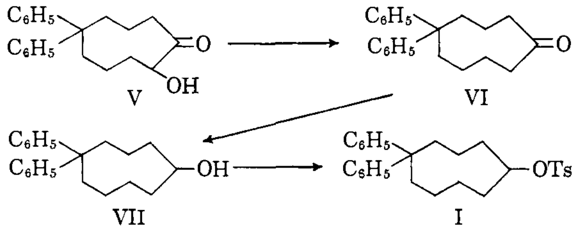
[3] B. F. H. wishes to thank the U. S. Educational Commission in the United Kingdom for the award of a Fulbright Travel Grant.

[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.

groups which occurred during, or subsequent to, the ionization step would be evident from a study of the products formed during acetolysis. Some of the possible rearrangements are shown in the diagram.

The tosylate I required for the solvolysis study was prepared from 2-hydroxy-6,6-diphenylcyclononanone by standard methods. The azeloin was first reduced by means of zinc and hydrochloric acid to the ketone VI, which was then converted to the alcohol VII by treatment with lithium aluminum hydride. Reaction of this alcohol in pyridine solution with *p*-toluenesulfonyl chloride afforded the tosylate I as a white crystalline solid, m.p. 103–104°, which could be kept at room temperature for several days without apparent decomposition. The stability of this tosylate is in marked contrast to that of the unsubstituted cyclononanol tosylate which underwent decomposition after several days at 0–10°.[6]



The rate of acetolysis of I was measured at 35° in anhydrous acetic acid containing excess acetic anhydride,[6] using the procedure for determination of rate constants which has been employed by Winstein and co-workers.[7] The products of acetolysis were separated by chromatography on alumina into two fractions, an olefin (71%) and an acetate fraction (20%), both obtained as white crystalline solids. The initial rate constant for acetolysis was found to be 6.7×10^{-6} sec.$^{-1}$,[8] a rate slower by a factor of ten than that observed for the acetolysis of cyclononanol tosylate.[6] This retardation of rate indicated that the phenyl groups were not providing anchimeric assistance of ionization and this fact was confirmed by a study of the products of solvolysis. The acetate fraction, after crystallization from petroleum ether, had m.p. 96–98°, undepressed on admixture with a specimen prepared by treatment of 5,5-diphenylcyclononanol with acetic anhydride in pyridine. The two specimens also had identical infrared spectra.

Infrared analysis of the olefin fraction indicated that it consisted of both *cis*- and *trans*-olefins. Hydrogenation of the olefin, m.p. 87–88°, led to the uptake of the theoretical volume of hydrogen for one double bond and afforded 1,1-diphenylcyclononane as a white crystalline solid, m.p. 92°. The infrared spectrum of this compound no longer showed bands at 10.06 and 13.78 μ, present in the spectrum of the diphenylcyclononene (III). The ultraviolet spectrum of III showed clearly that no rearrangement of phenyl groups had occurred, being identical with that reported for diphenylmethane[9] and also identical with the spectrum of 5,5-diphenylcyclononane. Any rearrangement of phenyl groups would lead to the formation of the styrene chromophore whose spectrum[9] is sharply contrasted with that of diphenylmethane.

In an attempt to determine the position of the double bond in III, a sample was subjected to oxidation by potassium permanganate in acetone. The acidic portion of the product (57%) was separated from neutral material and, after crystallization from petroleum ether had m.p. 213–214°, undepressed on admixture with a specimen of δ,δ-diphenylazelaic acid.[1] This result is consistent with the formulation of the olefin as 6,6-diphenylcyclononene (IIIa); but it is perhaps doubtful whether the oxidation products of compounds IIIa and IIIb would be distinguishable by mixed melting point determination.

Experimental Part[10]

2-Hydroxy-6,6-diphenylcyclononanone[1] (V) was obtained in 40% yield, using the method previously reported,[1] modified by use of a sodium–ester molar ratio of 6.7:1 instead of the reported 4.4:1.

5,5-Diphenylcyclononanone (VI) was prepared by a method first developed by Goldstein[11] for the conversion of sebacoin to cyclodecanone. The cyclic acyloin V (3.4 g., 0.011 mole) was dissolved in glacial acetic acid (5 ml.) and zinc dust (Allied Chemical and Dye Corporation, 90%) (4.1 g.) was added. The stirred mixture was maintained at 30° with ice cooling while 3.5 g. of concentrated hydrochloric acid was added dropwise. Stirring was continued for 15 min.; then two further quantites of hydrochloric acid were added at 15-min. intervals. Fifteen minutes after the final addition, the mixture was warmed on the steam-bath for 15 min. and then quickly chilled in an ice-bath. The zinc was filtered, 25 ml. of saturated sodium chloride solution was added, and the solution was extracted several times with ether. The extract was washed successively with saturated sodium chlroide solution, 10% sodium bicarbonate solution, and saturated sodium chloride solution, dried over sodium sulfate and evaporated. Addition of a little petroleum ether afforded 1.66 g. (55%) of the ketone VI as white crystals, m.p. 116°. The infrared spectrum of VI showed a carbonyl absorption peak at 5.87 μ.

Anal. Calcd. for $C_{21}H_{24}O$: C, 86.25; H, 8.27. Found: C, 86.23; H, 8.45.

5,5-Diphenylcyclononanol (VIII).—The ketone VI (6 g., 0.02 mole), diluted with 100 ml. of ether was reduced in the usual manner with 1 g. of lithium aluminum hydride in 50 ml. of ether. Decomposition was effected with dilute sulfuric acid and water, and the alcohol was extracted with ether. After drying over sodium sulfate and evaporation of solvent, the alcohol was obtained as a very viscous oil (6.2 g.) which resisted all attempts at crystallization.

Treatment of the alcohol with acetic anhydride and pyridine afforded the acetate IV, as white crystals, m.p. 96–98°, from petroleum ether.

Anal. Calcd. for $C_{23}H_{28}O_2$: C, 82.09; H, 8.39. Found: C, 81.89; H, 8.35.

---

[6] H. C. Brown and G. Ham, This Journal, **78**, 2735 (1956).

[7] S. Winstein, C. Hanson and E. Grunwald, *ibid.*, **70**, 812 (1948).

[8] After completion of 55% of reaction, the rate of solvolysis became appreciably slower. Some retardation of rate was noted also in the case of cyclononanol tosylate and 5,5-dimethylcyclononanol tosylate solvolyses, but in these cases this did not occur until after completion of at least 75% of reaction (Y. C. Meinwald, personal communication). One plausible explanation of this phenomenon is that the carbonium ion II may revert to a tosylate of different conformation from that of the starting material, and this second tosylate may then ionize at a slower rate. It is considered unlikely, although not impossible, in view of the sharp melting point of the initial tosylate, that this tosylate was itself a mixture of conformational isomers. (The authors are indebted to Dr. C. F. Wilcox for helpful discussion on this point.)

[9] V. Grignard, "Traité de Chimie Organique," Vol. II, Part I. Masson and Co., Paris, 1936, p. 72.

[10] All melting points are uncorrected. Infrared absorption spectra were determined with a Perkin–Elmer double beam spectrometer, model 21. Petroleum ether refers to the fraction b.p. 30–60°.

[11] A. Goldstein. Ph.D. Thesis, Cornell University (1954).

5,5-Diphenylcyclononanol tosylate (I), m.p. 103–104°, was prepared by the method of Brown and Ham[6] and crystallized from petroleum ether.

Anal. Calcd. for $C_{23}H_{32}O_3S$: C, 74.96; H, 7.19; S, 7.15; sapn. equiv., 448.6. Found: C, 75.20; H, 7.36; S, 7.16; sapn. equiv., 445.7.

Kinetic Measurements and Product Analysis.—The rate constant for the acetolysis of 2.026 g. of I was determined at 35° according to the procedure of Winstein, *et al.*,[7] using 120 ml. of anhydrous acetic acid[6] as solvent. Upon completion of the reaction the mixture was diluted with water and the products were extracted with ether. After drying and evaporation of solvent, 1.05 g. of the resultant colorless oil was subjected to chromatography on alumina. Elution with petroleum ether effected separation into two components. Both were crystallized from petroleum ether as white solids; the first (0.75 g., 71%) had m.p. 87–88° and the second (0.21 g., 20%) had m.p. 96–97°. This latter compound was shown by means of mixed melting point and infrared absorption spectrum determinations to be identical with the acetate IV, described above.

The infrared absorption spectrum of the first crystalline fraction, diphenycyclonene (III), showed *inter alia* bands at 10.09 and 13.78 μ. The ultraviolet spectrum of III, in isooctane solution, showed two bands, $\lambda_{\max}$ 260 mμ, log ϵ 2.93, and $\lambda_{\max}$ 270 mμ, log ϵ 2.86.

Anal. Calcd. for $C_{21}H_{24}$: C, 91.25; H, 8.75. Found: C, 91.40; H, 8.75.

When 0.10 g. of the olefin III in ethyl acetate solution was hydrogenated over palladium–carbon catalyst, 9.1 ml. (100 %) of hydrogen was taken up at 740 mm. and 26°. The product, 1,1-diphenylcyclononane, after evaporation of solvent and crystallization from petroleum ether, had m.p. 92°.

Anal. Calcd. for $C_{21}H_{26}$: C, 90.59; H, 9.41. Found: C, 90.48; H, 9.47.

Oxidation of III.—Finely ground potassium permanganate (0.75 g.) was added in small portions to a vigorously stirred solution of III (0.20 g.) and sodium bicarbonate (0.1 g.) in acetone (20 ml.). The mixture was stirred for 2 hr., acidified with dilute sulfuric acid and treated with sulfur dioxide until a clear solution was obtained. The products of oxidation were separated into neutral and acidic fractions in the usual way and the acidic fraction (1.4 g., 57%), after crystallization from glacial acetic acid, had m.p. 213–214°, underpressed on admixutre with authentic δ,δ-diphenylazelaic acid.[1]

ITHACA, N. Y.

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

Many-membered Carbon Rings. XX. Azacyclohendecane *via* Reduction of Cyclodecanone Oxime[1,2]

BY A. T. BLOMQUIST, B. F. HALLAM[3] AND A. D. JOSEY[4]

RECEIVED AUGUST 11, 1858

N,N-Dimethyl-9-decenylamine has been identified as an accessory product (*ca.* 10%) in the preparation of cyclodecene by pyrolysis of trimethylcyclodecylammonium hydroxide. It is proposed that this unsaturated amine arises as a result of rearrangement of cyclodecanone oxime to azacyclohendecane during reduction with lithium aluminum hydride.

trans-Cyclononene and *trans*-cyclodecene have been prepared[5,6] by the pyrolysis of the corresponding trimethylcycloalkylammonium hydroxides, obtained by a route involving the lithium aluminum hydride reduction of the cyclic ketoximes, cyclononanone oxime and cyclodecanone oxime. During the course of this work it was noted that the cycloalkenes were always contaminated with a substantial amount (*ca.* 10%) of an unsaturated amine.

It has been reported[7] earlier that the reduction of acetophenone oxime with lithium aluminum hydride yields a quantity (16%) of N-ethylaniline in addition to the expected α-phenylethylamine and under similar conditions proprionophenone oxime afforded a 14% yield of N-*n*-propylaniline. These N-alkylanilines were considered to arise by rearrangement of the oxime, under the conditions of the reaction, to an amide which was then reduced to a secondary amine.[7,8] In view of these reports it was considered desirable to establish the structure of the unsaturated amines formed as accessory products in the preparation of cyclononene and cyclodecene and a detailed study was made of the byproduct formed in the case of the latter preparation.

The unsaturated amine I was separated from cyclodecene in the usual way and distilled as a colorless liquid, b.p. 91–94° (6 mm.), $n^{25}\text{D}$ 1.4404, which gave a picrate derivative, m.p. 53–54°, and a methiodide derivative, m.p. 151–152°. The infrared spectrum of the amine showed strong absorption at 10.98 μ and medium absorption at 6.08 μ, consistent with the presence of a terminal vinyl group in the molecule.[9] Catalytic reduction of the amine I resulted in the absorption of the theoretical amount of hydrogen required for the presence of one carbon–carbon double bond, and the saturated amine II obtained gave a picrate derivative, m.p. 45–46°, and a methiodide derivative, m.p. 199–200°. This amine II was shown to be N,N-dimethyldecylamine by comparison of its infrared spectrum with that of an authentic specimen and by means of mixed melting point determinations on the picrate and methiodide derivatives. Authentic II was prepared for comparative purposes

---

(1) For the preceding paper in this series, see A. T. Blomquist and B. F. Hallam, THIS JOURNAL, **81**, 676 (1959).

(2) This research was supported in part 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) This author wishes to thank the U. S. Educational Commission in the United Kingdom for the award of a Fulbright Travel Grant.

(4) This article is in part abstracted from the dissertation presented by A. D. Josey in February, 1958, to the Graduate School of Cornell University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(5) A. T. Blomquist, R. E. Burge, Jr., and A. C. Sucsy, THIS JOURNAL, **74**, 3636 (1952).

(6) A. T. Blomquist, L. H. Liu and J. C. Bohrer, *ibid.*, **74**, 3643 (1952).

(7) D. Smith, M. Maienthal and J. Tipton, *J. Org. Chem.*, **17**, 294 (1952).

(8) N. Gaylord, "Reduction with Complex Metal Hydrides," Interscience Publishers, Inc., New York, N. Y., 1956, p. 751.

(9) L. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954, p. 42.