at 32 ± 2° for 34 hours, most of the starting material XVI was recovered. When XIX and XX were each subjected to the same solvolysis conditions (63 ± 1°, 24 hours), they were recovered unchanged.

Solvolysis of *exo*-Bicyclo[5.1.0]oct-4-yl Brosylate (XXI).—A mixture of 300 mg. of XXI, 1.8 ml. of glacial acetic acid and 3.0 ml. of 0.5 *M* sodium acetate in acetic acid was heated at 63 ± 1° for 24 hours. The solvolysis mixture was treated as described previously to give 95 mg. (77%) of a mixture containing 43% of XVII, 45% of XIX and 12% of XX, identified by gas chromatography on TCEP at 130° and on silicone oil at 150°, and by comparison of their infrared spectra with those of authentic samples. In another run conducted under the same conditions, 156 mg. (76%) of a mixture containing 43% of XVII, 43% of XIX and 14% of XX was obtained from 500 mg. of XXI in 3.0 ml. of glacial acetic acid and 5.0 ml. of 0.5 *M* sodium acetate in acetic acid. When the solvolysis was carried out at 32 ± 2° for 34 hours, most of the starting material was unchanged, as shown by an infrared spectrum of the crude reaction product.

Preparation of the Acetates XIX and XX.—Authentic samples of XIX and XX were prepared by the acetic anhydride–pyridine method from the corresponding alcohols. Starting with 85 mg. of *endo*-bicyclo[5.1.0]octan-4-ol, 300 μl. of dry pyridine and 200 μl. of acetic anhydride, 93 mg. (83%) of XIX was obtained. The product was shown to be homogeneous by gas chromatography on TCEP at 120°. A sample collected by gas chromatography (silicone oil, 150°) was analyzed.

Anal. Calcd. for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.48; H, 9.49.

The acetate XX (137 mg., 93%) was prepared from 110 mg. of the corresponding alcohol, 300 μl. of dry pyridine and 220 μl. of acetic anhydride. A sample collected by gas chromatography (silicone oil, 150°) was analyzed.

Anal. Calcd. for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.34; H, 9.52.

Preparation of Bicyclo[5.1.0]oct-3-ene (XVII).—The olefin XVII was prepared by the pyrolysis of bicyclo[5.1.0]oct-4-yl S-methyl xanthate prepared in the following manner.[6,7] Commercial 50% sodium hydride in mineral oil (0.7 g.) placed in a 50-ml. round-bottomed flask was washed with four 2-ml. portions of dry benzene. Benzene (15 ml.) and 0.55 g. of a mixture (1:1) of *endo*- and *exo*-bicyclo[5.1.0]-octan-4-ol were added to the flask and the mixture was heated under reflux for 24 hours. It was then cooled to 10° by means of an ice–water bath, and 4.5 ml. of carbon disulfide was added and the heating was resumed for 24 hours. The mixture was again cooled to room temperature, and 4.5 ml. of methyl iodide was added and the heating was continued for another 24-hour period. Water (25 ml.) was added to the mixture in small portions with cooling and the solution was extracted with three 20-ml. portions of benzene. The combined benzene layers were washed with three 25-ml. portions of water and 25 ml. of saturated sodium chloride solution. After drying (magnesium sulfate) the solvent was removed under reduced pressure to give 0.9 g. (95%) of a yellow oil. This crude xanthate mixture was heated in an oil-bath under atmospheric pressure. The temperature was gradually raised to 180° during a period of 2 hours. The yellow distillate was then passed through a column of alumina (5 g., base-washed, activity II) with pentane to give colorless liquid fractions weighing 90 mg. (45%). The product was shown to be homogeneous by gas chromatography on TCEP at 84°. It exhibited ultraviolet absorption[10] at 210 mμ (ε 800, not a maximum) and infrared absorption at 1021, 3040 cm.$^{-1}$ (cyclopropane) and 1650 cm.$^{-1}$ (C=C). A sample collected by gas chromatography was analyzed.

Anal. Calcd. for C_8H_{12}: C, 88.82; H, 11.18. Found: C, 89.00; H, 11.09.

A sample (30 mg.) collected by gas chromatography was dissolved in 4 ml. of absolute methanol, and hydrogenated in the presence of prereduced platinum oxide (*ca.* 50 mg.) at room temperature (24°) under atmospheric pressure. In 10 minutes, 97% of the calculated amount of hydrogen was absorbed. The catalyst was removed by filtration, and the filtrate was diluted with 15 ml. of water and extracted with four 3-ml. portions of ether. The combined ether extracts were washed with four 5-ml. portions of water and 5 ml. of saturated sodium chloride solution. After drying (magnesium sulfate), the solvent was carefully removed through a semi-micro column to yield 15 mg. (49%) of bicyclo[5.1.0]-octane, identified by gas chromatography on silicone oil at 150° and on TCEP at 120°, and by comparison of its infrared spectrum with that of an authentic sample.

Preparation of Bicyclo[5.1.0]oct-2-ene.—Bicyclo[5.1.0]-oct-2-ene was prepared by a procedure similar to the one employed for the preparation of XVII. Starting from 0.65 g. of a mixture (*ca.* 1:1) of *endo*- and *exo*-bicyclo[5.1.0]octan-2-ol, 0.8 g. of 50% sodium hydride in mineral oil, 17 ml. of benzene, 5.2 ml. of carbon disulfide and 5.2 ml. of methyl iodide, 1.1 g. (99%) of the crude S-methyl xanthate mixture was obtained. The xanthate mixture (0.6 g.) was pyrolyzed without purification to give 40 mg. (13%) of a clear liquid, which was shown to be at least 90% pure by gas chromatography on TCEP at 84°, and had a different retention time from that of XVII. A sample collected by gas chromatography exhibited infrared absorption at 1021, 3040 cm.$^{-1}$ (cyclopropane) and 1650 cm.$^{-1}$ (C=C), and ultraviolet absorption[10,11] at 210 mμ (ε 2400, not a maximum) and 237 mμ (ε 560).

Anal. Calcd. for C_8H_{12}: C, 88.82; H, 11.18. Found: C, 88.76; H, 10.84.

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(10) Determined as a solution in *n*-heptane.

(11) 1,3-Cycloöctadiene was reported to show ultraviolet absorption at 228 mμ (log ε 3.75); A. C. Cope and L. L. Estes, Jr., *J. Am. Chem. Soc.*, **72**, 1128 (1950).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, CAMBRIDGE 39, MASS.]

Proximity Effects. XXVIII. The Solvolysis of 5,5-Diphenylcycloöctyl *p*-Toluenesulfonate[1]

BY ARTHUR C. COPE, PAUL E. BURTON[2] AND MYRON L. CASPAR

RECEIVED JUNE 22, 1962

The mixture of olefins obtained from solvolysis of 5,5-diphenylcycloöctyl *p*-toluenesulfonate in trifluoroacetic acid 0.3 *M* in sodium trifluoroacetate was found to contain 1% of 1,5-diphenylcycloöctene. This constitutes the first known example of transannular phenyl migration in medium-ring compounds.

Although transannular hydride migration is a well-known reaction in medium-ring compounds, there have been no examples of similar transannular aryl or alkyl migrations. Attempts have been made recently to induce both methyl and phenyl migration in nine- and ten-membered rings without success.[3] It is noteworthy that in addition to the

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[1] Supported in part by a research grant (NSF-G5055) of the National Science Foundation; paper XXVII, A. C. Cope, S. Moon and C. H. Park, *J. Am. Chem. Soc.*, **84**, 4850 (1962).

[2] National Science Foundation Predoctoral Fellow, 1957–1960.

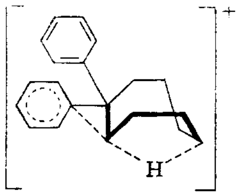
(3) (a) V. Prelog and W. Küng, *Helv. Chim. Acta*, **39**, 1394 (1956). (b) A. T. Blomquist and Y. C. Meinwald, *J. Am. Chem. Soc.*, **80**, 630 (1958); (c) A. T. Blomquist and B. F. Hallam, *ibid.*, **81**, 676 (1959). Products were determined in these cases by infrared spectroscopy; thus the presence of a small amount (of the order of 5% or less) of a minor product might not have been detected.

apparent absence of methyl or phenyl migration in the solvolyses of 5,5-diphenyl- and 5,5-dimethylcyclononyl tosylates in acetic acid, transannular hydride migrations were not observed.[3b,c] Recent work has shown that increasing amounts of transannular reactions may take place in formic acid and trifluoroacetic acid as compared to acetic acid.[4] Since all of the diphenylcyclooöctanes and a number of related olefins have been prepared in these laboratories[5] and were available for comparison, and since high temperature gas chromatography could be used for detection of trace amounts of products, it was felt that the problem of transannular migration of phenyl groups could be reinvestigated profitably by studying the solvolysis of 5,5-diphenylcyclooöctyl tosylate in formic acid and in trifluoroacetic acid.

The most convenient route to the 5-substituted cyclooöctyl system is through a Thorpe ring closure of a 5-substituted nonanedinitrile. 5-Phenylcyclooctanone has previously been synthesized in this manner.[5c] 5,5-Diphenylcyclooöctanone was prepared in 48% yield from 5,5-diphenylnonanedinitrile[6] by cyclization of the dinitrile with sodium methylanilide and hydrolysis of the resulting 2-cyano - 5,5 - diphenyl - 1 - cyclooöcten - 1 - ylamine with hydrochloric acid in acetic acid. The ketone was characterized by Wolf–Kishner reduction to 1,1-diphenylcyclooöctane and by chromium trioxide oxidation to 4,4-diphenyloctanedioic acid. The ketone was reduced to 5,5-diphenylcyclooöctanol with lithium aluminum hydride and the alcohol was converted to 5,5-diphenylcyclooöctyl tosylate. The tosylate was solvolyzed with anhydrous formic acid 0.05 M in sodium formate at 47–49°. After saponification of the formates the product mixture was chromatographed on alumina, giving a mixture of olefins (74.1%) and alcohols (22.4%). By a combination of repeated alumina chromatography, fractional crystallization and gas chromatography, it was possible to separate and identify the major components of this complex mixture. No products of transannular phenyl migration were isolated, although several trace components (present in amounts not greater than 0.1% of the total olefin mixture) with retention times similar to those of 1,3- and 1,5-diphenylcyclooöctene were detected by gas chromatography.

The main product of formic acid solvolysis was the normal elimination product, 5,5-diphenylcyclooctene (2), the amount of which could not be estimated by gas chromatography since both 4,4- and 5,5-diphenylcyclooöctene had the same retention times. The mixture of 4,4- and 5,5-diphenylcyclooöctene represented 57.2% of the olefin mixture, and 32% of 5,5-diphenylcyclooöctene was actually isolated from the middle and late fractions of the alumina chromatograms. The structure of 2 was proved by hydrogenation to 1,1-diphenylcyclooctane and by oxidative cleavage[7] to 4,4 - diphenyloctanedioic acid. The 4,4-diphenylcyclooctene (**3**), isolated from the late fractions of the alumina chromatograms, represented 6% of the total olefin fraction. The compound was characterized by hydrogenation to 1,1-diphenylcyclooctane. The position of the double bond was established by the n.m.r. spectrum which showed a doublet at $\tau = 7.08$ ($J = 8$ c.p.s.) which may be ascribed to the two methylene protons at the 3-position split by the vinyl proton at the 2-position. 4,4-Diphenylcyclooöctene must be presumed to arise from carbonium ions **11** and **13** which may be formed from carbonium ion **10** by a 1,3- or a 1,2-hydride shift. 3,3-Diphenylcyclooöctene (**15**), a third possible *gem*-diphenyl isomer which might have been expected to arise from carbonium ion **11** or **12**, was not detected.

cis-1,2-Diphenylcyclooöctene (**4**), 29.2% of the olefin mixture by gas chromatographic analysis, was isolated from the early fractions of the alumina chromatograms and identified by comparison with an authentic sample, and by hydrogenation to *cis*-1,2-diphenylcyclooöctane.[3a] Further proof for the position of the double bond was obtained from the n.m.r. spectrum which showed no peaks in the vinyl region. *cis*-1,2-Diphenylcyclooöctene may be obtained from the initially formed carbonium ion **10** by a 1,4-hydride shift to give carbonium ion **12** followed by a 1,2-phenyl migration to give carbonium ion **14** and loss of a proton. Alternatively, carbonium ion **12** may be formed from carbonium ion **10** by a two-step process involving either a 1,3-hydride shift followed by a 1,2- or a 1,4-hydride shift, or a 1,2-hydride shift followed by a 1,3- or a 1,5-hydride shift. Although a recent study[8] has shown that in the cyclooöctyl series 1,3- and 1,5-hydride shifts occur to the exclusion of 1,4-hydride shifts, it may be that *gem*-diphenyl substitution alters the conformation of the cyclooöctane ring so that 1,4-hydride migration can occur in the solvolysis of 5,5-diphenylcyclooöctyl tosylate. Examination of Stuart–Briegleb models shows that the hydrogen atoms in both the 3- and 4-positions are held in close proximity to the developing carbonium ion at the 1-position. It is possible that in this case a 1,4-hydride shift is favored due to the additional stabilization that may result from a synchronous 1,2-phenyl shift. At the present time, the available evidence does not allow a choice between this process and one of the multistep processes.



The other possible olefin that can be formed from carbonium ion **14** by loss of a proton, 2,3-diphenylcyclooöctene (**5**), was found to compose 7.4% of the olefin mixture by gas chromatographic analysis and

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(4) A. C. Cope, J. M. Grisar and P. E. Peterson, *J. Am. Chem. Soc*., **81**, 1640 (1959).

(5) (a) A. C. Cope and D. S. Smith, *ibid.*, **74**, 5136 (1952); (b) A. C. Cope, M. R. Kinter and R. T. Keller, *ibid.*, **76**, 2757 (1954); (c) A. C. Cope and R. J. Cotter, *J. Org. Chem.*, **28**, Jan. (1963); (d) A. C. Cope and W. R. Moore, *J. Am. Chem. Soc.*, **77**, 4939 (1955); (e) A. C. Cope and D. S. Smith, *ibid.*, **74**, 5136 (1952).

(6) A. T. Blomquist and C. J. Buck, *ibid.*, **81**, 672 (1959).

(7) B. Riegel, R. B. Moffett and A. V. McIntosh, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 234.

(8) A. C. Cope, G. A. Berchtold, P. E. Peterson and H. S. Sharman, *J. Am. Chem. Soc.*, **82**, 6366 (1960).

was isolated from the middle fractions of the alumina chromatograms. An authentic sample was obtained by the dehydration of 1,2-diphenylcyclooctanol,[3a] which gave a 43:57 mixture of two olefins. Since the first was identical with *cis*-1,2-diphenylcycloöctene[3a] the second could reasonably be only 2,3 diphenylcycloöctene. This sample was shown to be identical with the sample from the solvolysis by mixture melting point and by a comparison of ultraviolet and infrared spectra.

Two unidentified compounds, **7** and **8**, were present to the extent of 0.3% and 3.7%, respectively, in the olefin mixture. The mixture of alcohols was not investigated other than to show that the main component was 5,5-diphenylcycloöctanol.

The fact that a larger ratio of *cis*-1,2-diphenylcycloöctene to 4,4- plus 5,5-diphenylcycloöctene had been obtained from a preliminary solvolysis suggested the possibility that 4,4- and/or 5,5-diphenylcycloöctene might undergo acid-catalyzed isomerization to *cis*-1,2-diphenylcycloöctene in formic acid. Heating either 4,4- or 5,5-diphenylcycloöctene in formic acid 0.05 *M* in sodium formate under reflux was indeed found to give a mixture of *cis*-1,2 - diphenylcycloöctene and 2,3 - diphenylcycloöctene. However, at lower temperatures, under conditions similar to those used for the solvolysis of 5,5-diphenylcycloöctyl tosylate, only a small amount (*ca.* 0.5%) of isomerization of 5,5-diphenylcycloöctene occurred. It is difficult to draw a conclusion from these results concerning the amount of isomerization of 5,5-diphenylcyclooctene that would occur during the solvolysis, since in this case the olefin would be present, at least initially, in an homogeneous solution, while the isomerization experiments carried out at 40–50° were heterogeneous throughout.

In order to study the solvolysis under non-acidic conditions, 5,5-diphenylcycloöctyl tosylate was also solvolyzed in tetrahydrofuran 0.7 *M* in lithium perchlorate.[9] Under these conditions the mixture of olefins formed in 93% yield was found to contain 97% of 5,5-diphenylcycloöctene and only 3% of a mixture of the isomerization products **4** and **5**. No trace of transannular phenyl migration was detected. This result suggests that solvolyses of this type should serve as a useful opposite to solvolyses in trifluoroacetic acid if a minimum rather than a maximum amount of transannular reaction is desired.

The solvolysis of 5,5-diphenylcycloöctyl tosylate also was carried out in trifluoroacetic acid 0.3 *M* in sodium trifluoroacetate at 0° for 10 hours. After reduction with lithium aluminum hydride the product mixture was chromatographed on alumina, giving a mixture of at least six olefins (87.6%) and at least four alcohols (6.2%). The olefin mixture (see Table I) was similar to that obtained from the formic acid solvolysis except that the profusion of trace products found in the latter reaction was not present. Two additional components, one (compound **9**) having a retention time on gas chromatography only slightly longer than *cis*-1,2-diphenylcycloöctene, and the second having a retention time identical with that of 1,5-diphenylcycloöctene,[3c] also were present. The latter compound, 1% of the olefin mixture, was isolated by gas chromatography and shown to be identical with authentic 1,5-diphenylcycloöctene[3c] by comparison of ultraviolet and infrared spectra.

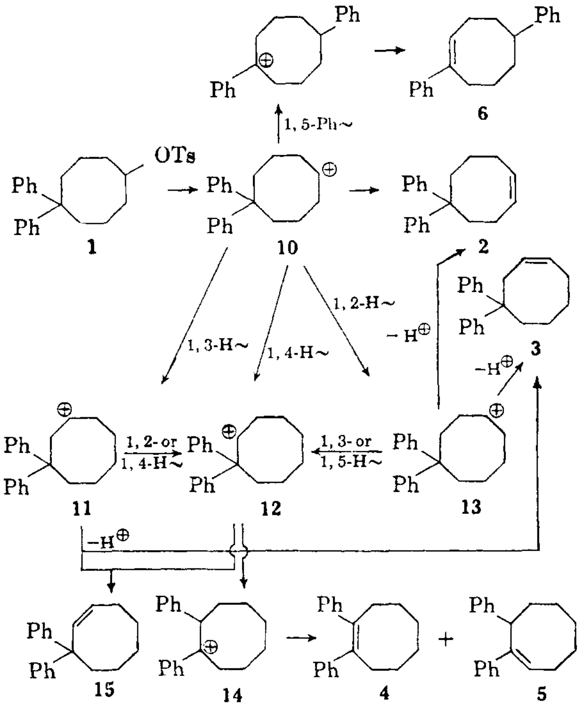


Fig. 1.

TABLE I

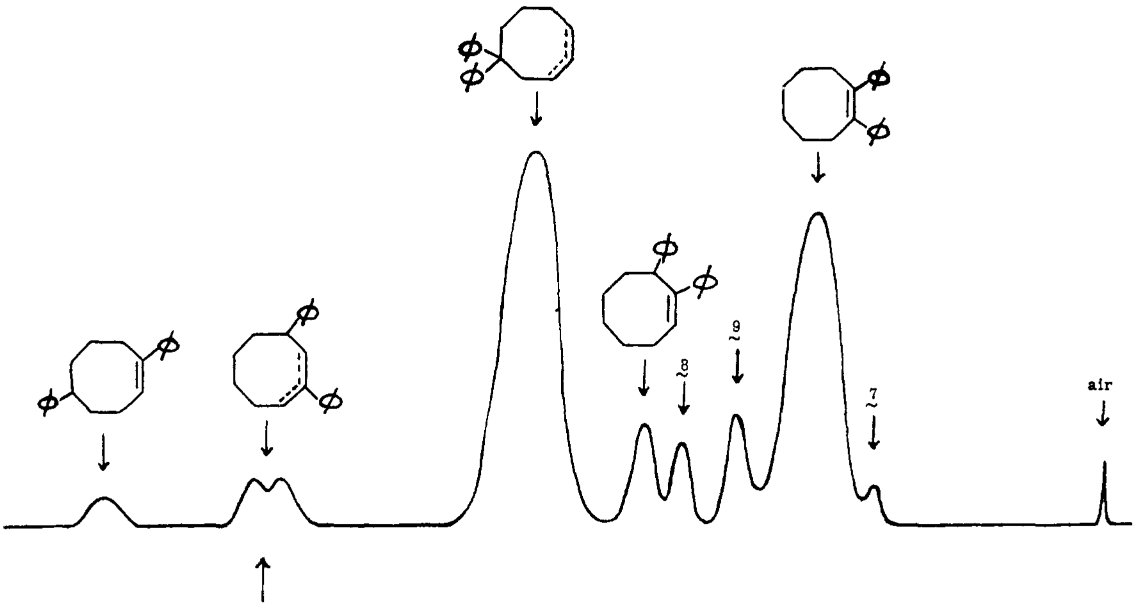
COMPOSITION OF OLEFIN MIXTURES FROM SOLVOLYSES OF 5,5-DIPHENYLCYCLOÖCTYL *p*-TOLUENESULFONATE[a]

Cycloöctene	% from HCO_2H	% from CF_3CO_2H
5,5-Diphenyl- (**2**) 4,4-Diphenyl- (**3**)	57.2[b]	43.0[b]
1,2-Diphenyl- (**4**)	29.2	39.5
2,3-Diphenyl- (**5**)	7.4	1.7
1,5-Diphenyl- (**6**)	..	1.0
7	0.3	..
8	3.7	6.5
9	..	8.2
Others[c]	*ca.* 2	<0.1

[a] Estimated by gas chromatography on Viton A-HV at 208–250°. [b] Mixture was not resolved. [c] Fifteen to twenty additional components, none constituting more than 0.1% of the total olefin mixture.

Under conditions similar to those of the solvolysis, 5,5-diphenylcycloöctene was found to isomerize to a mixture of *cis*-1,2-diphenylcycloöctene, 2,3-diphenylcycloöctene and compound **9**. No trace of either compound **8** or of 1,5-diphenylcycloöctene could be detected. A careful examination of the products showed that the only *gem*-diphenylcyclooctene present was the unchanged starting material, 5,5-diphenylcycloöctene. In contrast, at least several per cent. of 4,4-diphenylcycloöctene was formed in the solvolysis of 5,5-diphenylcycloöctyl tosylate. This suggested that isomerization of 5,5-diphenylcycloöctene results mainly from pro-

(9) S. Winstein, S. Smith and D. Darwish, *J. Am. Chem. Soc.*, **81**, 5511 (1959).



A mixture of 1,3- and 2,4-diphenylcycloöctenes (not found in the solvolysis products) was eluted at the point indicated

Fig. 2.—Order of elution from Viton A-HV of the solvolysis products of 5,5-diphenylcycloöctyl *p*-toluenesulfonate.

tonation of the double bond at the 1-position to give the 4,4-diphenylcycloöctyl carbonium ion **13** which could undergo a 1,3- or a 1,5-hydride shift to carbonium ion **12** leading to the formation of *cis*-1,2-diphenylcycloöctene and 2,3-diphenylcyclooctene. It is possible to envision this entire process as occurring in a synchronous manner. Protonation at the 2-position to give the 5,5-diphenylcycloöctyl carbonium ion **10** would have been expected to give observable amounts of 4,4-diphenylcycloöctene and 1,5-diphenylcycloöctene.

Experimental[10]

2-Cyano-5,5-diphenyl-1-cycloöcten-1-ylamine.—Redistilled N-methylaniline (87.5 g.), b.p. 92–92.5° (21 mm.), was added to 15 g. of sodium wire (cut into small pieces) and 50.6 g. of naphthalene in 2 l. of dry ether. The mixture was stirred and heated under reflux in a nitrogen atmosphere for 3 hr. 5,5-Diphenylnonanedinitrile (19.6 g.) in 1.5 l. of dry ether was added dropwise at a rate of *ca.* 1 drop per second over 30.5 hr. through a high dilution apparatus.[11] The reaction mixture was then heated under reflux for 8 hr., cooled, and water (1 l.) was added slowly. The ether layer was separated, and the aqueous layer was extracted with two 300-ml. portions of ether. The combined extracts were washed with three 500-ml. portions of water, treated with Norit (2 g.), and filtered through Celite. The solvent was removed by distillation at atmospheric pressure and the residue was steam distilled. The solid residue from the steam distillation was dissolved in methylene chloride and the solution was dried over magnesium sulfate and treated with Norit. The product was purified by fractional crystallization from *n*-hexane–methylene chloride and from benzene–petroleum ether (93–97°). The yield was 15.15 g. (77%). An analytical sample obtained from a similar preparation was purified by chromatography on neutral alumina (activity I) by elution with ether–pentane (1:1), followed by recrystallization from ether; m.p. 158.4–160.0°.

Anal. Calcd. for $C_{21}H_{22}N_2$: C, 83.40; H, 7.33; N, 9.26. Found: C, 83.27; H, 7.10; N, 9.40.

5,5-Diphenylcycloöctanone.—2-Cyano-5,5-diphenyl-1-cycloöcten-1-yl amine (17.73 g.) was heated under reflux with 350 ml. of glacial acetic acid and 850 ml. of concd. hydrochloric acid for 47.5 hr. After cooling, 3 l. of water was added and the mixture was extracted with four 400-ml. portions of ether. The combined extracts were washed with water and saturated sodium bicarbonate solution, and dried over magnesium sulfate. Neutral alumina (activity I, 50 g.) and Norit (1 g.) were added and the solution was filtered through Celite. The filtrate was evaporated to dryness under reduced pressure to give 14.03 g. (86%) of crude 5,5-diphenylcycloöctanone (m.p. 92.0–94.8°). Recrystallization from ethanol–petroleum ether (93–97°) gave 10.19 g. (62%), m.p. 96.3–97.8°. An analytical sample was prepared from the product of a similar reaction by distillation of the ketone in a short path still at 110–130° (bath temperature) (0.1–0.4 mm.), followed by recrystallization from methanol; m.p. 96.2–97.0°.

Anal. Calcd. for $C_{20}H_{22}O$: C, 86.28; H, 7.97. Found: C, 86.42; H, 8.01.

The 2,4-dinitrophenylhydrazone was prepared and purified by elution from alumina with benzene followed by three recrystallizations from methylene chloride–methanol; m.p. 198.0–198.6°.

Anal. Calcd. for $C_{26}H_{26}O_4N_4$: C, 68.10; H, 5.72; N, 12.22. Found: C, 68.29; H, 5.64; N, 12.20.

5,5-Diphenylcycloöctanol.—Finely ground 5,5-diphenylcycloöctanone (15.27 g.) was added to a solution of 1.10 g. of lithium aluminum hydride in 1 l. of dry ether. After being stirred 3 hr. at room temperature the reaction mixture was poured into 1 l. of ether containing 15 ml. of water and stirred for 1 hr. Magnesium sulfate (25 g.) was added and the solution was filtered through Celite and evaporated to dryness under reduced pressure yielding 15.00 g. (97.5%) of the pure alcohol, m.p. 146.8–149°. An analytical sample was obtained from a similar preparation by four recrystallizations from ether; m.p. 147.0–148.0°.

Anal. Calcd. for $C_{20}H_{24}O$: C, 85.71; H, 8.64. Found: C, 85.66; H, 8.63.

5,5-Diphenylcycloöctyl *p*-Toluenesulfonate.—A cold solution of 30.0 g. of *p*-toluenesulfonyl chloride in 150 ml. of dry pyridine was added to 21.65 g. of 5,5-diphenylcyclooctanol (m.p. 147.5–148.5°) in 100 ml. of dry pyridine cooled in an ice-bath. The reaction mixture was allowed to stand for 20 hr. in a refrigerator, then cooled in an ice–salt-bath and water (400 ml.) was slowly added. The cold mixture was extracted with five 200-ml. portions of ether, and the

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[10] Melting points are corrected and boiling points are uncorrected. We are indebted to Dr. S. M. Nagy and his associates for analyses.

[11] A. C. Cope and E. C. Herrick, *J. Am. Chem. Soc.*, **72**, 985 (1950).

combined extracts were washed with five 25-ml. portions of cold hydrochloric acid, three 25-ml. portions of cold water, three 50-ml. portions of cold saturated sodium bicarbonate solution, and dried over magnesium sulfate. The solution was concentrated to 100 ml. under reduced pressure, cooled overnight in a refrigerator and filtered to obtain 28.52 g. (85%) of pure tosylate, which melted at 106–107° and decomposed above 120°. An analytical sample obtained from an earlier preparation after four recrystallizations from hexane melted at 101.0–101.5° dec. (probably due to very slight contamination with the acid or dimorphism).

Anal. Calcd. for $C_{27}H_{30}SO_3$: C, 74.61; H, 6.96. Found: C, 74.46; H, 6.98.

Dimethyl 5,5-Diphenylnonanedioate.—5,5-Diphenylnonanedinitrile (5.00 g.), 4 ml. of concd. sulfuric acid, 2 ml. of water and 30 ml. of methanol were heated under reflux for 5 days. The reaction mixture was cooled, poured into 50 ml. of ice-water and extracted with three 50-ml. portions of ether. The combined extracts were washed with water, 10% sodium carbonate solution and saturated sodium chloride solution, and dried over magnesium sulfate. The crude product was purified by chromatography on neutral alumina (activity I), eluting with ether–pentane (1:9 to 1:3), and recrystallized from ether–pentane, pentane or hexane. The total yield was 2.60 g. (43%). An analytical sample had m.p. 82.0–82.8°.

Anal. Calcd. for $C_{23}H_{28}O_4$: C, 74.97; H, 7.66. Found: C, 75.08; H, 7.63.

Monomethyl 5,5-Diphenylnonanedioate.—A modification of the method of Walker was employed.[12] Dimethyl 5,5-diphenylnonanedioate (3.316 g.) and 0.522 g. of potassium hydroxide in 25 ml. of absolute methanol were stirred at room temperature for 18 hr., and then heated at 56–61° with stirring for an additional 3 hr. Most of the methanol was removed by distillation, and the mixture was cooled. Water (20 ml.) and ether (10 ml.) were added and the mixture was stirred, after which water and ether (10 ml. each) were added and the layers separated. The aqueous layer was extracted with an additional 20 ml. of ether and the combined extracts were dried over magnesium sulfate. Upon removal of the solvent, dimethyl 5,5-diphenylnonanedioate (0.905 g.), m.p. 79.8–82.2°, was recovered.

The aqueous phase was acidified with hydrochloric acid and extracted with three 20-ml. portions of ether. The combined extracts were dried over magnesium sulfate and the solvent was removed under reduced pressure. The monomethyl ester, a total of 1.80 g., was separated from the dicarboxylic acid by trituration of the residue with boiling hexane. After two recrystallizations from ether–hexane, 1.427 g. (45%) of monomethyl 5,5-diphenylnonanedioate was obtained, m.p. 107.2–108.6°.

Anal. Calcd. for $C_{22}H_{26}O_4$: C, 74.55; H, 7.39. Found: C, 74.77; H, 7.19.

The hexane-insoluble residue was 0.49 g. of 5,5-diphenylnonanedioic acid,[4] m.p. 210.0–216.6°.

5,5,9,9-Tetraphenyl-8-nonenoic Acid.—To the Grignard reagent prepared from 0.159 g. of bromobenzene and 0.029 g. of magnesium turnings in 9 ml. of tetrahydrofuran (freshly distilled from sodium) was added 0.099 g. of monomethyl 5,5-diphenylnonanedioate in 5 ml. of tetrahydrofuran. The mixture was stirred and heated under reflux for 1 hr., cooled in an ice-bath, and 5 ml. of saturated ammonium chloride solution was added with stirring. The tetrahydrofuran phase was separated and the aqueous phase was extracted with two 10-ml. portions of ether and the combined organic phases were dried over magnesium sulfate. After removal of the solvent under reduced pressure, the residue was heated under reflux for 5 hr. with 24 mg. of *p*-toluenesulfonic acid monohydrate in 20 ml. of benzene. The benzene solution was cooled, filtered and concentrated under reduced pressure. The residue was heated under reflux for 0.5 hr. with 0.40 g. of potassium hydroxide in 10 ml. of methanol. Water (5 ml.) was added, and most of the methanol was removed under reduced pressure. An additional 15 ml. of water was added and the mixture was extracted with three 10-ml. portions of ether. The aqueous layer was acidified with 10 ml. of 6 *N* hydrochloric acid and extracted with three 10-ml. portions of ether. These extracts were dried over magnesium sulfate, and the solvent was removed under reduced pressure. Trituration of the residue with boiling petroleum ether gave 0.073 g. of crude product which was recrystallized from methanol–water and then from methanol; 0.047 g. (36%), m.p. 135.3–137.7°. An analytical sample melted at 136.6–137.6°.

Anal. Calcd. for $C_{33}H_{32}O_2$: C, 86.05; H, 7.00. Found: C, 85.77; H, 7.14.

4,4-Diphenyloctanedioic Acid.—Chromium trioxide (0.201 g.), dissolved in 0.4 ml. of water and 2.8 ml. of glacial acetic acid, was added to a stirred solution of 91 mg. of 5,5,9,9-tetraphenyl-8-nonenoic acid in 0.8 ml. of chloroform and 5 ml. of glacial acetic acid. The temperature was kept below 50° during the addition. The solution was stirred at 50° for 20 min. and then cooled in an ice-bath while the excess chromic acid was destroyed with 0.5 ml. of methanol. The volatile components were removed under reduced pressure and water and sodium chloride solution were added to the residue, which was extracted with three portions of ether. The combined extracts were washed with water and 10% hydrochloric acid and dried over magnesium sulfate. The crude dicarboxylic acid (34 mg.) obtained by concentration was triturated twice with boiling hexane to remove any starting material present and recrystallized from glacial acetic acid and then from tetrahydrofuran–pentane, giving 9 mg. (14%), m.p. 191.4–193.0°.

Anal. Calcd. for $C_{20}H_{22}O_4$: C, 73.60; H, 6.79. Found: C, 73.60; H, 6.80.

1,1-Diphenylcycloöctane.—5,5-Diphenylcycloöctanone (0.126 g.), 0.29 g. of potassium hydroxide, 1 ml. of hydrazine hydrate (85%) and 10 ml. of diethylene glycol were heated at 190–193° for 1 hr., at 193–201° for 0.5 hr. and at 210–220° for 3 hr. Approximately 1 ml. of distillate was collected. The mixture was cooled, diluted with 50 ml. of water, and extracted with three 75-ml. portions of ether. The combined extracts were washed with water, dried over magnesium sulfate and evaporated, leaving a residue of 0.115 g. Chromatography on 6 g. of neutral alumina (activity I) yielded 0.112 g. of crude hydrocarbon (eluted with pentane), which was distilled at 0.1 mm. in a short-path still (bath temperature 77–90°). The distillate, 0.099 g., m.p. 57–64°, was recrystallized twice from methanol and 63 mg. (68%) of the pure hydrocarbon was obtained, m.p. 62.8–63.8°.

Anal. Calcd. for $C_{20}H_{24}$: C, 90.85; H, 9.15. Found: C, 90.83; H, 8.99.

Oxidation of 5,5-Diphenylcycloöctanone with Chromium Trioxide.—To a cold solution of 5,5-diphenylcycloöctanone (200 mg.) in 3 ml. of chloroform and 14 ml. of glacial acetic acid was added 700 mg. of chromium trioxide in 1 ml. of water and 10 ml. of glacial acetic acid. Concentrated sulfuric acid (0.5 ml.) was then added and the solution was heated at 72° for 105 min. The cooled reaction mixture was poured into 75 ml. of water and extracted three times with chloroform and once with ether. The combined organic layers were washed with water and a saturated solution of sodium chloride and dried over magnesium sulfate. The solution was evaporated to dryness under reduced pressure giving 222 mg. of a yellow semi-solid which was dissolved in 50 ml. of 10% potassium hydroxide solution and extracted with four 25-ml. portions of ether. The aqueous phase was acidified with concd. hydrochloric acid, allowed to cool slowly and filtered to give 94 mg. (40%) of 4,4-diphenyloctanedioic acid, m.p. 188–191°, undepressed on mixed m.p. with authentic material prepared as previously described. The infrared spectra of the two samples were identical.

Solvolysis of 5,5-Diphenylcycloöctyl *p*-Toluenesulfonate.—A stirred mixture of 28.24 g. of 5,5-diphenylcycloöctyl *p*-toluenesulfonate in 1.3 l. of anhydrous formic acid[13] 0.0545 *M* in sodium formate[14] was heated at 47–49° for 44 hr. At the end of the reaction period an oil floated on the colorless solution. A portion of this oil was removed and fractionally crystallized from pentane to yield 1.643 g. of a crystalline solid, later shown to be 5,5-diphenylcycloöctene. The balance of the mixture was poured into 2 l. of water and the turbid solution was extracted with five 200-ml. portions of ether. The combined extracts were washed with three 100-ml. portions of water and four 100-ml. portions of saturated sodium bicarbonate solution and evaporated to dryness under reduced pressure. The residual oil (including the

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[12] J. Walker, *J. Chem. Soc.*, **61**, 709 (1892).

[13] S. Winstein and H. Marshall, *J. Am. Chem. Soc.*, **74**, 1120 (1952).

[14] S. Winstein and R. Heck, *ibid.*, **78**, 4801 (1956).

mother liquors from the above crystallization) was stirred for 26 hr. in a mixture of 200 ml. of 20% aqueous sodium hydroxide and 400 ml. of methanol. Water was added and the mixture was extracted with six 100-ml. portions of ether and three 100-ml. portions of pentane. The combined extracts were washed twice with water, twice with saturated sodium chloride solution, dried over magnesium sulfate, and evaporated to dryness under reduced pressure. The residue was fractionally crystallized from petroleum ether (97–100°) to give 1.88 g. of 5,5-diphenylcycloöctanol, identified by mixture melting point and by comparison of its infrared spectrum with that of an authentic sample. The residues from the fractional crystallization were combined and chromatographed on 900 g. of neutral alumina (activity I). Eluting with pentane and collecting 200-ml. fractions gave 22 empty fractions. Eluting with pentane–ether (200:1), pentane–ether (50:1) and ether gave a mixture of olefins (10.96 g.) in fractions 23–56. Fractions 57–70 eluted with ether–ethanol (1:1) were empty. A mixture of alcohols (2.215 g.) was obtained in fractions 71–75. The total yields of olefins and alcohols obtained from the solvolysis were thus 74.1 and 22.4%, respectively. Gas chromatography[15] on SE-30 and Viton A-HV showed that fractions 23–44 (10.694 g.) contained a mixture of two major and at least four minor components. Fractions 45–56 (0.268 g.) contained at least 15 and perhaps 20 additional components. Several of the components in fractions 45–56 had retention times similar to those of 1,5-diphenylcycloöctene and of 1,3-diphenylcycloöctene; however, these mixtures could not be separated to give any single pure compound. The maximum amount (if any) of either transannular product would have been about 0.1% of the total olefin fraction. Gas chromatography on silicone grease and on SE-30 showed that the alcohol mixtures obtained in fractions 71–75 contained one major component with a retention time essentially identical to that of 5,5-diphenylcycloöctanol, and at least three minor components.

Since the olefin mixture was not completely resolved by gas or alumina chromatography, the olefins were separated by a combination of alumina chromatography, fractional crystallization and gas chromatography. Neutral alumina (activity I) was used for elution chromatography, using alumina:olefin mixture ratios of 100–600:1. The best separations were effected using pentane–methylene chloride 250–50:1. Individual fractions were checked by gas chromatography and fractions of similar compositions were combined. When further crystallization could not be induced by seeding, all the residues were combined, rechromatographed on alumina and the process repeated.

Identification of 5,5-Diphenylcycloöctene (2).—The oil removed from the surface at the completion of the formic acid solvolysis was crystallized from pentane and from ethanol to give 1.213 g., m.p. 93.5–94.2°. A total of 4.269 g. (33.8% based on total crude olefin) of this product was obtained in 12 separate fractions by the combination of alumina chromatography and fractional crystallization described above. The identity of each of these fractions was shown by mixture melting point and by retention time on gas chromatography. The ultraviolet spectrum of **2** in isoöctane exhibited maxima at 244 mμ (ϵ 207), 250 mμ (ϵ 307), 254 mμ (ϵ 401), 260 mμ (ϵ 481), 263 mμ (ϵ 459), 265 mμ (ϵ 405) and 270 mμ (ϵ 386). The n.m.r. spectrum determined in deuteriochloroform had a sharp singlet at $\tau = 2.8$ and multiplets centered at $\tau = 4.4$, $\tau = 7.7$ and $\tau = 8.6$ in the ratio 10:2:8:2.

Anal. Calcd. for $C_{20}H_{22}$: C, 91.55; H, 8.45. Found: C, 91.46; H, 8.49.

A 26.0-mg. sample hydrogenated over 25.3 mg. of 10% palladium-on-charcoal in 6 ml. of 1:1 ethyl acetate–methanol absorbed 136% of one molar equivalent of hydrogen. Gas chromatography of the product (25.0 mg.) showed a single peak which had essentially the same retention time as 1,1-diphenylcycloöctane. A 20.1-mg. sample of the product was recrystallized from methanol yielding 15.1 mg. (58%) of 1,1-diphenylcycloöctane, m.p. 62.9–63.3°, undepressed on admixture with an authentic specimen.

Oxidation of 5,5-Diphenylcycloöctene (2) with Chromium Trioxide.—Chromium trioxide (0.204 g.) in 0.4 ml. of water and 2.8 ml. of glacial acetic acid was added to a stirred solution of 0.054 g. of **2** in 0.8 ml. of chloroform and 4 ml. of glacial acetic acid maintained below 50° by an ice-bath. The mixture was warmed at 50° for 20 min., then cooled with an ice-bath, and 0.5 ml. of methanol was added to destroy the unchanged chromic acid. The volatile components were removed under reduced pressure. Water (7 ml.) was added to the residue, which was extracted with three 10-ml. portions of ether. The combined extracts were washed twice with water and three times with 10% hydrochloric acid solution, after which they were extracted with 20 ml. of 10% potassium hydroxide solution and then 20 ml. of water. The basic aqueous extracts were combined and acidified with hydrochloric acid, and the flocculent white precipitate was collected by filtration. It was recrystallized twice from glacial acetic acid and once from tetrahydrofuran–pentane, yielding 3.1 mg. (5%) of 4,4-diphenyloctanedioic acid, m.p. 189.5–192.5°, undepressed on mixed m.p. with an authentic specimen. The infrared spectra of the two were identical.

Identification of 4,4-Diphenylcycloöctene (3).—After six alumina chromatograms of the crude olefin mixture from solvolysis, there was obtained 1.497 g. of a colorless oil which by gas chromatography (Viton A-HV and SE-30) showed 87% of a component with the same retention time as 5,5-diphenylcycloöctene (**2**). This pentane-soluble oil was eluted from alumina after **2**, would not crystallize on seeding with **2**, and showed an infrared spectrum different from that of **2**. After standing for 6 months, 1.10 g. of this oil, which was now only partially soluble in pentane, was chromatographed on 400 g. of neutral alumina (activity I). After developing with 2 l. of pentane and pentane–methylene chloride (100:1), elution with pentane–methylene chloride (50–10:1) gave 0.828 g. of colorless oils in thirteen 200-ml. fractions. Fraction 1 (44 mg.) partially solidified on seeding with **2**. The infrared spectra of fractions 2–13 were all identical and showed only small absorption bands at 763 and 713 cm.$^{-1}$ attributable to **2**. After standing for 2 weeks a small crystal formed in fraction 7 and was used to crystallize fractions 2–13. Fractions 3–12 (602 mg.) were combined and recrystallized (Norit) three times from ethanol to give 84 mg., m.p. 64.5–66.2°. The ultraviolet spectrum of **3** in cyclohexane exhibited maxima at 244 mμ (ϵ 235), 250 mμ (ϵ 344), 254 mμ (ϵ 444), 260 mμ (ϵ 521), 263 mμ (ϵ 496), 265 mμ (ϵ 438), 270 mμ (ϵ 400). The n.m.r. spectrum determined in deuteriochloroform had peaks at $\tau = 2.82$, $\tau = 4.5$ (multiplet), $\tau = 7.08$ (doublet, $J = 8$ c.p.s.) and a complex band centered at $\tau = 8.1$, in the ratio 10:2:2:8.

Anal. Calcd. for $C_{20}H_{22}$: C, 91.55; H, 8.45. Found: C, 91.54; H, 8.50.

The yield of 4,4-diphenylcycloöctene isolated was about 0.750 g. (6% of the total olefins). A 36.7-mg. sample, which contained *ca.* 10% of **2** (estimated by infrared analysis), hydrogenated over 42.6 mg. of 10% palladium-on-charcoal in 6 ml. of 1:1 ethyl acetate–methanol absorbed 119% of one molar equivalent of hydrogen. On gas chromatography the product (36.0 mg.) showed a major peak (98%) with essentially the same retention time as 1,1-diphenylcycloöctane. Recrystallization of the crude product from methanol yielded 26.1 mg. (71%) of 1,1-diphenylcycloöctane, m.p. 61.7–62.7°, undepressed on admixture with an authentic specimen.

Identification of *cis*-1,2-Diphenylcycloöctene (4).—Using the same techniques described for the isolation of 5,5-diphenylcycloöctene, a total of 2.168 g. (17.2% of the total olefin mixture) of *cis*-1,2-diphenylcycloöctene (**4**) melting in the range 74.5–78.0° was obtained from the early fractions

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(15) Gas chromatographic analyses were carried out using 180 × 0.8-cm. Pyrex tubes. The samples were eluted with helium at 15 p.s.i. and thermistors were used as detectors. Columns packed with 20–33% SE-30 silicone rubber (General Electric Co.) on base-washed fire-brick (40–60 mesh) and Gas-Chrome P (60–80 mesh) were used at temperatures of 220–280°. Columns packed with 15–30% Viton A-HV rubber (du Pont Co.) on Chromosorb P (60–80 mesh) or Chromosorb W (60–80 mesh) were used at temperatures of 190–260°. The order of retention times on Viton A-HV of diphenylcycloöctenes and other solvolysis products was: compound **7** < *cis*-1,2-diphenylcycloöctene < compound **8** < 2,3-diphenylcycloöctene, < 4,4- and 5,5-diphenylcycloöctene < 1,3- or 2,4-diphenylcycloöctene < 2,4- or 1,3-diphenylcycloöctene < 1,5-diphenylcycloöctene. 5,5-Diphenylcyclooctanol could not be eluted from Viton A-HV at the same temperature as the olefins. The order on SE-30 was the same except that compound **8** and *cis*-1,2-diphenylcycloöctene had the same retention times, and a mixture of 1,3- and 2,4-diphenylcycloöctene gave a single peak. 5,5-Diphenylcycloöctanol was eluted after 1,5-diphenylcycloöctene. The polar Viton A-HV shows a higher separation efficiency than SE-30 and is comparable to QF-1; W. J. A. Vanden Heuvel, E. O. A. Haahti and E. C. Horning, *J. Am. Chem. Soc.*, **83**, 1513 (1961).

of the alumina chromatograms. The fractions were shown to be identical by mixture m.p. and by retention time on gas chromatography. A sample of **4** was purified for spectral data by recrystallization from ethanol; m.p. 75.2–75.7°. The ultraviolet spectrum in isoöctane showed a maximum at 254 mμ (ε 7,930) and an inflection at 224 mμ (ε 11,090). The infrared spectrum was identical with that of an authentic sample[3a] and the mixture m.p. was undepressed. The n.m.r. spectrum determined in deuteriochloroform had peaks at $\tau = 3.01$, $\tau = 7.34$ and $\tau = 8.30$ in the ratio 10:4:8.

A 41-mg. sample of **4** hydrogenated over 60 mg. of 10% palladium-on-charcoal in 8 ml. of ethyl acetate absorbed 100% of one molar equivalent of hydrogen. On gas chromatography the product (39 mg., m.p. 73.5–75.8°) showed a single peak with the same retention time as *cis*-1,2-diphenylcycloöctane. Recrystallization of the crude product from ethanol and from methanol yielded 21 mg. (51%) of *cis*-1,2-diphenylcycloöctane, m.p. 75.5–76.4°, undepressed on admixture with an authentic specimen.[3a]

Identification of 2,3-Diphenylcycloöctene (5).—After nine alumina chromatograms, during which *cis*-1,2-diphenylcycloöctene (**4**) and 5,5-diphenylcycloöctene (**2**) were isolated as described above, there was obtained 317 mg. (in three fractions) of an oil which was shown by gas chromatography on SE-30 to contain 5.2% of **8**, 25% of **4**, 55% of **5**, 9.8% of **2** and 4.7% of two compounds with retention times similar to that of **2**. A small amount of crystalline **5**, m.p. 83–89°, was isolated by gas chromatography and used to seed a 79-mg. fraction which contained 74% of **5**. Crystallization from ethanol gave 48 mg. of **5** (0.4% of the total olefin mixture) which partially melted, then partially resolidified and remelted in the range 88–113°. Further recrystallization from hexane, ethanol and methanol did not change this melting point. An analytical sample (m.p. 88–110°), after standing for 6 months at room temperature, melted sharply at 112.5–113.5°.

Anal. Calcd. for $C_{20}H_{22}$: C, 91.55; H, 8.45. Found: C, 91.34; H, 8.42.

The ultraviolet spectrum of **5** in isoöctane showed a maximum at 236 mμ (ε 6,820). The infrared spectrum was identical to that of the authentic sample (described below) and the mixture m.p. with this sample was not depressed.

Preparation of 2,3-Diphenylcycloöctene (5).—1,2-Diphenylcycloöctanol[3a] (40 mg.) was dehydrated according to the procedure of Smith,[5e] except that benzene was substituted for toluene. Gas chromatography on SE-30 showed that the product (38 mg.) was a 43:57 mixture of *cis*-1,2-diphenylcycloöctene (**4**) and 2,3-diphenylcycloöctene (**5**). Crystallization from 0.5 ml. of absolute ethanol plus 0.1 ml. of pentane gave (after seeding with **5**) 7.2 mg., m.p. 90–112°. Gas chromatography on Viton A-HV showed a single component. After standing at room temperature for 6 months this sample melted sharply at 112.5–113.5°. Its ultraviolet spectrum in isoöctane showed a maximum at 236 mμ (ε 6,750).

Isolation of Additional Components.—Compound **7**, present to the extent of 0.3% in the crude olefin mixture, was eluted from alumina in the early fractions and had the shortest retention time on gas chromatography. A small amount (1.63 mg.) was obtained from the same fractions from which 2,3-diphenylcycloöctene had been isolated. The ultraviolet spectrum of **7** in isoöctane showed maxima at 249 mμ (ε 1285), 254 mμ (ε 1370, 259 mμ (ε 1340) 263 mμ (ε 1320), 265 mμ (ε 1245), 270 mμ (ε 1245), 280 mμ (ε 1000). The compound was not further characterized.

Compound **8**, present to the extent of 3.7% in the crude olefin mixture, was the first component to be eluted from alumina. Compound **8** had the same retention time as *cis*-1,2-diphenylcycloöctene on gas chromatography on silicone grease and on SE-30, but had a retention time between *cis*-1,2-diphenylcycloöctene and 2,3-diphenylcycloöctene on Viton A-HV. The mother liquors from the crystallization of *cis*-1,2-diphenylcycloöctene and 5,5-diphenylcycloöctene, from the first five fractions of the third successive alumina chromatogram, contained 2.500 g. of the remaining 4.237 g. of the unseparated olefin mixture. This 2.500-g. fraction was chromatographed on 670 g. of neutral alumina (activity I). The column was developed with 4 l. of pentane, 4 l. of pentane–methylene chloride (1000:1), 2 l. of pentane–methylene chloride (500:1) and 1 l. of pentane–methylene chloride (250:1), and the olefins (2.456 g., in 110 fractions) were eluted with pentane–methylene chloride (250:1). Gas chromatography of fractions 1–6 (36 mg.) on SE-30 and Viton A-HV showed 100% of compound **8**. Fractions 7–17 (370 mg.) contained 71% of **8** and 29% of *cis*-1,2-diphenylcycloöctene. The ultraviolet spectrum of **8** in isoöctane showed maxima at 253 mμ (ε 540), 259 mμ (ε 850), 266 mμ (ε 1,148), 273 mμ (ε 1,182). Compound **8** was unchanged on attempted hydrogenation over palladium-on-charcoal.

Isomerization of 4,4- and 5,5-Diphenylcycloöctene in Formic Acid.—A mixture of 222 mg. of 5,5-diphenylcyclooctene (**2**) and 16 ml. of formic acid was heated to boiling and became homogeneous. After heating under reflux for 5 hr. the solution was cooled and the resulting mixture was evaporated to dryness under reduced pressure. The residue was dissolved in 50 ml. of ether–pentane (1:1) and the solution was dried over potassium carbonate. Evaporation to dryness gave 219 mg. (99%) of a colorless solid, m.p. 50–74°. Gas chromatographic analysis on SE-30 and on Viton A-HV indicated about 95% of a component with the same retention time as that of *cis*-1,2-diphenylcycloöctene (**4**). A second component had the same retention time as that of 2,3-diphenylcycloöctene (**5**). The infrared spectrum of the mixture was essentially identical to that of **4**. When the reaction was carried out at reflux in formic acid 0.05 *M* in sodium formate, after 15 minutes the mixture consisted of **2** (93%), **4** (4%) and **5** (3%). After 4 days at reflux, it consisted of **4** (80%), **5** (8%) and at least three other components. At lower temperatures the reaction mixture was heterogeneous and the isomerization proceeded much more slowly. Only 0.05% of **4** and a trace of **5** were formed when a mixture of **2** (50 mg.) and 6 ml. of formic acid 0.05 *M* in sodium formate was stirred for 5 days at 40–50°.

In a similar fashion 4,4-diphenylcycloöctene (**3**) was isomerized to a mixture of **4** (95%) and **5** (5%) by heating under reflux for 2 days in formic acid 0.05 *M* in sodium formate.

Isomerization of *cis*-1,2-Diphenylcycloöctene (4).—After heating under reflux 9 days, an aliquot of a solution of 57 mg. of *cis*-1,2-diphenylcycloöctene (**4**) in 5 ml. of formic acid 0.05 *M* in sodium formate was removed and worked up as described above. Gas chromatographic analysis on SE–30 and Viton A–HV showed the presence of **4** (93%) and **5** (6%) and two other components with retention times greater than **4**. The infrared spectrum was essentially identical to that of **4**.

Solvolysis of 5,5-Diphenylcycloöctyl *p*-Toluenesulfonate in Tetrahydrofuran–Lithium Perchlorate.—To a solution of anhydrous lithium perchlorate (7.5 g.) in 100 ml. of dry tetrahydrofuran was added 1.0 g. of anhydrous calcium carbonate and 1.470 g. of 5,5-diphenylcycloöctyl *p*-toluenesulfonate. The mixture, protected from atmospheric moisture, was heated under reflux for 38 hr. and then evaporated nearly to dryness under reduced pressure. The solids were extracted with pentane (100 ml.) and the residue diluted with water (100 ml.) and filtered. The aqueous filtrate was extracted with three 25-ml. portions of pentane and six 25-ml. portions of methylene chloride and the combined extracts, after drying over magnesium sulfate, were evaporated to dryness. A combination of fractional crystallization and alumina chromatography gave 0.822 g. (93%) of a mixture which, by gas chromatography on SE-30 and Viton A–HV, was shown to contain 97% of a component with the same retention time as 5,5-diphenylcycloöctene (**2**) and about equal amounts of two other components with retention times the same as *cis*- 1,2-diphenylcycloöctene and 2,3-diphenylcycloöctene. A total of 0.681 g. (77%) of **2** was isolated. No trace of transannular phenyl migration products, 1,3- or 2,4- or 1,5-diphenylcycloöctene, was detected.

Solvolysis of 5,5-Diphenylcycloöctyl *p*-Toluenesulfonate in Trifluoroacetic Acid.—A mixture of 5.830 g. of 5,5-diphenylcycloöctyl *p*-toluenesulfonate in 50 ml. of trifluoroacetic acid 0.30 *M* in sodium trifluoroacetate was stirred at 0° for 10 hours, then poured into a cold saturated sodium bicarbonate solution (500 ml.). The resulting mixture was extracted with four 100-ml. portions of ether and the combined extracts were washed with two 25-ml. portions of water, dried over magnesium sulfate and evaporated under reduced pressure. The infrared spectrum of the residual oil (3.530 g.) had a small carbonyl band at 1775 $cm.^{-1}$ and indicated the absence of unchanged tosylate. To the oil (3.490 g.) dissolved in 200 ml. of dry ether was added 0.25 g. of lithium aluminum hydride. The mixture was stirred for 0.5 hr., then 5 ml. of ethyl acetate and 1 ml. of water were added. After stirring for an additional 0.5 hr. the mixture was dried over magnesium sulfate, filtered through Celite, and the filtrate was evaporated under reduced pressure to a colorless oil (3.342 g.). The infrared spectrum of this oil had a weak hydroxyl band at *ca.* 3600 cm.$^{-1}$ and no bands in the carbonyl region. Gas chromatography on SE-30 and Viton A-HV indicated a mixture of at least six olefins (94%) and at least four alcohols (6%). On the basis of retention times the olefin mixture appeared to consist of *cis*-1,2-diphenylcyclooctene (39.5%), compound **8** (6.5%), a component (compound **9**) with a retention time (Viton A-HV) between that of *cis*-1,2-diphenylcycloöctene and compound **8** (8.2%), 2,3-diphenylcycloöctene (1.7%), 4,4- and 5,5-diphenylcycloöctene (43%) and 1,5-diphenylcycloöctene (1%). The alcohol mixture appeared to contain mainly 5,5-diphenylcycloöctanol (75%).

The crude solvolysis mixture (3.300 g.) was chromatographed on 70 g. of neutral alumina (activity I). Eluting with pentane and pentane-methylene chloride (100:1) gave a mixture of olefins (3.076 g.) in twenty-two 100-ml. fractions. Eluting with ether-methanol (10:1) gave a mixture of alcohols (0.232 g.) in two 100-ml. fractions. The yields of olefins and alcohols from the solvolysis were thus 87.6 and 6.2%, respectively. Fractions 6-20 (0.283 g.), containing *cis*-1,2-diphenylcycloöctene (17%), a mixture of 4,4- and 5,5-diphenylcycloöctene (74%) and 1,5-diphenylcycloöctene (9%), were fractionally crystallized from ethanol (1 ml.) to give 63 mg. of 5,5-diphenylcycloöctene, m.p. 91.0-93.2°. The balance of the mixture was separated by gas chromatography on Viton A-HV at 233°. Fraction 1 (12.3 mg.) was shown to be identical with *cis*-1,2-diphenylcycloöctene by comparison of its infrared spectrum with that of an authentic sample. The infrared spectrum of fraction 2 (70.8 mg.) showed all the bands for both 4,4- and 5,5-diphenylcyclooctene and appeared to represent about a 1:1 mixture of these two compounds. The third fraction (10.1 mg.) was shown to be identical with an authentic sample of 1,5-diphenylcycloöctene by comparison of retention times on SE-30 and Viton A-HV and by comparison of ultraviolet and infrared spectra.

Isomerization of 5,5-Diphenylcycloöctene in Trifluoroacetic Acid.—A mixture of 400 mg. of 5,5- diphenylcyclooctene in 50 ml. of trifluoroacetic acid 0.3 *M* in sodium trifluoroacetate was stirred at 0° for 10 hr. The mixture was allowed to stand overnight in a refrigerator, filtered, and the filtrate was evaporated to dryness under reduced pressure at 0°. The combined residues were taken up in ether (50 ml.), dried over potassium carbonate, and evaporated under reduced pressure to an oil (380 mg.). To a portion of this oil (324 mg.) in dry ether (25 ml.) was added 50 mg. of lithium aluminum hydride. The solution was stirred for 0.5 hr., and then poured into 100 ml. of wet ether and stirred for 0.5 hr. longer, then dried over magnesium sulfate and evaporated under reduced pressure. Gas chromatographic analysis of the residual oil (297 mg.) on SE-30 and on Viton A-HV showed a mixture which, on the basis of retention times, consisted of *cis*-1,2-diphenylcycloöctene (33%), compound **9** (3%), 2,3-diphenylcycloöctene (1%), 5,5-diphenylcycloöctene (57%) and 5,5-diphenylcycloöctanol (6%). No trace of ether 1,5-diphenylcycloöctene or compound **8** was detected. Crystallization from ethanol (with seeding) gave 125 mg. of **2** (in two fractions), identified by mixture melting point and the infrared spectrum. Seeding the residue with *cis*-1,2-diphenylcycloöctene (**4**) gave 61 mg., m.p. 58-76.5°, which by gas chromatographic analysis (Viton A-HV) consisted of 94% of **4** and 6% of **2**. Gas chromatography (Viton A-HV) of the residue (82 mg.) from this last crystallization showed the presence of **4** (48%), **9** (9.6%), **5** (3.4%) and **2** (39%). Examination of the infrared spectrum of the **2**, m.p. 85-92°, collected from this gas chromatogram did not indicate the presence of any 4,4-diphenylcycloöctene (**3**).

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Proximity Effects. XXIX. Solvolysis of Cycloheptenyl Derivatives[1,2]

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RECEIVED JUNE 22, 1962

Cycloheptenyl derivatives have been solvolyzed and the products compared with those obtained in the solvolysis of cyclooctenyl derivatives. Solvolysis of 4-cyclohepten-1-yl brosylate in either acetic acid or trifluoroacetic acid gave 4-cyclohepten-1-ol, 3-cyclohepten-1-ol and 1,3- and 1,4-cycloheptadiene in contrast to 4-cycloöcten-1-yl brosylate which gave bicyclic compounds in addition to the normal products. Acetolysis of 3-cyclohepten-1-yl brosylate produced *endo*- and *exo*-bicyclo[4.1.0]heptan-2-ol. The bicyclic alcohols also were prepared by an independent route, and their configurations were established. Solvolysis of 2-cyclohepten-1-yl bromide afforded the expected 2-cyclohepten-1-ol and 1,3-cycloheptadiene.

Previous papers[4-6] in this series described solvolyses of derivatives of the three isomeric cycloöctenols. In acetic acid, 4-cycloöcten-1-yl brosylate gave bicyclo[3.3.0]oct-2-ene and *endo*- and *exo*-bicyclo-[3.3.0]octan-2-ol in addition to the unrearranged 4-cycloöcten-1-ol and 1,4-cycloöctadiene.[4] With trifluoroacetic acid as solvent only bicyclic products were obtained from this brosylate.[5] Similarly, the major products of the acetolysis of 3-cycloöcten-1-yl brosylate were *endo*- and *exo*-bicyclo[5.1.0]octan-2-ol.[4,6] On the other hand, acetolysis of 2-cycloocten-1-yl bromide gave unrearranged products.[4]

Recent studies have shown that cycloheptane derivatives under appropriate conditions also may form transannular products to a large extent.[7] It was therefore of interest to investigate the solvolytic reactions of derivatives of the isomeric cycloheptenols, and compare the results with those obtained from the solvolysis of the corresponding cycloöctenyl compounds. The solvolyses of 4-cyclohepten-1-yl brosylate, 3-cyclohepten-1-yl brosylate and 2-cyclohepten-1-yl bromide are reported in this paper.

4-Cycloheptene-1-carboxylic acid prepared by the procedure of Stork and Landesman[8] was converted to 4-cyclohepten-1-yl acetate in 70% yield by treatment with lead tetraacetate in acetic acid. The use of lead tetraacetate for the decarboxylation of monocarboxylic acids has been reported by several workers.[9-11] Under the conditions employed

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[1] Supported in part by a research grant (NSF-G5056) of the National Science Foundation.

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