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

Proximity Effects. XXVII. Solvolysis of Derivatives of Bicyclo[5.1.0]octanols[1,2]

BY ARTHUR C. COPE, SUNG MOON AND CHUNG HO PARK

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The study of proximity effects in medium ring compounds has been extended to bicyclo[5.1.0]octane derivatives. *endo*- and *exo*-bicyclo[5.1.0]oct-2-yl trifluoroacetate, *endo*- and *exo*-bicyclo[5.1.0]oct-3-yl brosylate and *endo*- and *exo*-bicyclo-[5.1.0]oct-4-yl brosylate were solvolyzed in acetic acid containing sodium acetate, and the products were identified. Possible reaction mechanisms are discussed.

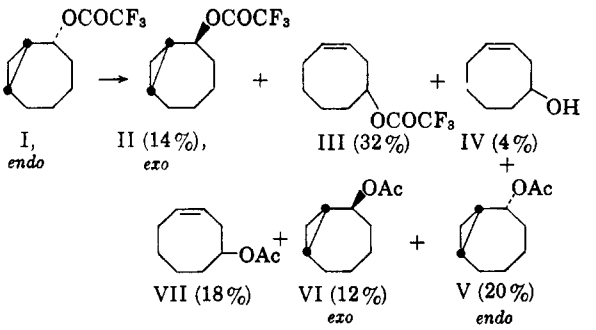
The influence of double bonds due to spatial proximity in the eight-membered ring was demonstrated by the solvolysis of 3- and 4-cycloöcten-1-ol derivatives.[3] Thus, *endo*- and *exo*-bicyclo[5.1.0]-octan-2-ol were obtained as principal products from the solvolysis of 3-cycloöcten-1-yl brosylate, and the solvolysis of 4-cycloöcten-1-yl brosylate yielded *cis*-bicyclo[3.3.0]oct-2-ene and *endo*- and *exo*-bicyclo[3.3.0]octan-2-ol in addition to the normal products.[3,4] A comparable example of reactions influenced by cyclopropane rings was shown in the solvolysis of *endo*- and *exo*-bicyclo[5.1.0]octan-2-ol and their derivatives.[4] Recently, Winstein[5] reported the formation of a symmetrical non-classical 3-bicyclo[3.1.0]hexyl cation in the solvolysis of *cis*-3-bicyclo[3.1.0]hexyl tosylate by the participation of the cyclopropane ring. Since the various bicyclo[5.1.0]octanols possess cyclopropane rings that are held in proximity to the hydroxyl group, it was of interest to investigate the solvolysis of suitable derivatives of these alcohols in order to study the influence of cyclopropane rings which are remotely situated from the initially formed carbonium ion. For this purpose, the solvolyses of derivatives of *endo*- and *exo*-bicyclo-[5.1.0]octan-2-ol, *endo*- and *exo*-bicyclo[5.1.0]octan-3-ol and *endo*- and *exo*-bicyclo[5.1.0]octan-4-ol were undertaken. The synthesis and stereochemistry of these bicyclic alcohols are described in the preceding paper.[2]

In selecting suitable derivatives of bicyclo[5.1.0]-octan-2-ols, it has been reported[4] previously that efforts to prepare their brosylates or tosylates were unsuccessful, probably due to the great instability of these esters, and their acetates and *p*-nitrobenzoates were too unreactive to be solvolyzed under mild conditions and had to be treated under severe conditions under which the bicyclo[5.1.0]oct-2-yl acetates, if initially formed, would have rearranged to 3-cycloöcten-1-yl acetate. Therefore, it was of importance to find derivatives of *endo*- and *exo*-bicyclo[5.1.0]octan-2-ol which would solvolyze rapidly enough under sufficiently mild conditions to permit isolation of intermediates in the solvolyses. *endo*- and *exo*-bicyclo[5.1.0]oct-2-yl trifluoroacetate proved suitable for this purpose, and their solvolyses are discussed in this paper. *endo*- and *exo*-bicyclo[5.1.0]octan-3-ol and *endo*- and *exo*-bicyclo[5.1.0]octan-4-ol were converted to the corresponding brosylates, and these sulfonic esters also were solvolyzed.

Solvolysis of 3-Cycloöcten-1-yl Trifluoroacetate and *endo*- and *exo*-Bicyclo[5.1.0]oct-2-yl Trifluoroacetate.—The trifluoroacetates were solvolyzed in acetic acid containing excess sodium acetate. The solvolysis products were analyzed and separated by gas chromatography, and identified by their infrared spectra.

3-Cycloöcten-1-yl trifluoroacetate (III) was too unreactive to be solvolyzed at room temperature, and had to be heated at 102° for 48 hours in order to bring the solvolysis to completion. The sole product was 3-cycloöcten-1-yl acetate (VII), which is the product expected to be formed from the solvolysis under reversible (equilibrating) conditions. It has been shown that, under these conditions, bicyclo[5.1.0]oct-2-yl acetates rearrange to 3-cycloöcten-1-yl acetate.[4]

When *endo*-bicyclo[5.1.0]oct-2-yl trifluoroacetate (I) was solvolyzed at 102° for 24 hours, 3-cycloocten-1-ol (IV, 6%), 3-cycloöcten-1-yl trifluoroacetate (III, 3%) and 3-cycloöcten-1-yl acetate (VII, 91%) were obtained; however, when the solvolysis was carried out at room temperature for 24 hours, the products were found to be *exo*-bicyclo-[5.1.0]oct-2-yl trifluoroacetate (II, 14%), 3-cycloöcten-1-yl trifluoroacetate (III, 32%), 3-cycloöcten-1-ol (IV, 4%), *endo*-bicyclo[5.1.0]oct-2-yl acetate (V, 20%), *exo*-bicyclo[5.1.0]oct-2-yl acetate (VI, 12%) and 3-cycloöcten-1-yl acetate (VII, 18%).



A possible mechanism for the formation of these products can be written, in which the ion pair A is formed as an intermediate; A can collapse to give I, II and III, or give rise to a bridged carbonium ion intermediate B, which would then yield IV, V, VI and VII by substitution.

endo-Bicyclo[5.1.0]oct-2-yl trifluoroacetate (I) thus formed would again be subjected to solvolysis until none of it remained in the reaction mixture, and

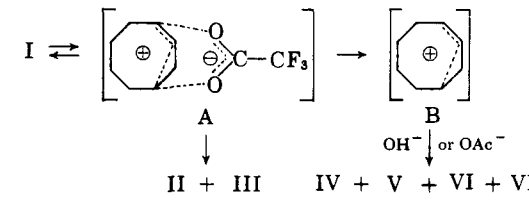
(1) Supported in part by a research grant (NSF-G5505) of the National Science Foundation.

(2) Paper XXVI, A. C. Cope, S. Moon and C. H. Park, *J. Am. Chem. Soc.*, **84**, 4843 (1962).

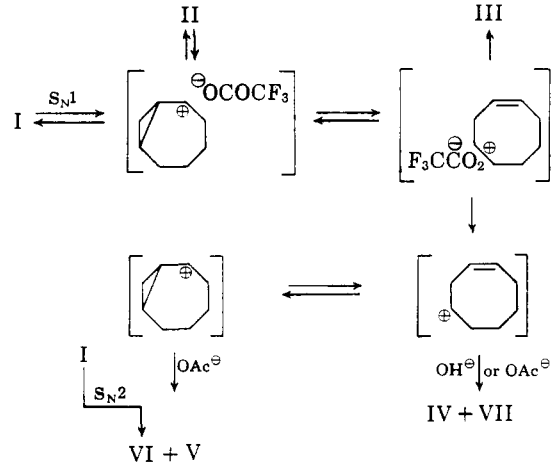
(3) A. C. Cope and P. E. Peterson, *ibid.*, **81**, 1643 (1959).

(4) A. C. Cope, S. Moon and P. E. Peterson, *ibid.*, **84**, 1935 (1962).

(5) S. Winstein and J. Sonnenberg, *ibid.*, **83**, 3244 (1961).

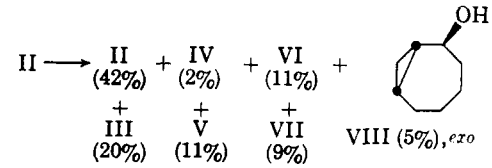


II so formed may undergo further solvolysis to some extent as shown in the solvolysis of *exo*-bicyclo[5.1.0]oct-2-yl trifluoroacetate (II). The solvolysis may have proceeded to some degree through classical carbonium ion intermediates as well as by an SN2 mechanism.



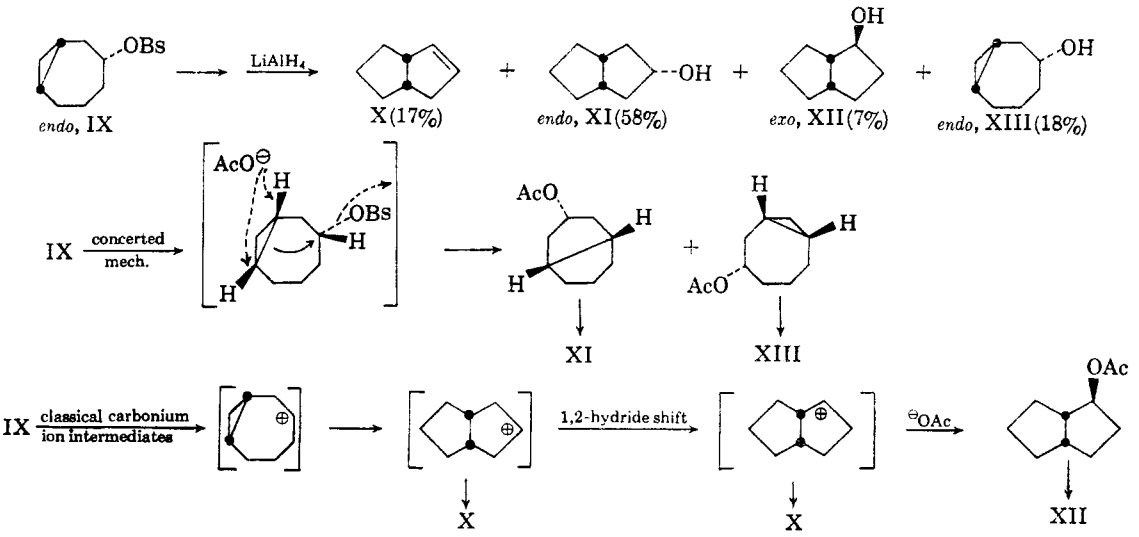
However, predominant formation of the thermodynamically less stable *endo*-bicyclo[5.1.0]oct-2-yl acetate (V, 20%) compared to the amount of the more stable *exo* isomer VI (12%) supports the bridged ion (nonclassical carbonium ion) intermediate. Had the solvolysis proceeded solely through classical carbonium ion intermediates, the thermodynamically more stable *exo*-acetate VI would have been formed principally due to the planar nature of the carbonium ion and the approach of acetic acid from the less hindered *exo* position. If the reaction proceeded solely by an SN2 mechanism, the *exo*-acetate VI is also expected to be formed predominantly by rearward approach of the attacking acetate ion. On the other hand, it has been predicted[3,4] that the *endo*-acetate V would be the principal product of solvolysis if the reaction proceeded through a bridged ion intermediate, in order to permit the favorable overlap of *p*-orbitals in the transition state; however, essentially equivalent reaction paths can be formulated involving classical carbonium ions in equilibrium provided their stereochemistry is preserved.

When *exo*-bicyclo[5.1.0]oct-2-yl trifluoroacetate (II) was solvolyzed under the same conditions, the products consisted of *exo*-bicyclo[5.1.0]oct-2-yl trifluoroacetate (II, 42%), 3-cycloöcten-1-yl trifluoroacetate (III, 20%), *exo*-bicyclo[5.1.0]octan-2-ol (VIII, 5%), 3-cycloöcten-1-ol (IV, 2%), *endo*-bicyclo[5.1.0]oct-2-yl acetate (V, 11%), *exo*-bicyclo[5.1.0]oct-2-yl acetate (VI, 11%) and 3-cycloöcten-1-yl acetate (VII, 9%). The acetates V, VI, VII and 3-cycloöcten-1-yl trifluoroacetate (III) were shown to be stable under these solvolysis conditions.



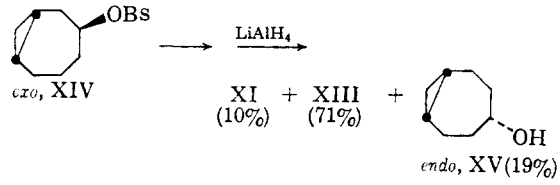
Solvolysis of *endo*- and *exo*-Bicyclo[5.1.0]oct-3-yl Brosylate (IX, XIV).—When the crystalline *endo*-bicyclo[5.1.0]oct-3-yl brosylate (IX) was solvolyzed in acetic acid containing sodium acetate at room temperature, the reaction proceeded to completion in 48 hours; however, the *exo* isomer XIV was too stable under these conditions, and had to be heated at 60° for 24 hours in order to bring the solvolysis to completion. Study of models shows that the higher ground state energy of the crowded *exo* isomer would tend to make it more reactive than the less crowded *endo* isomer. Therefore, the observed higher reactivity of the *endo* isomer can be attributed mainly to its favorable stereoelectronic arrangement which enables the cyclopropane ring to participate more easily, since the *p*-orbital vacated by the leaving group is in better position to accept electrons from the cyclopropane ring in the *endo* isomer. The solvolysis of IX, followed by lithium aluminum hydride reduction, yielded a mixture containing 17% of *cis*-bicyclo[3.3.0]oct-2-ene (X), 58% of *endo*-bicyclo[3.3.0]octan-3-ol (XI), 7% of *exo*-bicyclo[3.3.0]octan-2-ol (XII) and 18% of *endo*-bicyclo[5.1.0]octan-3-ol (XIII). Formation of these products can be explained by a combination of concerted mechanisms and one proceeding through classical carbonium ion intermediates. Absence of *exo*-bicyclo[5.1.0]octan-3-ol excluded the possibility of an SN2 mechanism. Predominant formation of XI (58%) supports the concerted mechanism, since XI and XIII rather than the corresponding *exo* isomers are expected to be formed as the principal products due to the nature of the rearward approach by the attacking electron pairs in the concerted mechanism. Although XIII was shown to be thermodynamically more stable than the corresponding *exo* isomer, formation of XIII with absence of the *exo* isomer also supports the concerted mechanism. On the other hand, formation of X and XII supports a mechanism proceeding through classical carbonium ion intermediates.

endo- and *exo*-bicyclo[3.3.0]octan-3-ol have not been described before, and authentic samples of the alcohols were prepared in the following manner. *cis*-Bicyclo[3.3.0]oct-2-ene[3] was epoxidized with 40% peracetic acid to give a mixture containing 13% of *endo*- and 87% of *exo*-*cis*-bicyclo[3.3.0]oct-2-ene oxide, which were then separated by gas chromatography. Lithium aluminum hydride reduction of the *endo*-epoxide yielded a mixture containing 74% of known[3] *endo*-bicyclo[3.3.0]octan-2-ol and 26% of XI. The *exo*-epoxide was reduced with lithium aluminum hydride to give a mixture of *exo*-bicyclo[3.3.0]octan-2-ol and *exo*-bicyclo[3.3.0]-octan-3-ol. Although these two alcohols were not separable by gas chromatography, their acetates were. The acetate mixture was shown to contain 19% of *exo*-bicyclo[3.3.0]oct-3-yl acetate and 81% of *exo*-bicyclo[3.3.0]oct-2-yl acetate. The pure acetates, separated by gas chromatography, yielded



the known *exo*-bicyclo[3.3.0]octan-2-ol and *exo*-bicyclo[3.3.0]octan-3-ol when reduced with lithium aluminum hydride.

Solvolysis of *exo*-bicyclo[5.1.0]oct-3-yl brosylate (XIV) at 60° for 48 hours, followed by lithium aluminum hydride reduction, yielded a mixture containing 10% of *endo*-bicyclo[3.3.0]octan-3-ol (XI), 19% of *endo*-bicyclo[5.1.0]octan-4-ol (XV) and 71% of *endo*-bicyclo[5.1.0]octan-3-ol (XIII).

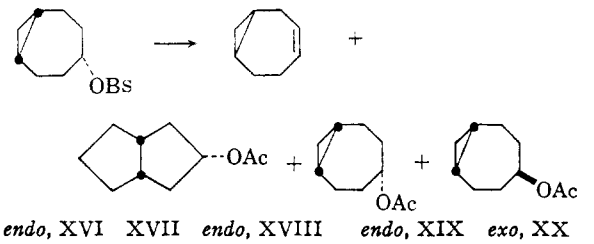


Formation of XI (10%) indicates that the reaction proceeded at least to a small extent by a concerted mechanism. Formation of XIII (71%) as the principal product indicates that the reaction may have proceeded mostly by an SN2 mechanism. Although formation of XIII rather than the corresponding *exo* isomer is also predicted by the concerted mechanism, the amount obtained seems too large compared to that obtained from the solvolysis of IX, in view of the smaller tendency for the cyclopropane ring of XIV to participate in the solvolysis. However, this reasoning has to be made with reservation since the solvolyses of IX and XIV were carried out at two different temperatures. Formation of the thermodynamically less stable *endo*-bicyclo[5.1.0]octan-4-ol (XV) can be explained by a mechanism in which a 1,2-hydride shift is followed by the rearrangement of the cyclopropane ring in a concerted manner.

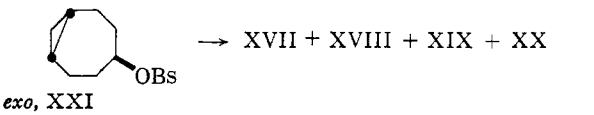
Solvolysis of *endo*- and *exo*-Bicyclo[5.1.0]oct-4-yl Brosylate (XVI, XXI).—The crystalline brosylates of *endo*- and *exo*-bicyclo[5.1.0]octan-4-ol were solvolyzed in acetic acid containing excess sodium acetate at 63° for 24 hours to give the products shown in Table I. When XIX and XX were subjected to the same solvolysis conditions, the starting materials were recovered unchanged, indicating that the initially formed acetates did not rearrange to other products. Authentic samples of XVII and

TABLE I

YIELDS OF PRODUCTS FROM SOLVOLYSIS OF *endo*- AND *exo*-BICYCLO[5.1.0]OCT-4-YL BROSYLATE

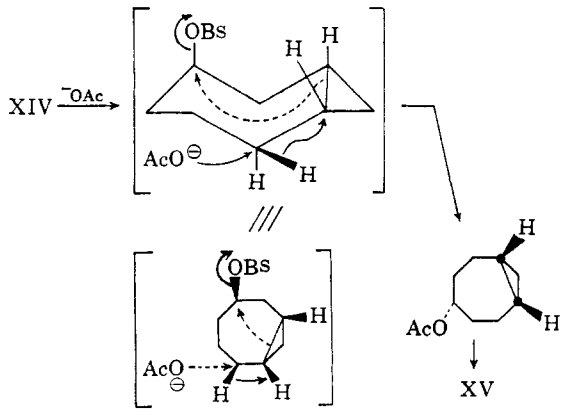


No.	Yield, %	Mole % of total product			
1	83	73	0.5	4	22.5
2	83	65	0.7	5	29



1	77	43	0	45	12
2	76	43	0	43	14

bicyclo[5.1.0]oct-2-ene have been prepared by the pyrolysis of the S-xanthates of bicyclo[5.1.0]octan-4-ols and bicyclo[5.1.0]octan-2-ols according to procedures similar to ones previously described.[6,7]

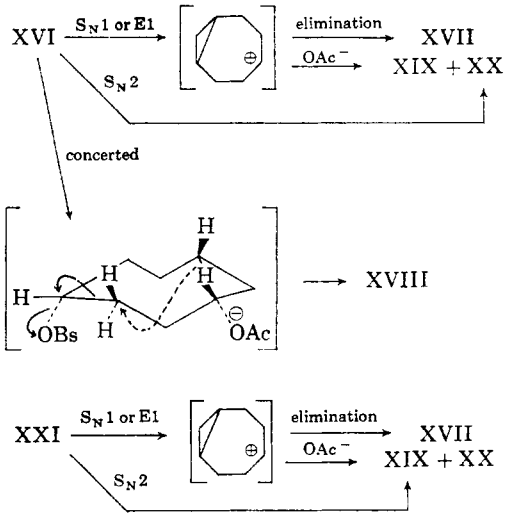


(6) A. T. Blomquist and A. Goldstein, *J. Am. Chem. Soc.*, **77**, 1001 (1955).

(7) G. L. O'Connor and H. R. Nace, *ibid.*, **74**, 5454 (1952).

Each of the bicyclic olefins obtained was free of the other isomer as shown by gas chromatography, and yielded bicyclo[5.1.0]octane on catalytic reduction after taking up one equivalent of hydrogen.

Solvolysis of XVI and XXI can be explained in the following manner.



Formation of bicyclo[5.1.0]oct-4-ene (XVII) in a large proportion suggests that bicyclo[5.1.0]oct-4-yl carbonium ion is formed in the first step, which can then give rise to the olefin by elimination, or yield the acetates XIX and XX by the attack of acetate ion. The presence of a considerable degree of an SN2 mechanism in addition to the SN1 mechanism was demonstrated by the relative amounts of *endo*- and *exo*-bicyclo[5.1.0]oct-4-yl acetate (XIX, XX) formed in the solvolyses, since formation of the *endo*-acetate XIX is expected from the *exo*-brosylate XXI and *vice versa* if the reaction had proceeded solely by an SN2 mechanism. On the other hand, if the reaction had proceeded solely through an SN1 mechanism, the more stable *exo*-acetate XX would have been formed principally from both the *endo*- and *exo*-brosylate, as they would both proceed through a common carbonium ion intermediate. In the solvolysis of the *exo*-brosylate XXI, absence of any product which would have been derived from rearrangement of the cyclopropane ring indicated that there had been little or no participation by the cyclopropane ring during the solvolysis. However, in the solvolysis of the *endo*-brosylate XVI, formation of a small but significant amount of *endo*-bicyclo[3.3.0]oct-3-yl acetate (XVIII) indicated a definite participation by the cyclopropane ring followed by a 1,2-hydride shift in a concerted manner. Such participation by a cyclopropane ring which is remotely situated from the initially formed carbonium ion appears to be the first example of its kind, attributable mainly to the proximity effect in the eight-membered ring.

Experimental[8,9]

Preparation of the Trifluoroacetates I, II and III.—3-Cycloöcten-1-ol (IV, 0.1 g.) dissolved in 1 ml. of ether was cooled in an ice–water bath and added to a solution of 0.33 g. of trifluoroacetic anhydride in 1 ml. of cold ether. After the mixture was allowed to stand overnight at 0–5°, the excess trifluoroacetic anhydride was hydrolyzed by addition of small portions of water while the temperature was maintained below 20°. Finally, 2 ml. of water was added and the ether layer was separated. The aqueous layer was extracted with two 1-ml. portions of ether, and the combined ether layers were washed with two 3-ml. portions of water, 3 ml. of 5% sodium carbonate and two 3-ml. portions of water. After drying (magnesium sulfate), the solvent was removed to give 0.17 g. (98%) of III. The product was shown to be homogeneous by gas chromatography on silicone oil at 180°, and exhibited infrared absorption at 1785 cm.$^{-1}$. An analytical sample, $n^{25}D$ 1.4160, was collected by gas chromatography.

Anal. Calcd. for $C_{10}H_{13}O_2F_3$: C, 54.05; H, 5.90. Found: C, 54.28; H, 6.01.

When pyridine was used in place of ether as solvent, the yield of III was very poor, as the solvent reacted with trifluoroacetic anhydride.

endo-Bicyclo[5.1.0]oct-2-yl trifluoroacetate (I) was obtained from the corresponding alcohol in 86% yield according to the procedure described for the preparation of III, except that the ether solution was washed with just enough 2.5% sodium carbonate to obtain a *p*H of 7. The product was shown to be homogeneous by gas chromatography on silicone oil at 140°, and exhibited infrared absorption at 3060 cm.$^{-1}$ (cyclopropane) and 1775 cm.$^{-1}$ (C=O). A sample collected by gas chromatography was analyzed.

Anal. Calcd. for $C_{10}H_{13}O_2F_3$: C, 54.05; H, 5.90. Found: C, 54.09; H, 6.03.

exo-Bicyclo[5.1.0]oct-2-yl trifluoroacetate (II) was prepared in 86% yield from the corresponding alcohol by the procedure used for the preparation of I. The product was shown to be homogeneous by gas chromatography on silicone oil at 140°, and exhibited infrared absorption at 3060 cm.$^{-1}$ (cyclopropane) and 1775 cm.$^{-1}$ (C=O). Infrared spectra of I and II were quite different in the fingerprint region. A sample collected by gas chromatography was analyzed.

Anal. Calcd. for $C_{10}H_{13}O_2F_3$: C, 54.05; H, 5.90. Found: C, 53.85; H, 5.80.

Preparation of the Brosylates.—The brosylates were prepared from the corresponding alcohols by the procedure used for the preparation of 3-cycloöcten-1-yl brosylate.[8]

endo-Bicyclo[5.1.0]oct-3-yl brosylate (IX), obtained in 68% yield, was more stable than 3-cycloöcten-1-yl brosylate at room temperature, and did not decompose when allowed to stand at room temperature for 1 day. It was analyzed after one recrystallization from a pentane–ether mixture; m.p. 43–45°.

Anal. Calcd. for $C_{14}H_{17}O_3SBr$: C, 48.70; H, 4.96. Found: C, 48.97; H, 4.95.

exo-Bicyclo[5.1.0]oct-3-yl brosylate (XIV) was prepared in 84% yield, and analyzed after one recrystallization from a pentane–ether mixture; m.p. 68–69° dec.

Anal. Calcd. for $C_{14}H_{17}O_3SBr$: C, 48.70; H, 4.96 Found: C, 48.56; H, 5.01.

endo-Bicyclo[5.1.0]oct-4-yl brosylate (XVI) was prepared in 98–99% yield, and did not decompose on standing at room temperature for 7 days. It was analyzed after two recrystallizations from ether; m.p. 102–103° dec.

Anal. Calcd. for $C_{14}H_{17}O_3SBr$: C, 48.70; H, 4.96. Found: C, 48.96; H, 4.82.

exo-Bicyclo[5.1.0]oct-4-yl brosylate (XXI) was prepared in 95–96% yield, and analyzed after two recrystallizations from ether; m.p. 86–87° (without decomposition).

Anal. Calcd. for $C_{14}H_{17}O_3SBr$: C, 48.70; H, 4.96. Found: C, 48.58; H, 4.90.

Solvolysis of 3-Cycloöcten-1-yl Trifluoroacetate (III).—A mixture of 0.1 g. of III, 1 ml. of 0.5 *M* sodium acetate in acetic acid and 0.6 ml. of glacial acetic acid was allowed to stand at room temperature for 24 hours. Then 10 ml. of water and 5 ml. of ether were added to the mixture, and the ethereal layer was washed with water and with 5% sodium carbonate until the washings became basic. The ethereal solution was dried over magnesium sulfate, and the solvent was removed. The residue was shown to contain only unchanged starting material by gas chromatography on silicone oil at 160° and by its infrared spectrum. When the solvolysis was repeated at 102° for 2 hours, 90% of the starting material

(8) Melting points are corrected and boiling points are uncorrected.

(9) Reference 3, footnote 24, describes the conditions and equipment used for gas chromatography.

was still present in the product. When III was solvolyzed at 102° for 24 hours, the product contained 30% of the starting material, 10% of IV and 60% of VII. Finally, when the solvolysis was repeated at 102° for 48 hours, the sole product (99%) was the corresponding acetate VII.

Solvolysis of *endo*-Bicyclo[5.1.0]oct-2-yl Trifluoroacetate (I).—A mixture containing 340 mg. of I, 2.03 ml. of glacial acetic acid and 3.4 ml. of 0.5 *M* sodium acetate in acetic acid was allowed to stand at room temperature for 24 hours. The mixture was diluted with 20 ml. of water and extracted with four 5-ml. portions of ether. The combined ether extracts were washed with two 5-ml. portions of water and neutralized to *p*H 7 with 2.5% sodium carbonate. The ether solution was again washed with two 5-ml. portions of water, dried over magnesium sulfate, and the solvent was removed to give a mixture containing 14% of II, 32% of III, 4% of IV, 20% of V, 12% of VI and 18% of VII, which were identified by gas chromatography on silicone oil and on TCEP at 140° and by comparison of their infrared spectra with those of authentic samples. The composition of products from another run conducted under the same conditions, was 10% of II, 36% of III, 3% of IV, 21% of V, 12% of VI and 18% of VII. A similar result was obtained when the solvolysis was carried out at room temperature for 36 hours; however, when compound I was solvolyzed at 102° for 24 hours, a mixture containing 3% of III, 6% of IV and 91% of VII was obtained.

Solvolysis of *exo*-Bicyclo[5.1.0]oct-2-yl Trifluoroacetate (II).—A mixture containing 0.6 g. of II, 6.0 ml. of 0.5 *M* sodium acetate in acetic acid and 3.6 ml. of glacial acetic acid was allowed to stand at room temperature for 48 hours. The mixture was treated as described for the solvolysis of I to give a mixture containing 42% of II, 20% of III, 2% of IV, 11% of V, 11% of VI, 9% of VII and 5% of VIII, which were identified by gas chromatography on silicone oil and on TCEP at 140° and by comparison of their infrared spectra with those of authentic samples. When the solvolysis was carried out at 102° for 24 hours, the product was shown to be a mixture of 3.5% of III, 5.5% of IV and 91% of VII.

Solvolysis of *endo*-Bicyclo[5.1.0]oct-3-yl Brosylate (IX).—A mixture of 440 mg. of IX, 2.64 ml. of glacial acetic acid and 4.4 ml. of 0.5 *M* sodium acetate in acetic acid was allowed to stand at room temperature for 48 hours. The white crystals of sodium *p*-bromobenzenesulfonate that formed were separated by filtration and the filtrate was diluted with 60 ml. of water and extracted with four 15-ml. portions of ether. The combined ether extracts were washed successively with three 15-ml. portions of water, two 50-ml. portions of 5% sodium carbonate and 10 ml. of saturated sodium chloride solution. After drying (magnesium sulfate), removal of the solvent yielded 290 mg. of a mixture with an infrared spectrum showing the absence of the unchanged brosylate IX. The mixture also contained 17% of a hydrocarbon, which was later shown to be the olefin X by gas chromatography on silicone oil at 120° and by comparison of its infrared spectrum with that of an authentic sample. One-half of the product mixture was reduced with lithium aluminum hydride in ether at room temperature for 0.5 hour to give 100 mg. of a mixture containing 17% of X, 58% of XI, 7% of XII and 18% of XIII, identified by gas chromatography on TCEP and on silicone oil at 120° and by comparison of their infrared spectra with those of authentic samples (with the exception of XII). Compound XII was isolated as the acetate prior to the hydride reduction, since the alcohols XI and XII did not separate on gas chromatography and the acetates of XI and XII were separable by gas chromatography on TCEP at 120°.

Solvolysis of *exo*-Bicyclo[5.1.0]oct-3-yl Brosylate (XIV).—A mixture of 230 mg. of XIV, 1.38 ml. of glacial acetic acid and 2.30 ml. of 0.5 *M* sodium acetate in acetic acid was heated at 60 ± 2° for 48 hours. The cooled reaction mixture was treated as described for the solvolysis of IX to give 60 mg. of an acetate mixture. An infrared spectrum of the mixture showed the absence of starting material XIV. The acetate mixture was reduced with lithium aluminum hydride in ether at room temperature for 0.5 hour to give 35 mg. of a mixture containing 10% of XI, 71% of XIII and 19% of XV, which were identified by gas chromatography on TCEP at 120° and by comparison of their infrared spectra with those of authentic samples.

Preparation of *endo*- and *exo*-Bicyclo[3.3.0]oct-2-ene Oxide.—To a solution of 500 mg. of bicyclo[3.3.0]oct-2-ene in 2.5 ml. of of acetic acid, 1 g. of a 40% peracetic acid solution (after its sulfuric acid content was neutralized with 250 mg. of sodium acetate trihydrate) was added at such a rate that the temperature of the mixture was maintained at 25 ± 2°. The flask was cooled with ice-water if necessary. After addition was complete, the mixture was maintained at 26 ± 1° for an additional 40 minutes, diluted with 30 ml. of water, and extracted with four 15-ml. portions of ether. The combined ether extracts were washed successively with three 10-ml. portions of water, 5 ml. of saturated sodium bisulfite, three 10-ml. portions of water, 10 ml. of 5% sodium carbonate, two 10-ml. portions of water and 10 ml. of saturated sodium chloride solution. After drying (magnesium sulfate), careful evaporation of ether through a semimicro column yielded 450 mg. of a mixture later shown to contain 13% of the *endo* and 87% of the *exo* epoxide by gas chromatography on silicone oil at 120°. An infrared spectrum of the crude mixture showed no hydroxyl or acetate absorption, indicating that no opening of the epoxide ring took place during the reaction. Analytical samples of the *endo*-epoxide, $n^{25}D$ 1.4765, and of the *exo*-epoxide, $n^{25}D$ 1.4753, were isolated by gas chromatography (silicone oil, 120°).

Anal. Calcd. for $C_8H_{12}O$: C, 77.37; H, 9.74. Found for the *endo* isomer: C, 77.19; H, 9.93. Found for the *exo* isomer: C, 77.60; H, 9.94.

In another preparation conducted under the same conditions, 3 g. (68%) of the epoxide mixture was obtained from 3.85 g. of the olefin dissolved in 5 ml. of acetic acid and 8 g. of the 40% peracetic acid solution containing 2 g. of sodium acetate trihydrate.

Preparation of *endo*-Bicyclo[3.3.0]octan-3-ol (XI).—*endo*-Bicyclo[3.3.0]oct-2-ene oxide (46 mg.) isolated by gas chromatography, was reduced with lithium aluminum hydride in ether under reflux for 1 hour to give 36 mg. of product which was shown to contain 74% of *endo*-bicyclo[3.3.0]octan-2-ol[3] and 26% of the desired alcohol XI, estimated by gas chromatography on TCEP at 120°. A sample of XI collected by gas chromatography was analyzed.

Anal. Calcd. for $C_8H_{14}O$: C, 76.14; H, 11.18. Found: C, 76.26; H, 11.31.

The alcohol mixture was converted to acetates by the acetic anhydride–pyridine method,[2] and pure *endo*-bicyclo-[3.3.0]oct-3-yl acetate was collected by gas chromatography on TCEP at 120°.

Anal. Calcd. for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.21; H, 9.70.

Preparation of *exo*-Bicyclo[3.3.0]octan-3-ol.—*exo*-Bicyclo-[3.3.0]oct-2-ene oxide (185 mg.) isolated by gas chromatography was reduced with lithium aluminum hydride as described for the preparation of XI to give 132 mg. of a mixture which showed a single peak on gas chromatography on TCEP and on silicone oil at 120°. The acetates prepared from this mixture by the acetic anhydride–pyridine method consisted of 81% of known *exo*-bicyclo[3.3.0]oct-2-yl acetate and 19% of the acetate of the desired alcohol, as shown by gas chromatography on TCEP at 120°. A sample of *exo*-bicyclo[3.3.0]oct-3-yl acetate collected by gas chromatography (TCEP, 117°) was analyzed.

Anal. Calcd. for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.38; H, 9.41.

exo-Bicyclo[3.3.0]oct-3-yl acetate (35 mg.), isolated by gas chromatography, was reduced with lithium aluminum hydride in ether at room temperature for 0.5 hour to give 20 mg. of *exo*-bicyclo[3.3.0]octan-3-ol. A sample purified by gas chromatography (TCEP, 120°) was analyzed.

Anal. Calcd. for $C_8H_{14}O$: C, 76.14; H, 11.18. Found: C, 75.98; H, 11.24.

Solvolysis of *endo*-Bicyclo[5.1.0]oct-4-yl Brosylate (XVI).—A mixture of 300 mg. of XVI, 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 cooled mixture was treated as described for the solvolysis of IX to give 90 mg. (83%) of a mixture containing 73% of XVII, 0.5% of XVIII, 4% of XIX and 22.5% 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, 200 mg. of XVI with 1.2 ml. of acetic acid and 2.0 ml. of 0.5 *M* sodium acetate in acetic acid yielded 62 mg. (83%) of a mixture containing 65% of XVII, 0.7% of XVIII, 5% of XIX and 29% of XX. When the solvolysis was carried out

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.

(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

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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

(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.