[Contribution from the Department of Chemistry, University of California, Los Angeles 24, Calif.]

Homoconjugation and Homoaromaticity. III.[1] The 3-Bicyclo[3.1.0]hexyl System[2,3]

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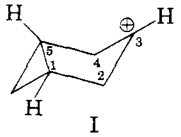
In order to study the nature of the theoretically interesting 3-bicyclo[3.1.0]hexyl cation, synthetic routes to 3-bicyclo[3.1.0]-hexanone and the epimeric bicyclohexanols have been devised. The *cis*- and *trans*-3-bicyclo[3.1.0]hexyl toluenesulfonates show contrasting behavior in acetolysis. Acetolysis is associated with a special salt effect and some anchimeric acceleration in the case of the *cis* epimer, but not the *trans*. Also, the *cis*-toluenesulfonate leads to *cis*-acetate with complete retention of configuration and no olefin, while the *trans*-toluenesulfonate gives rise to *cis*-acetate with complete inversion of configuration, together with considerable olefin. This behavior is suggestive of the intervention of a non-classical cation in acetolysis of the *cis*-toluenesulfonate, but not the *trans*.

Some years ago in another connection the question arose whether a 3-bicyclo[3.1.0.]hexyl cation I might have a symmetrical non-classical structure II. Examination of models suggested that the amount of reorganization and rehybridization required to make carbon atoms 1, 3 and 5 equivalent, as in the case of three alternate carbon atoms in chair cyclohexane, was not enormous. On the other hand, substantial quantum-mechanical delocalization energy could be anticipated on theoretical grounds[4,5] for a cation such as II. Therefore, structure II for the 3-bicyclohexyl cation appeared to us to be a definite possibility. It seemed to us also that the existence of a structure such as II would have far-reaching implications for organic chemistry.[1b] Therefore, we synthesized and studied the behavior of 3-bicyclo[3.1.0.]hexyl derivatives in acetolysis. Some of the results of this work are described and discussed in the present manuscript.



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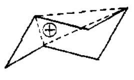
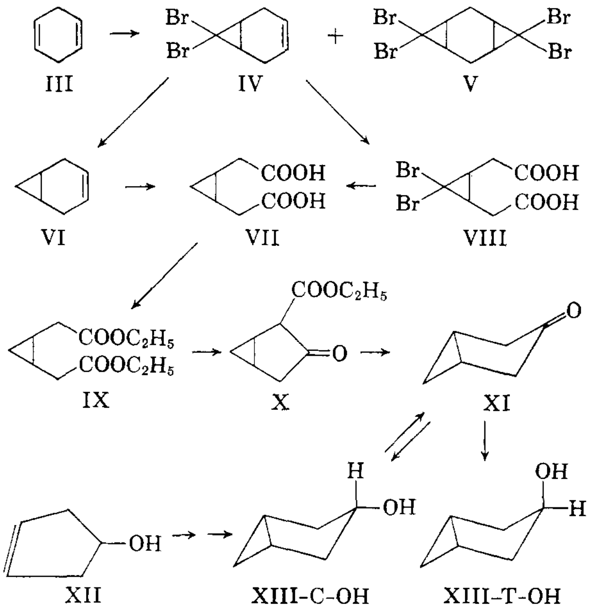

II

Synthesis of 3-Bicyclo[3.1.0.]hexanone.—Since neither 3-bicyclo[3.1.0.]hexanone (XI) nor the related alcohols XIII-C-OH and XIII-T-OH were known when we commenced this work, it was necessary to devise synthetic approaches to the 3-bicyclohexyl system. One of our two approaches involves formation of 3-bicyclo[3.1.0.]hexanone (XI) from cyclopropane-*cis*-1,2-diacetic acid (VII). The second method of synthesis involves methylene addition to Δ^3-cyclopentenol (XII) to yield 3-bicyclo[3.1.0.]hexanol (XIII-OH).



While our work was in progress, a Communication by Hofmann, Orochena and Yoho[6a] appeared which reported a synthesis of cyclopropane-*cis*-1,2-diacetic acid from 1,4-cyclohexadiene (III) by way of 7,7-dibromonorcar-3-ene (IV) and the 3,3-dibromocyclopropane-*cis*-1,2-diacetic acid (VIII). Our own synthesis of cyclopropane-*cis*-1,2-diacetic acid before the experimental details of their procedure were available[6b] was analogous to theirs, except that debromination of the dibromonorcarene IV was carried out before oxidation of the olefinic group to a dicarboxylic acid.

Treatment of 1,4-cyclohexadiene with dibromocarbene[7] gave rise to a satisfactory yield of dibromonorcarene[6b] IV, together with a small amount of tetrabromide[6b,8] V. Debromination of the dibromonorcarene IV proceeds in high yield with a large excess of sodium in moist methanol.[7,9,11]

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(1) First two papers in this series: (a) I, S. Winstein, J. Sonnenberg and L. de Vries, *J. Am. Chem. Soc.*, **81**, 6523 (1959); (b) II, S. Winstein, *ibid.*, **81**, 6524 (1959).

(2) This research was supported by a grant from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of this fund.

(3) The main results reported in the present manuscript were presented by S. Winstein at the Welch Foundation Conference on Molecular Structure and Organic Reactions, Houston, Tex., November 7-9, 1960.

(4) (a) E. Hückel, *Z. Physik*, **70**, 204 (1931); (b) J. D. Roberts, A. Streitwieser, Jr., and C. M. Regan, *J. Am. Chem. Soc.*, **74**, 4579 (1952).

(5) (a) M. Simonetta and S. Winstein, *ibid.*, **76**, 18 (1954); (b) C. F. Wilcox, Jr., S. Winstein and W. G. McMillan, *ibid.*, **82**, 5450 (1960).

(6) (a) K. Hofmann, S. F. Orochena and C. W. Yoho, *ibid.*, **79**, 3608 (1957); (b) K. Hofmann, S. F. Orochena, S. M. Sax and G. A. Jeffrey, *ibid.*, **81**, 992 (1959).

(7) W. E. Doering and A. K. Hoffmann, *ibid.*, **76**, 6162 (1954).

(8) A lachrymatory material, also reported by Hofmann, Orochena and Yoho,[6b] was observed in 2% yield in the present work. This proved to be benzyl bromide, formed probably from the adduct of dibromocarbene to 1,3-cyclohexadiene, a contaminant of the 1,4-cyclohexadiene employed.

(9) This dehalogenation also proceeds well with lithium and *t*-butyl alcohol in tetrahydrofuran[10] (unpublished work by P. Bruck).

(10) P. Bruck, D. Thompson and S. Winstein, *Chemistry & Industry*, 405 (1960).

(11) Norcar-3-ene has been prepared recently by H. E. Simmons directly from 1,4-cyclohexadiene with methylene iodide and the zinc-copper couple (H. E. Simmons, private communication).

Conversion of the norcarene VI to cyclopropane-*cis*-1,2-diacetic acid was carried out by ozonolysis in a 2:1 acetic acid–acetic anhydride mixture. The yield of acid (63%) was definitely better than in glacial acetic acid alone and far superior to that in ethyl acetate.[12]

The results of an attempted preparation of 3-bicyclo[3.1.0.]hexanone (XI) directly from the barium salt of cyclopropane-*cis*-1,2-diacetic acid were discouraging, so the Dieckmann condensation of the diethyl ester of the cyclopropane-*cis*-1,2-diacetic acid was resorted to. By this method the β-keto-ester X was obtained in over-all yields of 60–80% from the acid VII. By hydrolysis and decarboxylation the keto-ester X was converted to bicyclohexanone XI in 50% yield.

Methylene Addition to Δ^3-Cyclopentenol.—After we developed a convenient preparation of Δ^3-cyclopentenol[13] (XII), direct methylene addition appeared to provide an attractive possible alternative route to the 3-bicyclo[3.1.0.]hexyl system. Photolysis of diazomethane in the presence of Δ^3-cyclopentenol (XII) or its acetate in ether solution yielded no bicyclic derivative. The diethyl ether solvent was apparently attacked in preference to the olefinic group.[14] Preliminary work on the addition of dibromocarbene to Δ^3-cyclopentenyl derivatives showed that this method might be capable of development into a practical synthesis. However, our best results were obtained with the method of Simmons and Smith[16] for preparing cyclopropanes directly from olefins using methylene iodide and zinc–copper couple in ether.

A major problem in the olefin–methylene iodide synthesis of cyclopropanes is a good, reproducible zinc–copper couple. By modifying the procedure described by Hennion and Sheehan,[17] a fairly active zinc–copper couple was obtained which worked satisfactorily in the Simmons and Smith reaction. This method for preparing the couple is simple and easily reproducible. A similar procedure has recently been described.[18]

From the action of two parts methylene iodide and 4 parts zinc–copper couple on one part Δ^3-cyclopentenol (XII), a gratifying 75% yield of 3-bicyclo[3.1.0.]hexanol was obtained. Vapor phase chromatographic analysis of the product showed less than 0.5% of one of the two epimeric bicyclohexanols, the addition being highly stereospecific. From the configurational assignments in a later section of this paper, it is the *cis*-3-bicyclo[3.1.0.]hexanol (XIII-C-OH) which is produced by this method.

The above-described reaction of Δ^3-cyclopentenol is, apparently, the first example of the addition of iodomethylzinc iodide to an unsaturated alcohol. Not only does the hydroxyl group permit addition of methylene to the olefinic group, but it strongly facilitates this reaction. Thus, the reaction with Δ^3-cyclopentenol is much more rapid and proceeds with much higher yield than with Δ^3-cyclopentenyl acetate or cyclopentadiene. The latter two substances led to *ca.* 3% yields of bicyclic products under the identical conditions which gave rise to a high yield of bicyclohexanol from Δ^3-cyclopentenol.

Oxidation of the 3-bicyclo[3.1.0.]hexanol (XIII-C-OH) from the Simmons–Smith reaction by means of chromium trioxide in pyridine gave rise to bicyclohexanone XI in good yield.

3-Bicyclo[3.1.0.]hexanone and its Reduction.—The 3-bicyclo[3.1.0.]hexanone differs from the previously reported 2-bicyclo[3.1.0.]hexanone[19] in physical properties and in melting point and ultraviolet spectral properties of the corresponding 2,4-dinitrophenylhydrazones. The infrared spectrum of the 3-bicyclohexanone XI is summarized in the experimental section together with the ultraviolet spectrum of ketone XI and those of Δ^3-cyclopentenone, cyclopentanone and cyclohexanone for comparison.

The ultraviolet spectra of bicyclohexanone XI and its olefinic analog, Δ^3-cyclopentenone, are of some interest in connection with the subject of "interactions[3,5,20] between non-conjugated chromophores." In the $n \rightarrow \pi^*$-region of the spectrum (*ca.* 2800 Å.), neither 3-bicyclo[3.1.0.]hexanone (XI) nor Δ^3-cyclopentenone show the enhanced extinction coefficient characteristic of many β,γ-unsaturated ketones.[20a] Also, in the shorter wave length region of the spectrum down to *ca.* 1860 Å., neither compound shows evidence of any new $\pi \rightarrow \pi^*$ band such as those that appear in the spectra of certain β,γ-unsaturated ketones.[20b]

As regards the enhancement of the $n \rightarrow \pi^*$-extinction coefficient of certain β,γ-unsaturated ketones, Labhart and Wagniere[20b] have correlated this phenomenon with overlap of a non-bonding p-orbital on the oxygen atom with the bonding olefinic π-orbital. On this basis, no increase of $n \rightarrow \pi^*$-extinction coefficient would be anticipated for Δ^3-cyclopentenone, since the pertinent overlap integral has a value of zero for symmetry reasons.[3] Since Δ^3-cyclopentenone shows no increase in intensity of the $n \rightarrow \pi^*$-transition, none is expected for the bicyclohexanone XI.

Reduction of the 3-bicyclo[3.1.0.]hexanone by several methods gave rise to mixtures of the two epimeric *cis*- and *trans*-3-bicyclo[3.1.0.]hexanols (XIII-C-OH and XIII-T-OH). The reducing agents included lithium aluminum hydride in ether[21] at −78°, lithium tri-*t*-butoxyaluminohydride in tetrahydrofuran,[22] sodium borohydride in pyridine[23] and aluminum isopropylate in isopropyl

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[12] A. L. Henne and P. Hill, *J. Am. Chem. Soc.*, **65**, 752 (1943).

[13] (a) S. Winstein, E. L. Allred and J. Sonnenberg, *ibid.*, **81**, 5833 (1959); (b) E. L. Allred, J. Sonnenberg and S. Winstein, *J. Org. Chem.*, **25**, 26 (1960); (c) J. Sonnenberg, unpublished work.

[14] This is in line with Meerwein's report[15] that diazomethane reacts in diethyl ether to give ethyl n-propyl and ethyl isopropyl ether as products.

[15] H. Meerwein, H. Rathjen and H. Werner, *Ber.*, **75**, 1610 (1942).

[16] (a) H. E. Simmons and R. D. Smith, *J. Am. Chem. Soc.*, **80**, 5323 (1958); (b) **81**, 4256 (1959).

[17] G. F. Hennion and J. J. Sheehan, *ibid.*, **71**, 1964 (1949).

[18] R. S. Shank and H. Schechter, *J. Org. Chem.*, **24**, 1825 (1959).

[19] N. A. Nelson and G. A. Mortimer, *ibid.*, **22**, 1146 (1947).

[20] (a) R. C. Cookson and N. S. Wariyar, *J. Chem. Soc.*, 2302 (1956); (b) H. Labhart and G. Wagniere, *Helv. Chim. Acta*, **42**, 2219 (1959).

[21] A. Streitwieser, Jr., and W. D. Schaeffer, *J. Am. Chem. Soc.*, **79**, 6233 (1957).

[22] H. C. Brown and R. F. McFarlin, *ibid.*, **78**, 252 (1956); **80**, 5372 (1958).

[23] W. G. Dauben, G. J. Fonken and D. S. Noyce, *ibid.*, **78**, 2579 (1956).

alcohol.[24] The proportions of the two epimeric alcohols in the product could be determined by vapor phase chromatography, and the results are summarized in Table I.

TABLE I

FORMATION AND EQUILIBRATION OF BICYCLOHEXANOLS FROM 3-BICYCLO[3.1.0.]HEXANONE

Method	Temp., °C.	10^3 moles ketone	% yield (recovery)	Isomer ratio in distilled alcohol *cis:trans*
	Reductions			
$LiAlH_4$–ether	−78	29.0	85	89:11
		25.0		87.5:12.5
$LiAlH(OBu\text{-}t)_3$–THF	25	2.1		88:12
$NaBH_4$–pyridine	75	2.3	44	64 ± 2:36 ± 2
$Al(OPr\text{-}i)_3$–i-PrOH	75	31.3		40:60
		1.0		44:56
	Equilibration			
$Al(OPr\text{-}i)_3$–i-PrOH	82	2.5[a]	89	72:28
		2.1[b]	62	76:24

[a] 90:10 *cis:trans* mixture of the 3-bicyclo [3.1.0.]hexanols.
[b] 60:40 *cis:trans* mixture of the 3-bicyclo[3.1.0.]hexanols.

Equilibration of the two bicyclohexanols was carried out by the procedure of Eliel and Ro[24] using aluminum isopropylate with a trace of acetone in refluxing isopropyl alcohol. As summarized in Table I, a 74:26 equilibrium mixture of epimeric alcohols is approached from both directions.

From the 88:12 *cis*-rich alcohol mixtures obtained by hydride reduction of the bicyclohexanone, the pure *cis*-alcohol XIII-C-OH could be obtained by chromotography. The *trans*-alcohol XIII-T-OH could be obtained free from the *cis* epimer by chromatographic separation of the 60:40 *trans*-rich alcohol mixture from aluminum isopropylate reduction of the ketone.

Assignment of Configuration to the Bicyclohexanols.—The 3-bicyclo[3.1.0]hexyl derivatives can be expected to have a chair-like conformation resembling the chair conformation of cyclohexane and a puckered[25] conformation of the cyclopentane ring.[26] Due to the restriction of the fused 3-membered ring, the puckering of the cyclopentane ring occurs primarily at the 3-position and does not oscillate around the ring. For this reason the 5-membered ring may be expected to assume the C_s[27] or envelope[28] form, and the *cis*- and *trans*-3-bicyclo[3.1.0]hexanols will have largely *equatorial* and *axial* dispositions of the hydroxyl group, respectively. This is depicted in formulas XIII-C-OH and XIII-T-OH. With the available evidence it is possible to make a convincing assignment of configuration to the two bicyclohexanols obtained in reduction of 3-bicyclo[3.1.0]hexanone.

The results obtained in reduction of the bicyclohexanone and equilibration of the bicyclohexanols can be used to assign configurations to the epimeric 3-bicyclo[3.1.0]hexanols. Thus, reductions of relatively unhindered cyclohexanones with lithium aluminum hydride conventionally lead to a high proportion of the more stable *equatorial* alcohol,[23] while aluminum isopropylate tends to give more of the less stable *axial* alcohol. On this basis, the 3-bicyclo[3.1.0]hexanol favored at equilibrium and formed predominantly in the hydride reductions is the *equatorial cis*-alcohol XIII-C-OH. The bicyclohexanol which is formed predominantly by aluminum isopropylate reduction is therefore the axial *trans*-alcohol XIII-T-OH.

Observed relationships between other *cis* and *trans* pairs of cyclopentane derivatives as regards physical properties and relative stability also support the above configurational assignments to the 3-bicyclo[3.1.0]hexanols. In the cyclopentane series, the *trans* isomer tends to have the higher boiling point and refractive index.[29] With the 1,3-dimethylcyclopentanes, the *cis* isomer has been found to be the thermodynamically more stable one.[30] These are just the relationships which obtain with the *cis*-and *trans*-3-bicyclo[3.1.0]hexanols as regards boiling point, refractive index and relative stability.

Other chemical evidence strongly supports the above assignment of configuration to the 3-bicyclo[3.1.0]hexanols. One such piece of evidence is the facilitating stereospecific effect of the hydroxyl group of Δ^3-cyclopentenol in the Simmons–Smith reaction. This must be due to some participation by the hydroxyl group in the mechanism of methylene addition by the iodomethylzinc iodide.[16] Without attempting to go into details, the hydroxyl participation must involve oxygen atom coördination to zinc. This would make the methylene addition to the olefinic group occur *cis* to the hydroxyl group, *cis*-3-bicyclo[3.1.0]hexanol (XIII-C-OH) being the expected product from an hydroxyl group-facilitated reaction.[31] Another important piece of chemical evidence supporting the stated configurational assignment to the bicyclohexanols is the relative behavior of the corresponding toluenesulfonates XIII-C-OTs and XIII-T-OTs in acetolysis, which is described below and in the subsequent paper. Anchimeric acceleration of ionization of the *cis* epimer XIII-C-OTs compared to the *trans*, with formation of a non-classical carbonium ion, is in line with the present configurational assignment, but could not be understood with a reversed one.

Rates and Salt Effects in Acetolysis.—In Table II are summarized the measured first-order rates of acetolysis of the *cis*- and *trans*-3-bicyclo[3.1.0]-hexyl toluenesulfonates (XIII-C-OTs and XIII-T-OTs), as well as the cyclopentyl ester which was examined for comparison. Rates were measured at 50° and 75° in anhydrous acetic acid both with and without added sodium acetate or lithium per-

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[24] E. L. Eliel and R. S. Ro, *J. Am. Chem. Soc.*, **79**, 5992 (1957).

[25] (a) J. G. Aston, S. C. Schumann, H. L. Fink and P. M. Doty, *ibid.*, **63**, 2029 (1941); **65**, 341 (1943); (b) J. E. Kilpatrick, K. S. Pitzer and R. Spitzer, *ibid.*, **69**, 2483 (1947).

[26] In carbonyl stretching frequency (1739 cm.$^{-1}$), the 3-bicyclo-[3.1.0.]hexanone resembles cyclopentanone (1743 cm.$^{-1}$) much more closely than cyclohexanone (1709 cm.$^{-1}$). This resemblance exists also for the $n \rightarrow \pi^*$-absorption in the ultraviolet.

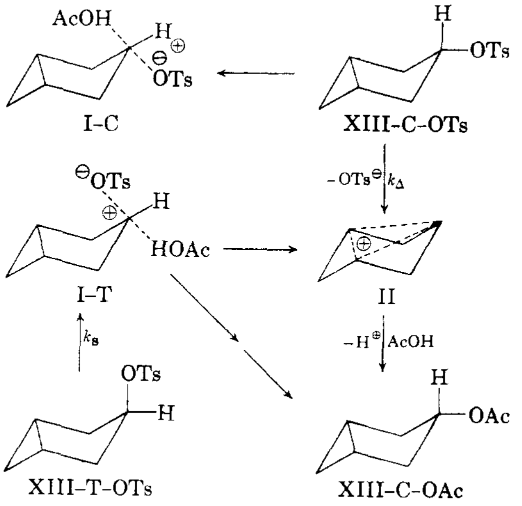
[27] K. S. Pitzer and W. Donath, *J. Am. Chem. Soc.*, **81**, 3213 (1959).

[28] F. V. Brutcher, *et al.*, *ibid.*, **81**, 4915 (1959).

[29] S. F. Birch and R. A. Dean, *J. Chem. Soc.*, 2477 (1953).

[30] J. N. Haresnape, *Chemistry & Industry*, 1091 (1953).

[31] The stereospecific facilitating effect of the hydroxyl group in the reaction of Δ^3-cyclopentenol with iodomethylzinc iodide is analogous to similar effects of the hydroxyl group in olefine addition reactions observed by Henbest [*e.g.*, H. B. Henbest and R. A. Wilson, *J. Chem. Soc.*, 1958 (1957)].



chlorate. The latter salt was added especially to determine whether acetolysis of any of the substances was subject to a special salt effect.[32]

With cyclopentyl toluenesulfonate, added sodium acetate increased the first-order titrimetric rate constant, k_t, by amounts corresponding to the so-called "normal" salt effect.[32,33] In Table III is summarized the corresponding b-value derived from the fit of the salt effects to the linear relation[33] 1, where $k_t{}^0$ is the titrimetric rate constant at zero salt concentration.

$$k_t = k_t{}^0\,[1 + b(\text{salt})] \qquad (1)$$

$$k_t = k_{\text{ext}}{}^0\,[1 + b(\text{LiClO}_4)] \qquad (2)$$

With the *cis*-3-bicyclo[3.1.0]hexyl toluenesulfonate (XIII-C-OTs), added 0.03 M sodium acetate caused an unusually large rate enhancement, the apparent b-value being 30 compared to 1–2 for the cyclopentyl and Δ^3-cyclopentenyl analogs. Added lithium perchlorate definitely gave rise to a steep special salt effect at low concentrations, followed by the normal, more shallow, linear pattern of salt effects at the higher concentrations. Fitting the normal linear portion of the k_t *vs.* [LiClO$_4$] plot to eq. 2, where $k_{\text{ext}}{}^0$ is a rate constant which includes the special but none of the normal salt effect, one obtains a $k_{\text{ext}}{}^0/k_t{}^0$ ratio of 3.2. This measures the magnitude of the special salt effect.[32] The efficiency of lithium perchlorate in the special salt effect may be gauged from the value of 4×10^{-3} M for $[\text{LiClO}_4]_{1/2}$, the salt concentration which introduces half of the special salt effect.

By contrast with its *cis* epimer, the *trans*-3-bicyclo[3.1.0]hexyl toluenesulfonate (XIII-T-OTs) displayed little or no special salt effect in its acetolysis. With this epimer, there is some uncertainty in the $k_t{}^0$ value because of difficulties discussed more fully in the Experimental section. However, any special salt effect of lithium perchlorate is quite small. For example, a $k_{\text{ext}}{}^0/k_t{}^0$ value of 1.17 is obtained by applying eq. 2 to the k_t values at 0.02, 0.04 and 0.08 M lithium perchlorate concentrations and comparing the derived $k_{\text{ext}}{}^0$ value with the $k_t{}^0$ values listed in Table III.

TABLE II

RATES OF ACETOLYSIS OF SOME TOLUENESULFONATES

[ROTs], 10^3 M	Temp., °C.	Other solute	Concn., 10^2 M	10^5 k, sec.$^{-1}$ Integ.	Graphical
			cis-3-Bicyclohexyl		
18.0[a]	50.0	....	..	2.31 ± 0.02	2.34
18.2[b]	50.0	....	..	2.53 ± .05	2.56[e]
18.2[b]	75.0	....	..	40.9 ± .3	40.9[e]
12.6[c]	50.0	....	..	2.44 ± .02	2.43
9.0[d]	50.0	....	..	2.47 ± .05	2.43
9.0[c]	50.0	....	..	2.46 ± .04	2.51
12.6[b]	50.0	NaOAc	3.05	4.60 ± .08	4.75[f]
12.6[b]	75.0	NaOAc	3.05	69.0 ± .29	72.0[f]
9.9[d]	50.0	LiClO$_4$	0.40	5.40 ± .05	5.36
12.3[c]	50.0	LiClO$_4$	1.00	7.69 ± .06	7.64
9.4[d]	50.0	LiClO$_4$	2.00	10.5 ± .1	10.5
9.3[d]	50.0	LiClO$_4$	3.00	12.7 ± .2	12.7
12.9[c]	50.0	LiClO$_4$	4.00	14.9 ± .2	14.9
12.4[c]	50.0	LiClO$_4$	6.00	18.9 ± .3	19.0
12.5[c]	50.0	LiClO$_4$	8.00	22.1 ± .2	22.1
			trans-3-Bicyclohexyl		
17.7[g]	75.0	....	..	....	3.80
5.3[g]	75.0	....	..	....	4.80
8.6[h]	50.0	....	..	0.266 ± 0.023	..
13.2[g]	75.0	NaOAc	3.05	....	5.10
8.3[h]	50.0	NaOAc	3.05	....	0.295
8.1[g]	75.0	LiClO$_4$	2.00	7.66 ± 0.07	7.64
8.0[g]	75.0	LiClO$_4$	4.00	9.92 ± .26	9.89
7.6[g]	75.0	LiClO$_4$	8.00	14.1 ± .2	14.0
			Cyclopentyl		
22.3	50.0	....	..	3.60 ± .13	..
29.5	50.0	NaOAc	3.05	3.76 ± .05	..
28.2	75.0	NaOAc	3.05	54.1 ± .8	..

[a] Toluenesulfonate prepared from an 89:11 *cis:trans* mixture of the 3-bicyclo[3.1.0]hexanols; m.p. 46–48°. [b,c] Toluenesulfonates prepared from the chromatographed *cis*-3-bicyclo[3.1.0]-hexanol; m.p. 51.6–51.8° and 51.5–52.°0, respectively. [d] Toluenesulfonate prepared from *cis*-alcohol from the Simmons and Smith reaction; m.p. 50.6–51.6°. [e] At 50.0°; $\Delta H^{\ddagger} = 24.1$ kcal./mole; $\Delta S^{\ddagger} = -5.0$ e.u. [f] At 50.0°; $\Delta H^{\ddagger} = 23.7$ kcal./mole; $\Delta S^{\ddagger} = -5.2$ e.u. [g] Toluenesulfonate, m.p. 70.5–72.0°. [h] Toluenesulfonate, m.p. 70.8–71.3°.

Solvolysis Products.—Vapor phase chromatographic analysis using *n*-decane as an internal standard showed that the product from solvolysis of the *cis*-3-bicyclo[3.1.0]hexyl toluenesulfonate (XIII-C-OTs) in acetic acid containing sodium acetate is quantitatively the bicyclohexyl acetate. The extent of olefin formation must have been less than 0.5%. On the other hand, the *trans*-3-bicyclo[3.1.0]hexyl toluenesulfonate (XIII-T-OTs) gave rise only to 67% of bicyclohexyl acetate. The remaining 33% must be attributed to olefin formation. Three new peaks were observed in vapor phase chromatography of the product, two of them with retention times similar to that of cyclohexene and the other with a somewhat longer retention time. However, the hydrocarbon fraction was not investigated further.

In order to determine the proportions of *cis* and *trans* isomers in the acetate products from solvolysis, they were reduced with lithium aluminum hydride and the product alcohols were ex-

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[32] S. Winstein, *et al.*, (a) *J. Am. Chem. Soc.*, **76**, 2597 (1954); (b) *Chemistry & Industry*, 664 (1954); (c) *Experientia Suppl. II*, 137 (1955); (d) *J. Am. Chem. Soc.*, **80**, 169 (1958).

[33] S. Winstein and A. H. Fainberg, *ibid.*, **78**, 2763 (1956).

TABLE III

SUMMARY OF OBSERVED SALT EFFECTS IN ACETOLYSIS OF SEVERAL TOLUENESULFONATES

ROTs	Temp., °C.	Special salt effect	10^5 k, sec.$^{-1}$ k_{ext}^0	k_t^0	k_{ext}^0/k_t^0	b-Values LiClO$_4$	Av. fit % of k	b-Values NaOAc
cis-3-Bicyclo[3.1.0]hexyl	50.0	Yes	7.87	2.48	3.17[a]	22.9	1.2	30[b]
trans-3-Bicyclo[3.1.0]hexyl	75.0	[f]	5.60	4.80	1.17	18.8	0.7	2.0[c]
Δ^3-Cyclopentenyl[e]	50.0	No	0.436	0.438	0.99	30.4	1.0	1.8
Cyclopentyl	50.0	No		3.60				1.5
Cyclohexyl[d]	50.0	No		0.179		37.2		

[a] $(LiClO_4)_{1/2}$ is 4×10^{-3} M. [b] Based on one point; includes contribution from the special salt effect. [c] Value observed at 50.0° is 3.6. [d] Data of Fainberg and Winstein.[34] [e] Data of Joseph Sonnenberg.[13c] [f] Small or none.

amined vapor phase chromatographically using a carbowax column. The product alcohols from both *cis*-and *trans*-toluenesulfonates were nearly pure *cis*, the one from *cis*-toluenesulfonate being at least 98.5% *cis*, and the one from *trans*-toluenesulfonate being at least 99.5% *cis*. The results are summarized in Table IV. A control experiment on a 70:30 *cis:trans* mixture of 3-bicyclo-[3.1.0]hexyl acetates showed that the acetates quantitatively survived the reaction conditions and confirmed the reliability of the whole workup and analytical procedure (Table IV).

Discussion.—Examining the available evidence for any indication that a unique carbonium ion species may intervene in solvolysis of a 3-bicyclo-[3.1.0]hexyl toluenesulfonate, we come first to the question of anchimeric acceleration. As is brought out in Table V, the rate data do give some indication of slight anchimeric acceleration of solvolysis of the *cis*-3-bicyclo[3.1.0]hexyl toluenesulfonate (XIII-C-OTs). However, the usual problem exists regarding what is the best compound for comparison with the *cis*-toluenesulfonate in assessing anchimeric acceleration in the latter. Cyclopentyl and cyclohexyl toluenesulfonates, either of which might be suggested as models, differ between themselves by a factor of 20 in acetolysis rate at 50°.

TABLE IV

SUMMARY OF PRODUCTS OF ACETOLYSIS OF 3-BICYCLO-[3.1.0]HEXYL TOLUENESULFONATES WITH 0.10 M SODIUM ACETATE

Compound	Temp., °C.	[ROTs], 10^2 M	Time, hr.	Products, % Acetate	Olefin	Alcohol compn., % *cis*	*trans*
cis-ROTs	50.0	8.1	42.0	100	0[a]	98.5	1.5
trans-ROTs	75.0	8.5	38.5	66.5	33[b]	100	0[a]
	75.0	4.9	38.5	67.8		...	..
cis- and *trans*-ROAc[c]	75.0	7.3	38.5	101	0[a]	70	30

[a] < 0.5%. [b] Difference between 100 and % yield of acetate. [c] 70:30 *cis:trans* mixture.

Reference to Table V shows that the *trans*-3-bicyclo[3.1.0]hexyl toluenesulfonate ranks between the cyclohexyl and Δ^3-cyclopentenyl analogs in reactivity, all three of these esters having closely similar acetolysis rate constants. On the other hand, the k_t for the *cis*-toluenesulfonate XIII-C-OTs is larger than that of the *trans* epimer by *ca.* one power of ten. Taking k_{ext}^0 for the *cis*-toluenesulfonate XIII-C-OTs, since this is a better lower limit to the ionization rate constant, makes the *cis:trans* rate ratio *ca.* 30. This estimate of the degree of anchimeric acceleration of ionization of the *cis*-toluenesulfonate would be increased further if we allowed for the fact that the *axial* disposition of the toluenesulfonoxy group in the *trans*-ester XIII-T-OTs may be associated with slight steric acceleration (as in the case of the *axial* *cis*-4-*t*-butylcyclohexyl[35] ester).

TABLE V

REACTIVITIES OF SOME p-TOLUENESULFONATES IN ACETOLYSIS AT 50.0°

ROTs	10^5 k, sec.$^{-1}$	Rel. k
Cyclopentyl	3.60	20.0
Δ^3-Cyclopentenyl	0.438	2.4
trans-3-Bicyclo[3.1.0]hexyl	.266	1.5
Cyclohexyl[34]	.179	1.00
cis-3-Bicyclo[3.1.0]hexyl	2.48, 7.87[a]	13.8, 44[a]

[a] Based on k_{ext}^0.

Another indication that there is something unique about the solvolysis of the *cis*-toluenesulfonate XIII-C-OTs is the contrast between the *cis* and *trans* epimers XIII-C-OTs and XIII-T-OTs as regards stereochemistry and products of acetolysis. Thus, the *trans* epimer gives acetate XIII-C-OAc with complete inversion of configuration and a substantial fraction of elimination product. This is similar to the behavior of both the *trans*- and *cis*-4-*t*-butylcyclohexyl toluenesulfonates.[35] On the other hand, the *cis*-3-bicyclo[3.1.0]hexyl toluenesulfonate (XIII-C-OTs) gives rise to *cis*-acetate XIII-C-OAc with complete retention of configuration and no accompanying olefin.

The most striking indication that a unique species intervenes in acetolysis of the *cis*-toluenesulfonate XIII-C-OTs is the special salt effect which is present in its acetolysis. A special salt effect does not occur in acetolysis of the cyclopentyl, Δ^3-cyclopentenyl[13c] and cyclohexyl analogs and is either absent or quite small with the *trans*-toluenesulfonate XIII-T-OTs. Here, as in other cases,[32] the special salt effect can be taken to be diagnostic for the occurrence of a carbonium ion pair with a relatively stable unique structure for the cation.

The anchimeric acceleration, stereochemistry, lack of olefin formation and special salt effect observed in its acetolysis all suggest that ionization of *cis*-3-bicyclo[3.1.0]hexyl toluenesulfonate (XIII-C-OTs) may indeed lead very predominantly to a non-classical ion II which leads stereospecifically to *cis*-acetate XIII-C-OAc. The anchimerically unassisted ionization to the classical ion pair IC (rate

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(34) A. H. Fainberg and S. Winstein, *J. Am. Chem. Soc.*, **78**, 2780 (1956).

(35) S. Winstein and N. J. Holness, *ibid.*, **77**, 5562 (1955).

constant k_s) would, on this basis, be negligible. On the other hand, ionization of the *trans*-toluenesulfonate XIII-T-OTs, with the wrong configuration for anchimeric assistance, is entirely anchimerically unassisted (k_s). The classical interneiate I-T leads partly to olefin, while the non-classical ion II does not.

The indications of a unique intermediate in acetolysis of the *cis*-toluenesulfonate appeared to us to warrant isotopic labeling experiments which would provide a definite check for the occurrence of a cation with the symmetrical structure II. These are described and discussed in the following paper.

Experimental

7,7-Dibromonorcar-3-ene.—Dibromocarbene[7] was allowed to react with a 69:31 1,4-cyclohexadiene–benzene mixture prepared by the procedure of Wibaut and Haak.[36] An equimolar amount of bromoform (330 g., 1.7 moles) in dry *t*-butyl alcohol (90 ml.) was added in one portion to the 1,4-cyclohexadiene (140 g., 1.75 moles) in benzene. To this stirred solution a 50 molar % excess of 1 *M* potassium *t*-butylate in *t*-butyl alcohol was slowly added. The reaction product in 1 liter of pentane was washed with a total of 10 liters of water to remove most of the *t*-butyl alcohol. This precipitated tetrabromide V, which was washed with pentane and dried. This product (66 g.), m.p. 205–206° (reported[6b] m.p. 205–207°), was obtained in 18% yield based on the available bromoform.

The remaining yellow pentane solution was dried over anhydrous magnesium sulfate. The solvent was evaporated and the residue was distilled at 2.8 mm., a portion of the material boiling at 68° and the remainder at 91°. Absolute ethanol was added to the distillate and the product cooled to give a first crop of 95.5 g. of 7,7-dibromonorcar-3-ene, m.p. 37.8–38.8° (reported[6b] m.p. 36.8–37.0°). After a second and third crop were obtained, the remaining mother liquor was redistilled. The distillate partly solidified after standing in the refrigerator. After decanting off a small liquid portion which was used later, the solid was recrystallized from absolute alcohol. A total of 188 g. (44% yield based on the available diene and bromoform) of 7,7-dibromonorcar-3-ene was obtained. The recrystallizations were unpleasant because of the presence of a lachrymatory material.

The small liquid portion remaining was distilled through a Podbielniak column and, following a small forerun (b.p. 39.2–40.0° at 6.7 mm.), about a 5-g. fraction, b.p. 56–59° at 3.8 mm., was collected. This colorless fraction had strong lachrymatory character and appeared to be benzyl bromide on the basis of its infrared spectrum. It formed an *sec*-alkylisothiouronium picrate, m.p. 188–188.5° (reported[37] m.p. 188° for the benzyl bromide derivative).

Norcar-3-ene.—The 7,7-dibromonorcar-3-ene (48 g., 0.19 mole) was dissolved in ether (200 ml.) in a 5-liter 3-neck flask cooled in ice and equipped with a stirrer, Dry-Ice condenser, addition tube and dropping funnel. Metallic sodium (3 g. atom) was added in roughly 2-cc. pieces during the course of the reduction. At the same time wet methanol (10 ml. of water in 300 ml. of methanol) was added dropwise with rapid stirring; 2.25 hours was required for the addition of the sodium. After the reaction mixture was stirred for 2 hours, ether (50 ml.) was added, followed by additional sodium (1 g. atom) and wet methanol (200 ml.). The reaction mixture was stirred an additional 3 hours (sodium was still present) and then water (350 ml.) was added cautiously, followed by the addition of ether (50 ml.). The combined ether solution was separated and the aqueous layer extracted successively with pentane (100 ml.), ether (150 ml.) and pentane (150 ml.). The combined organic layer was washed with water (4 × 50 ml.), the last wash being neutral to litmus. The combined organic layer was dried over anhydrous magnesium sulfate and anhydrous calcium chloride, filtered, and distilled carefully to remove most of the pentane and ether. The residue was fractionally distilled through a Podbielniak column and two colorless fractions were collected: (a) 1.05 g., b.p. 84–115°; and (b) 13.95 g. (77%), b.p. 115–115.5° at 751 mm., $n^{25.0}\text{D}$ 1.4740. A small colored residue remained. In another similar run, 0.5 mole of 7,7-dibromonorcar-3-ene yielded an 88% yield of norcar-3-ene, b.p. 115–115.5°. Vapor phase chromatographic analysis (v.p.c.) of fraction b on didecyl phthalate indicated one symmetrical peak.

Anal. Calcd. for C_7H_{10}: C, 89.29; H, 10.71. Found: C, 88.88; H, 10.63.

The hydrocarbon is a colorless liquid with a slight odor. It adds bromine in carbon tetrachloride, and in 95% ethanol immediately decolorizes aqueous permanganate. The in-infrared spectrum contains absorption bands at 1648 (C=C) and 1018 cm.$^{-1}$ (cyclopropane ring), as well as other bands at 3052(sh), 2995, 2865, 2832, 1440, 731 and 654 cm.$^{-1}$. The ultraviolet spectrum in cyclohexane shows no maximum above 2150 Å., the extinction coefficient at 2160 Å. being only 59.

Cyclopropane-*cis*-1,2-diacetic Acid.—The norcar-3-ene (12 g., 0.128 mole) dissolved in glacial acetic acid (160 ml.) and acetic anhydride (80 ml.) was ozonized (3% approximate weight concentration of the ozone) between 0° and 20° until ozone was detected in the exit tube. Ozone was consumed immediately and the solution was clear during most of the reaction. Toward the end of the reaction, the reaction mixture became cloudy and precipitated some white semi-solid. The excess ozone in the system was flushed out with an oxygen stream before 30% hydrogen peroxide (35 ml.) and water (240 ml.) were added and the solution refluxed overnight.

The following day the water and acetic acid were removed by distillation at atmospheric pressure; the last traces were removed with the aid of a water aspirator. A slightly yellow solid remained which was recrystallized from ethyl acetate and washed with ether. An over-all yield of 63% of crude diacid was obtained in four experiments. Ozonolyses in acetic acid and/or ethyl acetate gave much poorer yields (30–45%). The initial sample of the diacid was obtained using glacial acetic acid as the solvent. A sublimation and recrystallization from ethyl acetate gave crystals, m.p. 131–132° (reported[6] 131–133°).

Anal. Calcd. for $C_7H_{10}O_4$: C, 53.16; H, 6.37. Found: C, 53.11; H, 6.32.

2-Carbethoxy-3-bicyclo[3.1.0]hexanone.—A mixture of cyclopropane-*cis*-1,2-diacetic acid (19.0 g., 0.12 mole), absolute ethanol (43.2 ml., 0.36 mole), dry toluene (22 ml.) and concentrated sulfuric acid (0.10 ml.) was placed in a 200-ml. distilling flask connected with a downward condenser and magnetic stirrer. When heated in a 110–115° oil-bath, an azeotropic mixture of alcohol, toluene, and water began to distil at about 75°. Distillation was suspended when most of the toluene–alcohol azeotrope (76.7°) had distilled over. Distillation was continued after a fresh portion of alcohol and toluene was added and the procedure repeated. Toluene was finally added to remove all the ethanol by azeotropic distillation. The diester was not isolated but the residue used directly in the Dieckmann condensation.

After small pieces of sodium (4.5 g., 0.20 mole) were added at one time to the cooled residual toluene solution of the diester, the mixture was heated slowly to 110° while being stirred magnetically. (Approximately 3 ml. of absolute ethanol was added to reduce the induction period.) After a few minutes, a vigorous reaction commenced, and some ethanol distilled out. A cake of the sodium compound separated and the solution became orange. Dry toluene was added in order to keep the mixture fluid enough for efficient stirring. After the spontaneous reaction had abated, the mixture was refluxed for 30 minutes before being decomposed with ethanol. The cooled reaction mixture was then slowly poured into cold 10% acetic acid and the organic layer separated with the aid of pentane. The remaining aqueous portion was then extracted successively with two portions of pentane, toluene and ether. The united orange organic extract was then washed successively with water, 5% sodium bicarbonate, and water until neutral. Without drying the organic solution, the ether, pentane and toluene were removed by distillation. The residue was distilled under reduced pressure and this gave rise to 16.0 g. (79% over-all yield) of the keto-ester.

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(36) J. P. Wibaut and F. A. Haak, *Rec. trav. chim.*, **67**, 85 (1948).

(37) N. D. Cheronis and J. B. Entrikin, "Semimicro Qualitative Organic Analysis," Interscience Publishers, Inc., New York, N. Y., 2nd Ed., 1957.

An analytical sample was prepared in a similar manner in 60% over-all yield, b.p. 85–86° (2.2 mm.), $n^{27}D$ 1.4642.

Anal. Calcd. for $C_9H_{12}O_3$: C, 64.27; H, 7.19. Found: C, 64.21; H, 7.28.

The β-keto-ester is a colorless pleasant-smelling liquid which gives a purple color with ferric chloride. The infrared spectrum shows a small O–H absorption at 3460 cm.$^{-1}$. Other absorption bands occur at 1751, 1722, 1024 and 810 cm.$^{-1}$.

3-Bicyclo[3.1.0]hexanone.—Barium hydroxide crystals (28.2 g., 0.165 mole) were added to a mixture of water (282 ml.) and 2-carbethoxy-3-bicyclo[3.1.0]hexanone (16.0 g., 0.095 mole) in a 500-ml. round-bottom flask. The mixture was refluxed for 30 minutes (decomposition sets in suddenly) and then about 30 ml. was distilled and collected in pentane. The aqueous phase was returned to the flask and distillation continued. This process was repeated until ketone no longer distilled over (three times).

The combined pentane solution was first dried over calcium chloride for 15 minutes, then over anhydrous magnesium sulfate. The mixture was filtered, and then pentane was removed by distillation. The remaining residue was fractionally distilled through a Podbielniak column. Two fractions were collected and a small residue remained: (a) 0.44 g. (5%), b.p. 50–54° (24 mm.); (b) 3.92 g. (43%), b.p. 54–55° (25 mm.), $n^{2.50}D$ 1.4590.

The analytical sample was prepared in a similar manner in 44% yield. On distillation through a Podbielniak column, the ketone boiled at 51–52° at 18 mm., $n^{25.0}D$ 1.4590.

Anal. Calcd. for C_6H_8O: C, 74.97; H, 8.39. Found: C, 74.69; H, 8.43.

The bicyclohexanone is very volatile and has a pleasant odor resembling that of cyclopentanone. The analytical sample exhibited only one peak on v.p.c. using a Carbowax column. The infrared and ultraviolet spectra of the ketone are summarized in Table VI and VII.

TABLE VI

OBSERVED INFRARED ABSORPTION BANDS OF 3-BICYCLO-[3.1.0]HEXANONE

Cm.$^{-1}$	Cm.$^{-1}$	Cm.$^{-1}$	Cm.$^{-1}$	Cm.$^{-1}$	Cm.$^{-1}$
3462w	1763shs	1457m	1137s	962w	808m
3052m	1739vs	1407ms	1075w	918w	770shw
2915s	1700shm	1263s	1038m	903w	753m
2860ms	1643vw	1157s	1022shw	847vw	

The orange 2,4-dinitrophenylhydrazone of 3-bicyclo-[3.1.0]-hexanone was prepared in the usual manner and was recrystallized from aqueous alcohol; m.p. 149.2–149.8°; λ_{max}^{EtOH} 3595 Å., ε 23,100; $\lambda_{max}^{CHCl_3}$ 3625 Å., ε 23,600.

Anal. Calcd. for $C_{12}H_{12}O_4N_4$: C, 52.17; H, 4.38; N, 20.28. Found: C, 52.42; H, 4.15; N, 20.31.

***cis*- and *trans*-3-Bicyclo[3.1.0]hexanols.**—A mixture of these alcohols was obtained from lithium aluminum hydride reduction of the bicyclohexanone. After the lithium aluminum hydride (1.1 g., 0.029 mole) was stirred magnetically with anhydrous ether (100 ml.) for 1 hour, the 3-bicyclo-[3.1.0]hexanone (2.8 g., 0.029 mole) in ether (75 ml.) was added dropwise over 30 minutes while being cooled in a Dry Ice–acetone-bath. The solution was stirred for 4 hours at −78°, then an additional hour at room temperature. While the solution was being cooled in ice, water (2.2 ml.) followed by 10% sodium hydroxide (1.75 ml.) was added. After the reaction mixture was stirred for 2 hours, the inorganic salts were filtered and the ethereal solution dried over magnesium sulfate. Distillation through a Podbielniak column gave 2.40 g. (85%) of 3-bicyclo[3.1.0]hexanol, b.p. 68–69.5° (17.5 mm.), $n^{25.0}D$ 1.4774. Analysis by v.p.c. using a 2-meter column containing 25% Carbowax 1500 (polyethylene glycol) on 40–80 mesh firebrick operated at 140–150° showed the product to be an 89:11 *cis–trans* mixture.

Anal. Calcd. for $C_6H_{10}O$: C, 73.43; H, 10.27. Found: C, 73.61; H, 10.35.

The bicyclohexanone was reduced also on a small scale (200 mg.) with lithium tri-*t*-butoxyaluminohydride in tetrahydrofuran[22] and sodium borohydride in pyridine,[23] and the resulting alcohol mixtures were determined by v.p.c. (Table I).

TABLE VII

ULTRAVIOLET SPECTRA OF SEVERAL KETONES

Water		Isoöctane		Isoöctane	
λ_{max}, Å.	ε	λ_{max}, Å.	ε	λ_{max}, Å.	ε
		Cyclohexanone			
<1855[a]	1980	<1860[a]	840	2910sh	14.9
2764	21.0	2768sh	12.8	2950sh	14.6
		2847sh	14.6	3054sh	11.6
		Cyclopentanone			
<1850[a]	1260	1897	1100	2894	17.1
2799	22.0	2597	6.2	2935sh	15.5
		2684	9.5	2998	18.5
		2711sh	10.2	3057sh	13.0
		2768sh	13.3	3110	15.0
		2799	13.7	3234	6.7
		2864sh	16.2		
		Δ^3-Cyclopentenone			
<1860[a]	4390	<1860[a]	4300	2887sh	11.0
2593	48.5	2592	6.2	2941sh	10.0
		2676	8.1	2991	10.9
		2765	10.0	3104	8.4
		2803sh	9.7	3230	4.2
		2862	11.1		
		3-Bicyclo[3.1.0]hexanone			
<1855[a]	1460	<1860[a]	1510	2860sh	13.7
2797	18.9	2600	5.7	2888	14.7
		2683	8.7	2993	15.1
		2766	11.8	3102	11.3
		2799	12.1	3217	4.6

[a] Not a maximum.

A 20.4-g. (0.1 mole) quantity of distilled aluminum isopropoxide was added to 3-bicyclo[3.1.0]hexanone (3.0 g., 0.031 mole) in isopropyl alcohol (98 ml.) in a flask equipped with a downward condenser. The mixture was magnetically stirred and heated at 92° for 17 hours. After the reaction mixture was cooled, water (2 ml.), ether (40 ml.) and then 16 *M* sodium hydroxide (25 ml.) were added. The aqueous portion was extracted three times with pentane and ether and then the combined organic layer washed with brine. After the solution was dried over anhydrous magnesium sulfate, pentane and ether were distilled at atmospheric pressure, and the isopropyl alcohol was removed carefully at 96 mm. Using a Podbielniak column, a slightly yellow liquid (3.35 g.) with a distinct odor, distilling mostly at 78° (20 mm.), was obtained. A yellow residue remained. The v.p.c. analysis of the distillate indicated a 40:60 *cis–trans* mixture of the 3-bicyclo[3.1.0]hexanols, along with a 10% impurity of unknown identity.

For the equilibration of the *cis*- and *trans*-bicyclohexanols, isopropyl alcohol (40 ml.), acetone (0.7 ml.) and the 3-bicyclo[3.1.0]hexanol (0.24 g.) were added to a small quantity of freshly distilled aluminum isopropoxide in a 100-ml. round-bottom flask. After the reaction mixture was refluxed for 112 hours, 5 ml. was distilled and the cloudy mixture refluxed for another 24 hours. The mixture was worked up in the usual way, and the bicyclohexanols were isolated by distillation and analyzed by v.p.c. (Table I).

By careful chromatography on alumina, essentially pure *cis*-3-bicyclo[3.1.0]hexanol was obtained from the product of reduction of bicyclohexanone with lithium aluminum hydride. Distillation of the earlier fractions eluted with pentane yielded a material, b.p. 69° (19.5 mm.), $n^{25}D$ 1.4771, with a *cis*-alcohol content greater than 98.5%.

From 900 mg. of *cis*-3-bicyclo[3.1.0]hexanol the toluenesulfonate, m.p. 52.0–52.4°, was prepared in the usual way in 66% yield.

Anal. Calcd. for $C_{13}H_{10}O_3S$: C, 61.88; H, 6.39; S, 12.71. Found: C, 61.77; H, 6.22; S, 12.49.

The toluenesulfonate formed directly from the lithium aluminum hydride reduction product from 3-bicyclo[3.1.0]-hexanone had m.p. 46–48°.

By systematic chromatography on alumina, 3-bicyclo-[3.1.0]hexanol, b.p. 75–76° (18 mm.), with the *trans* content greater than 97%, was obtained from the alcohol mixture which arises from aluminum isopropoxide reduction of bicyclohexanone. From 450 mg. of the *trans*-alcohol the toluenesulfonate, m.p. 71–72°, was prepared in 60% yield in the usual manner.

Anal. Calcd. for $C_{13}H_{16}O_3S$: C, 61.88; H, 6.39; S, 12.71. Found: C, 62.02; H, 6.22; S, 12.76.

Treatment of Δ^3-Cyclopentenol and its Acetate with Diazomethane.—An ethereal solution of diazomethane (0.02 mole) was added to Δ^3-cyclopentenol[13] (0.014 mole) in ether and irradiated by an internal ultraviolet source until the solution became colorless. This reaction was performed at three temperatures, room temperature, 0° and −78°. In all three experiments, a v.p.c. analysis of the ether residue on a Carbowax column showed only starting alcohol and several peaks right after the ether solvent peak. The starting alcohol was recovered in each case.

An ethereal solution of diazomethane (0.024 mole) and Δ^3-cyclopentenyl acetate [13,38] (0.014 mole) was allowed to stand several months at 0° until the yellow color disappeared. After distilling away most of the ether, the residue was analyzed by v.p.c. using a didecyl phthalate column. No bicyclic acetate was visible; only the starting acetate and a few new peaks, which appeared right after the ether solvent peak, were observed. The starting acetate was recovered as the corresponding alcohol.

Zinc–Copper Couple.—Couple A was one described by Howard[39] and recommended by Simmons and Smith.[16]

Couple B was prepared as follows. Mallinckrodt analytical reagent zinc dust (24.8 g., 0.38 mole) was washed successively with 3% hydrochloric acid (4 × 20 ml.), distilled water (3 × 25 ml.), 2% copper sulfate solution (2 × 40 ml.), and finally distilled water (3 × 50 ml.). The last water washings were decanted directly on a Büchner funnel. After most of the water was removed by suction (too much air drying by suction caused the couple to heat up), the zinc–copper couple was dried using a rotary vacuum dryer, and a uniform finely divided active couple was obtained. On a molar scale, less active couple was produced.

Methylene Addition to Δ^3-Cyclopentenyl Acetate and Cyclopentadiene.—Zinc–copper couple A (5.4 g.) was added in one portion to a solution of Δ^3-cyclopentenyl acetate [13,38] (6.3 g., 0.05 mole) and methylene iodide (13.4 g., 0.05 mole) in ether (50 ml.). The reaction mixture was stirred magnetically and refluxed for 48 hours with no noticeable effect. After the reaction mixture was filtered, the crude acetate was analyzed by v.p.c. on a Carbowax column. This analysis indicated the formation of 10–18% bicyclohexyl acetate, the yield varying with the couple and the reaction time. Since the *cis*- and *trans*-3-bicyclohexyl acetates are not separated on a Carbowax column, nor on didecyl phthalate or silicone columns, the acetate mixture was reduced to alcohol with lithium aluminum hydride in ether and worked up by the usual basic treatment. Analysis of the alcohol by v.p.c. on a Carbowax column showed it to be predominantly *cis*, but the presence of a little methylene iodide makes the analysis inaccurate because its retention time falls between those of the two 3-bicyclo[3.1.0]hexanols. On a didecyl phthalate column, methylene iodide is well separated from the bicyclohexanols, but these two alcohols are not separated from each other. The infrared spectrum of a 3-bicyclo[3.1.0]-hexanol fraction obtained by preparative v.p.c. of a combination of various reaction residues indicated that the bicyclohexanol contained no more than 10% of the *trans* epimer.

In an experiment similar to the one above, refluxing tetrahydrofuran being substituted in place of ether as the solvent, Δ^3-cyclopentenyl acetate gave only 1% bicyclic acetate as shown by v.p.c. analysis. The reaction of Δ^3-cyclopentenyl acetate and methylene iodide with a moderately active zinc–copper couple B gave a 2% yield of bicyclic acetate as shown by v.p.c. analysis after 48 hours of gentle refluxing in ether. The same zinc–copper couple worked smoothly with Δ^3-cyclopentenol, however.

An ethereal solution of methylene iodide (26.8 g., 0.1 mole) and freshly distilled cyclopentadiene (34 g., 0.52 mole) was added to a moderately active zinc–copper couple B (13.1 g., 0.2 mole), and the mixture was magnetically stirred and refluxed for 48 hours. Work-up of the reaction mixture and v.p.c. examination of the fraction of intermediate boiling point indicated the presence of two new components with retention times appropriate for C_6-hydrocarbons. However, these were present in only very low yield, and the reaction mixture was not examined further.

***cis*-3-Bicyclo[3.1.0]hexanol from Δ^3-Cyclopentenol.**—Anhydrous ether (60 ml.) was added to zinc–copper couple B prepared from 24.8 g. of zinc dust in a flask equipped with a magnetic stirrer, dropping funnel, reflux condenser and drying tube. To the above slurry, an intimate mixture of methylene iodide (53.4 g., 0.20 mole) and Δ^3-cyclopentenol[13] (8.4 g., 0.10 mole) was added rapidly. This was followed by anhydrous ether (40 ml.). After a short induction period (5 min.), an exothermic reaction occurred which lasted for several minutes.

After the mixture was refluxed for an hour, it was cooled and filtered through a Super-Cel pad on a Büchner funnel to remove the excess zinc which was thoroughly washed with ether. The filtrate was distilled carefully at atmospheric pressure (bath temperature to 80°) and a yellow solution remained to which pentane was added. On addition of water to the organic solution, a very slight exothermic reaction was noticed and a massive white precipitate formed. More water and pentane were added and the mixture was again suction filtered on a Super-Cel pad. Even after repeated pentane and ether washings, the smell of bicyclic alcohol persisted on the pad.

The pentane solution was separated and the aqueous portion continuously extracted with ether–pentane mixtures. The combined organic material developed a light purple color which was removed by washing with aqueous sodium thiosulfate. After the organic solution was dried over anhydrous magnesium sulfate, a crude distillation gave 7.6 g. of material, b.p. 63–69° (17 mm.). On v.p.c. analysis this crude product proved to be *cis*-3-bicyclo[3.1.0]hexanol contaminated with up to 2% of methylene iodide, 2% of the starting Δ^3-cyclopentenol, and the impurities contained in the latter, namely, 4% cyclopentanol and 2% of an unidentified component.[13] Fractionation of the crude product gave rise to a material, b.p. 68° (18 mm.), n^{25}D 1.4781, whose infrared spectrum was identical to that of authentic *cis*-3-bicyclo[3.1.0]hexanol, n^{25}D 1.4770.

The fractionated *cis*-3-bicyclo[3.1.0]hexanol (containing a trace of methylene iodide) gave rise to a *p*-toluenesulfonate, m.p. 46.2–49.5°. This crude product was dissolved in ether and washed with sodium thiosulfate and water. Recovery and recrystallization of the toluenesulfonate led to a 66% yield of colorless product, m.p. 50.5–51.4°, m.p. 50.5–51.5° on admixture with authentic *cis*-toluenesulfonate. On acetylation with acetic anhydride in pyridine, the fractionated alcohol gave rise to a quantitative yield of acetate. The analytical sample had b.p. 71° (15 mm.), n^{25}D 1.4492.

Anal. Calcd. for $C_8H_{12}O_2$: C, 68.54; H, 8.63. Found: C, 68.49; H, 8.65.

Methylene iodide, which was not effectively removed from the *cis*-3-bicyclo[3.1.0]hexanol by fractional distillation, was eliminated by chromatography on alumina. Analysis of the chromatographed alcohol by v.p.c. on a Carbowax column showed the absence of *trans*-alcohol, and on didecyl phthalate the absence of methylene iodide.

In another experiment starting with Δ^3-cyclopentenol (7.8 g.) and a moderately active zinc–copper couple B, a work-up involving one filtration was used. After being refluxed for an hour, the reaction mixture was cooled to room temperature. When water was added, the reaction mixture became exothermic and ether refluxed for several minutes while precipitation occurred. The mixture was then suction filtered and washed several times with ether. The organic layer was separated and the aqueous layer extracted with ether. The combined ether solution was washed successively with brine, sodium thiosulfate solution, and finally with brine. The resulting colorless solution was dried over anhydrous magnesium sulfate and the ether removed. The resulting residue was chromatographed on alumina, ether being used to recover all the alcohol product. The slightly colored ether solution was washed with sodium thiosulfate solution, brine, dried and distilled. A crude distillation gave 7.5 g. (79%) of material, b.p. 65–66° (15 mm.). Redistillation through a Podbielniak column gave a fraction of *cis*-3-bicyclo[3.1.0]-hexanol, b.p. 76° (27 mm.), n^{25}D 1.4775. As noticed with

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(38) J. Sonnenberg, unpublished work.

(39) F. L. Howard, *J. Research Natl. Bur. Standards*, **24**, 677 (1940).

other samples of the *cis*-alcohol, the refractive index decreased on contact with air.

A 2.2-g. portion of the *cis*-3-bicyclo[3.1.0]hexanol was converted to acid phthalate by a procedure adapted from that of Levene and Mikeska.[40] Evaporation of the ether solution of the acid phthalate gave rise to 5.42 g. (98.5%) of material, m.p. 122–125°. This crude ester was recrystallized once from ether–pentane, which led to 3.6 g. (65%) of product, m.p. 125.5–126.5°. Recrystallization of a portion of this material led to a melting point of 126.0–127.0°.

Anal. Calcd. for $C_{14}H_{14}O_4$: C, 68.28; H, 5.73. Found: C, 68.49; H, 5.81.

Saponification of a 2.46 g. of acid phthalate, m.p. 125.5–126.5°, gave rise to 0.86 g. (88%) of *cis*-alcohol, b.p. 71.0–71.5° (22 mm.). From a redistillation a center cut, b.p. 66° (16 mm.), $n^{25}D$ 1.4770, was collected.

Anal. Calcd. for $C_6H_{10}O$: C, 73.43; H, 10.27. Found: C, 73.63; H, 10.53.

Oxidation of *cis*-3-Bicyclo[3.1.0]hexanol.—To a solution of chromic trioxide (4.5 g., 0.045 mole) in pyridine[41] (45 ml.), a solution of the alcohol (1.0 g., 0.01 mole) in pyridine (10 ml.) was added, and the resulting mixture was stirred magnetically at room temperature for 20 hours. During the first half-hour, the mixture turned from yellow to dark brown. Water (112 ml.) was added and the solution extracted with ether (3 × 100 ml.). The combined organic layer was washed successively with water, 1.8 *M* sulfuric acid, water, sodium bicarbonate, and water, and then dried over magnesium sulfate. The odor of pyridine was still present so the organic solution was washed with portions of hydrochloric acid. After washing away the acid as before and drying the resulting organic phase, the ether was removed by distillation and 0.50 g. (51%) of material, b.p. 49–50° (20 mm.), was isolated. The infrared spectrum of this material was identical with that of authentic 3-bicyclo-[3.1.0]hexanone.

Acetolysis Products.—A 102.8-mg. quantity of *cis*-3-bicyclo[3.1.0]hexyl toluenesulfonate, m.p. 50.6–51.4°, and 62.5- and 108.0-mg. samples of *trans*-toluenesulfonate, m.p. 70.8–71.3° and 69.5–70.3°, respectively, were each solvolyzed under the conditions summarized in Table IV. A control run with a 51.3-mg. sample of a 70:30 *cis–trans* mixture of 3-bicyclo[3.1.0]hexyl acetates, b.p. 68.5–70.5° (14 mm.), n^{2} D 1.4488, was also carried out (Table IV).

After the acetolysis solutions were cooled, the ampoules were opened and their contents transferred to a separatory funnel with the aid of pentane and water. Then a known weight of *n*-decane (53.0 mg. for the *cis*-toluenesulfonate) was added. A total of 45 ml. of distilled water was added to the acetolysis products and the decane, and this mixture extracted with pentane (4 × 50 ml.). The combined pentane solution was then washed successively with water (2 × 5 ml.), 5% sodium bicarbonate (1 × 5 ml.), and water (1 × 5 ml.). After the pentane solution was dried with magnesium sulfate, the pentane was carefully distilled through an efficient column with the bath temperature maintained below 60°. The inside of the column was washed with a small quantity of pentane, and the acetate residue analyzed directly by v.p.c. using a didecyl phthalate column. With the aid of a detector response factor determined on four synthetic mixtures of decane and *cis*-3-bicyclo[3.1.0]hexyl acetate, the yield of acetate is given by the relative v.p.c. areas of decane and acetate.

After the v.p.c. analyses of the acetates were performed, anhydrous ether was added to the remaining pentane solution and the pentane removed by azeotropic distillation. More anhydrous ether was added to the residue and the mixture cooled to 0°. As the mixture was being magnetically stirred and cooled, an ethereal 0.8 *M* lithium aluminum hydride solution (10 ml.) was added over several minutes. The reaction mixture was stirred for a half-hour at room temperature, and then the excess hydride decomposed by water (0.6 ml.) followed by 10% sodium hydroxide (0.5 ml.). Following an additional half-hour of stirring, the reaction mixture was allowed to stand overnight. The following day the mixture was carefully suction filtered and the salts washed thoroughly with ether. The ether solution was dried with anhydrous magnesium sulfate and the ether carefully distilled through an efficient column with the bath temperature maintained below 60°. After the inside of the column was washed with a small quantity of pentane, the alcohol residue was analyzed directly by v.p.c. on a Carbowax column.

The alcohol product from the *cis*-toluenesulfonate was very predominantly the *cis*-alcohol, no more than 1.5% of *trans*-alcohol being present. This was indicated by comparison with a synthetic mixture of 2% *trans*-alcohol in *cis*-alcohol from saponification of the acid phthalate. This synthetic mixture suggested that 0.5% of the *trans*-alcohol could be observed in the presence of the *cis*-alcohol. The v.p.c. analysis of the alcohol product from the *trans*-toluenesulfonate showed only *cis*-alcohol, no *trans*-alcohol being detected.

Control experiments showed that the extraction technique caused no change in the ratio of decane to acetate, and that conversion of acetate to alcohol introduced no error. The latter point was checked on pure *cis*-acetate and on the 70:30 *cis-trans* mixture.

Kinetic Measurements.—Cyclopentyl toluenesulfonate, m.p. 28–29° (reported[42,43] m.p. 28–29°; 27–28°), was prepared in the usual way.

Solvents and reagents for measurement of acetolysis rates in acetic acid, 0.01 *M* in acetic anhydride, by the sealed ampoule technique were prepared as usual.[33–35] In the acetolysis runs in the presence of sodium acetate, all three toluenesulfonates listed in Table II displayed infinity titers within *ca.* 1% of theoretical. With the *cis*-3-bicyclohexyl ester, the first-order rate constant drifted down slightly in a run due to the special salt effect of sodium acetate and the accumulation of the common ion salt, sodium toluenesulfonate.[32,44]

In the absence of sodium acetate the infinity titer was still close to theoretical in the case of cyclopentyl toluenesulfonate. However, it was only *ca.* 95% of theoretical in the case of the *cis*-3-bicyclohexyl ester. The reason for the low infinity titer was not further investigated, but steady first-order rate constants were obtained on the basis of the experimental infinity titers. With the *trans*-3-bicyclohexyl ester, an infinity titer could not be measured because of darkening of the acetolysis solution. The first-order rate constant evaluated on the basis of the theoretical infinity titer drifted down in a run, making the values listed in Table II somewhat inaccurate. For the run at 75° with 0.0053 *M* ester, the $10^5 k$ value given by a plot of log $(a-x)$ *vs.* time is 5.72, 4.80 and 4.25 for the reaction ranges, 6–17%, 17–47% and 39–64%, respectively. The intermediate value of k is listed in Tables II and III. For the run at 75° with 0.0177 *M* ester, the 10^5k value obtained graphically is 4.72 for the 1–38% reaction range and 3.80 for the 38–71% range. The lower figure is listed in Table II. It seems quite probable that the correct infinity titer to be employed under these conditions should be lower, as in the case of the *cis*-ester, but an experimental figure was not available.

In the presence of added lithium perchlorate, darkening of the acetolysis solutions prevented determination of an infinity titer with both *cis*- and *trans*-bicyclohexyl esters. Acetolysis was followed to *ca.* 60% and 30% solvolysis with the *cis*- and *trans*-esters, respectively, steady first-order rate constants being obtained on the basis of theoretical infinity titers.

Spectral Measurements.—The Δ^3-cyclopentenone was prepared by pyrolysis[45] of dicyclopentadienol-3. Fractionation of the ketone fraction through a Podbielniak column gave a sample of Δ^3-cyclopentenone, b.p. 39.0–40.5° (39 mm.), $n^{25}D$ 1.4521. On redistillation, material, b.p. 41–43° 41–43° (42–45 mm.), $n^{25}D$ 1.4518, was obtained (reported[45] b.p. 41° (40 mm.), $n^{20}D$ 1.4536).

The infrared spectral measurements were performed with the neat liquids in 0.018–0.031 mm. sodium chloride cells on a Perkin–Elmer model 21 double beam spectrophotometer with sodium chloride prisms.

The ultraviolet spectral measurements were carried out with a Cary model 14 spectrophotometer, the instrument being swept with nitrogen to exclude oxygen. To reach

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(40) P. A. Levene and L. A. Mikeska, *J. Biol. Chem.*, **75**, 587 (1927).

(41) G. I. Poos, G. E. Arth, R. E. Beyler and L. H. Sarett, *J. Am. Chem. Soc.*, **75**, 422 (1953).

(42) (a) H. C. Brown and G. Ham, *ibid.*, **78**, 2735 (1956); (b) J. D. Roberts and V. C. Chambers, *ibid.*, **73**, 5034 (1951).

(43) S. Winstein, *et al.*, *ibid.*, **74**, 1127 (1952).

(44) S. Winstein, P. Klinedinst, Jr., and G. C. Robinson, *ibid.*, **83**, 885 (1961).

(45) K. Alder and F. H. Flock, *Ber.*, **89**, 1732 (1956).

1850 Å. it was necessary to use thin cells (0.1-cm. and 0.01-cm. path length), a maximum phototube voltage (setting 4 or 5), and a slit control of 25. In the far ultraviolet region a scanning speed of 0.5 Å./sec. with a chart speed of 2 in./min. was used; in the near ultraviolet region a scanning speed of 2.5 Å./sec. with a chart speed of 2 in./min. was employed. Negligible scattering was found in the instrument down to 1850 Å.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, LOS ANGELES 24, CALIF.]

Homoconjugation and Homoaromaticity. IV. The Trishomocyclopropenyl Cation. A Homoaromatic Structure[1,2]

BY S. WINSTEIN AND JOSEPH SONNENBERG

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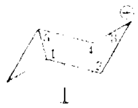
3-Deuterated-3-bicyclo[3.1.0]hexanols have been prepared and the corresponding toluenesulfonates acetolyzed in order to check for the occurrence of a uniquely symmetrical non-classical cation as an intermediate in solvolysis of the *cis*-toluenesulfonate. In acetolysis of the *trans*-toluenesulfonate very little redistribution of deuterium is visible in the solvolysis product. In acetolysis of the *cis*-toluenesulfonate, however, deuterium is distributed equally over carbon atoms 1, 3 and 5 in the product. Further, deuterium on the cyclopropane ring of the initial *cis*-toluenesulfonate is also symmetrically distributed during acetolysis. The results obtained are uniquely consistent with the intervention of the trishomocyclopropenyl cation as an intermediate in solvolysis of *cis*-3-bicyclo[3.1.0]hexyl toluenesulfonate. The theoretical relationship between trishomocyclopropenyl and cyclopropenyl cations is discussed, and some of the implications of the present results for organic chemistry are outlined. Regarding the trishomocyclopropenyl cation as the first example of a homoaromatic structure, the authors discuss a generalized concept of homoaromaticity.

The contrasting behavior of the *cis*- and *trans*-3-bicyclo[3.1.0]hexyl toluenesulfonates as regards anchimeric acceleration, special salt effects, stereochemistry and olefin formation in acetolysis[3] was an indication that the *cis*-epimer does indeed give rise to the symmetrical non-classical cation II. We had anticipated the possibility of such a structure for the 3-bicyclo[3.1.0]hexyl cation I on theoretical grounds. Suitable isotopic labeling of the 3-bicyclohexyl ring system was obviously the way to establish whether solvolysis does indeed involve an intermediate such as II with equivalent carbon atoms 1,3 and 5. In this paper we report and discuss the results of such a study which prove that the 3-bicyclo[3.1.0]hexyl cation does indeed have the non-classical structure II. Regarding this so-called trishomocyclopropenyl cation as the first-recognized homoaromatic structure, we go on to propose and discuss a generalized concept of homoaromaticity.[4]



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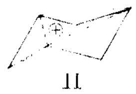

II

Deuterium Labeling and Kinetic Isotope Factor.—The simplest way to label the bicyclo[3.1.0]-hexyl ring system is by substitution of a deuterium atom for hydrogen on the carbinol carbon atom 3. For this reason, 3-bicyclohexanone was reduced with lithium aluminum deuteride as shown in the Reaction Scheme. The bicyclohexanone was derived from oxidation of a mixture of *cis*- and *trans*-3-bicyclohexanols, designated A-OH and F-OH, respectively. A large portion of the deuterated *cis*-alcohol B-OH was separated from the contaminating *trans*-epimer by chromatography on alumina and then purified further by way of the crystalline acid phthalate.[3] Combustion analysis of the deuterated *cis*-alcohol B-OH showed it to have 9.85 atom % excess deuterium or 98.5% of theoretical for one deuterium atom per molecule.

Saponification of the non-crystalline portion of the acid phthalate of the deuterated alcohol gave rise to a 60:40 *cis-trans* mixture of deuterated alcohols. A small amount of deuterated *trans*-alcohol G-OH was isolated by preparative vapor phase chromatography, but this sample was still slightly impure.

Rates of acetolysis of the toluenesulfonates of the deuterated and ordinary *cis*-3-bicyclo[3.1.0]-hexanols B-OH and A-OH were determined simultaneously at 50.0°. From these rate runs, summarized more fully in the Experimental section, a small kinetic isotope effect is indicated, (k_H/k_D) being equal to 1.05.

Deuterium Scrambling and Spectra.—Acetolysis of the toluenesulfonate B-OTs of the deuterated *cis*-alcohol B-OH at 50° in acetic acid solvent 0.10 *M* in sodium acetate and reduction of the resulting acetate with lithium aluminum hydride in the usual way[3] gave rise to a *cis*-alcohol C-OH. The infrared spectra of the three *cis*-alcohols A-OH, B-OH and C-OH, summarized in the Experimental section, show qualitatively that solvolysis of B-OTs is accompanied by the type of deuterium scrambling expected from a symmetrical non-classical intermediate II.

The substitution of deuterium for hydrogen on the carbinol carbon atom 3 of the *cis*-3-bicyclo-[3.1.0]hexanol causes the appearance of a number of new infrared absorption bands, while others disappear or are shifted. The two most prominent new absorption bands in alcohol B-OH are the C-D stretching absorption at 2151 cm.$^{-1}$ and an absorption at 723 cm.$^{-1}$. These two bands can be

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(2) The main results presented in this manuscript were reported in outline form: (a) in a preliminary Communication, S. Winstein, J. Sonnenberg and L. de Vries, *J. Am. Chem. Soc.*, **81**, 6523 (1959); (b) by S. Winstein at the Welch Foundation Conference on Molecular Structure and Organic Reactions, Houston, Tex., November 7-9, 1960.

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

(4) S. Winstein, *ibid.*, **81**, 6524 (1959).