Strained Ring Systems. IV.[1a] The Synthesis and Solvolysis of *exo*-Bicyclo[2.2.0]hex-2-yl Tosylate

Richard N. McDonald and Charles E. Reineke[1b]

Department of Chemistry, Kansas State University, Manhattan, Kansas 66502

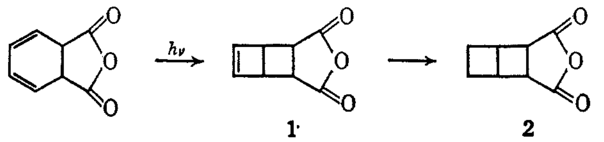
Received August 8, 1966

The synthesis of bicyclo[2.2.0]hex-2-ene and its hydroboration to *exo*-bicyclo[2.2.0]hexan-2-ol (**5a**) is reported. Acetolysis of **5a** tosylate produces 53% ion pair return to *exo*-bicyclo[2.1.1]hex-2-yl tosylate and an acetate mixture composed of 4-cyclohexenyl acetate (51%), *exo*-bicyclo[2.1.1]hex-5-yl acetate (41%), 3-cyclohexenyl acetate (5%), and *exo*-bicyclo[2.2.0]hex-2-yl acetate (3%). Formolysis gave a similar distribution of products. *It is concluded that anchimeric assistance occurs in the solvolyses leading to a nonclassical carbonium ion.* Certain other synthetic routes leading to this interesting strained ring system were also investigated.

Simple derivatives of bicyclo[2.1.1]hexane with substituents at the 1 and 5 positions have been synthesized and some reactions of these systems have been studied.[2,3] More recently, the synthesis and reactions of some 2-substituted bicyclo[2.1.1]hexanes have been reported.[4] Likewise, several 2- and 3-substituted bicyclo[3.1.0]hexyl derivatives have been reported[5,6] as well as acid-catalyzed additions to bicyclo[3.1.0]hex-2-ene.[7]

Although there have been many studies concerned with the synthesis of highly substituted bicyclo[2.2.0]hexanes,[8,9] only recently have methods become available[10–13] which make possible the synthesis of simply substituted bicyclo[2.2.0]hexanes. It is the purpose of this paper to describe the synthesis and reactions of bicyclo[2.2.0]hex-2-ene and some bicyclo[2.2.0]hex-2-yl derivatives.

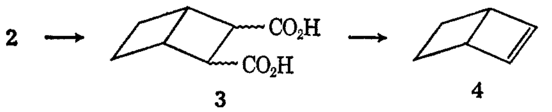
Utilizing the method of van Tamelen and Pappas[10,14] as an entry into bicyclo[2.2.0]hexene (**4**), bicyclo[2.2.0]hexane-2,3-dicarboxylic anhydride (**2**) was prepared by the catalytic reduction of **1**.



1 **2**

Anhydride **2** exhibited nuclear magnetic resonance (nmr) absorption at τ 6.53 as a finely split multiplet and continuous absorption from τ 6.65 to 7.84. The melting point of **2** was found to be 84.5–86° which disagrees with those previously reported values of 98–100°[10] and 158–160°.[14] This latter melting point agrees well with that of bicyclo[2.2.0]hexan-2,3-dicarboxylic acid (**3**), which is produced in 87% yield by basic hydrolysis of **2**.

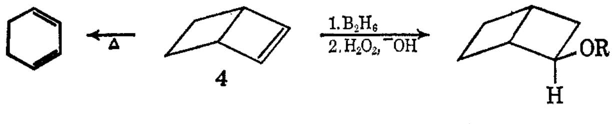
Bicyclo[2.2.0]hex-2-ene (**4**) was produced in 15% yield by the lead tetraacetate decarboxylation of anhydride **2**. Yields as high as 52%, as determined by gas chromatography (gc) analysis, were produced when diacid **3** was decarboxylated in pyridine solution with lead tetraacetate.



3 **4**

Good olefin yields have previously been produced by decarboxylation of anhydrides;[15] however, the original reactions involving such decarboxylations with lead tetraacetate by Grob[16] were performed on the dicarboxylic acids.

Gas chromatography was an effective means of studying the thermal isomerization of **4**. At injection port temperatures above 130° partial isomerization of **4** to 1,3-cyclohexadiene occurred and at 330° total isomerization to cyclohexadiene resulted. Because of the possibility of thermal isomerization, olefin **4** was first distilled at reduced pressure to avoid excessive distillation pot temperatures. However, some distillations were performed using a semimicro spinning-band column at atmospheric pressure without extensive rearrangement. The later fractions in these distillations were usually enriched in 1,3-cyclohexadiene.



4

5a, R = H
b, R = Ts
c, R = $COCH_3$

As expected, thermal isomerization of **4** occurs at temperature intermediate between those for bicyclo[2.2.0]hexane, which thermally rearranges to biallyl at 230°,[17] and bicyclo[2.2.0]hexa-2,5-diene, which rearranges to benzene by heating at 90°.[10] That bicyclo[2.2.0]hexa-2,5-diene exhibits considerable sta-

---

(1) (a) For paper III in this series, see R. N. McDonald and C. E. Reineke, *Tetrahedron Letters*, 2739 (1966). (b) This work comprises a portion of the dissertation submitted by C. E. Reineke to the Graduate School of Kansas State University in April 1966, in partial fulfillment of the requirements for the Ph.D. degree. A portion of this research was communicated in *J. Am. Chem. Soc.*, **87**, 3020 (1965).

(2) K. B. Wiberg, B. R. Lowry, and T. H. Colby, *ibid.*, **83**, 3998 (1961); K. B. Wiberg and B. R. Lowry, *ibid.*, **85**, 3188 (1963), and references therein.

(3) K. B. Wiberg and R. Fenoglio, *Tetrahedron Letters*, 1273 (1963).

(4) J. Meinwald and J. K. Crandall, *J. Am. Chem. Soc.*, **88**, 1292 (1966).

(5) E. J. Corey and R. L. Dawson, *ibid.*, **85**, 1782 (1963), and references therein.

(6) S. Winstein and J. Sonnenberg, *ibid.*, **83**, 3235, 3244 (1961).

(7) P. K. Freeman, M. F. Grostic, and F. A. Raymond, *J. Org. Chem.*, **30**, 771 (1965).

(8) For a brief review of the chemistry of bicyclo[2.2.0]hexane, see the Ph.D. Thesis of C. E. Reineke.[1b]

(9) D. Seebach, *Angew. Chem. Intern. Ed. Engl.*, **4**, 121 (1965).

(10) E. E. van Tamelen and S. P. Pappas, *J. Am. Chem. Soc.*, **85**, 3297 (1963).

(11) R. Pettit and co-workers, *ibid. Soc.*, **87**, 131, 3253 (1965); *Chem. Commun.*, 517 (1965); *J. Am. Chem. Soc.*, **88**, 623, 1328 (1966).

(12) K. V. Scherer, *Tetrahedron Letters*, 5685 (1966).

(13) R. Srinivasan and F. I. Sonntag, *Tetrahedron Letters*, 603 (1966).

(14) S. P. Pappas, Ph.D. Thesis, University of Wisconsin, 1963.

(15) E. Grovestein, D. V. Rao, and J. W. Taylor, *J. Am. Chem. Soc.*, **83**, 1075 (1961).

(16) C. A. Grob, *Angew. Chem.*, **70**, 343 (1958); *Helv. Chim. Acta*, **41**, 1191 (1958).

(17) C. Steel, R. Zand, P. Hurwitz, and S. G. Cohen, *J. Am. Chem. Soc.*, **86**, 679 (1964).

bility has been explained by van Tamelen[18] as being due to a disfavored mode of stereoisomerization to benzene. He suggests that the preferred conrotatory[19] course of thermal isomerization of bicyclo[2.2.0]hexa-2,5-diene cannot operate since a highly strained *cis,cis,trans*-cyclohexa-1,3,5-triene would result. To undergo the less preferred disrotatory course of ring opening, rehybridization must take place which results in an increased transition state energy for the transformation, and, therefore, an increased stability for bicyclo[2.2.0]-hexa-2,5-diene. The same argument can apply to bicyclo[2.2.0]hex-2-ene, since a highly strained *cis,-trans*-1,3-cyclohexadiene would result by the preferred conrotatory mode of cyclobutene ring opening. The 1,3-cyclohexadiene product does not possess the resonance stabilization as does benzene, causing the rehybridization for the disrotatory process in **4** to be energetically less favorable than in the case of bicyclo[2.2.0]hexa-2,5-diene.

The nmr spectrum of bicyclo[2.2.0]hex-2-ene **4** in carbon tetrachloride was also in agreement with the assigned structure exhibiting olefinic proton resonance at τ 3.85 as a finely split doublet, methine proton resonance centered at τ 6.83, and methylene proton resonance as absorption from τ 7.6–8.7 appearing in the expected ratio of 1:1:2. The mass spectrum exhibited a parent peak at m/e 80 with the most intense peak at m/e 79 and a cracking pattern almost identical with that of 1,3-cyclohexadiene.

Hydroboration[20] of **4** with a diborane solution in tetrahydrofuran, followed by oxidation at 35–45°, gave *exo*-bicyclo[2.2.0]hexan-2-ol (**5a**) in 77% yield. Vapor phase chromatography of the product mixture indicated only one product alcohol. The mass spectrum exhibited a parent peak at m/e 98. The *exo* configuration as assigned by analogy to the hydroboration of norbornene which gives *exo*-norborneol. The neat nmr spectrum of **5a** exhibited a singlet at τ 4.59 which was assigned to the hydroxyl hydrogen since it was solvent dependent.[21] Other absorptions were observed as continuous absorptions from τ 7.0–8.4 (bridgehead methine and methylene protons) and a triplet at τ 5.63, assigned to the C-2 methine hydrogen. The triplet absorption at τ 5.63 was further evidence for the *exo* configuration of **5a**,[22a] since a similar absorption is observed[22b] for *exo*-norbornyl compounds. *endo*-Norborneol derivatives exhibits a greater multiplicity for the absorption of the C-2 methine proton.[22b]

The conversion of **5a** to the *p*-toluenesulfonate ester **5b** was accomplished by reaction with *p*-toluenesulfonyl chloride in ether solution in the presence of potassium hydroxide.[2] Tosylate **5b** was purified for acetolysis by repeated molecular distillations and checked for purity by recording the nmr spectrum which was in accord with that expected, being similar to **5a**. The infrared spectrum was also in agreement with that expected.

Before the acetolysis rate constant of **5b** was determined, the procedure and reagents were tested by the determination of the known acetolysis rate constant of *exo*-norbornyl tosylate. The value observed by the sealed ampoule technique[23] was $4.66 \pm 0.28 \times 10^{-4}$ sec^{-1} at 49.84°. The most recently reported[24] value for this rate constant was $4.67 \pm 0.09 \times 10^{-4}$ sec^{-1} at 49.84°. The acetolysis rate constant of *exo*-norbornyl tosylate at 25° was found to be $2.28 \pm 0.04 \times 10^{-5}$ sec^{-1} as an average of three independent runs. These values are in excellent agreement with the reported value of 2.33×10^{-5} sec^{-1} at this temperature.[24]

The acetolysis rate constant (Table I) of the *exo*-bicyclo[2.2.0]hex-2-yl *p*-toluenesulfonate (**5b**) was determined by the sealed-ampoule technique. These rate constants were the average from three independent runs at each temperature. Extrapolation to 25° gives $k_{\mathrm{HOAc}} = 9 \times 10^{-8}$ sec^{-1}. A plot of log $(C_i - C_t)$ *vs.* time showed a downward curvature which leveled off at about 50% reaction. When plots of log $(C_\infty - C_t)$ *vs.* time were made, straight lines were obtained. The average infinity titer for the six acetolysis runs was 46.7 ± 2.7% of the theoretical amount based on starting **5b**. This observation was rationalized by ionization of **5b** with ion pair return to a much more slowly solvolyzing tosylate. This was confirmed by isolation of *exo*-bicyclo[2.1.1]hex-5-yl tosylate (**6**) from the acetolysis mixture in 50% yield. Acetolysis of **6** was not detected after 10 half-lives of **5b** at the temperatures of the present work. The acetolysis data of **5b** are summarized in Table I.

TABLE I

SOLVOLYSIS RATE CONSTANTS FOR *exo*-BICYCLO[2.2.0]HEX-2-YL TOSYLATE (**5b**)

	Temperature, °C	k, sec^{-1}
Acetolysis[a]	75.00	$4.20 \pm 0.19 \times 10^{-5}$
	90.00	$1.93 \pm 0.10 \times 10^{-4}$
Formolysis[b]	25.00	$1.14 \pm 0.02 \times 10^{-4}$
	35.00	$3.78 \pm 0.15 \times 10^{-4}$

[a] ΔH = 24.7 kcal/mole; ΔS = −8.2 eu (75°). [b] ΔH = 21.3 kcal/mole; ΔS = −5.1 eu (25°).

The acetolysis products of **5b** were composed of 51% of 4-cyclohexenyl acetate (**7a**), 41% of *exo*-bicyclo-[2.1.1]hex-5-yl acetate (**8a**), 5% of 3-cyclohexenyl acetate (**9a**), and 3% of *exo*-bicyclo[2.2.0]hex-2-yl acetate (**5c**). These products were separated from the tosylate product **6** and identified by comparison of their gc retention times with those of authentic samples. The major products, **7a** and **8a**, were confirmed by collection by gc and characterization by their infrared and nmr spectra.

The amounts of these acetates were estimated in a sample of the crude acetate mixture to be present in a ratio of 11:7 by integration of the nmr peak areas of

---

[18] E. E. van Tamelen, *Angew. Chem. Intern. Ed. Engl.*, **4**, 738 (1965).

[19] R. B. Woodward and R. Hoffman, *J. Am. Chem. Soc.*, **87**, 395 (1965).

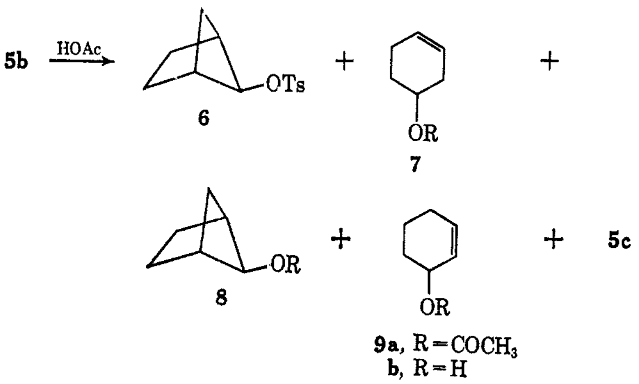
[20] G. Zweifel and H. C. Brown, *Org. Reactions*, **13**, 1 (1963).

[21] L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy to Organic Chemistry," The Macmillan and Co., New York, N. Y., 1959.

[22] (a) The C-2 proton of *endo*-bicyclo[2.2.0]hexan-2-ol appears as a multiplet from τ 5.4–5.9; see accompanying paper, R. N. McDonald and C. E. Reineke, *J. Org. Chem.*, **32**, 1888 (1967). (b) The *endo*-2 proton of *exo*-norborneol (18% carbon tetrachloride solution, tetramethylsilane internal standard) shows up as a broad doublet centered at τ 6.37 with each peak having further poorly resolved splitting. In the corresponding tosylate this C-2 proton appears as a triplet centered at τ 5.61. Also, see E. W. C. Wong and C. C. Lee, *Can. J. Chem.*, **42**, 1245 (1964), for the spectra of the brosylate, and S. J. Cristol, *et al.*, *Tetrahedron Letters*, 185 (1963), who report that the C-2 proton of *endo*-5,6-trimethylene-*exo*-norborneol appears as a doublet with evidence of further splitting.

[23] S. Winstein, E. Grunwald, and L. L. Ingraham, *J. Am. Chem. Soc.*, **70**, 821 (1948).

[24] P. von R. Schleyer, M. N. Donaldson, and W. E. Watts, *ibid.*, **87**, 375 (1965).



the C-5 methine hydrogen of **8a** and the C-4 methine hydrogen of **7a**. This ratio was considered only approximate, because the C-2 methine hydrogen of **5c** and the C-3 methine hydrogen of **9a** also absorb at the same τ value as that of **7a**. The most reliable yield data was obtained by gc analysis. The minor products, **9a** and **5c**, were identified only by gc retention times. The total isolated yield of acetate products was 24% based on **5b** and a 50% yield of **6** was obtained; a total of 74% of **5b** used in the acetolyses was, therefore, accounted for in products. No attempt was made to detect any possible elimination products of the acetolysis.

A sample of acetate **8a** was prepared by detosylation[25] of **6** by reaction with lithium in liquid ammonia followed by acetylation. Acetate **5c** was found to be stable to the acetolysis conditions at 90°.

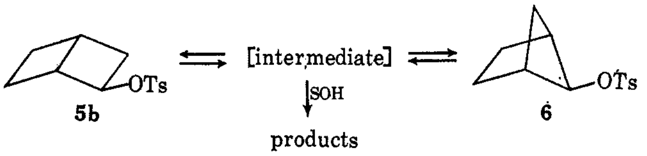
The formolysis rate constant (Table I) of **5b** was determined titrimetrically by the usual technique[26] using ether as diluent. The infinity titer corresponded to 51% of the theoretical again indicating 49% ion pair return to **6**. Tosylate **6** was isolated from the formolysis mixture in 36% yield. The formolysis technique was tested by measuring the rate of formolysis of cyclohexyl tosylate at 25°. The rate constant obtained, $3.98 \pm 0.21 \times 10^{-5}$ sec^{-1}, was in excellent agreement with the reported[27] value of 3.98×10^{-5} sec^{-1} at 25°.

The formate products were separated from tosylate **6** by distillation and the relative amounts of the distilled formate products, determined by integration of the gc peak areas, were found to be 53.5% of 4-cyclohexenyl formate, 42.3% of *exo*-bicyclo[2.1.1]hex-5-yl formate, and about 4% of *exo*-bicyclo[2.2.0]hex-2-yl formate. 3-Cyclohexenyl formate was not detected. The total yield of isolated formate products was 29%.

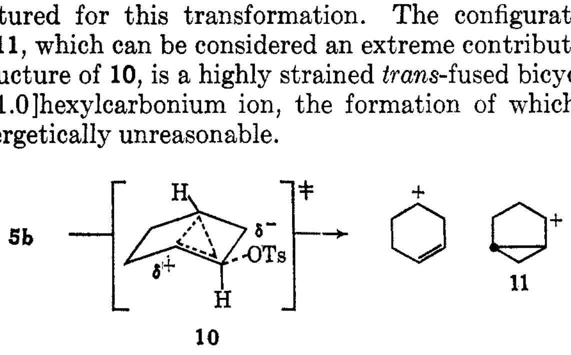
The formolysis products of **5b** were reduced to the corresponding alcohols with lithium aluminum hydride. The alcohol mixture produced was shown to consist of 40.6% of *exo*-bicyclo[2.1.1]hexan-5-ol (**8b**), 56.0% of 3-cyclohexenol (**7b**), and 3.4% of *exo*-bicyclo[2.2.0]hexan-2-ol (**5a**). The major alcohols, **7b** and **8b**, were collected by gc and identified by comparison of their infrared spectra with those of authentic samples. *exo*-Bicyclo[2.2.0]hexan-2-ol (**5a**) was indicated by its retention time, but under the gc conditions the isomeric alcohol *trans*-bicyclo[3.1.0]hexan-2-ol exhibited the same retention time.

It thus became necessary to convert the alcohol mixture to the acetates which could be separated by gc. The acetate mixture produced corresponded to the same mixture as previously observed in the acetolysis of **5b**. Neither the *cis*- nor the *trans*-bicyclo[3.1.0]hex-2-yl acetate corresponded in retention time to any of the acetate products. 3-Cyclohexenyl acetate (**9c**) was observed in trace amount indicating that 3-cyclohexenyl formate was a formolysis product. That this formate or the parent alcohol **9b** was not observed in the respective gc analyses was probably due to the low yield and incomplete resolution on the gc columns. It does not seem probable that **9a** would have arisen during the hydride reduction of the formates or conversion of the alcohol mixture to the acetates. The fact that the alcohol mixture from the formates gave essentially the same acetate mixture as that obtained from the acetolysis helps confirm the identity of *exo*-bicyclo[2.2.0]-hex-2-yl acetate and formate as products of these solvolyses.

The solvolysis products of **5b** can be explained on the basis of a norbornyl-type carbonium ion rearrangement by analogy with the intensively studied norbornyl system.[28,29] It was expected that an equilibrium between **5b** and **6**, involving some common carbonium ion intermediate, would be observed. That this is not the case cannot be assumed from the information available. In order to induce a reasonable rate of acetolysis of **6**, a temperature of 164.2° was necessary.[3] It is probable that at such a temperature any common intermediate would rearrange to a more stable system and not be detected in the products. This appears to be the case, since the only observed product from **6** was 4-cyclohexenyl acetate (**7a**).



Since 4-cyclohexenyl acetate (**7a**) was observed as a major acetolysis product of **5b** one might consider that this product could arise directly from **5b** (path a, Scheme I). This could be visualized by the cleavage of the 1,4-bridge σ bond of **5b**, simultaneously with ionization of the tosylate anion. This pathway appears unlikely on the basis of a stereochemical argument.[30] A highly strained transition state such as **10** can be pictured for this transformation. The configuration of **11**, which can be considered an extreme contributing structure of **10**, is a highly strained *trans*-fused bicyclo[3.1.0]hexylcarbonium ion, the formation of which is energetically unreasonable.



---

[25] J. Meinwald and P. G. Gassman, *J. Am. Chem. Soc.*, **85**, 57 (1963).

[26] S. Winstein and R. Heck, *ibid.*, **78**, 4801 (1957).

[27] S. Winstein, B. K. Morse, E. Grunwald, H. W. Jones, J. Corse, D. Trifan, and H. Marshall, *ibid.*, **74**, 1127 (1952).

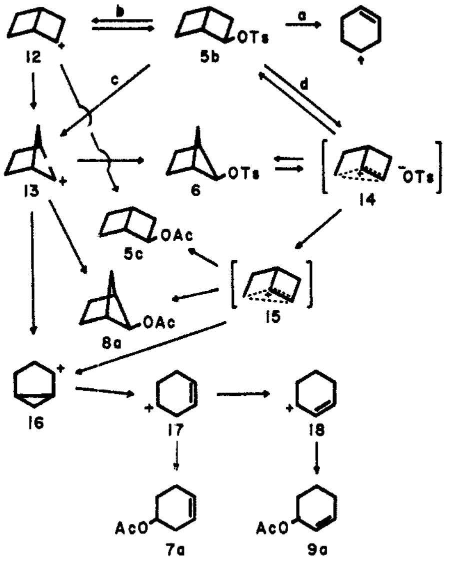
[28] J. A. Berson, "Molecular Rearrangements," Vol. 1, P. deMayo, Ed., Interscience Publishers, Inc., New York N. Y., 1963, p 111.

[29] A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962.

[30] K. B. Wiberg and A. J. Ashe, *Tetrahedron Letters*, 1553 (1965).

SCHEME I

POSSIBLE MECHANISTIC ROUTES FOR THE SOLVOLYSIS OF *exo*-BICYCLO[2.2.0]HEX-2-YL TOSYLATE



There are three possible ways for the ionization of **5b** under the solvolytic conditions which should be considered. These are illustrated by paths b–d in Scheme I. The observed products can be explained by paths b and c as shown; however, there is considerable evidence to suggest that a pathway similar to d may be the favored one. We will first discuss paths b and c.

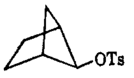
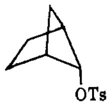
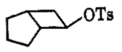
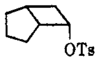
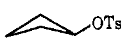
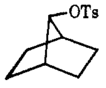
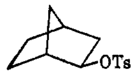
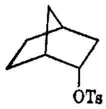
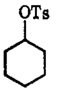
The acetolysis rate constant of **5b** is compared with those of cyclic and bicyclic tosylates in Table II. The rate of acetolysis of **5b** is 10^2 times as fast as that of **6**. Cyclobutyl tosylate solvolyzes about nine times faster than **5b**, and it and other cyclobutyl derivatives[28,29] have been found to solvolyze considerably faster than expected by consideration of bond-angle deformations. The rate of acetolysis of cyclobutyl tosylate is somewhat faster than cyclohexyl tosylate even though the introduction of an sp^2 hybridized carbon atom accompanying ionization in the cyclobutyl system would be expected to increase the strain in the system.[31] This enhancement is solvolysis rate has been rationalized[28,32] as due to the formation of a stabilized bicyclobutonium ion rather than the classical cyclobutyl cation.

The low reactivity of *exo*-bicyclo[2.1.1]hex-5-yl tosylate (6), compared to that of cyclobutyl tosylate, has been attributed[3] to bond-angle deformation of the C-5 carbon atom. A similar increase in angle strain in passing from the tetrahedral carbon at C-7 in 7-norbornyl tosylate to a trigonal carbon has been suggested as the most important contributing factor to the very slow rate of acetolysis of this compound.[31] The internal $C_1C_7C_4$ bond angle in 7-norbornyl tosylate has been estimated[31] to be 98.3°. The internal bond angle of cyclobutyl tosylate approaches 90°.

Cyclobutane and its simple derivatives, according to most evidence[33,34] exist in a bent or folded conformation.

TABLE II

ACETOLYSIS RATE CONSTANTS OF SOME CYCLIC AND BICYCLIC *p*-TOLUENESULFONATE ESTERS

Compound	Temp., °C	k, sec^{-1}	ΔH, kcal/ mole	ΔS, eu	Ref Registry no.
	25.00	9×10^{-8}			Present
	75.00	4.20×10^{-5}	24.7	−8.2	study
	90.00	1.93×10^{-4}			
	25	9×10^{-10}			*a*
	164.2	5.82×10^{-4}			
	25	2.79×10^{-3}			*a*
					10437-83-9
	49.01	2.33×10^{-6}	26.3	−3	*b*
	79.75	9.0×10^{-5}			10464-98-9
	15.58	1.44×10^{-5}			
	30.02	1.04×10^{-4}	23.3	0	*b*
					10437-84-0
	70	2.67×10^{-4}			*c*
	80	7.38×10^{-4}			10437-85-1
	90	1.65×10^{-3}			
	25	6.4×10^{-15}	35.7	−3.5	*d*
					10265-27-7
	25.24	2.33×10^{-5}	21.6	−7.2	*e*
	74.84	5.19×10^{-3}			959-42-2
	25.0	8.28×10^{-8}	25.8	−4.4	*e*
	74.84	5.09×10^{-5}			840-90-4
	50	1.82×10^{-6}			*c*
	70	2.37×10^{-5}			953-91-3
	90	2.22×10^{-4}	27.3	−0.5	

[a] Reference 3. [b] F. F. Nelson, Ph.D. Thesis, University of Wisconsin, 1960. [c] H. C. Brown and G. Ham, *J. Am. Chem. Soc.*, **78,** 2735 (1956). [d] S. Winstein, M. Shatavsky, C. Norton, and R. B. Woodward, *ibid.*, **77,** 4183 (1955). [e] Reference 24.

Models illustrate the suggestion[35] that the cyclobutane ring is forced into near planarity when fused to another cyclobutane ring as in **5b**. Thus, it appears that the cyclobutane ring in **5b** would be more highly strained than cyclobutyl tosylate itself and is probably more strained than the cyclobutane ring in **6** due to increased nonbonded interactions, since in the latter compound the four-membered ring retains the bent conformation. Ionization of **5b** according to path b, to the bicyclohexylcarbonium ion **12**, which would lead to a still more highly strained ring by introduction of an sp^2 carbon atom, would be expected to be less favorable than the ionization of cyclobutyl tosylate. Also, since the bond-angle deformation in **5b** compares more closely with that in 7-norbornyl tosylate and **6**, the rate of acetolysis would be expected to be at least as slow as their rate. Because compound **5b** undergoes acetolysis only nine times slower than cyclobutyl tosylate at 90°, direct ionization to **12** (path b, Scheme I) does not appear to be the case.

Another possibility would be ionization of **5b** with assistance by the C-1,6 σ bond leading directly to the bicyclo[2.1.1]hex-5-ylcarbonium ion (**13**) (path c,

---

[31] P. von R. Schleyer and R. D. Nicholas, *J. Am. Chem. Soc.*, **83**, 182 (1961).

[32] R. H. Mazur, N. N. White, D. A. Semenow, C. C. Lee, M. S. Silver, and J. D. Roberts, *ibid.*, **81**, 4390 (1959).

[33] J. B. Lambert and J. D. Roberts, *ibid.*, **87**, 3884 (1965).

[34] I. L. Karle, J. Karle, and K. Britts, *ibid.*, **88**, 2918 (1966).

[35] K. B. Wiberg and A. J. Ashe, *Tetrahedron Letters*, 4265 (1965).

Scheme I). However, on the basis of the stereochemistry of the products observed in the solvolysis of **5b** it seems reasonable to conclude that the classical carbonium ion **13** is not an intermediate in the solvolysis. It would be expected that **13** would lead preferentially to *endo*-bicyclo[2.1.1]hex-5-yl acetate which was not observed. That both *exo* and *endo* acetates should be observed from the classical ion **13** is argued by analogy to the work of Gassman and Marshall[36] on the acetolysis of 2-*exo*- and 2-*endo*-hydroxybicyclo[2.2.1]heptan-7-one tosylate. The observance of both the *exo* and *endo* acetates from the solvolysis of both of these compounds was explained by a classical norbornyl cation. Preferential formation of the *endo* isomer from ion **13** would be in agreement with the observation of hydride attack at the *endo* position of bicyclo[2.1.1]hexan-5-one on reduction with lithium aluminum hydride.[2]

The fact that **5c**, with retained configuration, and *exo*-bicyclo[2.1.1]hex-5-yl acetate (**8a**) are observed among the acetolysis products might be argued on the basis of a rapid equilibration of carbonium ions **12** and **13**. Such a rapid equilibration has been suggested to prevent solvation from the *endo* position of the norbornylcarbonium ion, causing formation of only *exo* products upon reaction with solvent.[37]

In the present case, however, carbonium ions **12** and **13** should be of different energies. An approximation of this energy difference can be realized by considering the thermal isomerization data for the parent hydrocarbons, bicyclo[2.1.1]hexane[38] and bicyclo[2.2.0]hexane,[17] to hexa-1,5-diene. The activation energy for this isomerization is 19 kcal lower for the [2.2.0] system. Allowing for some differences in the two transition states due to differences in ground-state geometries, possibly as much as 3–5 kcal, this indicates a pronounced greater stability of the bicyclo[2.1.1]hexane system. Since similar factors will be operative in cations **12** and **13**, this would indicate that an equilibrium between them would be essentially nonexistent, and that only **13** would be present. As mentioned above, this should produce *endo*-bicyclo[2.1.1]hex-5-yl acetate, a product which is not observed.

By analogy to the proposals for the solvolysis of cyclobutyl and *exo*-norbornyl tosylates, ionization of **5b** with anchimeric assistance forms a more stable ion than either **12** (path b, Scheme I) or **13** (path c, Scheme I). This leads to the conclusion that the delocalized ion pair **14** (path d, Scheme I) is the initially formed solvolytic intermediate. Ion pair **14** could undergo internal return of tosylate at C-1 to give rise to **6** or at C-2 to give back **5b**. Further separation of **14** by solvent would give **15** which by reaction with solvent from above the upper face of the molecule at C-2 would produce **5c** and at C-1 would give **8a**. Ion **15** could also further rearrange to the 4-cyclohexenyl cation (**17**), probably *via* **16**, which upon reaction with solvent would give the major product **7a**. The 4-cyclohexenylcarbonium ion **17** could rearrange further to the 3-cyclohexenylcarbonium ion (**18**) by a 1,2- or 1,3-hydride shift. Acetate **9a** has been observed as a major product of the acetolysis of 4-cyclohexenyl tosylate.[39a]

The fact that the formation of **8a** is preferred over **5c** can be rationalized by considering that the product-forming transition states leading from the nonclassical ion **15** to these acetates are of different energies with the one leading to **8a** being of lower energy. This is reasonable if these transition states are beginning to assume the strain present in the products **8a** and **5c**.[39b]

endo-Bicyclo[2.1.1]hex-5-yl tosylate has been observed to undergo acetolysis 3 × 10^6 times as fast as the *exo* isomer **6**.[3] An 80% pair return to 4-cyclohexenyl tosylate was observed with the major acetate products being **7a** (8%) and bicyclo[3.1.0]hex-2-yl acetate (8%). The greatly enhanced rate of acetolysis of this tosylate was attributed to the possibility of bicyclobutonium ion formation.[3] A similar ion could be involved in the transformation of ion **15** to ion **17**, although no bicyclo[3.1.0]hexyl acetates were observed. Rearrangement of the bicyclo[2.1.1]hexane structure to the bicyclo[3.1.0]hexane structure has been observed elsewhere.[40]

On the basis of the products of acetolysis and formolysis of **5b**, it appears that tosylates **6** and **5b** may solvolyze by way of a common intermediate. If this is the case, however, it seems from the relative rates of acetolysis that there is considerably more assistance to ionization of the *exo*-bicyclo[2.2.0]hexyl tosylate (**5b**) than the *exo*-bicyclo[2.1.1]hexyl tosylate (**6**). By consideration of nonbonded interactions[41,42] between the tosylate goup and the *exo* C-6 hydrogen of **6**, ionization of the tosylate group should be sterically enhanced over that of **5b**. It has been suggested that the steric effect of such nonbonded interactions in *endo*-norbornyl tosylate may contribute a factor of 5 in the *exo*:*endo* rate ratio.[42] Further, Dreiding molecular models indicate that these interactions are greater in **6** than in *endo*-norbornyl tosylate. In spite of these considerations, **5b** is seen to solvolyze faster than **6** by a factor of 100 at 25°.

The greater stability exhibited by bicyclo[2.1.1]hexane may mean that the difference in the rate of solvolysis of *exo*-bicyclo[2.1.1]hex-5-yl tosylate and *exo*-bicyclo[2.2.0]hex-2-yl tosylate is due mainly to the difference in their ground-state energies, assuming the same intermediates for the solvolysis of the two compounds.

A rationalization of the energy difference between **5b** and **6** can be given in terms of the effective alignment for overlap of the developing p orbital as tosylate ionizes at C-2 of **5b** or C-5 of **6** with the σ-bond orbital between C-1 and C-6 of **5b** or C-1 and C-2 of **6**. Again, for lack of the necessary molecular structure data, Dreiding molecular models of the two systems indicate that such overlap may be possible at an earlier point in the ionization of **5b** because of the close proximity of the C-1,6 σ orbital to the reaction center. It should be stated that these are only qualitative considerations not based on calculations and that detailed molecular

---

[36] P. G. Gassman and J. L. Marshall, *J. Am. Chem. Soc.*, **88**, 2822 (1966).

[37] H. C. Brown, Special Publication No. 16, The Chemical Society, London, 1962, pp 140–157 and 176–178, as cited by S. Winstein, *J. Am. Chem. Soc.*, **87**, 381 (1965).

[38] R. Srinivasan and A. A. Levi, *ibid.*, **85**, 3363 (1963).

[39] (a) M. Hanack and W. Keberle, *Ber.*, **96**, 2937 (1963). (b) A referee has pointed out that since the product studies were not carried out in buffered medium conclusions about the kinetically controlled formation of products and their distribution may be in error.

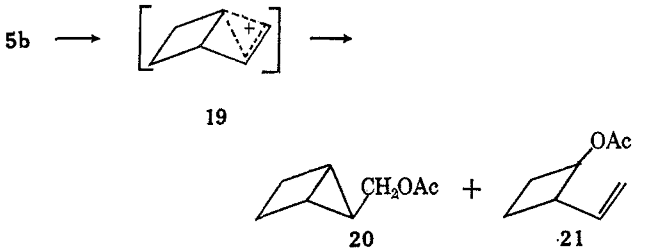
[40] J. Meinwald and R. A. Schnedier, *J. Am. Chem. Soc.*, **87**, 5218 (1965).

[41] P. von R. Schleyer, *ibid.*, **86**, 1854 (1964), and references therein.

[42] P. von R. Schleyer, Symposium on Linear Free Energy Correlation, Durham, N. C., Oct 19, 1964, reprints of papers, p 225, as cited in ref 39a.

structure data for both systems will be necessary for a determination of the validity of this argument.

Further evidence for a relatively stable carbonium ion species in the solvolysis of **5b** is the fact that the same product mixture, in nearly the same distribution, was obtained in both the acetolysis and formolysis. Because of the greater ionizing ability of formic acid, less stable carbonium ions should possess a long enough life-time before being trapped by solvent to undergo rearrangements to more stable systems. The greater nucleophilicity of acetic acid would cause interception by solvent molecules of such carbonium ions at an earlier stage of development.[29]



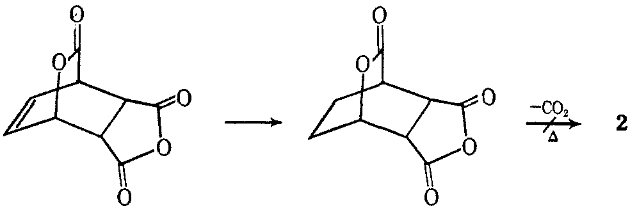
19 **20** **21**

Another possible rearrangement pathway available to **5b** should be mentioned, even though the products of the solvolyses show that this reaction path is not chosen. If rearrangement were to occur by assistance to ionization of the C-3,4 σ bond, the bicyclobutonium ion **19** could form. The possible products from this ion or by rearrangement in this manner would be *exo*-bicyclo[2.1.0]pentane-5-methyl acetate (**20**) and 2-vinylcyclobutyl acetate (**21**). Additional products from the 2-vinylcyclobutylcarbonium ion precursor of **21** are also conceivable. This pathway is in analogy with the proposed mechanism[43] for the acetolysis of *exo*-bicyclo[3.2.0]hept-6-yl tosylate (**22**), which would be considered to be a much less strained molecule, but nevertheless contains a fused cyclobutane ring which would be expected to be more strained than cyclobutyl itself. The products were explained by formation from a bicyclobutonium ion. The acetolysis rate of **22** is seen in Table II to be about twice that of **5b** at 75° again indicating that if anchimeric assistance is invoked in one system it should also apply to the other.

The acetolysis of *exo*-bicyclo[2.1.0]pentane-5-methyl tosylate (**23**) gave the corresponding acetate as the major product with a rate constant of 1.35×10^{-4} sec^{-1} at 17°. This rate was considered accelerated[35] and explained on the basis of a relatively stable cyclopropylcarbinyl cation. That **23** did not react by way of the bicyclobutonium ion **19** was attributed to an unfavorable geometry.

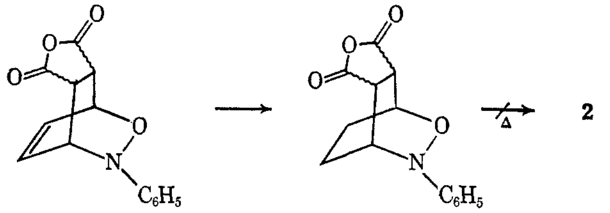
The rationalization of why intermediate **19** is not formed is that the four-membered rings in the bicyclo[2.2.0]hexane system are forced into near planarity, preventing the orbital arrangements necessary for formation of the bicyclobutonium ion.[35] Since the bicyclobutonium ion is believed to have a bent geometry similar to that of bicyclo[1.1.0]butane,[35] apparently, the bicyclobutonium ion **19** would be so strained by adapting to a more planar geometry that its formation would not be energetically justified.

Some alternative methods for the synthesis of **2** were also investigated. The Diels-Alder adduct **24** of α-pyrone and maleic anhydride was prepared and hydrogenated to the saturated adduct **25** as previously reported.[44] It was expected that carbon dioxide could be eliminated from **25** by pyrolysis to produce anhydride **2** by analogy to the previously reported[45] elimination of nitrosobenzene from a similar adduct. Pyrolysis attempts, however, were unsuccessful giving only sublimed **25** and charring at high temperatures.



24 **25**

The Diels-Alder adduct **26** of nitrosobenzene and 1,2-dihydrophthalic anhydride was conveniently prepared in quantitative yield. A broad melting range was observed for adduct **26** which suggested that the two possible isomers may have been produced. Adduct **26** was catalytically reduced to give **27** in 77% yield.



26 **27**

The nmr spectrum of **26** showed no absorption at higher field than τ ~7 as would be expected. Methylene absorption at about τ 7.9–8.7 for the reduced adduct **27** was observed. A liquid, obtained as the minor product from the reduction of **26**, appeared to be a product of cleavage of the heterocyclic ring as evidenced by a strong hydroxyl absorption in the infrared spectrum. The structure of this product was not studied, but such cleavage reactions of nitrosobenzene adducts are known.[46] The solid reduced adduct **27** was found to exhibit considerable thermal stability when pyrolyzed in a sublimination apparatus at reduced pressure. The only identifiable material from the pyrolysis was unchanged **27**, which was sublimed. The unsublimed material remained as a charred residue. None of the desired adduct **2** could be detected by the infrared spectrum of the sublimate.

An attempt to hydroborate the Diels-Alder adduct **26** gave a mixture of products among which starting material was detected by a small-scale column chromatograph on a sample of the mixture. Alcohol products were also indicated and, since at least four isomers were possible, the mixture was converted directly to the acetate derivative without attempts to purify the product. This reaction gave a detectable amount of 4-cyclohexenyl acetate as the only distillable product.

---

[43] See Table II footnote *a*.

[44] B. R. Landau, Ph.D. Thesis, Harvard University, 1950.

[45] C. E. Griffin, N. F. Hepfinger, and B. L. Shapiro, *J. Am. Chem. Soc.*, **85**, 2683 (1963).

[46] G. Kresge and G. Shultz, *Tetrahedron*, **12**, 7 (1961).

Experimental Section

All melting points were taken on a Kofler hot stage and are corrected. Boiling points are uncorrected. Infrared spectra were determined on a Perkin-Elmer 137 double-beam recording spectrophotometer. Nmr spectra were determined on a Varian A-60 recording spectrometer. Microanalyses were by Galbraith Laboratories, Inc., Knoxville, Tenn. Molecular weights were determined using a Mechrolab osmometer or with a Bendix time-of-flight mass spectrometer. The gc data was obtained using an F & M Model 500 temperature-programmed gas chromatograph with a disk integrator.

***trans*-1,2-Dihydrophthalic Acid.**[44]—A vigorously stirred solution of 170 g (1.02 moles) of phthalic acid and 281 g of sodium acetate in 1700 ml of water was cooled in an ice bath while a total of 3400 g of 3% sodium amalgam[47] was added in 50–100-g portions. With each portion of amalgam there was also added 10–20 ml (500-ml total) of 50% acetic acid. When hydrogen evolution had ceased after the addition of an amalgam portion, another addition was made until all the amalgam was added (4–8 hr). The solution was decanted from the mercury deposit through a filter and the cold filtrate was treated with 1700 ml of cold 20% sulfuric acid. Crystllization of the acid began immediately. After standing 8–10 hr, the acid was collected by suction filtration and washed well with ice water to remove the sulfuric acid. The average yield of crude, vacuum-dried acid from three representative runs was 124 g (72%). The crude acid was used in most cases for conversion to the anhydride.

For minimum loss during recrystallization, the crude acid was immediately divided into two portions and each portion added to 1.2–1.5 l. of rapidly stirred, boiling water to effect as rapid a solution as possible. When the acid was dissolved, the solution was poured through a fluted filter and the filtrate was cooled in an ice bath to induce crystallization. The Norit treatment previously reported[44] was found unnecessary if the sodium amalgam was washed free of mineral oil with petroleum ether (bp 30–60°) before use. The white crystals were collected by filtration and dried *in vacuo* to give 107 g (62% yield) of the acid, mp 207–214° (lit.[44] 50% yield, mp 213–214°). The infrared spectrum was identical with that reported.[44]

***cis*-1,2-Dihydrophthalic Anhydride.**—The procedure was similar to that of Pappas.[14] To 600 ml of acetic anhydride, which was magnetically stirred in a nitrogen atmosphere and heated to 98–100°, was added 137 g (0.82 mole) of *trans*-1,2-dihydrophthalic acid. After solution of the diacid was complete (10–12 min), the clear, yellow solution was cooled to room temperature and the acetic anhydride was carefully removed *in vacuo* using an oil pump and Dry Ice cooled traps to collect the distillate. Sublimation of the yellow crystalline residue at 50–70° and 0.01–0.03 mm gave an average yield of 78%, mp 104–108°, from 10 reactions. Recrystallization from Skelly B gave crystals, mp 108–109.5°, $\lambda_{\max}^{\text{ether}}$ 264 and 256 mμ [lit.[14] mp 111–113°, $\lambda_{\max}^{\text{ether}}$ 264 mμ (ϵ 4.8 × 10^3) and 256 mμ (ϵ 5.0 × 10^3)]. The sublimed anhydride was used in the ultraviolet irradiation reactions without further purification.

Bicyclo[2.2.0]hex-5-ene-2,3-dicarboxylic Anhydride.—The procedure was that of Pappas[14] with modification. A solution of 14 g (0.076 mole) of sublimed *cis*-1,2-dihydrophthalic anhydride in 4.5 l. of anhydrous ether was photolyzed under a purified nitrogen atmosphere using a 450-w mercury vapor lamp (Hanovia type L), which was immersed in the solution in a water-cooled quartz well containing a Vycor filter. The solution was stirred magnetically and by nitrogen ebullition and photolyzed until the ultraviolet absorption of the *cis*-1,2-dihydrophthalic anhydride at 256 mμ diminished to a constant value. The quartz well was removed every 4 hr and wiped free of yellow deposit which blocked the effective irradiation. The reaction was complete after 14 hr. The ether was removed from the reaction mixture by distillation and the orange, viscous residue was transferred to a sublimation apparatus. Sublimation at 50° and 0.01 mm gave 2.8 g (24% yield) of photoanhydride, mp 157–161°. Recrystallization from a Skelly B–ether mixture gave crystals [mp 160–164° (lit.[14] 22% yield, mp 162–163°)] which exhibited only end absorption in the ultraviolet spectrum as reported.[14] The infrared and nmr spectra of this photoanhydride were in agreement with those reported.[10,14]

In some photolysis reactions the orange glass, which remained after sublimation of the product, was finely ground and Soxhlet extracted with petroleum ether to obtain additional product.

The work-up used most in this work was one whereby the reaction mixture was condensed to a volume of 5–100 ml by distillation of the ether. The orange solution was then cooled for several hours to induce crystallization of the photoanhydride, which was collected by filtration and sublimed. The sublimed product was employed in the next step without further purification.

Bicyclo[2.2.0]hexane-2,3-dicarboxylic Anhydride.—A solution of 18.3 g (0.122 mole) of bicyclo[2.2.0]hex-5-ene-2,3-dicarboxylic anhydride in 200 ml of ethyl acetate was hydrogenated over prereduced platinum oxide catalyst at room temperature in a Parr hydrogenation apparatus. The initial pressure was 55.5 psi. Hydrogen uptake ceased at 105% of the theoretical uptake (8.5 psi/0.1 mole) after 1.5 hr. The catalyst was removed by filtration and the ethyl acetate removed *in vacuo* to give 18.2 g of crude product. Sublimation at 60° (0.01 mm) gave 16.6 g (90% yield), mp 79–84°. Recrystallization of a sample of the anhydride to a constant melting point from an ether–petroleum ether mixture yielded fine, colorless needles, mp 84.5–86°.

Anal. Calcd for $C_8H_3O_3$: C, 63.15; H, 5.30. Found: C, 63.06; H, 5.17.

Bicyclo[2.2.0]hexane-2,3-dicarboxylic Acid.—To a stirred slurry of 14 g (0.092 mole) of bicyclo[2.2.0]hexane-2,3-dicarboxylic anhydride in 100 ml of water, which was cooled in an ice bath and contained several drops of phenolphthalein indicator solution, was added dropwise 3 *N* sodium hydroxide (61.3 ml) until the solution was pink and homogeneous. The ice-cooled solution was then acidified by the dropwise addition of 10% hydrochoric acid (64 ml). The solution was extracted with ten 100-ml portions of ether. The ether extracts were combined and dried over anhydrous sodium sulfate and evaporated *in vacuo* to give 13.6 g (87% yield), mp 145–154°. Aftr six recrystallizations from ether–petroleum ether, fine white needles (mp 160–165°) were obtained.

Bicyclo[2.2.0]hex-2-ene.—The procedure for the preparation of this compound was similar to that of Pappas[14] in the synthesis of bicyclo[2.2.0]hexa-2,5-diene. In a 1-l. three-necked flask, which was fitted with an Adjustatherm thermometer and a nitrogen bleed and connected to a receiving flask by means of a curved adapter, was placed 260 ml of dry pyridine and 6.22 g (36.6 mmoles) of bicyclo[2.2.0]hexane-2,3-dicarboxylic acid. The receiving flask was cooled in a Dry Ice–isopropyl alcohol bath and attached to two additional Dry Ice cooled traps and finally to a vacuum pump *via* a manostat and manometer. The solution was flushed with nitrogen (purified) for 15–20 min and 16.0 g (37.0 mmoles) of lead tetraacetate was added in one portion with stirring. The reaction flask was then heated in a water bath at 52–55°. The nitrogen flow was then stopped and the temperature of the reaction mixture maintained near 50° (2.3° below the water-bath temperature) by adjusting the vacuum (50–80 mm). During the first 5 min, a yellow flocculent precipitate formed which dissolved with an exothermic reaction and the temperature of the reaction mixture temporarily rose above the bath temperature. The resulting orange solution turned dark red during the course of the reaction. Reaction was continued for 2 hr during which time 38.7 g of pyridine distillate was collected in the receiving flask. Analysis of the reaction mixture by gc showed no olefin. Analysis of the pyridine distillate by gc and integration of the peak areas indicated that 2.8% of the mixture was bicyclo[2.2.0]hex-2-ene (1.08 g, 37% yield).

The gc analysis was performed on a 10% Apiezon L on 60–80 mesh Chromasorb W column maintained at 75°. The retention time of bicyclo[2.2.0]hex-2-ene was 2.1 min and that of pyridine was 3.6 min. The only impurity was 1,3-cyclohexadiene with a retention time of 2.6 min.

Another reaction of 7.1 g (41.7 mmoles) of bicyclo[2.2.0]-hexane-2,3-dicarboxylic acid, 18.6 g (43 mmoles) of lead tetraacetate, and 270 ml of pyridine gave 88 g of pyridine distillate over a reaction period of 1.5 hr. Gc showed the distillate to contain 1.6% bicyclo[2.2.0]hex-2-ene (1.40 g, 42% yield).

The pyridine distillates from the two reactions above were combined and distilled through a 30-cm Vigreux column until the boiling point of pyridine was reached. Four fractions were collected: fraction 1, bp 43–48° (277 mm), 0.93 g; fraction 2, bp 45–56° (266 mm), 0.72 g; fraction 3, bp 56–74° (270 mm), 0.58 g; and fraction 4, bp 74–82° (270 mm), 1.43 g.

Each fraction was analyzed by gc. Fraction 1 contained only bicyclo[2.2.0]hex-2-ene and fractions 2, 3, and 4 contained 95,

---

[47] W. B. Renfrow and C. R. Hauser, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p 609.

62, and 32%, respectively, of the desired olefin. This corresponded to a total average yield for the two reactions of 2.39 g (38%).

For a series of similar reactions the yields ranged from 40–52% by gc analysis of the pyridine distillates and 30–38% after distillation. The reaction times varied and appeared dependent upon the rate of distillation of pyridine. The above reaction time was typical, but if olefin was detected in the reaction mixture by gc analysis, the reaction was continued to obtain additional product.

A reaction of bicyclo[2.2.0]hexane-2,3-dicarboxylic anhydride under the above conditions on a smaller scale gave a 15% yield of bicyclo[2.2.0]hex-2-ene as determined by gc analysis of the pyridine distillate.

Gc analysis of the olefin distillates on a 6 ft × 0.25 in. 30% α-nitro-α-methylpimelonitrile (NMPN) on a firebrick column maintained at a temperature of 100° with the injection port temperature at 225° showed two major products with retention times of 1.3 and 2.2 min. The retention time of pyridine under these conditions was greater than 20 min. When the injection port temperature was increased to 330° only the component at 2.2 min was observed and at an injection port temperature of 130°, only the 1.3-min component was observed. The component with a retention time of 1.3 min was bicyclo[2.2.0]hex-2-ene as shown by the infrared and nmr spectra on the collected material. Bicyclo[2.2.0]hex-2-ene was injected onto the NMPN column at an injection port temperature of 330° and the component with retention time of 2.2 min was collected and identified a 1,3-cyclohexadiene by its infrared and nmr spectrum. The nmr spectrum in carbon tetrachloride with tetramethylsilane internal standard exhibited two sharp singlets of equal intensity at τ 4.34 and 7.96.

***exo*-Bicyclo[2.2.0]hexan-2-ol.**—To a stirred solution of 2.78 g (34.7 mmoles) of bicyclo[2.2.0]hex-2-ene in 15 ml of dry tetrahydrofuran was added dropwise 16 ml (9.1 mmoles) of 0.58 *M* diborane[20] solution in tetrahydrofuran, while maintaining the temperature of the reaction mixture at 5–10° by cooling in an ice–water bath. When the addition was complete (40 min), the solution was stirred at 5° for 20 min and then at room temperature for 2.25 hr. The excess hydride was decomposed by the addition of 7 ml of water while cooling the mixture.

The organoborane was oxidized at 35–45° (water bath) by the addition of 4.4 ml of 3 *N* sodium hydroxide, followed by the dropwise addition of 4.4 ml of 30% hydrogen peroxide. After the hydrogen peroxide addition was complete (30 min), the mixture was stirred at room temperature for 1 hr and then saturated with sodium chloride. The resulting heterogeneous mixture was treated with 30 ml of ether and the layers were separated. The aqueous layer was extracted twice with 20-ml portions of ether and the organic layers were combined, washed once with saturated sodium chloride solution, and dried over anhydrous sodium sulfate. After removal of the solvents by distillation the crude *exo*-bicyclo[2.2.0]hexan-2-ol (3.4 g) was distilled through a 6-in. vacuum-jacketed Vigreux column to give 2.73 g (80%), bp 69–70.5°, $n^{20.4}\text{D}$ 1.4772.

Anal. Calcd for $C_6H_{10}O$: C, 73.42; H, 10.27. Found: C, 73.20; H, 10.43.

***exo*-Bicyclo[2.2.0]hex-2-yl Acetate.**—According to the general procedure of Shriner, Fuson, and Curtin,[48] a solution of 70 mg (0.71 mmole) of *exo*-bicyclo[2.2.0]hexan-2-ol, 0.5 ml of acetic anhydride, and 1 ml of dry pyridine was stirred at room temperature for 46 hr. The solution was treated with 1 ml of water and extracted four times with 6-ml portions of pentane. The combined pentane extracts were washed once with 20 ml of 5% hydrochloric acid, once with water, and dried over anhydrous sodium sulfate. Most of the pentane was removed by distillation and the residue (110 mg) was analyzed on a 6 ft × 0.25 in. 10% diisodecyl phthalate on 60–80 mesh Chromasorb W column. Integration of the peak areas indicated 68% of the mixture was the acetate (75 mg, 75% yield). Collection of the acetate by gc gave 60 mg (60% yield). The nmr spectrum in carbon tetrachloride with tetramethylsilane internal standard showed proton resonance at τ 4.93 as an triplet, continuous absorption from τ 6.90–7.95, and a sharp singlet at τ 8.05 in a ratio of 1:8:2.8.

Anal. Calcd for $C_8H_{12}O_2$: C, 68.54; H, 8.63. Found: C, 68.81; H, 8.74.

***exo*-Bicyclo[2.2.0]hex-2-yl *p*-Toluenesulfonate.**—The method for the preparation of this ester was that previously used yb Wiberg, Lowry, and Colby[2] with some modification. To a stirred solution of 1.16 g (11.8 mmoles) of *exo*-bicyclo[2.2.0]-hexan-2-ol in 65 ml of anhydrous ether, cooled in an ice–salt–water bath at 0°, was added in one portion 2.25 g (11.8 mmoles) of *p*-toluenesulfonyl chloride. To the resulting solution was added 1.92 g (34.2 mmoles) of powdered potassium hydroxide at such a rate that the temperature did not exceed 0°. When the addition was complete, the mixture was stirred at room temperature for 4.5 hr. The resulting mixture was poured onto 50 g of ice and the layers were separated. The aqueous layer was extracted three times with 25-ml portions of ether. The combined ether layers were washed with water, dried over anhydrous potassium carbonate, and evaporated *in vacuo* to give 2.58 g (87%) of a colorless oily product. The pure ester was isolated as a colorless, viscous liquid by molecular distillation (modified Hichman still) of the crude product at 75° (0.02–0.01 mm) to obtain 2.08 g (70%), $n^{25.8}\text{D}$ 1.5323.

The nmr spectrum in carbon tetrachloride with tetramethyl silane internal standard exhibited absorptions at τ 2.42 as a quartet, τ 5.01 as a triplet, and as continuous absorption from τ 7.04 to 8.40 in a ratio of 4.4:1:11.3.

Anal. Calcd for $C_{13}H_{16}O_3S$: C, 61.88; H, 6.41; mol wt, 252. Found: C, 61.88; H, 6.33; mol wt, 251 (osmometer, chloroform solvent).

Kinetic Acetoylsis of *exo*-Bicyclo[2.2.0]hex-2-yl *p*-Toluenesulfonate.—The rate constant was determined by the sealed-ampoule technique[23,49] and calculated by the infinity titer method.[49] A summary of the acetolysis data is given in Table I. A plot of log (C_i − C_t) *vs.* times for runs 1 and 2 showed a steady downward drift in rate. In this plot, C_i is the initial concentration of tosylate and C_t is the concentration of ester at time *t*. Similar plots using C_∞ in place of C_i gave good straight lines.

Preparative Acetolysis of *exo*-Bicyclo[2.2.0]hex-2-yl *p*-Toluenesulfonate.—A solution of 1.31 g (5.2 mmoles) of *exo*-bicyclo-[2.2.0]hex-2-yl tosylate dissolved in 200 ml of anhydrous acetic acid was heated in a constant-temperature bath at 75° for 46.5 hr (10 half-lives). The acetolysis mixture was diluted to 500 ml with water and extracted with two 100-ml portions of pentane. The aqueous layer was then extracted continuously with pentane for 48 hr. The pentane extracts were combined, washed three times with 100-ml portions of 6% sodium bicarbonate solution, washed once with 100 ml of water, and dried over anhydrous sodium sulfate. The pentane was removed by distillation on a 30-cm Vigreux column. The residue which still contained pentane, was transferred to a modified Hickman still which was heated by a heating mantle. The approximate pot temperature was monitored by means of a thermocouple positioned between the heating mantle and the still pot. The residue was separated into three major fractions, and additional product was isolated from the Dry Ice cooled trap.

Fraction 1 was collected at atmospheric pressure at a pot temperature of 50° to remove the last traces of pentane. This fraction was analyzed by gc on a 6 ft × 0.25-in. 30% NMPN on firebrick column maintained at 125°. It was composed mainly of pentane, with two minor components with retention times of 9.8 and 14.3 min.

Fraction 2 (66 mg) was collected at a pot temperature of 54° while the pressure was reduced to 0.4 mm. Gc analysis of this fraction under the above conditions showed four components with retention times of 10.9, 13.2, 14.9, and 17 min. By peak area integration (disk integrator) the percentage composition of this mixture, assuming equal detector response for all components, was 39.8, 3.6, 48.3, and 5.4%, respectively. By retention time comparisons these components corresponded to *exo*-bicyclo-[2.1.1]hex-5-yl acetate (10.9 min), *exo*-bicyclo[2.2.0]hex-2-yl acetate (13.2 min), 4-cyclohexenyl acetate (14.9 min), and 3-cyclohexenyl acetate (17 min). Confirmation of the structures of the two major acetates was obtained from the nmr spectrum of the mixture, which exhibited absorptions characteristic of a mixture of *exo*-bicyclo[2.1.1]hex-5-yl acetate and 4-cyclohexenyl acetate. A sample of the acetate with a retention time of 10.9 min was collected by gc under the above conditions and the nmr spectrum was in agreement with that of the assigned structure and similar to that of *exo*-bicyclo[2.1.1]hexan-5-ol.[50]

---

[48] R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," 4th ed, John Wiley and Sons, Inc., New York, N. Y., 1956, p 212.

[49] H. Tanida, T. Tsuji, and H. Ishitobi, *J. Am. Chem. Soc.*, **86**, 4904 (1964).

[50] K. B. Wiberg, B. R. Lowry, and B. J. Nist, *ibid.*, **84**, 1594 (1962).

Fraction 3 was distilled at 60° (0.01 mm) to give 556 mg of a viscous oil which solidified on standing. This fraction contained no acetates as shown by the infrared spectrum. The infrared spectrum of this material was characteristic of a tosylate. The nmr spectrum in carbon tetrachloride with tetramethylsilane internal standard was similar to that of *exo*-bicyclo[2.1.1]hexan-5-ol,[50] exhibiting absorptions at τ 2.36 (quartet), 5.79 (doublet), 7.57 (broad singlet), 8.42 (singlet), and 8.91 (triplet) in a ratio of 4:1:7:4:2, respectively. On this basis and its detosylation to the alcohol, it was assigned structure of *exo*-bicyclo[2.1.1]hex-5-yl tosylate.

The product mixture which was recovered from the Dry Ice trap was combined with fraction 1 and the pentane removed by distillation. The residue was shown to contain both acetates and tosylate by the infrared spectrum. An additional 97 mg of acetate-free *exo*-bicyclo[2.1.1]hex-5-yl tosylate was obtained by short-path distillation *in vacuo*. The acetates were collected in a Dry Ice cooled receiver. The composition of this acetate mixture (129 mg) was determined by integration of the gc peak areas. Some pentane was still present.

The total yield of acetate products was determined by gc integration of all the acetate fractions to be 174 mg (24% yield). The mixture was composed of 41% of *exo*-bicyclo[2.1.1]hex-5-yl acetate, 3% of *exo*-bicyclo[2.2.0]hex-2-yl acetate, 51% of 4-cyclohexenyl acetate, and 5% of 3-cyclohexenyl acetate. The total yield of *exo*-bicyclo[2.1.1]hex-5-yl tosylate was 653 mg (50% yield).

3-Cyclohexenol.—By the procedure of Gogek, Moir, and Purves,[51] 1,4-cyclohexanediol (11.8 g) was heated with 0.045 ml of 65% sulfuric acid until 8.7 g of crude product was obtained by continuous distillation during the reaction. The crude product was redistilled through a 6-in. vacuum-jacketed Vigreux column to give fractions of cyclohexadiene (bp 70–85°, $n^{20}{}_{\mathrm{D}}$ 1.4708) and water at atmospheric pressure. The 3-cyclohexenol distilled at reduced pressure to yield 2.70 g (27%), bp 72° (15 mm), $n^{19.5}{}_{\mathrm{D}}$ 1.4847 (lit.[51] 38% yield, bp 164–165°). Gc analysis showed only one component.

4-Cyclohexenyl Acetate.—This acetate was prepared from the alcohol by the general procedure of Shriner, Fuson, and Curtin.[48] Distillation of the crude product through a 6-in. vacuum-jacketed Vigreux column gave a fraction of the acetate [bp 58–60° (4 mm), $n^{28}{}_{\mathrm{D}}$ 1.4625] which showed one major components by gc on a 6 ft × 0.25-in. NMPN column at 125°. The nmr spectrum in carbon tetrachloride with tetramethylsilane internal standard exhibited absorptions at τ 4.36 (multiplet), 5.05 (multiplet), and continuous absorption from τ 8.3 to 8.4 with a sharp methyl singlet at τ 8.01.

***exo*-Bicyclo[2.1.1]hexan-5-ol.**—The lithium in ether–liquid ammonia detosylation of *exo*-bicyclo[2.1.1]hex-5-yl tosylate was carried out on 280 mg of toslylate according to the reported procedure.[25] After work-up and evaporation of the solvent the residue was heated in a small sublimation apparatus at atmospheric pressure and 50°. The product was isolated from the cold finger as a colorless liquid, 68 mg (62% yield). Gc analysis on a 6 ft × 0.25-in. diisodecyl phthalate column at 125° showed only one component. The infrared spectrum of this material corresponded to that of *exo*-bicyclo[2.1.1]hexane-5-ol.[3]

***exo*-Bicyclo[2.1.1]hex-5-yl Acetate.**—The alcohol prepared above was converted to the acetate by the procedure previously described for the preparation of *exo*-bicyclo[2.2.0]hex-2-yl acetate. The crude product was analyzed by gc on a 6 ft × 0.25-in. NMPN column at 125°. Two peaks were observed at retention times of 9.4 and 10.3 min in a ratio of about 2:1, respectively. The major peak corresponded by retention time to the acetate product previously identified from the acetolysis mixture of *exo*-bicyclo[2.2.0]hex-2-yl tosylate. The infrared and nmr spectra of this collected gc peak established its structure as *exo*-bicyclo[2.1.1]hex-5-yl acetate. The minor component was not identified.

***cis*-Bicyclo[3.1.0]hexan-2-ol.**—The method employed for this reaction was that of Corey and Dawson.[5] The methylene iodide was prepared from methylene chloride by the procedure of Perkin and Scarborough.[52] The zinc–copper couple was prepared by the method of Schank and Schechter.[53] The crude product was distilled through a 6-in. vacuum-jacketed Vigreux column to give two main fractions: fraction 1, bp 42–45° (3.5–4 mm), $n^{29.5}{}_{\mathrm{D}}$ 1.4761; fraction 2, bp 42–41° (3.5–3 mm), $n^{29.5}{}_{\mathrm{D}}$ 1.4817 [lit.[54] 78–79.5° (20 mm)].

Fraction 2 was analyzed by gc on a 6 ft × 0.25-in. diisodecyl phthalate column at 100°. One major peak was observed and collected from the column, $n^{22}{}_{\mathrm{D}}$ 1.4796 (lit.[54] $n^{25}{}_{\mathrm{D}}$ 1.4742). The infrared spectrum of this material was in agreement with that previously reported.[54,55] The nmr spectrum was also in agreement with that previously reported showing absorption for the cyclopropane methylene hydrogens at τ 9.20–9.85.

***cis*-Bicyclo[3.1.0]hex-2-yl Acetate.**—This acetate was prepared by the procedure previously described.[48] The crude product showed one major component with a retention time of 12.6 min when analyzed by gc on a 6 ft × 0.25 in. NMPN column at 125° This material was used for retention time comparisons.

Equilibration of the Bicyclo[2.1.0]hexan-2-ols.—The procedure followed was that of Corey and Dawson.[5] From 0.56 g of *cis*-bicyclo[2.1.0]hexan-2-ol there was obtained 0.51 g of a crude product containing the *trans*- and *cis*-bicyclo[2.1.0]hexan-2-ols in a ratio of 1:2.2 as reported.

***cis*- and *trans*-Bicyclo[3.1.0]hex-2-yl Acetates.**—The bicyclo[2.1.0]hexan-2-ol equilibration mixture from the previous section was converted to the acetate derivative by the usual method.[48] The product mixture obtained was analyzed on a 15 ft × 0.25-in. 30% NMPN on firebrick column maintained at 150°. Two peaks were observed at 27.4 and 28.5 min in the ratio of 2.5:1, respectively. The major component at 27.4 min compared favorably with *cis*-bicyclo[3.1.0]hex-2-yl acetate. This mixture was used for retention time comparisons.

2-Cyclohexenol.—To a stirred solution of 0.87 g (9.2 mmoles) of 2-cyclohexenone, dissolved in a 5 ml of 95% ethanol and cooled in an ice bath, was added a solution of 0.12 g (5 mmoles) of sodium borohydride in 8 ml of 50% ethanol. The addition required 15 min after which time the mixture was allowed to react at room temperature for 3.5 hr. The solution was treated with 5 ml of 3 *N* sodium hydroxide and extracted first with pentane and then with ether. After drying and removing the solvents by distillation there was obtained 0.70 g of crude product. A short-path distillation gave 0.53 g of distillate. Analysis of this product by gc on a 6 ft × 0.25-in. β,β'-oxydipropionitrile at 90° showed two major components in a ratio of 2.3:1. Each component was collected from the column and the component of shortest retention time was identified by its infrared spectrum as cyclohexanol. The peak of longer retention time was taken as 2-cyclohexenol on the basis of its infrared spectrum.

3-Cyclohexenyl Acetate.—The product mixture from the previous section was converted to the corresponding acetate mixture by the usual method.[48] The product mixture was analyzed by gc on a 15 ft × 0.25-in. NMPN column under the conditions described for the bicyclo[3.1.0]hex-2-yl acetates above. Two peaks were observed at retention times of 18.6 and 29.5 min. The component with a retention time of 29.5 min was the major peak, corresponding to the acetate of 2-cyclohexenol since this alcohol was the major component of the alcohol mixture. This mixture was used for retention time comparisons.

Kinetic Formolysis of *exo*-Bicyclo[2.2.0]hex-2-yl *p*-Toluenesulfonate.—The formolysis procedure was that used by Winstein and Heck.[26] The formic acid used was Eastman 97% purity formic acid which was purified by the method of Winstein and Marshall.[56] The water content of the purified acid determined by titration with Karl Fisher reagent was less than 0.01%. A modification in the reported[26] procedure was made by substituting ether as the quenching solvent in place of dioxane. This modification was made to facilitate the isolation of the formolysis products from the titrated aliquots. For *exo*-bicyclo[2.2.0]hex-2-yl tosylate, aliquots were titrated with 0.0164 *M* sodium acetate in acetic acid. Two runs were made at each temperature.

Preparative Formolysis of *exo*-Bicyclo[2.2.0]hex-2-yl *p*-Toluenesulfonate.—The titrated aliquots from the kinetic runs were combined and chilled to avoid further reaction with acetic acid. That further reaction did not occur was evidenced by no color change in several test aliquots which were allowed to stand at room temperature for several hours after titration to the end point. The combined aliquots (~300 ml/run) were kept cold until the kinetic runs at each temperature were complete. They were then washed three times with 250-ml portions of water,

---

(51) C. J. Gogek, R. Y. Moir, and C. B. Purves, *Can. J. Chem.*, **29**, 949 (1951).

(52) W. H. Perkin, Jr., and H. A. Scarborough, *J. Chem. Soc.*, **119**, 1400 (1921).

(53) R. S. Schank and H. Schechter, *J. Org. Chem.*, **24**, 1825 (1959).

(54) W. G. Dauben and G. H. Berezin, *J. Am. Chem. Soc.*, **85**, 468 (1963).

(55) P. K. Freeman, M. F. Grostic, and F. A. Raymond, *J. Org. Chem.*, **30**, 771 (1965).

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

once with 100 ml of water, and then with 50-ml portions of 10% sodium bicarbonate solution until the aqueous layer was a deep blue color, which is the basic color for bromocresol green indicator in aqueous solution. The ether solutions were then washed once more with 100 ml of water and dried over anhydrous sodium sulfate. The sodium sulfate was removed by filtration and the ether was carefully distilled through a 39-cm Vigreux column. The products from the runs at 25 and 35° obtained in this manner gave identical infrared spectra and were combined. The infrared spectrum showed absorptions characteristic of a mixture of *exo*-bicyclo[2.2.0]hex-2-yl tosylate, *exo*-bicyclo[2.1.1]hex-5-yl tosylate, and formate products.

The combined products at this point amounted to 740 mg. The total amount of *exo*-bicyclo[2.2.0]hex-2-yl tosylate used in the four kinetic runs was 778 mg. The combined products were dissolved in 200 ml of anhydrous formic acid and placed in a constant-temperature bath at 35° for 4.5 hr. (9 half-lives). The formolysis mixture was then poured into 500 ml of ether and the resulting solution was washed twice with 250-ml portions of water, twice with 100-ml portions of water, six times with cold 5% sodium bicarbonate solution, and once with 100 ml of water. The ether layer was dried over anhydrous sodium sulfate, and, after removal of the drying agent by filtration, most of the ether was carefully distilled through a 30-cm Vigreux column. The final traces of ether were removed through a 6-in. vacuum-jacketed Vigreux column to give 585 mg of yellow oily residue. The infrared spectrum of this material exhibited bands which agreed well with the spectrum of *exo*-bicyclo[2.1.1]hex-5-yl tosylate. Strong carbonyl absorption was also present.

The formolysis product mixture was transferred with ether to a modified Hickman still and the formates removed by distillation of 35–55 mm and a pot temperature of 65–75°. The infrared spectrum of the undistilled residue corresponded to *exo*-bicyclo-[2.1.1]hex-5-yl tosylate (280 mg, 36% yield based on starting tosylate). A weak carbonyl absorption was present in the sample, but no further attempt was made to recover additional formate products from it.

The distilled formate products amounted to 67 mg (17% yield based on starting tosylate). This mixture was analyzed by gc on a 6 ft × 0.25-in. 30% NMPN on firebrick column at 125°. Three peaks other than ether were observed at retention times of 9.5, about 10 (as a shoulder), and 16.2 min. These peaks comprised 42.3, 4.1, and 53.5%, respectively, of the total mixture.

The formate mixture (67 mg), dissolved in 2 ml of ether, was added dropwise over a 15-min period to a stirred suspension of 40 mg of lithium aluminum hydride in 2 ml of ether at room temperature and the mixture was stirred at room temperature for 11 hr. The excess hydride was decomposed with water and the mixture was stirred until the salts were white (~30 min). The salts were removed by filtration and the filtrate was dried over anhydrous sodium sulfate. After the drying agent was removed by filtration, the ether was distilled through a 6-in. vacuum-jacketed Vigreux column to give 56 mg (16% yield based on starting tosylate) of an alcohol mixture. This mixture showed three peaks by gc on a 6 ft × 0.25-in. 10% β,β'-oxydipropionitrile on Chromasorb W column at 90°. The retention time and per cent of each component present as determined by integration of gc peak areas were 11.9 (40.6%), 15.1 (3.4%), and 17.2 min (56.0%). Injection of a mixture of *exo*-bicyclo-[2.2.0]hexan-2-ol and the alcohol mixture onto the column under the above conditions showed enhancement of the component at 15.1 min. The peak at 17.2 min showed enhancement when 3-cyclohexenol was mixed with the alcohol mixture and injected under the above conditions.

A sample of the component of retention time 11.9 min was collected from the column and identified as *exo*-bicyclo[2.1.1]-hexan-5-ol by its infrared spectrum.[57] The component of retention time 17.2 min was confirmed to be 3-cyclohexenol by collection and comparison of its infrared spectrum with that of an authentic sample.

Under the above gc conditions, *trans*-bicyclo[3.1.0]hexan-2-ol and *exo*-bicyclo[2.2.0]hexan-2-ol were not resolved. It was, however, possible to resolve these compounds as the acetate derivatives.

A sample of the alcohol mixture (48 mg) from the formolysis products was converted to the acetate derivative by the usual method.[48] The products were analyzed by gc on a 15 ft × 0.25-in. 30% NMPN on firebrick column maintained at 150°. The three major components corresponded by retention times to *exo*-bicyclo[2.1.1]hex-5-yl acetate (19.2 min), *exo*-bicyclo[2.2.0]-hex-2-yl acetate (24.0 min), and 4-cyclohexenyl acetate (26.4 min). A fourth component was detected in minor amount and corresponded by retention time to 3-cyclohexenyl acetate (29.3 min). Under these conditions the *cis*- and *trans*-bicyclo[3.1.0]-hex-2-yl acetates did not correspond to any of the components.

Diels–Alder Adduct of Nitrosobenzene and *cis*-1,2-Dihydrophthalic Anhydride.—The procedure followed was similar to that of Kresge and Schulz.[46] A solution of 2.9 g (0.027 moles) of nitrosobenzene and 4.5 g (0.03 moles) of 1,2-dihydrophthalic anhydride in 130 ml of anhydrous ether was stirred at 0°. The green color of the nitrosobenzene still remained after 3 hr. After further reaction at room temperature for 17 hr, the solution had turned light yellow and a white solid was collected by filtration, 4.81 g (65% yield), mp 120–145°. After three recrystallizations from methylene chloride–petroleum ether mixtures a grey crystalline product, mp 122–147°, was obtained, which darkened on standing at room temperature. The nmr spectrum in dimethyl sulfoxide showed absorptions centered at τ 2.72 (aromatic protons), 3.41 (olefinic protons), 4.71 (bridgehead methine protons), and 6.40 (anhydride methine protons).

Catalytic Reduction of the Diels–Alder Adduct of Nitrosobenzene and *cis*-1,2-Dihydrophthalic Anhydride.—A 10-ml tetrahydrofuran solution of 0.78 g (3.3 mmoles) of the Diels–Alder adduct, prepared in the previous section, was hydrogenated in a microhydrogenation apparatus over prereduced platinum oxide catalyst at atmospheric pressure and room temperature. After 1.5 hr, hydrogen uptake ceased at 88% of the theoretical amount. The catalyst was removed by filtration and the solvent was removed *in vacuo*. The crude product was a mixture of a viscous liquid and a solid, which were separated by crystallization of the solid from an ether solution of the mixture. There was obtained 0.60 g (77% yield) of the solid product (mp 152–160°) after one recrystallization from a tetrahydrofuran–petroleum ether mixture.

The nmr spectrum in dimethyl sulfoxide was in accord with the assigned structure showing absorptions at τ 2.80 (aromatic multiplet), 5.52 (doublet, bridgehead methines), 4.31 (multiplet, bridgehead methines), and 8.25 (saturated protons).

The liquid product (0.81 g) exhibited a strong hydroxyl absorption in the infrared and was not further characterized.

3-Phenyl-2-oxa-3-azabicyclo[2.2.2]oct-5-ene.—This compound was prepared according to Kresge and Schulz[46] to give the crude product in 100% yield, mp 65–67.5°. This compound showed nmr absorptions (carbon tetrachloride with tetramethylsilane internal standard) at τ 3.00 (aromatic protons), a multiplet centered at τ 3.74 (olefinic protons), a very broad doublet at τ 5.55 (bridgehead protons), and a multiplet centered at τ 8.26 (saturated protons).

Registry No.—**2**, 3097-61-8; **3**, 3097-62-9; **4**, 3097-63-0; **5a**, 3097-64-1; **5b**, 3097-59-4; **5c**, 4348-32-7; **6**, 3097-76-5; **7a**, 10437-78-2; **8a**, 4348-33-8; **8b**, 10437-80-6; **26**, 10437-81-7; **27**, 10437-82-8; 3-phenyl-2-oxa-3-azabicyclo[2.2.2]oct-5-ene, 10437-90-8.

Acknowledgments.—The authors wish to express their gratitude to the National Science Foundation (GP-1916, and GP-4888) for support of this research, and for a departmental grant used to purchase the Varian A-60 nmr spectrometer.

---

[57] K. B. Wiberg kindly provided infrared spectra of several derivatives of bicyclo[2.1.1]hexanes.