HOMOCONJUGATION AND HOMOAROMATICITY-XVII1

THE NATURE AND BEHAVIOR OF THE UNSUBSTITUTED TRISHOMOCYCLOPROPENYL CATION^{2, 3}

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Abstract—A more extensive investigation of the solvolysis of the 3-bicyclo-[3.1.0]hexyl tosylates has been carried out using kinetic, NMR and VPC techniques not employed previously. For labeled starting materials, 6,6-dideuterated species have been used. The trishomocyclopropenyl cation is here discussed on the basis of the new information.

In line with the presence of a special salt effect in acetolysis of the *cis*-tosylate, the latter exhibits equilibration of the deuterium label, originally at C_6 , over positions 2, 4 and 6 during acetolysis. The sum of the first order equilibration rate constant, k_{eq} , and the titrimetric rate constant, k_t , represents a minimum value for the ionization rate constant, k_1 . Lithium perchlorate reduces considerably the gap between k_t and $(k_{eq} + k_t)$, but it does not eliminate it entirely. Thus, the special salt effect eliminates only part of the ion pair return during the acetolysis. With respect to salt effects, ion pair behavior and lack of common ion rate depression, the *cis*-3-bicyclo[3.1.0]hexyl system is analogous to the 3-anisyl-2-butyl analog.

As regards mechanism of solvolysis of *cis*-tosylate, the essentially exclusive formation of *cis*acetate with retention of configuration and complete equilibration of the label, the absence of elimination, the lack of rearrangement to 2-bicyclo[3.1.0]hexyl and monocyclic structures, and the special salt effect and ion pair return phenomena provide a complete contrast with the behavior of

¹ Previous papers in this series:

^a XVI, M. Ogliaruso, R. Rieke and S. Winstein, J. Amer. Chem. Soc. 88, 4731 (1966); ^b XV, R. Rieke, M. Ogliaruso, R. McClung and S. Winstein, Ibid. 88, 4729 (1966); ^c XIV, S. Winstein, C. G. Kreiter and J. I. Brauman, Ibid. 88, 2047 (1966); ^d XIII, H. D. Kaesz, S. Winstein and C. G. Kreiter, Ibid. 88, 1319 (1966); ^e XII, S. Winstein, H. D. Kaesz and E. C. Friedrich, Ibid. 87, 3267 (1965); ^f XI, S. Winstein and F. P. Lossing, Ibid. 86, 4485 (1964); ^e X, S. Winstein, P. Bruck, P. Radlick and R. Baker, Ibid. 86, 1867 (1964); ^h IX, P. Radlick and S. Winstein, Ibid. 86, 1866 (1964); ⁱ VIII, R. Boikess and S. Winstein, Ibid. 85, 343 (1963); ^j VII, P. Radlick and S. Winstein, Ibid. 85, 344 (1963); ^k VI, R. J. Piccolini and S. Winstein, Tetrahedron 19, 423 (1963); ^l V, S. Winstein, L. deVries and R. Orloski, J. Amer. Chem. Soc. 83, 2020 (1961); ^m IV, S. Winstein and J. Sonnenberg, Ibid. 83, 3244 (1961); ⁿ III, S. Winstein, J. Sonnenberg, Ibid. 83, 3244 (1959); ^p I, S. Winstein, J. Sonnenberg and L. de Vries, Ibid. 81, 6524 (1959); ^p I, S. Winstein, J. Sonnenberg and L. de Vries, Ibid. 81, 6524 (1959); ^p I, S. Winstein, J. Sonnenberg and L. de Vries, Ibid. 81, 6524 (1959); ^p I, S. Winstein, J. Sonnenberg and L. de Vries, Ibid. 81, 6524 (1959); ^p I, S. Winstein, J. Sonnenberg and L. de Vries, Ibid. 81, 6524 (1959); ^p I, S. Winstein, J. Sonnenberg and L. de Vries, Ibid. 81, 6524 (1959); ^p I, S. Winstein, J. Sonnenberg and L. de Vries, Ibid. 81, 6524 (1959); ^p I, S. Winstein, J. Sonnenberg and L. de Vries, Ibid. 81, 6524 (1959); ^p I, S. Winstein, J. Sonnenberg and L. de Vries, Ibid. 81, 6523 (1959).

² Reported in part at: ^a The Chemical Society International Symposium on Aromaticity. Sheffield, England, July 6-8 (1966); ^b Kekule Celebration Meeting of the German Chemical Society. Bonn, Germany, Sept. 14 (1965); ^c Annual Meeting of the Japanese Chemical Society. Osaka, Japan, April 4 (1965) and The Japanese-American Seminar in Physical Organic Chemistry. Kyoto, Japan, April 6-10 (1965); ^d Ninth Organic Reaction Mechanisms Conference. Brookhaven, New York, Sept. 5-8 (1962).

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the *trans*-tosylate. All of the results are explicable on the basis of the trishomocyclopropenyl intermediate formed by anchimerically assisted ionization (k_d) of *cis*-tosylate. Rate constant k_d evidently exceeds the rate constant for anchimerically unassisted solvolysis, k_s , by a factor of ca. 50 in acetolysis and by a somewhat smaller factor in aqueous acetone.

The most striking aspect of the solvolysis of *trans*-tosylate is the complete absence of equilibration of the deuterium label in the *cis*-acetate part of the acetolysis product. Leakage from the classical cation to the nonclassical trishomocyclopropenyl structure competes unusually poorly with its other reactions. Probably the most important reason for this very inefficient leakage is that the geometry of the classical ion is unfavorable for the change. The reason for this goes back to the preferred boat conformation of 3-bicyclo[3.1.0]hexyl derivatives. This preferred boat conformation also provides part of the reason for the relatively low (k_d/k_e) ratios in solvolysis of the *cis*-tosylate.

Corey's alternative suggestion of three rapidly equilibrating "almost classical" nonclassical ions instead of the trishomocyclopropenyl species is discussed. None of the data require this modification, so the application of "Ockham's razor" to the three species and the retention of the simpler interpretation are recommended.

INTRODUCTION

ACETOLYSIS of the *cis*- and *trans*-3-bicyclo[3.1.0]hexyl toluenesulfonates I-OTs and III-OTs was originally investigated and discussed several years ago.^{1m-p} The *cis*-epimer was somewhat more reactive than the *trans*, and it showed a "special salt effect" in acetolysis, whereas the *trans*-isomer did not. The product from *cis*-tosylate was essentially exclusively the *cis*-acetate I-OAc, while the *trans*-tosylate gave considerable olefin, along with a substantial amount of *cis*-acetate. Acetolysis of *cis*-tosylate deuterium labeled in the 3-position (I-3D-OTs) gave acetate in which the deuterium was, within experimental error, equally distributed over the 1-, 3- and 5-positions. In the case of the *trans*-tosylate, acetate was formed with very little redistribution of the label. The results were interpreted in terms of anchimerically assisted ionization of the *cis*-tosylate directly to the unique nonclassical cation II, a homoaromatic trishomocyclopropenyl species. The *trans*-tosylate was presumed to ionize classically.



Since the original work, the nitrous acid deamination of the *cis*- and *trans*-3bicyclo[3.1.0]hexyl amines, I-NH₂ and III-NH₂ has been investigated^{4a} and the effect of phenyl substituents in the 1- and 5-positions of the *cis*-tosylate I-OTs on acetolysis rate studied.^{4b} The interpretation of the results has tended to create a certain amount of confusion.⁵ More recently, still other pertinent studies have been reported dealing with acid-catalyzed additions to 2-bicyclo[3.1.0]hexane⁶ and electrolytic decarboxylation of the *cis*- and *trans*-3-bicyclo[3.1.0]hexanecarboxylic acids.⁷

In the present manuscript, the results of a more extensive investigation of the solvolysis of the 3-bicyclo[3.1.0]hexyl tosylates is described using kinetic, NMR and VPC techniques not employed previously. For labeled starting materials we have now used 6,6-dideuterated systems, and considerable new or more accurate data have

⁴ ^a E. J. Corey and R. L. Dawson, J. Amer. Chem. Soc. 85, 1782 (1963); ^b E. J. Corey and H. Uda, Ibid. 85, 1788 (1963).

⁵ e.g., A. K. Katritzky et al., Chem. & Ind. 1452 (1963).

⁶ P. K. Freeman, M. F. Grostic and F. A. Raymond, J. Org. Chem. 30, 771 (1965).

⁷ P. G. Gassman and F. V. Zalar, J. Amer. Chem. Soc. 88, 2252 (1966).

thus become available. The trishomocyclopropenyl cation is here discussed on the basis of the information presented in the present paper and that in the literature.

3-Bicyclo[3.1.0]hexyl derivatives. The cis- and trans-3-bicyclo[3.1.0]-hexanols were prepared by methods similar to those employed previously, 1m,n however with certain convenient variations described in the experimental section. Hydroboration-oxidation of cyclopentadiene to Δ^3 -cyclopentenol was carried out using Brown's "in situ" method.^{8a} Oxidation of cis-3-bicyclo-[3.1.0]hexanol was carried out using chromium trioxide in ether-water,^{8b} and separation of the trans-3-bicyclo[3.1.0]hexanol from aluminum isopropoxide reduction of the ketone was by means of preparative VPC.

2,2,4,4-Tetradeuterated 3-bicyclo[3.1.0]hexanone was obtained from base-catalyzed protium-deuterium exchange on the bicyclohexanone.



6,6-Dideuterio-cis-3-bicyclo[3.1.0]hexanol (I-6D₂-OH) was prepared by the use of CD_2I_2 in the Simmons-Smith reaction on Δ^3 -cyclopentenol. The CD_2I_2 was derived from a convenient recipe for base-catalyzed deuterium exchange of CH_2I_2 which was developed as a modification of the one described.⁹

The preparation of labeled *trans*-3-bicyclo[3.1.0]hexanol depended on $S_N 2$ conversion of labeled *cis*-tosylate to *trans*-acetate with tetra-n-butylammonium acetate. In the aprotic solvent acetone, *cis*-tosylate is quite reactive towards the acetate nucleophile, the second order rate constant for reaction being $3.4 \times 10^{-3} 1 \text{ mole}^{-1}$

Compound	No. of Cyclopropane Methylene H
CD ₂ I ₂	(0·044±0·006)
cis-Alcohol I-6D2-OH	0.050 ± 0.010
cis-Tosylate I-6D ₂ -OTs	0.050 ± 0.010
trans-Tosylate III-6D2-OTs	0.060 ± 0.020
cis-Acetate from acetolysis ^a of cis-I-6D ₂ -OTs	1.37 ± 0.05
Calculated ^b	1.35
cis-Acetate from acetolysis ^a of trans-III-6D ₂ -OTs	0·040±0·004
cis-Tosylate recovered from formolysis ^c of cis-I-6D ₂ -OTs	
(51 % solvolysis)	0.076 ± 0.006

TABLE 1. ANALYSES FOR CYCLOPROPANE METHYLENE PROTONS IN DEUTERATED MATERIALS

^aCa, 0.01M NaOAc.

^bCalculated on basis of intermediate ion II, allowing for 6-protium in starting material.

°Ca. 0·1M LiOCHO.

⁸^a H. C. Brown, *Tetrahedron* 12, 118 (1961); ^b H. C. Brown and C. P. Garg, *J. Amer. Chem. Soc.* 83, 2952 (1961).

9 E. P. Blanchard and H. E. Simmons, J. Amer. Chem. Soc. 86, 1337 (1964).

Compound	$\mathrm{H_{1}}_{m{eta}}$	H_{2a}	$\mathrm{H}_{2\beta}$	Н _{3а}	Η _{3β}	$\mathrm{H}_{6_{\mathbf{d}}}$	H6β
3-Bicvelo[3.1.0]hexvl							
3-Ketone	8.50	<i>L</i> 6- <i>L</i>	7-49	ı	I	10-08	9-11
2,2,4,4-D ₄ -Ketone	8-49	D	D	ı	I	10-04	9-11
trans-3-Alcohol	8.73	7-96	8.40	6.15	HO	10-02	9-70
trans-3-Tosylate	8-75	7.92	8.12	5-50	OTs	10-05	9-63
cis-3-Alcohol	8-80	8.39	8-03	HO	5.78	9.5:	~
3-D-cis-3-Alcohol	8-80	8-35	7-99	HO	Q	9-51	
6,6-D ₂ -cis-3-Alcohol	8.80	8·32	8-00	НО	5.75	D	Ð
cis-3-Acetate	8·73	8·18	8.00	OAc	4-88	9.5.6	
cis-3-Tosylate	8-77	8·10	8-01	OTs	5.12	9-51	-
6,6-D ₂ -cis-3-Tosylate	8-77	8-06	7-93	OTs	5.12	D	D
d ³ -Cyclopentenyl							
Δ^3 -Ketone	3·88	7·20	7-20	I	ı	ı	I
d³-Alcohol	4-42	7.70	7-53	НО	5.62	1	I

^bRun as 10 to 20% by wt sols in CCI₄ on a Varian Associates Model A-60 instrument.

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Compound	J ₁ g. 2a	J _{1,8,2,8}	J _{2a} , 2β	J _{2a. 3}	J _{28, 3}	J _{6a, 6} g	J _{6a} 1β	J _{68,18}	J ₆₈ , 28
3-Bicycol[3.1.0]hexyl						1	4	ł	•
3-Ketone	0	~ 3	19-0	I	ı	5:3	3 .	¢.	∽ 1.>
2.2.4.4.D3-Ketone	1	1	1	1	1	5.3	 	7.5	1
	0	~3	13-0	7-0	۲~	4·5	4 0	7.5	5
trans. 2. Toculate	c	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	13-0	7-5	۲~	4·5	4-0	0.8 8	~ 1 ~
rie-3-Alcohol	0		14-0	1~	5.8	4.0 ⁵	4-0 ⁶	8.0°	۲ ۲
3-D-cis-3-Alcohol	0	~ 3	13-5	ł	ı	unres.	unres.	unres.	unres.
6.6-Dcir-3-Alcohol	0	۳ ۲	13-5	~	5.8	1	I	1	I
cir-3-Acetate	0	~3	13-8	7	6.0	unres.	unres.	unres.	unres.
cis-3-Tosylate	unres.	unres.	~14	~2	~6 ~	unres.	unres.	unres.	unres.
6,6-D2-cis-3-Tosylate	unres.	unres.	~ 14	~2	~6	1	t	1	ı
d ³ -Cyclopentenyl									
d ³ -Ketone	0	0	unres.	I !	I (I	I	I	1
d ³ -Alcohol	0	0	15-0	3.7	6.0	I	ł	I	I
,									

^{α}Reported in c/s. ^bDetermined in benzene solvent; unresolved in CCl₄.

sec⁻¹ at 25.0°. Since bimolecular substitution is accompanied by only 13% elimination, this represents an efficient method for inverting the system. The inverted acetate was cleaved by LAH and the alcohol product was converted directly into *trans*-tosylate III-6D₂-OTs. The 6,6-dideuterated materials could be assayed for protium in the 6-position by NMR, the analyses being summarized in Table 1.

NMR observations. The NMR spectra of the 3-bicyclo[3.1.0]hexanols and some of their derivatives and precursors have been examined at 60 M/s. While most of the molecules containing both cyclopropane and cyclopentane rings are of interest in connection with effects of geometry and substituents on proton chemical shifts and coupling constants, application of the present results will be mainly directed to proof of conformation of 3-bicyclo-[3.1.0]hexyl derivatives. In Tables 2 and 3 are summarized the proton chemical shifts and coupling constants which were derived, protons being designated as in structures IV and V. Assignments of the various chemical shifts and coupling constants were made taking into account the changes produced by variations of the 3-substituents and introduction of deuterium at various positions. The data confirm the structures and configurations of the compounds studied, but in addition, provide information regarding preferred conformations.



As regards conformations, Table 4 summarizes pertinent observed coupling constants along with the corresponding ones estimated for chair (VI) and boat (VII) forms, as well as a planar five-ring bicyclohexane (VIII). To obtain these estimates Dreiding models were used, a ca. 30° angle¹⁰ between the C₁-C₂-C₄-C₅ and C₂-C₃-C₄ planes being employed in the chair and boat forms. Pertinent proton-proton dihedral angles (\times) were measured from the Dreiding models and the corresponding estimated coupling constants were derived using the Karplus¹¹ equation.



Although the methods employed are only approximate, it is quite evident from Table 4 that the *cis*- and *trans*-3-bicyclo[3.1.0]hexanols and their esters tend to avoid the chair conformation and to prefer a boat form. This apparent preference of bicyclo[3.1.0]hexyl systems for a boat conformation has been observed by other

¹⁰ A corresponding angle of 22° 16' has been estimated for cyclopentene from a microwave spectral analysis. G. W. Rathjens, J. Chem. Phys. 36, 2401 (1962).

¹¹ M. Karplus, J. Chem. Phys. 30, 11 (1959).

investigators,^{6, 12} chiefly with various thujyl derivatives. In some of the systems^{12a, d} long-range coupling between 6β and 2β protons is also observed.

Conform	nation		$J_{1\beta, 2\alpha}$	J _{1β.2β}	J _{2a, 3a}	J _{2α, 3β}	J _{2β. 3α}	J _{2β.3β}
Chair		X =	120°	0°	30°	150°	90°	30°
	Calc.	J ==	2	8	6	7	0	6
Planar		X =	95°	25°	0°	120°	120°	0°
	Calc.	$\mathbf{J} =$	0	7	8	2	2	8
Boat		X =	75°	45°	30°	90°	150°	30°
	Calc.	J =	0	4	6	0	7	6
Observed	for:							
trans-3-	Alcohol	J =	0	~3	7.0	-	~7	-
trans-3-	Tosylate	e J=	0	~3	7.5	-	~7	-
cis-3-Al	cohol	$\mathbf{J} =$	0	~3	_	~1	_	5.8
cis-3-Ac	cetate	$\mathbf{J} =$	0	~3	_	~1	_	6.0
cis-3-To	osylate	$\mathbf{J} =$	unres.	unres.	-	~2	-	~6

TABLE 4. DETERMINATION OF CONFORMATION FROM COUPLING CONSTANTS IN BICYCLO[3.1.0]HEXYL SYSTEMS

Solvolysis rates and salt effects. Titrimetric solvolysis rate constants, k_t , for the *cis*- and *trans*-3-bicyclo[3.1.0]hexyl toluenesulfonates were previously¹ⁿ measured only in acetic acid, and these have now been studied also in formic acid and 60% aqueous acetone solvents. The data for these latter two solvents are summarized in Table 5. In acetic acid solvent, the previous data on the *cis*-tosylate have been supplemented with a more extensive study of salt effects, those of common ion tosylate salts as well as those of lithium perchlorate as a special salt. Titrimetric rates of acetolysis were measured for the 6,6-dideuterio-*cis*-tosylate as well, in order to provide a valid basis for comparison in connection with the kinetics of deuterium scrambling described below. In Table 6 are summarized the titrimetric acetolysis rate studies.

ROTs Epimer	Temp.	$(10^2 M)$	$10^4 k_{\rm t}$, (sec ⁻¹)
HCOOH ^a	······································		· · · · · · · ·
cis	25·0°	1.44	1·41±0·8
cis	25·0°	1.52	1.31 ± 0.6
trans	25·0°	1.46	0.285 ± 0.012
trans	25·0°	1· 49	0.299 ± 0.009
60% Acetone			
cis	25·0°	1.00	0-334±0-003
cis	50·0°	1.00	6·56±0·10
cis	50·0°	1.00	6·64±0·13
trans	25·0°		0.0152
trans	50·0°	1.00	0.313 ± 0.001
trans	75·0°	1.00	4.21 ± 0.02
trans	75·0°	1.00	4.21 ± 0.04

 TABLE 5. Some solvolysis rates of the 3-bicyclo[3.1.0]hexyl

 p-toluenesulfonates

"In the presence of 0-0300M lithium formate.

^bExtrapolated from values at other temperatures.

¹² ^a M. S. Bergqvist and T. Norin, Arkiv Kemi 22, 137 (1964); ^b K. Tori, Chem. Pharm, Bull. Tokyo 12, 1439 (1964); ^c H. E. Smith, J. C. D. Brand, E. H. Massey and L. J. Durham, J. Org. Chem. 31, 690 (1966); ^d A. Diefferbacker and W. von Philipsborn, Helv. Chim. Acta 49, 897 (1966).

Equilibration of deuterated cis-tosylate during solvolysis. Re-isolated deuterated cis-tosylate after varying solvolysis reaction times in acetic acid solvent showed a degree of deuterium equilibration which depended on the reaction time. The extent of tosylate equilibration was determined by an NMR analysis for cyclopropane methylene protons in the 6-position (τ 9.57). The signals for the four aromatic protons (τ 2.58), the one a-proton in the 3-position (τ 5.12) and the two tertiary cyclopropane protons (τ 8.77) were used as internal standards.

[ROTs]	~ 1.	[Salt]	
10 ² M	Salt	10º M	$10^{7} k_{\rm t} ({\rm sec}^{-1})$
1.43ª	_	-	237±5
1·73ª	-	_	243 ± 4
1·94ª	-		246±5
1.49		-	247±3°
2.18	-	-	247±5°
0.66	Bu₄NOTs	0.220	247 ± 3
0.92	Bu ₄ NOTs	0.200	246±7
0.92	Bu ₄ NOTs	1.00	250±5
1.15	LiOTs	3.00	290±6
1.25	LiOTs	5-00	308±5
0.99	LiClO ₄	0.40	540±5′
1.18	LiClO ₄	0.200	541±9
1.23	LiClO ₄	1.00	769±6'
2.05	LiClO ₄	2.00	1072±7°
0.93	LiClO ₄	3.00	1270±20 ^r
1.29	LiClO ₄	4.00	1490±20'
0.98	LiClO ₄	5.00	1664±14
1.39	LiClO ₄	6.00	1893±33 ^d
1.19	LiClO ₄	7.00	2156±19
1.06	LiClO ₄	8.00	2239±27"
1.48	LiClO ₄	9.00	2463±29
1.15	LiClO ₄	10.0	2630±40

TABLE 6. ACETOLYSIS RATES OF *cis*-3-BICYCL0[3.1.0]HEXYL *p*-TOLUENESULFONATE AT 50.0°

^e6,6 Dideuterio-ROTs.

^bPreviously reported:¹ⁿ 244 \pm 2, 247 \pm 5, 246 \pm 4.

Previously reported:¹ⁿ 1050 \pm 10.

^dPreviously reported:¹ⁿ 1890 \pm 30.

Previously reported:^{1#} 2210 \pm 20.

'Previously reported.ⁱⁿ

First order tosylate equilibration rate constants, k_{eq} , were evaluated with the aid of Eq. (1), where H and H_{∞} represent the number of cyclopropane methylene protons corresponding to time, t, and at infinity, respectively. Since complete equilibration of carbon atoms 2, 4 and 6 corresponds to 4/3 cyclopropane methylene protons, 4/3 was employed for H_{∞} in Eq. (1). As illustrated with the data for a typical run in Table 7, tosylate equilibration displayed satisfactorily first order kinetics.

$$2.303 \log \left[\frac{H_{\infty}}{H_{\infty} - H} \right] = k_{eq} t \tag{1}$$

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In the presence of increasing concentrations of added LiClO₄, tosylate equilibration becomes progressively less competitive with solvolysis, the first order k_{eq} values at a series of LiClO₄ concentrations being summarized in Table 8 along with the corresponding k_t values.

Solvolysis products. The products of acetolysis of the cis- and trans-3-bicyclo-[3.1.0]hexyl tosylates were re-examined using analytical methods which distinguished the cis- and trans-2 and 3-bicyclohexyl, and Δ^3 - and Δ^2 -cyclohexenyl substitution products, as well as the three olefinic products, bicyclo[3.1.0]hexene-2, 1,4-cyclohexadiene and 1,3-cyclohexadiene. The cis- and trans-2-bicyclo[3.1.0]hexyl and Δ^3 cyclohexenyl acetates and alcohols were available from another study.¹³

As summarized in Tables 9 and 10, the product from the *cis*-3-bicyclohexyl tosylate is almost exclusively *cis*-3-bicyclohexyl acetate, confirming the earlier work.¹ⁿ The *trans*-3-bicyclohexyl tosylate, on the other hand, gives rise to a product mixture¹ⁿ consisting of five isomeric acetates (70%) and three olefins (30%). The acetate mixture contains inverted *cis*-3-bicyclohexanol in the majority (54%), but appreciable quantities of hydrogen-shifted *cis*- and *trans*-2-bicyclohexyl and ring-opened Δ^3 - and Δ^2 -cyclohexenyl acetates are also present. The olefinic product is predominantly bicyclic (75%), but 1,4- and 1,3-cyclohexadienes constitute a fourth of the olefinic material.

Deuterium scrambling in acetolysis products. Examination by NMR of the cis-3acetate from acetolysis of the 6,6-dideuterio-cis-3-bicyclo-[3.1.0]hexyl tosylate provides a more accurate analysis of scrambling accompanying acetolysis than was possible in the earlier work.^{1m} The cis-3-acetate product contained 1.37 ± 0.05 protons in the 6-position (Table 1). For complete equivalence of carbon atoms 2, 4 and 6 in an intermediate, one would expect 4/3 cyclopropane methylene proton. Allowing for the ca. 3% 6-protium in the starting tosylate, 1.35 protons becomes the expected figure, and this is within experimental error of the observed figure. Thus, the present data confirm the earlier work with the 3-deuterated cis-tosylate.

% Equilibration	$10^5 k_{eq}$, sec ⁻¹	
0	-	
26	7.18	
48	7-27	
48	7.08	
67	7-39	
77	6.80	
-	% Equilibration 0 26 48 48 67 77	% Equilibration $10^5 k_{eq}$, sec ⁻¹ 0 - 26 7.18 48 7.27 48 7.08 67 7.39 77 6.80

TABLE 7. RATE OF EQUILIBRATION OF 0.040 M 6,6-DIDEUTERIO-cis-3-
bicyclo[3.1.0]hexyl p-toluenesulfonate during acetolysis at 50.0°
$k_{eq} = (7.12 \pm 0.14) \times 10^{-5} \text{ sec}^{-1}$

"With tosylate which had been carefully washed to remove traces of common ion salt.

The complete scrambling in the acetolysis product from *cis*-3-tosylate is in complete contrast with the result observed with the 6,6-dideuterio-*trans*-3-tosylate. The *cis*-3-acetate portion of the acetolysis product from *trans*-tosylate contained, within experimental error, no more cyclopropane methylene proton than was present in the original tosylate (Table 1).

¹³ E. C. Friedrich and M. Battiste, unpublished work.

DISCUSSION

Salt effects and ion pair return. As is clear from Table 6 and Fig. 1, lithium and tetra-n-butylammonium tosylates as added salts produce no common ion rate depression^{14a} in acetolysis of *cis*-3-bicyclo-[3.1.0]hexyl tosylate and give only small normal salt effects (Eqn 2). On the other hand, as was already clear from the previous work,¹ⁿ LiClO₄ shows the special salt effect^{14b, c} concerned with reduction of ion pair return.^{14b, c} A least squares treatment of the linear portion of the plot of k_t vs. [LiClO₄] in the 0.04–0.10 M LiClO₄ range gives a revised¹ⁿ estimate of 740 × 10⁻⁷

 [ROTs]	[LiClO ₄]		107 k (sec-1)	
10 ² M	10 ² M	k_{eq}	k_{t}	$(k_{eq} + k_{l})$	
 4.00		712±14	247	959	
4.77	0.500	539 ± 13	541	1080	
4.67	1.00	475 ± 10	769	1244	
7.35	2.00	465 ± 10	1072	1537	
7.35	3.00	436 ± 13	1270	1706	

Table 8. Summary of equilibration rates of 6,6-dideuterio-cis-3-bicyclo[3.1.0]hexyl p-toluenesulfonate during acetolysis at 50.0°

sec⁻¹ for k_{ext}^{o} , the intercept which includes the special but not the normal salt effect (Eqn 3). The general behavior of the *cis*-3-bicyclo[3.1.0]hexyl system in acetolysis is similar to that of the *threo*-3-*p*-anisyl-2-butyl analog,^{14b, c} which similarly shows a special salt effect but no common ion rate depression. As in similar situations,¹⁴ we can decide that acetolysis of *cis*-3-bicyclo[3.1.0]hexyl tosylate involves carbonium tosylate ion pairs but not dissociated carbonium ions.

$$k_{\rm t} = k_{\rm t}^{\rm o} \left[1 + b \, ({\rm MOTs}) \right]$$
 (2)

$$k_{t} = k_{\text{ext}}^{\text{o}} \left[1 + b \left(\text{LiClO}_{4} \right) \right]$$
(3)

$$(k_{eq} + k_t) = [k_{eq}^o + k_t^o] [1 + b (LiClO_4)]$$
(4)

As a consequence of ion pair return during acetolysis, *cis*-3-bicyclo-[3.1.0]hexyl toluenesulfonate deuterium labeled at C_6 , namely I-6D₂-OTs, tends to equilibrate and approach equal distribution of the label over carbon atoms 2, 4 and 6 (Tables 7 and 8). In other words, I-2D₂-OTs and I-4D₂-OTs are formed from I-6D₂-OTs.

	D-BIC	1010[3.1.0]	HEATL TOST	AIES		
Compound	10 ² M [Conc.]	Temp.	Olefin % yield	Bicyclo- [3.1.0] hexene	1,3-Cyclo hexadiene	1,4-Cyclo hexadiene
cis-3-Tosylate	7.57	75°	0.3 ± 0.2	ca 80	ca 0	ca 20
trans-3-Tosylate	6.77	75°	27 ± 2	74	5	21
	6.89	100°	b, c	75	6	19

 TABLE 10. OLEFIN PRODUCTS FROM ACETOLYSIS^a OF

 3-bicyclo[3.1.0]hexyl tosylates

^aIn dry AcOH containing 0.10M NaOAc.

^bLess exact analysis procedure employed.

"No internal standard.

¹⁴ e.g., ^a S. Winstein, E. Clippinger, A. H. Fainberg, R. Heck and G. C. Robinson, J. Amer. Chem. Soc. 78, 328 (1956); ^b S. Winstein and G. C. Robinson, *Ibid.* 80, 169 (1958); S. Winstein, R. Baker and S. Smith, *Ibid.* 86, 2072 (1964); ^c S. Winstein, B. Appel, R. Baker and A. Diaz, *The Chemical Society Special Publ.* No. 19, 109 (1965).

TABLE 9. ACETATE PRODUCTS^d FROM THE 3-BICYCLO[3.1.0]HEXYL TOSYLATES

Compound	10 ² M	Temp	Acetate % Yield	cis-3	Bicyclo[3 trans-3	.1.0]hexyl cis-2	trans-2	Cycloh ¹³ .	exenyl 42-
cis-3-Tosylate	7-57	75°	66	8	1±0-3	<0-3	<0-3	<0-3	<0.3
trans-3-Tosylate	6-77	75°	11	\$	<0·3	7.5	12	24	2.5
	68.9	100°	69 ₀	55	<0·3	ŝ	15	22	3
cis-3-Tosylate ^e	0-97	5 0-0°	<i>₅</i> 2.66	6-79	2.1	1	I	,	I
⁴ In AcOH containing 0-1	10M NaOAc.	n an							

^bLess exact analysis procedure employed. ^{660%} aqueous acetone solvent; product alcohol plus 0.1% olefin.



In formolysis the tendency for solvolyzing systems to display ion pair return is very much less^{14b, c} than in acetolysis, and this is again illustrated in the case of the *cis*-3-bicyclo[3.1.0]hexyl tosylate. Recovered I-6D₂-OTs from formolysis after 51% acid production showed less than 2% equilibration by ion pair return (Table 1), in contrast with the situation in acetolysis, where the same amount of acid production was accompanied by ca. 87% equilibration.

From the presently available data, the best estimate of the ionization rate constant, k_1 , in acetolysis of *cis*-3-bicyclo[3.1.0]hexyl tosylate is the sum of equilibration and titrimetric rate constants, namely ($k_{eq} + k_t$). As shown in Table 6, deuterium isotope effects in acetolysis of I-6D₂-OTs are relatively negligible, so k_t values for unlabeled tosylate may be employed for the labeled one. The ($k_{eq} + k_t$) values at different LiClO₄ concentrations summarized in Table 8 are plotted *vs*. [LiClO₄] in Fig. 1.

The reason that $(k_{eq} + k_t)$ is merely an estimate of the ionization rate constant is that it is not clear whether all ion pair return involves carbon atoms 1, 3 and 5 equally. To the extent that ion pair return favors the original carbon atom carrying the OTs group, namely carbon atom 3 in I-6D₂-OTs, $(k_{eq} + k_t)$ falls below k_1 . Thus, $(k_{eq} + k_t)$ represents a lower limit to k_1 . Further information could be gained from O¹⁸-equilibration studies,^{14c} but such data are not yet available.

As is clear from Fig. 1, the estimated ionization rate constants, $[k_{eq} + k_l]$, show a fair linear dependence on [LiClO₄], as is represented by Eq. (4). This is similar to other cases previously reported, ^{14b, c} where k_t values show a special salt effect, while k_1 values show a linear dependence on [LiClO₄]. As is also evident from Fig. 1, the special salt effect reduces ion pair return substantially but does not eliminate it. In this respect, the behavior of the *cis*-3-bicyclo[3.1.0]hexyl system is again similar to that of the 3-anisyl-2-butyl analog.^{14b}

While the necessary data are still lacking for a really complete analysis of ion pair return, it is instructive to treat the present acetolysis data according to the solvolysis scheme involving two varieties of ion pair (II and III), which was employed for the 3-anisyl-2-butyl and some other bridged carbonium ion systems¹⁴ (Eq 5).

Assuming that carbon atoms 1, 3 and 5 are equivalent in both II and III, that product formation is from III, and that the special salt effect eliminates ion pair return from III but not II, one may estimate the percent of return from each ion pair. The results



are summarized in Table 11 along with other data concerning salt effects. The derived values for percent return from II and III are fairly similar to those reported for the 3-anisyl-2-butyl system.¹⁴⁶

I II III

$$R-X \xrightarrow{k_{1}} R+X^{-} \xrightarrow{k_{2}} R+||X^{-} \xrightarrow{k_{4}^{III}} ROAc$$
(5)

cis/trans Solvolysis rate ratios. The solvolysis rate data in formic acid and aqueous acetone solvents, as well as the tosylate equilibration data in acetic acid solvent, provide new information on *cis/trans* reactivity ratios summarized in Table 12. In acetic acid at 50°, three values of this ratio are now available, depending on whether the ratio is based on k_t° , k_{ext}° or $(k_{eq}^\circ + k_t^\circ)$ for the *cis*-3-bicyclo[3.1.0]hexyl tosylate. The use of $(k_{eq}^\circ + k_t^\circ)$, which is closer to the ionization rate constant, k_1 , than either k_{ext}° or k_t° , leads to the highest *cis/trans* rate ratio in acetolysis, the value being 36.

In formic acid solvent, more ionizing and dissociating than acetic acid, k_t° for the *cis*-tosylate is essentially equal to the ionization rate constant, and the *cis/trans* rate ratio at 25° is 47, somewhat larger than the value in acetic acid. In the more nucleophilic 60% aqueous acetone solvent, where k_t° for the *cis*-tosylate is also very probably¹⁴ close to k_1 , the *cis/trans* rate ratio is 22, substantially smaller than in formic acid.

		LiClO₄	b Values LiOTs	Bu₄NOTs
$10^7 (k_{eq}^0 + k_t^0)$, sec ⁻¹	959 ^a	26		_
$10^7 k_{\rm ext}^0 {\rm sec}^{-1}$	740	26		-
$10^7 k_{eq}^{\circ}$ sec ⁻¹	712	-	-	-
$10^7 k_0^{1} \text{ sec}^{-1}$	247	-	5	ca. 0
$\frac{k_{eq}^{o}+k_{t}^{o}}{k_{t}^{o}}=\frac{k_{1}^{o}}{k_{t}^{o}}$	3.88			
$\frac{k_{ext}^{o}}{k_{ext}^{o}}$	3.0			
$1 - \frac{k_t^o}{k_t^o}$	0.74	(Fracti retui	ion of total m)	ion pair
$\frac{k_{-1}}{k_{-1}+k_{-2}}$	0.23	(Fracti pair	on of retur II)	rn from ion
$\frac{\hat{k}_{-2}}{k_{-2}+k_{\rm s}^{\rm III}}$	0 ·90	(Fracti pair	on of retur III)	n from ion

TABLE 11. SUMMARY OF SALT EFFECTS AND ION PAIR RETURN IN ACETOLYSIS OF *cis*-3-bicyclo[3.1.0]hexyl *p*-toluenesulfonate

"Least squares $(k_{eq} + k_t)$ vs. [LiClO₄] line gives 921 as the intercept $(k_{eq}^{\circ} + k_t^{\circ})$ value.

Solvolysis mechanisms. All of the available lines of evidence in solvolysis of the 3-bicyclo[3.1.0]hexyl tosylates point to preferred nonclassical ionization of the *cis*-epimer leading to the symmetrical trishomocyclopropenyl cation II. Writing k_d for the rate constant of this anchimerically assisted ionization and k_s for the anchimerically unassisted version, we can decide that the (k_d/k_s) ratio must be substantial. As regards products of solvolysis and deuterium scrambling, it is best to examine first the results with the *trans*-tosylate, since this epimer provides some perspective on the behavior of classical 3-bicyclo-[3.1.0]hexyl cations.^{1m, n}



Solvent	k	Temp	k _{cis} /k _{trans}	
НСООН	k ^o t	25·0°	47	
АсОН 60% Ме2CO	$\begin{cases} & (k_{eq}^{o} + k_{t}^{o}) \\ & k_{ext}^{o} \\ & k_{t}^{o} \\ & k_{t}^{o} \\ & k_{t}^{o} \end{cases}$	50-0° 50-0° 50-0° 25-0° 50-0°	36-0 27-8 9-3 22-0 21-1	

TABLE 12.	COMPARISO	N OF cis/tra	ans RATE	RATIOS IN	SOLVOLYSIS	OF
3-BICYCLO[3.1.0]HEXYL p-TOLUENESULFONATES						

Ionization of *trans*-tosylate III-OTs without anchimeric assistance (k_a) leads to the classical cation X. The latter may obviously collapse to inverted *cis*-acetate I-OAc. It may also set off a series of rearrangements via a $2\rightarrow 3$ hydride shift¹⁵ leading to 2-bicyclo[3.1.0]hexyl cations XI. The latter are related to the Δ^3 -cyclohexenyl cation XII by ring opening, and XII can lead to the allylic cyclohexenyl cation XIII by hydride shift. On this basis, one can understand the complex array of acetolysis products from *trans*-tosylate, the bicyclic acetates I-OAc, XIV and XV, the monocyclic acetates XIX and XX, bicyclic olefin XVI and the monocyclic dienes XVII and XVIII (Tables 9 and 10). Classical structures are written here for XI and XII only for simplicity, and a fuller discussion of the importance and structure of corresponding nonclassical cations will be given when the results of other studies of solvolysis of 2-bicyclo[3.1.0]hexyl and Δ^3 -cyclohexenyl systems are reported.¹³

The most striking aspect of the solvolysis of *trans*-tosylate III-OTs is the complete absence of equilibration of the deuterium label in the *cis*-acetate part of the product from III-6D₂-OTs (Table 1). Evidently, leakage from the classical cation X to the nonclassical ion II competes unusually poorly with its other reactions. This is in sharp contrast with the relatively efficient leakage into nonclassical structures in the case of ions like those in solvolysis of *endo*-norbornyl^{17a, b} and *cis*-2-bicyclo[3.2.0]-heptyl^{17c} bromobenzenesulfonates. Probably the most important reason for the very inefficient leakage from classical ion X to nonclassical II is that the geometry of X is unfavorable for this change. The *trans*-tosylate III-OTs, with a preferred boat conformation, has no reason to ionize to a cation with a chair conformation. Instead, the classical cation X probably contains a relatively flat 5-membered ring, and an unusual amount of reorganization would be required for conversion to the chair-like nonclassical cation II.

¹⁵ More direct formation of a 2-bicyclo[3.1.0]hexyl cation by C₂-hydrogen participation in ionization of III-OTs is conceivable. However, this is rendered less probable by consideration of effects of 2-alkyl substituents on rate of solvolysis.¹⁶

^{16 a} T. Norin, Tetrahedron Letters No. 1, 37 (1964); ^b Y. Lin, unpublished work.

^{17 a} S. Winstein and D. Trifan, J. Amer. Chem. Soc. 74, 1147 (1952); S. Winstein, E. Clippinger, R. Howe and E. Vogelfanger, *Ibid.* 87, 376 (1965); ^b S. Winstein, *Ibid.* 87, 381 (1965); ^c S. Winstein, F. Gadient, E. T. Stafford and P. E. Klinedinst, Jr., *Ibid.* 80, 5895 (1958); F. Gadient, unpublished work.

Turning to the acetolysis of the *cis*-tosylate I-OTs, the essentially exclusive formation of *cis*-acetate I-OAc with retention of configuration and complete equilibration of the label, the absence of elimination, the lack of rearrangement to 2-



bicyclo[3.1.0]hexyl and monocyclic structures, and the special salt effect and ion pair return phenomena provide a complete contrast with the behavior of the *trans*tosylate III-OTs. All of the results are explicable on the basis of the trishomocyclopropenyl intermediate II. Since we can expect a classical cation IX from *cis*-tosylate to behave analogously to the classical cation X from *trans*-tosylate, it is apparent that IX can play only a very minor role.

 (k_d/k_s) Ratios. Judging from the $1.0 \pm 0.3\%$ of inverted trans-accetate III-OAc and the $0.3 \pm 0.2\%$ olefin observed in acctolysis of the cis-tosylate (Tables 9 and 10), k_s may be of the order of 2% as great as k_d . In other words, (k_d/k_s) must be ca. 50. In the more nucleophilic 60% acctone solvent, (k_d/k_s) is probably slightly smaller, judging by the increased proportion of inverted trans-alcohol III-OH (2.1%; Table 9) from hydrolysis of cis-tosylate. The (k_d/k_s) ratios based on the nature of the solvolysis products from cis-tosylate are of the same order of magnitude and slightly larger than the cis/trans 3-bicyclo[3.1.0]hexyl solvolysis rate ratios (Table 12). According to this, k_s for trans-tosylate is slightly larger than k_s for cis-tosylate. This relationship of the k_s values happens to correspond with the greater ground-state free energy of cis-alcohol relative to trans.¹ⁿ

The (k_d/k_s) ratios in solvolysis of *cis*-3-bicyclo[3.1.0]hexyl tosylate are not large by comparison with some of the other known nonclassical systems. One of the factors lowering the (k_d/k_s) ratio in the present case is conformational, since the 3-bicyclo[3.1.0]hexyl systems prefer a boat conformation. This may be seen as follows.



Anchimerically assisted ionization of I-OTs may be formulated for present purposes as an ionization of the chair form (chair I-OTs) with the corresponding rate constant k_{α}^{c} . If we denote the equilibrium constant between boat and chair conformations by K, the apparent k_{Δ} is expressed by $[K/(1 + K)]k_{\Delta}^{c}$. Since K is considerably less than unity, the apparent k_{Δ} is well below the intrinsic k_{Δ}^{c} value appropriate to the favorable chair conformation.

Other reactions of 3-bicyclo[3.1.0] hexyl systems. In nitrous acid deamination of the cis- and trans-3-bicyclo[3.1.0] hexyl amines, each epimeric amine gives rise to a mixture of cis- and trans-3- and rearranged cis- and trans-2-bicyclo[3.1.0]hexanols, with only little scrambling of the deuterium label in the 3-alcohol product.^{4a} While the authors stressed the disparity between the products from deamination and those from tosylate solvolysis, we are struck by the considerable similarity between the results of deamination of the two epimeric amines and those in solvolysis of the trans-tosylate, the epimer which prefers to ionize classically. Thus, in deamination of the two epimeric amines and solvolysis of the trans-tosylate, one observes 3-bicyclo-[3.1.0] hexyl product with predominant inversion of configuration and little scrambling of a deuterium label, as well as rearranged 2-bicyclo[3.1.0]hexyl product with the trans-epimer preferred over the cis. This similarity in behavior is easily understandable if both epimeric amines deaminate classically, a possibility which could certainly be expected on the basis of all that is known about deamination.^{4a} Just as in solvolysis of trans-tosylate, a classical 3-ion from deamination rearranges to a 2-ion, but leakage between the classical 3-ion and the nonclassical trishomocyclopropenyl cation II is relatively inefficient.

In acid-catalyzed methanol addition to bicyclo[3.1.0]hexene-2, the formation of 2-bicyclo[3.1.0]hexyl ether, but no 3-product was observed.⁶ Apparently, a 2-bicyclo-hexyl cation is preferred over a 3-ion, even nonclassical II. This is in line with considerable other evidence¹³ that a 2-bicyclohexyl cation is more stable than II. For example, solvolysis rates of the 2-bicyclo[3.1.0]hexyl tosylates are very much greater than that of the *cis*-3-bicyclo[3.1.0]hexyl analog.¹³

Recently, the results of an interesting investigation of the electrolytic oxidative decarboxylation of the epimeric bicyclo-[3.1.0]hexane-3-carboxylic acids in aqueous pyridine at a smooth platinum electrode was reported.⁷ Only small proportions of the epimeric 3-alcohols were observed, the main products being the rearranged 2-alcohols with *cis*-epimer predominating slightly from *cis*-acid and the *trans*-epimer in slight excess from the *trans*-acid. Furthermore, no scrambling of a deuterium label was observed. While it is evident that the trishomocyclopropenyl cation II plays essentially no role in the reaction of either epimeric acid, no definitive mechanistic comparison between this electrolytic decarboxylation and tosylate solvolysis is yet

possible. As is clear from the excellent discussion provided,⁷ one does not know for certain when and how carbon dioxide is eliminated and how many reaction steps occur at the electrode surface.

Other formulations of the trishomocyclopropenyl cation. Recently, an alternative mechanistic formulation⁴ of cis-3-bicyclo[3.1.0]-hexyl tosylate solvolysis was suggested based on the observations in amine deamination⁴ and on substituent rate effects of phenyl groups in the 1- and 5-positions in solvolysis of cis-1,5-diphenyl-3-bicyclo[3.1.0]hexyl tosylate^{4b} XXI. According to Corey and Uda,^{4b} the latter represent a test of the hypothesis of the trishomocyclopropenyl intermediate in acetolysis of cis-3-bicyclo[3.1.0]hexyl tosylate. These authors expected 1,5-phenyl substituents to stabilize a trishomocyclopropenyl cation XXII and the corresponding ionization transition state relative to the ground state. Therefore, if acetolysis of cis-3-bicyclo-[3.1.0]hexyl tosylate involves direct formation of the trishomocyclopropenyl cation, the 1,5-phenyl substituents were expected to be markedly rate-accelerating. What was observed^{4b} was that the 1,5-phenyl substituents were slightly rate-retarding, but the products from acetolysis of the 1,5-phenylsubstitued cis-tosylate XXI were totally rearranged.



It was concluded⁴⁶ that the 1,5-phenyl substituent rate effect argued strongly against the idea of anchimerically assisted ionization of *cis*-3-bicyclo[3.1.0]hexyl tosylate to give directly the trishomocyclopropenyl cation II. As an alternative to the trishomocyclopropenyl cation II, they suggested structure XXIII. In this cation a weak interaction involving the vacant orbital at C_3 and the "loose" electrons of the 3-membered ring is responsible for stereo-specific reaction of the cation and presumably also the anchimeric assistance in its formation from covalent I-OTs. Further, rapid equilibration of three such "almost classical" nonclassical ions XXIII a, b, c is invoked to accommodate the observed complete scrambling of a deuterium label. Another symbol, namely XXIIId, has been employed recently by Dewar¹⁸ for ion XXIIIa.



¹⁸ This symbol is related to Dewar's π-complex symbol. In his recent review of nonclassical ions, Dewar has stated that all nonclassical carbonium ions are π-complexes and has employed corresponding symbols for them. [M. J. S. Dewar and A. P. Marchand, Ann. Review of Phys. Chem. 16, 321 (1965)]. The differences between our formulations and those of Dewar are largely semantic, and we plan to discuss this matter separately. As we have already remarked elsewhere.²⁶ many of Dewar's symbols are, in our opinion, clumsy and unnatural for the organic chemist.

In view of the complex blend of steric, inductive and conjugative effects of the phenyl substituents, the assumed test based on phenyl substituent rate effects is rather naive.¹⁹ The problem is rendered even more complex in the present case than it usually is because phenyl substituents modify the rate constant for anchimerically assisted ionization (k_d) by their effect on the boat \rightleftharpoons chair equilibrium constant K, as well as their effect on k_d^2 , the rate constant for anchimerically assisted ionization of the chair form. As regards the phenyl substituent effect on k_d^2 , this involves a stabilizing interaction between phenyl and cyclopropane groups²⁰ in the ground state. Further, it involves the blend of rate-retarding inductive and rate-accelerating conjugative effects appropriate to the degree of 1,3,5-three center bridging, charge development at C₁ and C₅, and the nature of the orbital hybridization at C₁ and C₅ in the ionization state. As regards the degree of bridging at the transition state in anchimerically assisted ionizations, there are good reasons for this to be considerably less than the degree of ionization of the heterolyzing bond in the ionization.¹⁷⁶

As is illustrated by a number of examples in the literature, the phenyl group, with its opposing inductive and conjugative effects, is a treacherous one as a probe for positive charge development at a carbon atom.¹⁹ Thus, phenyl groups are often less accelerating than alkyl groups and are sometimes even rate-retarding. In the case of *cis*-3-bicyclo[3.1.0]hexyl tosylate systems, 1-isopropyl or 1-methyl substitution is substantially rate accelerating,¹⁶ in contrast to the retardation by phenyl groups observed.⁴⁰ Alkyl and phenyl substituent effects in ionizing 3-bicyclo[3.1.0]hexyl systems have been studied more extensively in these laboratories^{2a, b, 166} and the results will be reported in detail elsewhere. These observed substituent effects,¹⁶ as well as the phenyl substituent effects observed,^{4b} provide no evidence in favor of three rapidly equilibrating "almost classical" non-classical ions XXIIIa, b, c as opposed to the symmetrical trishomocyclopropenyl cation II. Since we see no need or advantage for the substitution of three species (XXIIIa, b, c) for one (II), we recommend the application of "Ockham's razor" to the three species and the retention of the simpler interpretation.

There has appeared recently further theoretical and experimental support for the trishomocyclopropenyl formulation of the cation from ionization of *cis*-tosylate I-OTs. According to extended Hückel calculations,²¹ an unsymmetrical ion in the form of a chair to simulate Corey's "almost classical" non-classical ion XXIII is predicted to be slightly less stable than a classical ion with a planar 5-ring. On the other hand, the calculations²¹ predict a deep minimum in energy (ca. 1 eV) for a symmetrical trishomocyclopropenyl cation II, symmetrization of the chair being definitely favored.

In solvolysis of the epimeric 3-bicyclo[3.1.0]hexyl tosylates in aqueous acetone, a volume of activation of -17.4 cc/mole for the *trans*-epimer, almost identical with the values for the cyclopentyl and cyclohexyl analogs, and a less negative value of -13.9 cc/mole for the *cis*-epimer has been observed.²² The authors conclude that

¹⁹ See G. D. Sargent, *Quarterly Reviews* 20, pp. 367–371 (1966), for an excellent review of this situation.

²⁰ G. L. Closs and H. B. Klinger, J. Amer. Chem. Soc. 87, 3265 (1965).

²¹ R. Hoffmann, Tetrahedron Letters No. 43, 3819 (1965); R. Hoffmann, private communication.

²² W. J. leNobel and B. L. Yates, Abstracts of 150th Meeting of the American Chemical Society p. 39S. Atlantic City, N.J., Sept. 13-17 (1965).

there is significant charge delocalization in the *cis* ionization transition state, and the data therefore support the suggestion that the trishomocyclopropenyl cation II is the direct product of ionization of the *cis*-tosylate.

Other homoaromatic species. Since the first discovery and discussions^{1m-p} of the unsubstituted trishomocyclopropenyl cation II, a number of substituted trishomocyclopropenyl species have been recognized and studied, examples being XXIV¹⁶ and XXV,¹⁶ XXVI^{16b} and XXVII,^{16b} and XXVIII^{1g} and XXIX.^{1g} Thus, such species are of fairly general occurrence in carbonium ion reactions of the corresponding substrates.



As we have pointed out previously, the trishomocyclopropenyl species, with a delocalized 2-electron system, is only one type in the larger theme of homoaromaticity. Recently recognized examples of 6-electron homoaromatics are the monohomotropylium cation^{1c-e, 23a} XXX, its molybdenum tricarbonyl complex^{1d, e} XXXI, the 1-methylsubstituted cation^{23b} XXXII and the 1-hydroxy analog XXXIII,^{2a, 24} as



^{23 a} J. L. Rosenberg, J. E. Mahler and R. Pettit, J. Amer. Chem. Soc. 84, 2842 (1962); ^b C. E. Keller and R. Pettit, *Ibid.* 88, 604 (1966).

²⁴ M. Brookhart and M. Ogliaruso, unpublished work.

well as the bishomocyclopentadienide ion $2^{a, 25}$ XXXIV. Examples of 9- and 10electron systems are the monohomocyclooctatetraene anion radical^{1b, 2a} XXXV and the monohomocyclooctatetraene dianion^{1a, 2a} XXXVI, respectively.

EXPERIMENTAL

All m.ps and b.ps are uncorrected. IR spectra were measured on a Perkin-Elmer Model 21 spectrophotometer. NMR spectra were determined on a Varian Associates Model A-60 instrument using either TMS or hexamethyldisiloxane as the internal standard. In those cases where the hexamethyldisiloxane standard was employed, suitable corrections were made based on the observation that its chemical shift is 3.6 c/s at 60 Mc/s. downfield from TMS. Microanalyses were performed by Miss Heather King.

 Δ^3 -Cyclopentenol. A mixture of 19.6 g (0.520 mole) of finely powdered NaBH₄ and 200 g (3.10 moles) cyclopentadiene in 800 ml dry THF was placed in a 2 l. 3-neck flask fitted with an overhead stirrer, a N inlet tube and a press equalizing dropping funnel. To this well-stirred slurry, 97.6 g (0.686 mole) distilled BF₃-etherate in 200 ml dry THF was added dropwise over the period of 1 hr. During this addition the temp of the reaction mixture remained at about 25°. After the addition was completed, stirring was continued at room temp for 2 hr. Excess diene and solvent were then removed at about 45° with a water aspirator to give a white pasty mass which was pumped on at 1 mm to remove the last traces of diene. This was treated with 800 ml ether and 250 ml 3N NaOH and, with stirring, 250 ml of 30% H_2O_2 was added over a period of 3 hr at a rate such that the refluxing of the ether did not become too vigorous. The ether layer was then separated and the aqueous layer was extracted with 2-100 ml portions ether. The combined ether solns were washed with 3-100 ml portions sat NaCl aq, and the combined aq layers were continuously extracted with ether for 110 hr. After drying over MgSO₄ and concentrating on the steam bath through a short Rashig ring column, the previous ether fraction was distilled under vacuum through a 30-in. tantalum spiral column; b.p. 63-65° (30 mm), wt. 26.7 g, n_D^{25} 1.4685. Analysis by VPC showed that this material contained 93% Δ^3 -cyclopentenol and was contaminated with several percent each of dicyclopentadiene, cyclopentanol and Δ^2 -cyclopentenol. The pot residue from this distillation along with the material obtained from continuous extraction of the aqueous layer from workup was also distilled and this gave 30.15 g viscous oil, b.p. 104-107° (1.5 mm), n_D^{25} 1.4933.

3-Bicyclo[3.1.0]hexanone. A soln of 27 g (0.267 mole) CrO₃ in 40 ml distilled water was added with cooling over a period of 20 min to a mixture of 10.0 g (0.10 mole) cis-3-bicyclo[3.1.0]hexanol in 40 ml ether. The resulting mixture was then stirred at room temp for 4 hr before workup by addition of another 20 ml ether and extraction of the ether layer with 3-30 ml portions sat NaHCO₃ aq and 2-20 ml portions sat NaCl aq. After drying over MgSO₄ and concentration of the ether sols, the product was distilled through a 30 cm tantalum spiral column; b.p. 58-59° (30 mm), wt. 6.6 g n_{D}^{25} 1.4585.

trans-3-Bicyclo[3.1.0]hexanol. Reduction of 6.5 g 3-bicyclo[3.1.0]hexanone with 40 g of freshly distilled aluminum isopropoxide in 200 ml dry isopropanol was carried out in the usual manner at reflux over a period of 18 hr. Analysis of the product by VPC showed that it consisted of 60% of the desired *trans*-isomer and 40% of the *cis*. The *trans*-3-bicyclo[3.1.0]hexanol was separated by preparative scale VPC on a 1 in. $\times 2 \text{ m } 30\%$ 3-nitro-3-methylpimelonitrile on 40/60 mesh firebrick column at 127° and flash distilled at 30 mm to give 1.8 g viscous light yellow oil, n_{10}^{25} 1.4729.

Found: C, 73·39; H, 10·19. Calc. for C₆H₁₀O: C, 73·43; H, 10·27.

trans-3-Bicyclo[3.1.0]hexyl p-toluenesulfonate. This was prepared in the usual manner from trans-3-bicyclo[3.1.0]hexanol and p-toluenesulfonyl chloride in pyridine and recrystallized twice from methylcyclohexane; m.p. 70-72°.

cis-3-Bicyclo[3.1.0]hexyl p-toluenesulfonate. This material was prepared in the usual manner and recrystallized from methylcyclohexane; m.p. 51.2-52.8°.

Bicyclo[3.1.0]hex-2-ene. A rapidly stirred slurry of 10 g commercial potassium t-butoxide in 120 ml dry *p*-xylene was heated in an oil bath at 140° in a 200 ml round bottom flask fitted with a Claisen distilling head and a takeoff condenser. To this mixture, a soln of 5.0 g cis-3-bicyclo-[3.1.0]-hexyl *p*-toluenesulfonate in 30 ml *p*-xylene was added dropwise over the period of 1 hr. During the addition, about 10 ml volatile material distilled over. Slow distillation of the xylene was continued

^{25 a} J. M. Brown and J. L. Occolowitz, Chem. Comm. 376 (1965); ^b J. Nicholson, unpublished work.

for another hr until a total of about 30 ml distillate had been collected. This material was then redistilled to give 3.35 g product boiling at 80-90° which was shown by analytical VPC to contain 70% t-butanol. Purification by preparative scale VPC on a 1 in. $\times 2 \text{ m } 30\%$ 3-nitro-3-methylpimelonitrile column on 40/60 mesh firebrick at 40° gave 0.9 g bicyclo[3.1.0]hex-2-ene as a vile smelling colorless liquid, b.p. 71° (750 mm), n_D^{25} 1.4503. The NMR spectrum of this material in CCl₄ shows 6 separate groups of proton signals at $\tau 4.16$ (1H); 4.72 (1-H); 7.58 (2-H); 8.33 (2-H); 9.25 (1-H) and 10.22 (1-H). Its IR spectrum is consistent with the bicyclohexene structure and its UV spectrum in n-heptane showed no absorption above 230 m μ . At this point however, the baseline began rising toward a broad maximum at 202 m μ (t_{max} 4, 260).

2,2,4,4-Tetradeuterio-3-bicyclo[3.1.0]hexanone. A mixture of 1.0 g 3-bicyclo[3.1.0]hexanone, 15 g D₂O, 10 g dry dioxan and 0.25 g MeONa was prepared and allowed to stand at room temp for 3 hr. The product was worked up by extracting into pentane and distilled through a small one-piece apparatus at 30 mm (pot 70°); wt. 1.0 g. Examination of this material by NMR showed that complete exchange of the α -protons at positions 2 and 4 had taken place.

Dideuteriomethylene iodide. Base catalysed deuterium exchange of CH_2I_2 is feasible if the exchange mixture is saturated with iodide ion to reverse carbene formation.⁹ The method, however, which requires the use of EtOD and refluxing for several week-long periods, is not readily adapted to simple large-scale exchanges. By employing the iodide saturation technique, but using suitable quantities of dioxan and D₂O instead of EtOD, we have found that a nearly theoretical exchange of CH_2I_2 can be accomplished conveniently in only 10 hr reflux time. The extent of exchange was followed qualitatively by IR and measured quantitatively by NMR.

A mixture of 45 g NaI and 18 g MeONa was weighed into a 500 ml round bottomed flask and dried at room temp under 1 mm press for several hr. To this was then added 100 ml dioxan (freshly distilled from CaH₂), 60 ml (3·0 mole) 99·8% D₂O and 100 g (0·37 mole) CH₂I₂. The resulting mixture, with exclusion of light and protection from atm moisture, was then refluxed vigorously for 10 hr. After cooling to room temp, the entire mixture was extracted with 3-150 ml portions pentane and the combined pentane extracts washed with 1-100 ml portion water, dried over MgSO₄, and concentrated on an aspirator. Distillation through a short Vigreaux column gave 78·5 g material b.p. 68° (15 mm). Analysis by NMR using a chf internal standard indicated that 13·5% unexchanged protons still remained. Reexchange of this material using 50 g D₂O and proportionate amounts of the other reagents and solvent gave 48 g of CD₂I₂, b.p. 68° (15 mm), which contained 2·2 \pm 0·3% of two protons by quantitative NMR measurement.

The extent of exchange was also followed qualitatively by the disappearance of the major 3045 (m), 1105 (vs) and 710 (s) cm⁻¹ IR absorptions of diprotiomethylene iodide and the appearance of the 2290 (m) and 830 (vs) cm⁻¹ absorptions of CD_2I_2 . After only partial exchange, bands at 1075 (s) and 780 (s) cm,⁻¹ probably due to CHDI₂, were seen to appear and later disappear.

6,6-Dideuterio-cis-3-bicyclo[3.1.0]hexanol. A stirred slurry of 25 g (0.38 mole) freshly prepared Zn-Cu couple in 100 ml anhyd ether was treated with a small crystal of I₂. When the brown iodine color had disappeared, 45 g (0.168 mole) CD₂I₂ followed by 7.6 g (0.090 mole) chromatographed Δ^3 -cyclopentenol were added. After refluxing gently for about 15 min a very vigorous spontaneous reaction occurred with evolution of gas and heat. Gentle refluxing was continued for 2 hr before working up the reaction by addition of sat NH₄Cl aq, extraction with ether, and washing the combined ether extracts with sat Na₂CO₃ aq and NaCl sols. The ether soln was then concentrated on a steam bath through a Raschig ring column and the product distilled using a N capillary through a 30-in. glass spiral column to give 4.1 g material, b.p. 75–76° (30 mm), n_{25}^{25} 1.4763. Analysis by VPC on a 2 meter 30% 3-methyl-3-nitropimelonitrile supported on 80/100 mesh Chromosorb W column indicated that this fraction contained 93% of the bicyclic alcohol, the remainder being mainly unreacted Δ^3 -cyclopentenol. (Found: C, 71.84; H and D, 11.86. Calc. for C₆H₈D₂O: C, 72-00; H and D, 12:00).

Analysis for protium in the 6-position was based on NMR integration of the $\tau 9.53$ signal for the 6-protons using the $\tau 5.78$ (area 1) triplet of the 3-proton and the $\tau 8.80$ (area 2) multiplet of the 1- and 5-protons as internal standards. A similar method was used for the corresponding *p*-toluenesulfonate. (Table 1).

6,6-Dideuterio-cis-3-bicyclo[3.1.0]hexyl p-toluenesulfonate. A soln of 2.75 g (0.028 mole) 6,6dideuterio-cis-3-bicyclo[3.1.0]hexanol in 40 ml dry pyridine was cooled in an ice bath and treated while swirling with 5.8 g (0.030 mole) recrystallized p-toluenesulfonyl chloride. After standing in the refrigerator at $+4^{\circ}$ for 26 hr, this was worked up by pouring into ice and water and filtering with suction. The resulting solid was dissolved in about 20 ml ether, dried over MgSO₄, filtered, diluted with 90 ml pentane and cooled in a freezer at -24° to give 3.5 g white crystals. To eliminate any common-ion salts which might be present, this material was dissolved in 80 ml ether and washed with 10-100 ml portions distilled water. After drying over MgSO₂ and filtering, the ether was removed on an aspirator. Recrystallization at -24° from a mixture of 90 ml pentane and 20 ml ether gave 3.20 g white crystals, m.p. 48.0-50.0°. (Found: C, 61.41; H and D, 6.79. Calc. for C₁₃H₁₄D₂SO₃: C, 61.42; H and D, 7.08).

Tetra-n-butylammonium acetate. A soln of tetra-n-butylammonium hydroxide in MeOH was prepared from 25.9 g (0.070 mole) tetra-n-butylammonium iodide and 15 g (0.065 mole) AgO. After neutralization to a phenolphthalein in water endpoint with 4.10 g (0.068 mole) glacial AcOH, 100 ml benzene was added and the solvents removed on a rotary evaporator. The resulting oil was dissolved in 100 ml dry AcOEt which was also removed on a rotary evaporator. After drying in a vacuum desiccator at 1 mm press over P_2O_5 for 4 days, the resulting semi-solid material was recrystallized at -25° from a mixture of 100 ml benzene, 80 ml n-pentane and 30 ml AcOEt. The extremely hygroscopic crystals, wt. 15 g, were filtered in a dry box, washed with pentane, and dried in an Abderhalden over P_2O_5 at 80° and a press of 1 mm for 3 hr, followed by cooling while under vacuum for an additional 3 hr; m.p. 95–98°. (Found: C, 71.78; H, 13.07. Calc. for $C_{18}H_{39}NO_2$: C, 71.70; H, 13.04).

Titration of a sample of the salt by addition of excess perchloric acid in AcOH and back titration with AcONa in AcOH to a bromophenol blue endpoint showed that it contained 3.34 meq/g of basic acetate. (Calc. 3.32 meq/g).

6,6-Dideuterio-trans-3-bicyclo[3.1.0]hexyl p-toluenesulfonate. A mixture of 7.0 g (0.278 mole) 6,6-dideuterio-cis-3-bicyclo[3.1.0]hexyl p-toluenesulfonate in 500 ml dry acetone containing 9.2 g (0.332 mole) tetra-n-butylammonium acetate was heated at 50.0° for 6 hr. The soln was then concentrated to about 15 ml and poured into 75 ml pentane. This was washed successively with 3-50 portions of water and 2-20 ml portions dil. NaHCO₃ aq and dried over MgSO₄. The acetate obtained after removal of the solvent was reduced with 1.5 g LAH in about 40 ml ether. Direct conversion of the crude alcohol into its p-toluenesulfonate derivative was carried out in the usual manner with p-toluenesulfonyl chloride in pyridine followed by recrystallization from ether-pentane; wt. 4.2 g (60% yield); m.p. 71-72°.

Analysis for protium in the 6-position was based on integration of the $\tau 9.63$ and 10.05 regions in its NMR spectrum using the $\tau 2.30$ (area 4) quartet of the aromatic protons and the $\tau 5.50$ (area 1) quintet of the 3-proton as internal standards. As is clear from Table 1 no scrambling of deuterium occurred during the tosylate displacement reaction.

Solvolysis kinetics. Anhyd AcOH was prepared and acetolyses followed as previously described.^{26a} Anhyd HCO₂H was prepared and formolyses carried out as previously described,^{26b} except that runs were done in glass stoppered flasks because of the high rates involved.

Tetra-n-butylammonium acetate substitution kinetics. These were carried out at 25.0° in dry acetone using a procedure developed in these laboratories.^{26c} This involved titration for acetate ion by addition of excess perchloric acid in AcOH followed by back-titration with AcONa in AcOH to a bromophenol blue endpoint. Titration for fraction of elimination was done with MeONa in MeOH to a *p*-hydroxyazobenzene endpoint. In a typical run, where the concentration of salt was 0.01662M and of cis-3-bicyclo[3.1.0]hexyl *p*-toluenesulfonate was 0.00925M, k_2 was 3.4×10^{-3} 1 mole⁻¹ sec⁻¹ and the fraction of elimination, F_E , was 0.131 ± 0.004 . In a second run with 0.0139M salt and 0.0116M tosylate, k_2 was 3.1×10^{-3} 1 mole⁻¹ sec⁻¹ and F_E was 0.139 ± 0.006 .

Quantitative NMR measurements. All spectra were run as 10-20% sols in CCl₄. The areas of the proton signals of interest were determined by making at least 5 and sometimes as many as 10 successive integrations. An average of the values thus obtained was used in calculating the percent protium in the region measured. In a control experiment on a synthetic mixture of deuterated and undeuterated cis-3-bicyclo[3.1.0]hexyl p-toluenesulfonate calculated to contain 2-04% of 2 protons in the 6-position, a measured value of $3\cdot29 \pm 0.35\%$ of 2-protons was obtained.

Deuterium equilibration rates in solvolysis of 6,6-dideuterio-cis-3-bicyclo[3.1.0]hexyl p-toluenesulfonate. In a typical run, 0.1035 g 6,6-dideuterio-cis-3-bicyclo[3.1.0]hexyl p-toluenesulfonate was

^{26 a} S. Winstein, E. Grunwald and L. Ingraham, J. Amer. Chem. Soc. 70, 821 (1948); ^b S. Smith, A. Fainberg and S. Winstein, Ibid. 83, 618 (1961); ^c P. Beltrame and G. Biale, unpublished work. dissolved in 10-0 ml dry AcOH (0.01M in Ac₂O) and heated at 50-0° for 154 mins. This was then worked up by pouring into 100 ml pentane followed by washing with 3-20 ml portions of water and 1-20 ml portion 5% NaHCO₃ aq. After drying over MgSO₄ and filtering, the pentane was removed at aspirator press to give a white solid which was dissolved in 5 ml pentane and cooled to -24° . The white crystals obtained were filtered, dried in an Abderhalden over P₂O₅ at 1 mm press for 15 min and dissolved in CCl₄ to give approximately a 10% soln. Examination by NMR showed the presence of 0.64 protons in the τ 9.55 6-position. This corresponds to 48% complete scrambling of the 2, 4 and 6 positions in the unreacted tosylate. Runs containing added LiClO₄ were done in a similar manner.

A soln of 0.5787 g (0.0451M) 6,6-dideuterio-cis-3-bicyclo[3.1.0]hexyl p-toluenesulfonate in 50 ml of dry HCO₂H containing 0.2843 g (0.107M) HCO₂Li was allowed to react at 25.0° for 9 min. This was then worked up in a manner similar to that used for the acetolysis runs and the recovered tosylate, m.p. 49-51°, was examined by NMR for deuterium equilibration (Table 1).

Deuterium scrambling in the cis-acetate product from acetolysis of 6,6-dideuterio-cis-3-bicyclo[3.1.0]hexyl p-toluenesulfonate. A soln of 0.1282 g (0.0049M) 6,6-dideuterio-cis-p-toluenesulfonate in 10 ml dry AcOH which was 0.01106M in AcONa was placed in sealed ampoules and heated at 75.0° for 5 hr. The mixture was then poured into pentane, washed with water and dil. NaHCO₃ aq, dried over MgSO₄ and concentrated. After being purified by VPC on a 3-nitro-3-methylpimelonitrile column, the cis-3-acetate product was analysed by NMR measurements. The $\tau 4.88$ (area 1) 3proton signal was used as an internal standard for measuring the number of protons in the 6-position ($\tau 9.55$). An average of 5 consecutive integrations showed the presence of 1.37 ± 0.05 protons in this position. (Table 1).

Deuterium scrambling in the cis-3-acetate product from acetolysis of 6,6-dideuterio-trans-3-bicyclo-[3.1.0]hexyl p-toluenesulfonate. A soln of 0.5367 g 6,6-dideuterio-trans-3-bicyclo[3.1.0]hexyl ptoluenesulfonate was dissolved in 50 ml 0.01M AcONa in AcOH soln and heated at 75.0° for 45 hr. The acetate products were extracted into pentane, and the pentane soln washed several times with water and finally with dil. NaHCO₃ aq. This was then concentrated to about 1 ml, diluted with 5 ml MeOH and ozonized at 78° for 10 mins with a Welsbach Laboratory Ozonator set at 90 V and 0.03 scfm O₂ to remove all olefinic materials. The resulting soln was worked up by pouring into pentane, extracting with 2–15 ml portions of water, drying, and concentrating. The remaining acetates were then treated with LAH in ether and the *cis*-3-bicyclo[3.1.0]hexanol portion of the product was separated by VPC on a 2 meter 30% 3-nitro-3-methylpimelonitrile column. The protium content at the 6-position of this material was determined by NMR measurement using the $\tau 5.78$ (area 1) 3-proton as an internal standard. As shown in Table 1, no scrambling was detected.

Vapor phase chromatography. Acetolysis product analyses were carried out on a 2 meter 0.25 inch diam column packed with 30% by wt. 3-nitro-3-methylpimelonitrile on 80/100 mesh Chromosorb W. He was used as the carrier gas. On this column, the retention times in minutes of the compounds studied are as follows:

At 120°, 15 psi

Compound	Acetate	Alcohol
Cyclohexyl	11.0	12.5
trans-3-Bicyclo[3.1.0]hexyl	15.5	21.0
⊿ ³ -Cyclohexenyl	16.5	21.0
trans-2-Bicyclo[3.1.0]hexyl	17.0	18-5
cis-2-Bicyclo[3.1.0]hexyl	17.3	22.0
cis-3-Bicyclo[3.1.0]hexyl	17.5	16.5
A ² -Cyclohexenyl	18.8	1 9 ·0

At 50°, 7 psi

Compound	
Cyclohexene	5.5
Bicyclo[3.1.0]hex-2-ene	6.3
1,3-Cyclohexadiene	9.0
1,4-Cyclohexadiene	13·0
Benzene	19-0

Acetolysis products from trans-3-bicyclo[3.1.0]hexyl p-toluenesulfonate. As an example of the analysis procedure which was normally followed, 0-0848 g trans-3-bicyclo[3.1.0]hexyl tosylate was weighed into a Pyrex vial, dissolved in 4.969 ml 0.101M AcONa in dry AcOH soln, and 9.9 mg benzene internal standard weighed in from a hypodermic syringe. The vial was then sealed and heated at 75.0° for 45 hr.

At the end of this period, the vial was cooled and opened and about 0.3 ml of the AcOH soln was analysed directly for olefinic products using a VPC machine equipped for column backflushing. The olefin yield from the reaction was determined by comparison with the benzene internal standard.

To the remaining product soln was added 24.7 mg cyclohexyl acetate as an internal standard. This was then worked up by pouring into 40 ml pentane and extracting with 2-10 ml portions of water and 1-10 ml portion 5% NaHCO₃ aq followed by 1-10 ml portion of water. After drying over solid MgSO₄, the pentane soln was concentrated to about 5 ml through a short glass helice column. Analysis of this solution by VPC showed that a 71% yield of acetate products had been obtained as a symmetrical peak with a small trailing shoulder. This small shoulder amounted to about 2.5% of the total area and had a retention time like that of Δ^2 -cyclohexenyl acetate. Absence of any *trans*-3-bicyclo[3.1.0]hexyl acetate product was indicated by the lack of a leading shoulder on the main acetate peak.

The remaining pentane soln was then dil. with 5 ml MeOH and ozonized at -78° for 10 min in a large pyrex test tube with a Welsbach Laboratory Ozonator set at 90 volts and 0.03 scfm 0₂. This procedure has been shown to remove any olefinic acetate products from the mixture but not to disturb the bicyclic acetates. Workup was carried out by pouring into 40 ml pentane, extracting with 2–15 ml portions of water, drying over MgSO₄, and concentrating the pentane extract to about 4 ml through a short glass helice column. Analysis by VPC showed that the small Δ^2 -cyclohexenyl acetate shoulder had now disappeared and that the main acetate peak had decreased by about 23 %. This latter observation indicated that the original acetate product must have contained 24% Δ^3 cyclohexenyl acetate which was removed by the ozonolysis.

The pentane soln of the bicyclic acetates which still remained was diluted with 50 ml ether and treated with 0.25 g LAH for 30 min at room temp. After workup with NH₄Cl aq, drying with MgSO₄ and concentrating to about 4 ml, VPC analysis showed the presence of 3 bicyclic alcohol products. The first, with the retention time of *cis*-3-bicyclo[3.1.0]hexanol, amounted to 73% of the total; the second, with the retention time of *cis*-2-bicyclo[3.1.0]hexanol, amounted to 17% of the total; the third, with the retention time of *cis*-2-bicyclo[3.1.0]hexanol, amounted to 10% of the total.

Analyses were also carried out by LAH treatment of the acetate product followed by ozonolysis of the resulting alcohols. Although this procedure showed the same general product composition as the method described above, it is considered less accurate due to the partial solubilities of the alcohols in water.

Acetolysis products from cis-3-bicyclo[3.1.0]hexyl tosylate. Analysis was carried out using exactly the same procedures as were employed for the *trans*-tosylate. Only a trace of olefinic product was found, and neither of the 2-bicyclo[3.1.0]hexyl or cyclohexenyl acetate products were observed.

Stability controls on the acetolysis products. Controls were run on representative examples of the olefinic and bicyclic acetolysis products, and these were all relatively stable under the conditions used for acetolysis of the *cis*- and *trans*-3-bicyclo[3.1.0]hexyl tosylates.

Hydrolysis products from cis-3-bicyclo[3.1.0]hexyl tosylate. The tosylate (0-0097 M) was kept 3 hr at 50° in 60% aq acetone containing 0-0195 M NaHCO₃. The hydrolysis products were salted out with NaCl and extracted further with several portions of ether. The extract was dried over MgSO₄. VPC analysis on a 5% dioctyl phthalate on 80/100 Chromosorb W column using benzene as an internal standard showed 0.1% olefin with the retention time of the bicyclohexene. Concentration of the extract and VPC analysis on a 5% hyprose column showed the alcohol product to be 97.9% cis-3-bicyclo[3.1.0]hexanol and 2.1% trans-epimer.