

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<sup>1,2</sup>

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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<sup>3</sup> 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.<sup>4</sup>



**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.<sup>3</sup> 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<sup>3</sup> 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.

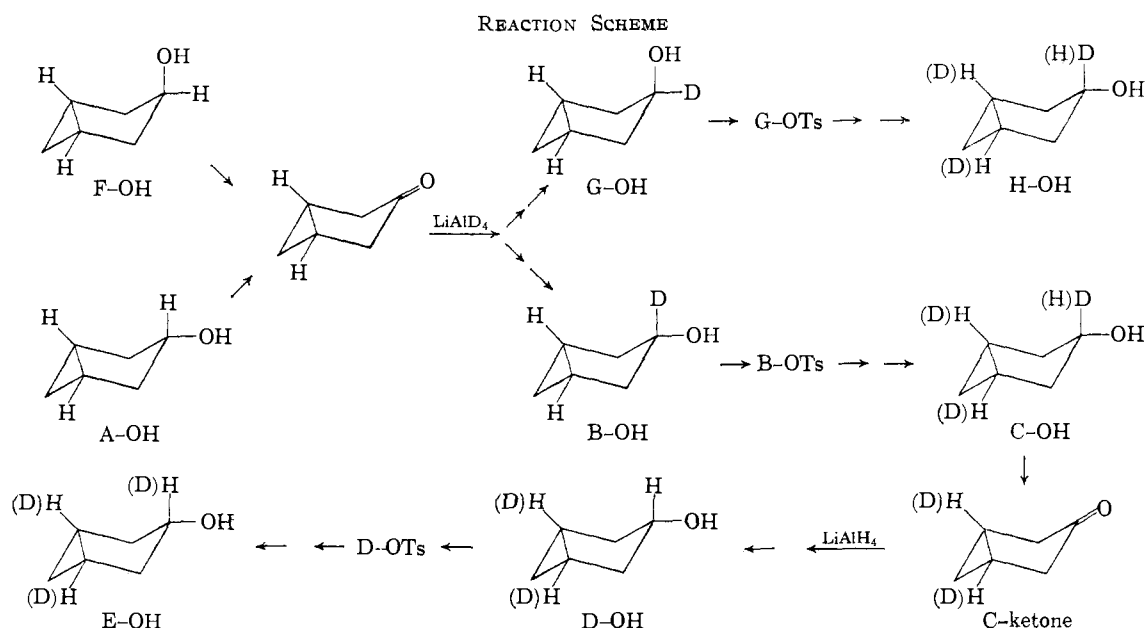
The substitution of deuterium for hydrogen on the carbinol carbon atom 3 of the *cis*-3-bicyclo[3.1.0]hexanol causes the appearance of a number of new infrared absorption bands, while others disappear or are shifted. The two most prominent new absorption bands in alcohol B-OH are the C-D stretching absorption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

(1) 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.

(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**, 3225 (1961).

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



assigned to the deuterium on the carbinol carbon atom 3. The strong absorption band at  $745\text{ cm}^{-1}$  in alcohol A-OH is absent in B-OH, and it can, therefore, be assigned to hydrogen on the carbinol carbon atom.

The infrared spectrum of the product alcohol C-OH shows all the bands of the deuterated B-OH as well as some additional ones. The  $2151$  and  $723\text{ cm}^{-1}$  bands for carbinyl deuterium occur with decreased intensities in C-OH. The additional bands for C-OH not present for B-OH include the carbinyl hydrogen band at  $746\text{ cm}^{-1}$  and two others, namely, at  $2266$  and  $670\text{ cm}^{-1}$ . As pointed out below, the latter two are quite clearly to be assigned to tertiary cyclopropyl deuterium.

Inspection of the infrared spectrum of *cis*-3-bicyclo[3.1.0]hexanol in the  $3.2\text{--}3.6\ \mu$  region using lithium fluoride optics reveals three frequencies logically associated with cyclopropyl hydrogen atoms,  $3070$ ,  $3028$  and  $3000\text{ cm}^{-1}$ . For the *trans*-epimer the corresponding frequencies are at  $3062$ ,  $3032$  and  $2995\text{ cm}^{-1}$ . By analogy with the in-phase and out-of-phase vibrations at *ca.*  $2926$  and  $2853\text{ cm}^{-1}$  for  $\text{CH}_2$  groups and the band at *ca.*  $2890\text{ cm}^{-1}$  for tertiary C-H observed in ordinary unstrained aliphatic compounds,<sup>5</sup> one can ascribe the  $3070$  and  $3000\text{ cm}^{-1}$  frequencies for the *cis*-3-bicyclo[3.1.0]hexanol to the  $\text{CH}_2$  group and the  $3028\text{ cm}^{-1}$  band to the tertiary hydrogen atom of the cyclopropane ring. Analogously, the  $3062$  and  $2995\text{ cm}^{-1}$  frequencies are due to methylene, and the  $3032\text{ cm}^{-1}$  frequency arises from tertiary hydrogen in the *trans*-alcohol.<sup>6</sup>

(5) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 2nd Ed., 1958.

(6) S. E. Wiberly and S. C. Bunce, *Anal. Chem.*, **24**, 623 (1952), have suggested the use of C-H stretching frequencies at  $3.23\ \mu$  ( $3096\text{ cm}^{-1}$ ) and  $3.23\ \mu$  ( $3013\text{ cm}^{-1}$ ) for identification of cyclopropane  $\text{CH}_2$  groups. Their data indicated that a third band sometimes occurs in this region, but this additional band did not appear regularly and was not commented on. For a number of cyclopropane derivatives, A. R. H. Cole, *J. Chem. Soc.*, 3807 (1954), has reported only a single cyclopropane hydrogen stretching frequency in the  $3042\text{--}3058\text{ cm}^{-1}$  region. For the cyclopropane ring-containing alcohol, 2-bicyclo[5.1.0]octanol,

The assignment of the  $3028$  or  $3032\text{ cm}^{-1}$  band for the *cis*- and *trans*-3-bicyclo[3.1.0]hexanols to the tertiary cyclopropyl hydrogen is supported by the fact that deuteration on the carbinol carbon atom 3 does not affect its intensity. On the other hand, the intensity is lowered in alcohol C-OH, which does have some tertiary cyclopropyl deuterium and thus less tertiary hydrogen. Also, 6,6-dibromobicyclo[3.1.0]hexane<sup>7</sup> (III) with no cyclopropyl methylene hydrogen atoms still shows a band at  $3030\text{ cm}^{-1}$ . Further support for the assignment is provided by the observations of Henbest, *et al.*, on epoxides,<sup>8</sup> whose strained 3-membered ring has considerable analogy to the cyclopropane ring. These investigators have observed characteristic C-H stretching bands which are useful in identification of the epoxide group. In cyclohexene oxide, the methine C-H band occurs at *ca.*  $3000\text{ cm}^{-1}$ , while in the more strained cyclopentene oxide IV, which bears a close analogy to bicyclo[3.1.0]hexane, the methine C-H stretch occurs at  $3037\text{ cm}^{-1}$ , quite similar to the  $3028$  or  $3032\text{ cm}^{-1}$  band observed with the bicyclohexanols. The new  $2266\text{ cm}^{-1}$  band observed in the product alcohol C-OH, not present in the spectrum of the deuterated alcohol B-OH, is quite clearly to be ascribed to tertiary cyclopropyl deuterium, because the position of this new band is reasonably close to that which can be anticipated from the effect of isotopic substitution on the  $3028\text{ cm}^{-1}$  C-H band.<sup>9</sup>

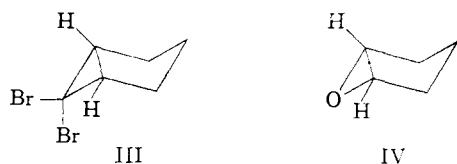
**Conversion of Cyclopropyl to Carbinyl Deuterium.**—It is quite obvious from the infrared spectra of A-OH, B-OH and C-OH and the band assignments discussed above that solvolysis of the

A. C. Cope and P. E. Peterson, *J. Am. Chem. Soc.*, **81**, 1643 (1959), have reported bands at  $3070$  and  $2990\text{ cm}^{-1}$ , attributed to the cyclopropane  $\text{CH}_2$  group.

(7) J. Sonnenberg, unpublished work.

(8) H. B. Henbest, G. D. Meakins, B. Nicholls and K. J. Taylor, *J. Chem. Soc.*, 1459 (1957).

(9) A. Streitwieser, Jr., R. H. Jagow, R. C. Fahey and S. Suzuki, *J. Am. Chem. Soc.*, **80**, 2326 (1958).



3-deuterated B-OTs is attended by some loss of deuterium from the carbinol carbon atom 3 and some appearance of tertiary deuterium on the cyclopropane ring. In order to obtain independent evidence on the amount of deuterium on the cyclopropane ring and to demonstrate the return of deuterium from the cyclopropane ring to the carbinol carbon atom, the product alcohol C-OH was carried through another sequence of reactions.

Chromium trioxide oxidation of the scrambled alcohol product C-OH yielded the partially deuterated C-ketone. On reduction of this ketone with lithium aluminum hydride and separation of the *cis*-3-bicyclo[3.1.0]hexanol from the small amount of contaminating *trans*-epimer<sup>3</sup> by preparative vapor phase chromatography, partially deuterated *cis*-alcohol D-OH was obtained. The infrared spectrum of D-OH showed that it contained only cyclopropyl deuterium, the 2266 and 670  $\text{cm}^{-1}$  bands being present and the carbinol C-D absorptions at 2151 and 723  $\text{cm}^{-1}$  being absent. Combustion analysis of D-OH showed it to contain 64% of the original deuterium in B-OH.

Acetylation of the toluenesulfonate D-OTs prepared from alcohol D-OH and the usual conversion of the product acetate to alcohol gave rise to *cis*-alcohol E-OH. In the infrared spectrum of this alcohol the cyclopropyl deuterium bands at 2266 and 670  $\text{cm}^{-1}$  were weaker than in the spectrum of D-OH and the carbinol C-D bands at 2151 and 723  $\text{cm}^{-1}$  were evident. Clearly, cyclopropyl deuterium was converted in part to carbinyl deuterium during solvolysis of D-OTs.

**Quantitative Spectral Analysis of Deuterium Scrambling.**—Absorbance measurements on the various *cis*-alcohols at some of the characteristic infrared frequencies as summarized in Table I give

TABLE I  
INTENSITY RATIOS OF CHARACTERISTIC ABSORPTION BANDS  
IN THE *cis*-3-BICYCLO[3.1.0]HEXANOLS

Alcohol ratio	Observed ratios at frequencies ( $\text{cm}^{-1}$ )				Predicted ratio <sup>a</sup>
	Carbinyl 2151	Cyclopropyl D 2266	D 670	Carbinyl H 745	
C/B	0.33				0.33
C/A				0.63	0.67
D/A				.96	1.00
D/C		0.99	0.99		1.00
E/A				.81	0.78
E/B	.20				.22
E/C	.62	.65	.66		.67
E/D		.66	.67		.67
H/A				.06	.00 <sup>b</sup>
H/B	.99				1.00 <sup>b</sup>
H/C			.07		0.00 <sup>b</sup>

<sup>a</sup> On the basis of the non-classical cation. <sup>b</sup> On the basis of the classical cation.

a more quantitative view of the degree of deuterium scrambling in the various specimens. Some intensity ratios between various pairs of alcohols

at pertinent frequencies are listed in Table I. For example, one sees that the C/B ratio at the carbinyl deuterium frequency of 2151  $\text{cm}^{-1}$  is 0.33, the value predicted on the basis of the non-classical cation II. An average value of  $0.32 \pm 0.01$  was obtained using two different instruments. The figure of 0.64 for the D/B ratio of deuterium content given by combustion analyses is also in line, (0.64/0.32) being equal within experimental error to the value 2.00 for the ratio of cyclopropyl to carbinyl deuterium predicted by equal distribution of the deuterium label among carbon atoms 1,3 and 5. Other ratios of infrared intensities listed in Table I further support the conclusion that solvolysis of *cis*-3-bicyclo[3.1.0]hexyl toluenesulfonate renders carbon atoms 1,3 and 5 effectively equivalent.

From Table I it is clear that in solvolysis of D-OTs, the fraction of deuterium which becomes carbinyl in type is close to one-third, the E/B ratio at 2151  $\text{cm}^{-1}$  being close to the value of two-ninths expected on the basis of the cation II. Similarly, the E/C and E/D ratios at cyclopropyl deuterium frequencies are very close to the predicted two-thirds. Thus, in solvolysis of D-OTs with deuterium solely on the cyclopropane ring, deuterium was again distributed equally among carbon atoms 1,3 and 5.

The occurrence of deuterium distribution during solvolysis of B-OTs is also substantiated by proton magnetic resonance spectra of alcohols A, B, C and D. The spectra of alcohols A and B indicate that the carbinyl proton resonates at the same frequency as the hydroxylic one. Comparison of the spectra of the four alcohols shows the line at +140 c.p.s. relative to water is due to tertiary cyclopropyl hydrogen. In Table II are summarized the area ratios of combined carbinyl and hydroxyl hydrogen to total hydrogen in the spectra of the four alcohols. Although this analysis is less accurate than the one based on infrared spectra, it is clear that the ratios are quite close to the ones calculated on the basis of the non-classical cation II.

TABLE II  
ANALYSIS OF DEUTERIUM SCRAMBLING BY PROTON MAGNETIC RESONANCE SPECTRA

<i>cis</i> -ROH	Total no. H atoms	No. of carbinyl and hydroxyl H atoms	Area ratio; carbinyl + hydroxyl/total	
			Calcd.	Found
A	10	2	0.200	0.183
B	9	1	.111	.115
C	9	1.67 <sup>a</sup>	.186 <sup>a</sup>	.183
D	9.33 <sup>a</sup>	2	.214 <sup>a</sup>	.230

<sup>a</sup> On the basis of non-classical cation II.

**Solvolysis of *trans*-Toluenesulfonate.**—The small amount of impure deuterated *trans*-alcohol G-OH was converted to crystalline toluenesulfonate G-OTs and acetylated similarly to the *cis*-epimer, except that the temperature was 75°. Conversion of the acetate product to alcohol in the usual way<sup>3</sup> gave rise to alcohol H-OH. The infrared spectrum of this material contained all the bands of alcohol B-OH and weak absorption bands attributed to C-OH. From Table I it is evident that no more than a few per cent. of redistribution of deuterium

occurs in solvolysis of the *trans*-toluenesulfonate G-OTs.

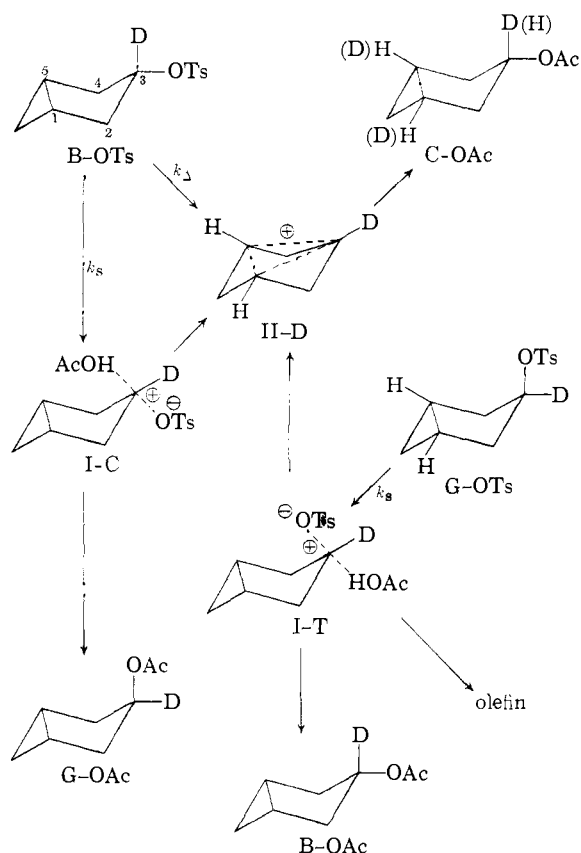
**Classical vs. Non-classical Cations.**—The previous paper<sup>3</sup> reported the contrasting behavior of the *cis*- and *trans*-3-bicyclo[3.1.0]hexyl toluenesulfonates in acetolysis. Thus, acetolysis is associated with a special salt effect and some anchimeric acceleration in the case of the *cis*-epimer, 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. It is instructive to compare the *cis*- and *trans*-bicyclohexyl toluenesulfonates with the *cis*- and *trans*-4-*t*-butylcyclohexyl<sup>10</sup> analogs for these both give inverted acetate and large amounts of olefin in acetolysis.

The behavior of the bicyclohexyl esters was suggestive of the intervention of the non-classical cation II in acetolysis of the *cis*-toluenesulfonate, but not the *trans*. It could be supposed that anchimerically assisted ionization of *cis*-toluenesulfonate gives rise to ion II which leads stereospecifically to *cis*-acetate. On the other hand, anchimerically unassisted ionization of *trans*-toluenesulfonate presumably leads to classical cation I-T which gives rise to *cis*-acetate, together with olefin. The observed deuterium scrambling during acetolysis of deuterated *cis*-3-bicyclo[3.1.0]hexyl toluenesulfonate B-OTs in exact accord with ion II-D provides compelling support for this interpretation.

As regards deuterium scrambling, the behavior of the *trans*-bicyclohexyl toluenesulfonate is in sharp contrast with that of the *cis*, just as in the case of the special salt effect, stereochemistry and elimination during acetolysis. This fact is very helpful in delineating the possible role of a classical ion in the deuterium scrambling during acetolysis of *cis*-toluenesulfonate. For example, one might attempt to explain this deuterium scrambling by way of three distinct classical cations in rapid equilibrium. However, the *trans*-toluenesulfonate solvolyzes by just such a classical cationic intermediate, and yet it displays very little deuterium scrambling in its acetolysis. Alternatively, one might consider a classical cation as a precursor of the non-classical one in accounting for the observed deuterium scrambling. On this basis, however, the *trans*-toluenesulfonate would also be expected to show extensive deuterium scrambling, but it does not. The behavior of the *trans*-toluenesulfonate indicates that a classical 3-bicyclo[3.1.0]hexyl cation neither equilibrates nor turns non-classical at a rate competitive with collapse to substitution and elimination products.

The deuterium scrambling, together with the special salt effect and stereochemistry in acetolysis, all are uniquely consistent with direct formation of the non-classical cation II by ionization of *cis*-3-bicyclo[3.1.0]hexyl toluenesulfonate. All the facts suggest that the ( $k_{\Delta}/k_s$ ) ratio, that is the ratio of anchimerically assisted and unassisted ionization rates, must be substantial and of the order of 30–50 or more. In the case of the *trans*-toluenesulfonate,

(10) S. Winstein and N. J. Holness, *J. Am. Chem. Soc.*, **77**, 5562 (1955).



only a small fraction (<10%) of the classical cation I-T first formed becomes non-classical, most of it collapsing to products without becoming bridged.

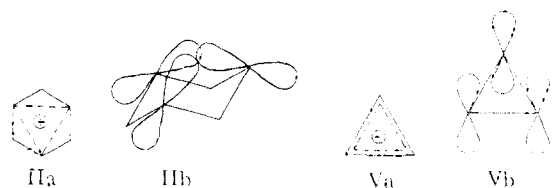
The kinetic isotope effect of the 3-deuterium atom on the rate of ionization of *cis*-3-bicyclo[3.1.0]hexyl toluenesulfonate is of obvious interest, but the present work has not supplied a direct measure of it. The observed ( $k_H/k_D$ ) ratio of 1.05 is smaller than the values reported for similar model systems, e.g., 1.15 and 1.19 for cyclopentyl-1-*d*<sup>9</sup> and cyclohexyl-1-*d*<sup>11</sup> toluenesulfonates, respectively. However, the apparent ( $k_H/k_D$ ) ratio of 1.05 applies to titrimetric rather than ionization rate constants. Since ion pair return accompanies acetolysis of *cis*-3-bicyclo[3.1.0]hexyl toluenesulfonate,<sup>3</sup> the titrimetric rate is only a fraction of the ionization rate and the residual toluenesulfonate rapidly becomes scrambled during a run. Until the extent of ion pair return and the kinetic isotope effect of deuterium on the cyclopropane ring are more directly assessed,<sup>12</sup> we should defer further discussion of the question of deuterium isotope effects.

**Stereoelectronic Considerations.**—The non-classical ion II, which may also be represented by IIa, may be expected to have a chair conformation, the atomic orbitals on atoms 1, 3 and 5 overlapping in such a manner that the electron cloud involved in the three-center bonding is concentrated on one side of the molecule. This orbital overlap is portrayed in IIb. While IIb is represented with tri-

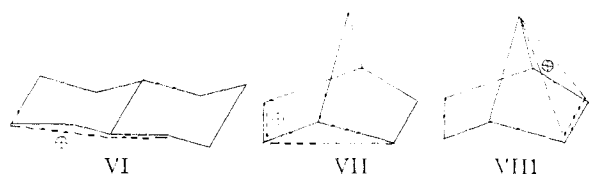
(11) K. Mislow, S. Borčić and V. Prelog, *Helv. Chim. Acta*, **40**, 2477 (1957).

(12) This matter is being investigated in collaboration with Dr. S. Borčić of the Institute Rudjer Bošković, Zagreb, Yugoslavia.

gonal hybridization at atoms 1, 3 and 5 and overlapping  $p$ -orbitals, some rehybridization would be permissible. Also, we can anticipate that introduction of some angle strain to decrease the C-C-C angles at the  $\text{CH}_2$  groups will be more than compensated for by increased delocalization energy.<sup>13</sup>



The stereospecific attack by solvent or other nucleophiles on the non-classical cation II to regenerate a *cis* configuration in the product is quite similar to the stereospecific formation of  $\beta$ -cholesteryl or 3,5-cyclocholestan-6 $\beta$ -yl derivatives from the non-classical cholesteryl cation<sup>13,14</sup> VI, *exo*-5-norbornenyl derivatives from the 5-norbornenyl ion<sup>2b,14d,15,16</sup> VII or *anti*-7-norbornenyl derivatives from the *anti*-7-norbornenyl cation<sup>17</sup> VIII.



**The Trishomocyclopropenyl Cation and the Generalized Concept of Homoaromaticity.**—The non-classical 3-bicyclo[3.1.0]hexyl cation II is related to the cyclopropenyl cation V by interposition of a  $\text{CH}_2$  group between the CH groups on all three sides of the molecule. Because of this analogy, cation II may be referred to as "tris-homocyclopropenyl." This species may well be merely the first example in an interesting new chapter of organic chemistry, namely, homoaromatic chemistry. This general idea is explained below.

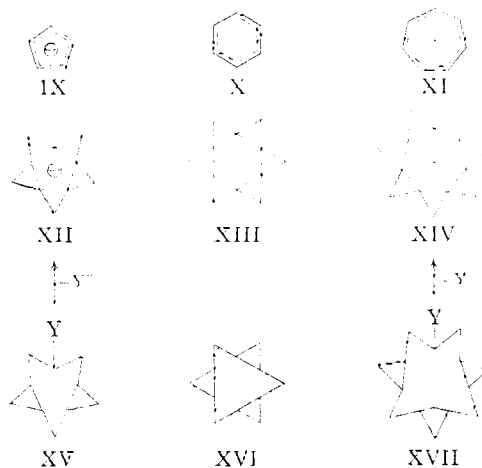
Simple molecular orbital theory applied to cyclic unsaturated systems predicts unique stability for those systems which have  $(4n + 2)$   $\pi$ -electrons.<sup>18</sup> These are the cases in which the bonding molecular orbitals are just fully filled. With the three-membered ring, two  $\pi$ -electrons are involved, unique stability being predicted for the cyclopropenyl cation V. This prediction has been confirmed recently with the preparation of relatively stable cyclopropenylum salts by Breslow.<sup>19</sup> With the 5-, 6- and 7-membered rings, the aromatic

sixtet of electrons is involved. This is contained in the cyclopentadienide ion IX, benzene X and tropylium ion XI, respectively, all three of these species being predicted by molecular orbital theory to have unique stability. Supporting evidence has long existed regarding cyclopentadienide ion and benzene, and the prediction has been strikingly confirmed more recently for tropylium ion by the preparation of very stable tropylium salts by Doering.<sup>20</sup>

Comparing the non-classical cation II with the cyclopropenyl analog V, we see that orbital overlap in II is not  $\pi$ , but intermediate between  $\sigma$  and  $\pi$ . Also, overlap and exchange integrals are 1, 3 rather than 1,2. Otherwise, the bicyclohexyl cation II is wave-mechanically analogous to the cyclopropenyl ion V. The two cations have the same pattern of molecular orbital energy levels,<sup>18</sup> with the resulting delocalization energy smaller for II than V, however. From this point of view the bicyclohexyl cation II is the trishomo counterpart of a species which fits the  $(4n + 2)$  electron rule. Conceptually, this homo relationship may be generalized to include homo counterparts of the other aromatic examples of the  $(4n + 2)$  rule. Thus, we can visualize pentahomocyclopentadienide ion XII, hexahomobenzene XIII and heptahomotropylium ion XIV. These are summarized and compared with their classical counterparts in Table III. Species XII could be visualized to arise from a material such as XV, structure XVI would

TABLE III  
AROMATIC AND HOMOAROMATIC SPECIES FITTING THE  
 $(4n + 2)$  RULE

$n$	$4n + 2$	Formula	Name
0	2	$\text{C}_3\text{H}_3^+$	Cyclopropenyl
		$\text{C}_6\text{H}_9^+$	Trishomocyclopropenyl
1	6	$\text{C}_5\text{H}_5^+$	Cyclopentadienide
		$\text{C}_{10}\text{H}_{15}^+$	Pentahomocyclopentadienide
1	6	$\text{C}_6\text{H}_6$	Benzene
		$\text{C}_{12}\text{H}_{18}$	Hexahomobenzene
1	6	$\text{C}_7\text{H}_7^+$	Tropylium
		$\text{C}_{14}\text{H}_{21}^+$	Heptahomotropylium



(13) M. Simonetta and S. Winstein, *J. Am. Chem. Soc.*, **76**, 18 (1954).

(14) S. Winstein, *et al.*, *ibid.*, (a) **70**, 838 (1948); (b) **70**, 3528 (1948); (c) **78**, 4347, 4354 (1956); (d) **81**, 4399 (1959).

(15) S. Winstein, H. M. Walborsky and K. Schreiber, *ibid.*, **72**, 5795 (1950).

(16) S. Winstein, *Experientia Suppl.* **11**, 137 (1955).

(17) (a) S. Winstein, M. Shatavsky, C. Norton and R. B. Woodward, *J. Am. Chem. Soc.*, **77**, 4183 (1955); (b) S. Winstein and M. Shatavsky, *ibid.*, **78**, 592 (1956).

(18) (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); (c) S. L. Menatt and J. D. Roberts, *J. Org. Chem.*, **24**, 1336 (1959).

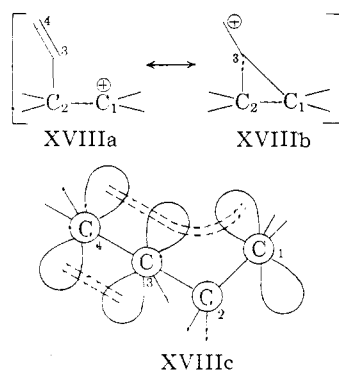
(19) (a) R. Breslow and C. Yuan, *J. Am. Chem. Soc.*, **80**, 599 (1958); (b) R. Breslow and H. Höver, *ibid.*, **82**, 2644 (1960).

(20) (a) W. v. E. Doering and L. H. Knox, *ibid.*, **76**, 3203 (1954); (b) see W. v. E. Doering and H. Krauch, *Angew. Chem.*, **68**, 661 (1956) for an excellent review of this and related matters.

represent one of the "Kekulé" structures for hexahomobenzene, and the heptahomotropylium ion XIV could be formulated as the product of ionization of a material with structure XVII.

The question whether species XII–XIV will prove to be truly homoaromatic is one of balance between quantum-mechanical delocalization energy and the compression energy necessary to force classical structures (like the "Kekulé" structures of type XVI) into the same geometry. It is quite clear that quantum-mechanical delocalization energies in homoaromatic cases XII–XIV will be less than in aromatic cases, perhaps *ca.* 40% as large,<sup>2b,13,21</sup> but the compression energies may not be large enough to preclude formation of hybrid homoaromatic structures. The balance seems no more discouraging for XII–XIV than for the trishomocyclopropenyl cation II, and we have experiments under way in an effort to prepare new homoaromatic compounds.

**Homoconjugation and Homoaromaticity.**—The concept of homoconjugation first arose in considering the behavior of cholesteryl and *i*-cholesteryl derivatives in solvolytic reactions.<sup>13,14</sup> A non-classical intermediate VI was visualized which was termed "homoallyl." The latter designation is made clearer with formulas XVIIIa–c which portray a carbonium ion with a  $\beta$ -olefinic group and show explicitly the overlapping atomic *p*-orbitals on the two olefinic carbon atoms C<sub>3</sub> and C<sub>4</sub> and the cationic carbon atom C<sub>1</sub>. The idea behind the homoallyl designation is that a methylene group (C<sub>2</sub>) is a poor insulator of conjugation if the proper rotational positions about the C<sub>1</sub>–C<sub>2</sub> and C<sub>2</sub>–C<sub>3</sub> bonds are assumed. With proper rotational positions, there is very appreciable 1,3-orbital overlap<sup>13</sup> of a type intermediate between  $\sigma$  and  $\pi$ . Semi-empirical molecular orbital calculations<sup>13</sup> suggest substantial stabilization from electron delocalization.

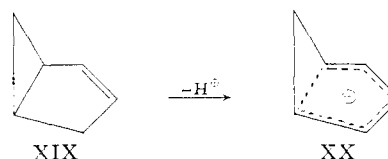


From the above point of view, one may say that the homoallyl cation XVIII is homoconjugatively stabilized. In conjugation there is electron delocalization over adjacent carbon atoms. Homoconjugation involves electron delocalization across intervening carbon atoms, a single intervening carbon atom in the case of cation XVIII. Such homoconjugation, involving electron delocalization across intervening carbon atoms, is present, also,

(21) (a) C. F. Wilcox, Jr., S. Winstein and W. G. McMillan, *J. Am. Chem. Soc.*, **82**, 5450 (1960); (b) S. Winstein and R. Piccolini, unpublished work.

in the trishomocyclopropenyl cation II and the other visualized homoaromatic species XII–XIV. The striking behavior of the *cis*-3-bicyclo[3.1.0]hexyl system has confirmed our anticipations on theoretical grounds that such homoconjugation could be important in systems possessing no  $\pi$ -electrons in the original classical structures.

If we consider the stepwise insertion of the methylene groups which convert species like the cyclopropenyl cation V and benzene X to their homoaromatic counterparts II and XIII, the designation bishomocyclopropenyl<sup>22</sup> is appropriate for cation VIII, and the pseudo-aromatic structure for tropilidene visualized by Doering<sup>23</sup> can be termed monohomobenzene. Only by explicit stepwise insertion of methylene groups may we appreciate the full ramifications of all the possible molecules which may represent discrete species. For illustration, monohomocyclopentadienide ion XX is a conceivable anion from proton removal from XIX. The homoaromatic species II and XII–XIV, with a methylene group inserted between all alternate CH groups, are unique in having complete equivalence of the classical contributing structures. While a systematic nomenclature system will ultimately be desirable, the designation "perhomoaromatic" may be a useful one to distinguish cases like II and XII–XIV from analogs with fewer interposed methylene groups.<sup>24</sup>



### Experimental

***cis*-Alcohol B-OH.**—3-Bicyclo[3.1.0]hexanone was obtained by oxidation of *cis*-3-bicyclo[3.1.0]hexanol<sup>3</sup> containing a small proportion of *trans*-epimer with chromic trioxide in pyridine.<sup>7</sup> Reduction<sup>3</sup> of the ketone with lithium aluminum deuteride in ether at  $-78^\circ$  gave rise to a 5.0-g. quantity of crude deuterated alcohol. From chromatography on alumina<sup>3</sup> three main fractions were obtained: (a) 2.9 g. of the essentially pure *cis*-alcohol (maximum of 4% of the *trans*-alcohol); (b) an intermediate fraction which was mostly the *cis*-alcohol; and (c) the remaining residue which came off with the ether eluent.

Each alcohol fraction was converted separately to acid phthalate.<sup>3a</sup> Fraction a yielded 7.1 g. of crude acid phthalate, m.p. 118–121.5°. After two recrystallizations from ether–pentane, 4.9 g. (67%) of product, m.p. 122.5–125.5°, was obtained. A second crop of 1.3 g., m.p. 118–123°, was also obtained. The combined crude acid phthalates from fractions b and c amounted to 1.2 g. of material, m.p. 120–123.5°. The mother liquors from all the recrystallizations were combined and saved for later use in obtaining the deuterated *trans*-alcohol.

Saponification<sup>3</sup> of the 4.9 g. of acid phthalate, m.p. 122.5–125.5°, yielded 1.7 g. (87%) of the deuterated *cis*-alcohol, b.p. 67–68° (17.0 mm.). The center fraction of 1.4 g., b.p. 67.5° (17.0 mm.),  $n_{25}^{20}D$  1.4770 was used in all the analytical work. A v.p.c. analysis indicated the presence of only the *cis*-alcohol, no more than 0.5% of the *trans*-alcohol being present. Deuterium combustion analysis<sup>25</sup> indicated 9.85 atom % excess deuterium.

(22) W. G. Woods, R. A. Carboni and J. D. Roberts, *J. Am. Chem. Soc.*, **78**, 5653 (1956).

(23) W. v. E. Doering, *et al.*, *ibid.*, **78**, 5448 (1956).

(24) This type of distinction is also desirable in the non-cyclic cases, such as those based on allyl. It is necessary to consider bishomoallyl as well as homoallyl.

(25) By Dr. J. Nemeth, Urbana, Ill.

*Anal.* Calcd. for  $C_6H_9DO$ : C, 72.68; H and D, 11.18. Found: C, 72.88; H and D, 11.09.

Saponification of the combined lower melting acid phthalates (2.5 g.) led to 0.90 g. of alcohol. A v.p.c. analysis indicated contamination by only 2% of the *trans*-isomer, so this material was used in the preparation of the deuterated *cis*-toluenesulfonate.

Conversion of deuterated *cis*-alcohol to toluenesulfonate<sup>3</sup> led to a 70% yield of product, m.p. 51.5–52.0°, in addition to a second crop, m.p. 51.0–51.5°, obtained from the last mother liquor.

*Anal.* Calcd. for  $C_{13}H_{13}DO_3S$ : C, 61.63; H and D, 6.76. Found: C, 61.79; H and D, 6.52.

**Acetolysis of B-OTs.**—The toluenesulfonate (m.p. 51.0–52.0°, 1.25 g., 5.0 mmoles) and 65 ml. of anhydrous acetic acid, 0.01 *M* in acetic anhydride and 0.1005 *M* in sodium acetate, was heated at 50.0° for 48 hours in a sealed flask. After the acetolysis products were subjected to the standard extraction and reduction procedure,<sup>3</sup> a v.p.c. analysis of the undistilled alcohol product indicated the presence of more than 99% of *cis*-alcohol. Distillation of the residue yielded 0.45 g. of *cis*-alcohol C-OH, b.p. 64–66° (18.5 mm.).

**C-Ketone and *cis*-Alcohol D-OH.**—Alcohol C-OH (ca. 0.45 g.) in pyridine (5 ml.) was oxidized<sup>3</sup> with chromic trioxide (2.3 g.) in pyridine (23 ml.) and worked up in the usual way. The product in ether was analyzed by v.p.c., and this showed the presence of the desired ketone, a relatively large amount of pyridine, and several minor impurities of times. No bicyclic alcohol was detected. The ketone in ether was reduced<sup>3</sup> with lithium aluminum hydride at –78° to yield 0.35 g. of alcohol product, b.p. 65–66° (16 mm.). A v.p.c. analysis indicated a 90:10 *cis-trans* mixture. Using preparative v.p.c., the *cis*-alcohol was purified and separated from the *trans*-alcohol. The deuterated *cis*-alcohol D-OH thus obtained was used in all the analytical work;  $n_D^{25} 1.4760$ . Deuterium combustion analysis<sup>32</sup> indicated 6.27 atom % excess deuterium. Conversion of alcohol D-OH (ca. 0.30 g.) to toluenesulfonate<sup>3</sup> gave rise to 0.35 g. of product, m.p. 50.5–51.5° after two recrystallizations.

**Acetolysis of D-OTs.**—Toluenesulfonate D-OTs (317 mg.) was dissolved in 16 ml. of anhydrous acetic acid, 0.01 *M* in acetic anhydride and 0.1005 *M* in sodium acetate, and was heated at 50.0° for 48 hours in a sealed ampoule. After the standard work-up and reduction procedure,<sup>3</sup> 0.10 g. of alcohol was obtained by distillation. A v.p.c. analysis of the distillate indicated that the *cis*-alcohol was contaminated with an unknown component (3%) with retention time slightly less than that of the *cis*-alcohol. Therefore, the *cis*-alcohol E-OH was reisolated using preparative v.p.c.

***trans*-3-Bicyclo[3.1.0]hexanol G-OH.**—The combined mother liquors from the preparation of the acid phthalate of deuterated *cis*-alcohol B-OH were saponified.<sup>3</sup> A v.p.c. analysis of the alcohol product indicated that it contained numerous components, most of them probably arising from the original chromic trioxide oxidation. However, the *trans*-alcohol constituted 40% of the bicyclic alcohol. Using preparative v.p.c., the *trans*-alcohol was isolated and partially purified. At the same time, more of the *cis*-alcohol was also collected.

The accumulated *trans*-alcohol (ca. 0.30 g.) was not pure, a small unknown component being present as evidenced by the asymmetrical peak on v.p.c. analysis. The infrared spectrum of the alcohol product exhibited C–D stretching absorption in the 4.5–5.0  $\mu$  region, which was weaker (about one third the absorbance) than that observed for the deuterated *cis*-alcohol B-OH. The infrared analysis of the deuterated *trans*-alcohol G-OH indicated the presence of 2% alcohol B-OH.

Conversion of alcohol G-OH (ca. 0.30 g.) to toluenesulfonate<sup>3</sup> gave 0.50 g. of crude product, m.p. 35–50°. One recrystallization from ether–pentane gave 0.35 g. of material, m.p. 58–66°. Utilizing fractional crystallization from ether–pentane, 0.22 g. of toluenesulfonate G-OTs, m.p. 68.5–70.0°, was obtained.

**Acetolysis of Toluenesulfonate G-OTs.**—The toluenesulfonate m.p. 68.5–70.0°, 0.22 g.) and 12 ml. of anhydrous acetic acid, 0.01 *M* in acetic anhydride and 0.1005 *M* in sodium acetate, was heated at 75.0° for 44.5 hours in a sealed ampoule. After the standard work-up and reduction<sup>3</sup> of the acetolysis product, alcohol H-OH was isolated using preparative v.p.c. The infrared spectrum of alcohol H-OH

TABLE IV  
OBSERVED INFRARED ABSORPTION BANDS OF THE  
ORDINARY AND DEUTERATED 3-BICYCLO[3.1.0]HEXANOLS  
(FREQUENCY OF ABSORPTION BANDS IN CM.<sup>-1</sup>)

<i>cis</i> -Alcohols			<i>trans</i> -Alcohols	
A-OH	B-OH	C-OH	F-OH	G-OH
(3310–3400vs)	(3310–3400vs)	(3310–3400vs)	(3280–3450vs)	(3280–3450vs)
3070w	3070w	3070w	3062m	3062m
3028s	3028s	3028s	3032ms	3032ms
3000m	3000m	3000m	2995m	2995m
				2950sh
(2920–2937vs)	(2920–2937vs)	(2920–2937vs)	(2926–2941vs)	(2926–2941vs)
			2900sh	2900sh
2846m	2846m	2846m	2860s	2860s
2732vw		2732vw		
		2266m		2366vw <sup>a</sup>
	2224w	2224vw		2342vw <sup>a</sup>
		2177mw		2193w
		2151m		2152m
		2137sh		2135sh
		2124sh		
		2086w		2092w
		2038vw		2030vw
1460sh	1454w	1454w	1460sh	
1434m	1435m	1435m	1445m	1453m
1360m	1359m		1363m	1372m
1342m		1351m	1346m	1353w
		1335m		1328w
1315m	1310w	1305m	1313m	
1290s	1288s	1288s	1293mw	1295s
		1240w	1272s	1274m
	1240vs	1242m		1245w
1230m		1225m		
			1210w	1208slw
				1190shw
1175m	1175ms	1175w	1170m	1177s
1165shw		1162sh	1155sh	
		1135m		
1102s	1120sh <sup>a</sup>	1109s	1105s	1125s
	1108vs	1087s		1115shw <sup>a</sup>
1068w				
	1062s	1060s		1060vs
1045vs	1044m	1041s	1048vs	
			1026m	1026m
1022sh	1019m	1020sh		1020sh
			1005w	1005w
		990s		
	978m	980sh		978shw
956vs		964w	965w	965ms
	941vs	944s	945shw	945w
935m	932sh	932sh		
		918m	919w	920w
		893w	899w	904w
	884vw <sup>a</sup>		875shw	879w
856w	855w	854w	862w	860w
	821shw	821w	833w	
807s	810ms	811w	810s	812s
	794m	763w		
		770w		
745s		746m	762s	763s
	723s	723m		723vw <sup>a</sup>
		670m		

<sup>a</sup> Probably due to impurities.

indicated it was primarily the deuterated *cis*-alcohol B-OH contaminated with a small amount of the scrambled *cis*-alcohol C-OH.

**Preparative V.p.c.**—By the use of a  $\frac{3}{8}$  inch copper tube column, 2.5 meters long, packed with 30% Carbowax 4000 suspended on 70% by weight of 40–60 mesh Johns–Mansville firebrick, and by attaching a collection system to the exit tube, it was possible to adapt the analytical<sup>3</sup> apparatus for separation of 0.2–0.5-ml. samples of the deuterated *cis*-

and *trans*-bicyclohexanols with considerable success. The final alcohol fractions were of ca. 98% purity.

**Spectral Measurements.**—The quantitative infrared spectral measurements were made with two spectrophotometers, each operated as a double beam instrument. The following control settings were used with the Perkin-Elmer model 21 equipped with sodium chloride prisms: resolution, 960; gain, 5.5; response, 1; speed, 5; and suppression, 0. The 2.5–16.0  $\mu$  range was scanned. The following control settings were used with the Beckman model IR-4 equipped with lithium fluoride prisms: gain, 2.0%; speed, 0.17  $\mu$ /min.; period, 2.0 sec.; and slit, 2  $\times$  standard. The 3.0–5.0  $\mu$  range was scanned. The liquid alcohols were determined neat in a 0.018-mm. sodium chloride cell compensated against a sodium chloride block.

The complete infrared spectra of the various *cis*- and *trans*-3-bicyclohexanols are given in Table IV for neat liquid films. The data for the 3.0–5.0  $\mu$  region are from the Beckman IR-4 instrument with lithium fluoride optics, and for the 5.0–16.  $\mu$  region from the Perkin-Elmer model 21 instrument with sodium chloride optics. The frequency ranges in parentheses indicate uncertain positions of maxima because of broadness of absorption bands.

TABLE V

OBSERVED PEAK HEIGHTS OF CHARACTERISTIC ABSORPTION BANDS OF THE *cis*-3-BICYCLO[3.1.0]HEXANOLS

Alcohol	(In absorbance units) <sup>a</sup>			Carbinyl H 745
	Carbinyl D 2151	Cyclopropyl D 2266	670	
A-OH	0.0	0.0	0.0	0.710
B-OH	.246	.0	.0	.0
C-OH	.081	.098	.335	.445
D-OH	.0	.097	.331	.680
E-OH	.050	.064	.222	.574
H-OH <sup>b</sup>	.163		.016	.026
	(.245)		(.024)	(.039)

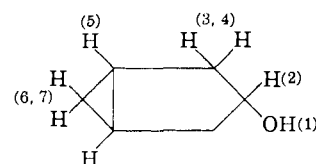
<sup>a</sup> Measured on Perkin-Elmer model 21 spectrophotometer equipped with sodium chloride optics; frequencies in  $\text{cm}^{-1}$ .  
<sup>b</sup> The available material at hand was insufficient to fill the infrared cell. Therefore, the values need to be increased. A factor of 1.5 has been chosen so that the intensity at the 2151  $\text{cm}^{-1}$  band represents about 100% deuterium. These increased values are given in the parentheses and are used in the calculations.

In Table V are summarized some of the quantitative measurements on the various alcohol specimens for the analysis of deuterium scrambling made in Table I.

Proton magnetic resonance spectra of the *cis*-3-bicyclo[3.1.0]hexanols were measured by R. Gillespie using a Varian V-4300-B high resolution spectrometer equipped with a 12-inch magnet and super-stabilizer. The frequency was fixed at 40 Mc./sec., and a magnetic field of about 9400 gauss was used. Determinations were made on the pure neat liquids. Sample tubes of 5-mm. outside diameter were used, and a sealed capillary tube of about 1-mm. diameter filled with distilled water was placed inside the sample tube. Samples were spun during the measurements. The line of the water peak was used as reference to measure shifts. The shifts of the peaks were determined by the use of the 60 c.p.s. audio-frequency side band method. The sign of the shift is chosen to be positive when the resonance falls at a higher applied field than the reference. In Table VI are summarized the observations on undeuterated *cis*-3-bicyclo[3.1.0]hexanol.

TABLE VI

PROTON MAGNETIC RESONANCE SPECTRUM OF *cis*-3-BICYCLO[3.1.0]-HEXANOL



Cycles per second <sup>a</sup>	Relative area		Hydrogen assignment
	Obsd.	Theory	
8	1.84	2	1,2
91	0.24	4	3,4
112 <sup>b</sup>	3.44		
140	2.48	2	5
161	2.16	2	6,7

<sup>a</sup> Relative to water, uncorrected for a bulk diamagnetic effect at 40 Mc. <sup>b</sup> Sharp peak; little, if any, splitting.

**Kinetic Measurements.**—First-order rate constants for acetolysis of 0.01 *M* toluenesulfonates A-OTs and B-OTs at 50.0° were determined simultaneously by the procedure employed previously.<sup>3</sup> For the undeuterated A-OTs the observed 10<sup>5</sup> *k* was 2.46 ± 0.04, while for the deuterated B-OTs it was 2.35 ± 0.04. In the latter case, there was some indication of a slight upward trend in the rate constant during the run.

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

## Allylic Rearrangements. L. Reactions of $\alpha$ - and $\gamma$ -Trifluoromethylallyl Alcohols with Thionyl Chloride and Thermal Decomposition of the Chlorosulfinate Intermediates<sup>1</sup>

BY J. A. PEGOLOTTI AND W. G. YOUNG

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The reaction of  $\alpha$ - and  $\gamma$ -trifluoromethylallyl alcohols with thionyl chloride in the solvents diethyl ether and thionyl chloride has been investigated. The effect of added tri-*n*-butylamine and its hydrochloride in these reactions was also studied.  $\gamma$ -Trifluoromethylallyl chloride was the only allylic chloride formed in these reactions. Kinetic and product studies from the thermal decomposition of  $\alpha$ - and  $\gamma$ -trifluoromethylallyl chlorosulfonates were carried out with results indicating that the secondary chlorosulfinate decomposes by an S<sub>N</sub>i' process of concerted nature.

In previous studies of the mechanism and products from the reaction of allylic alcohols with thionyl chloride, attention has been directed primarily toward allyl alcohol itself,<sup>2</sup>  $\alpha$ - and  $\gamma$ -methylallyl alcohols<sup>3</sup> and similar compounds where

(1) This work was supported in part by a grant to W. G. Young from the National Science Foundation.

(2) S. H. Sharman, F. F. Caserio, R. E. Nystrom, J. C. Leak and W. G. Young, *J. Am. Chem. Soc.*, **80**, 5965 (1958).

(3) (a) F. Caserio, G. E. Dennis, R. H. De Wolfe and W. G. Young, *ibid.*, **77**, 4182 (1955); (b) W. G. Young, F. Caserio and D. Brandon, *Science*, **117**, 473 (1953); (c) W. G. Young, F. F. Caserio, Jr., D. D. Brandon, *J. Am. Chem. Soc.*, **82**, 6163 (1960).

the basic allylic skeleton has alkyl substituents.<sup>4</sup> The present investigation was initiated to study the effect which a non-reactive, highly electronegative substituent would evince in this reaction. The trifluoromethyl group appeared most suitable for a substituent with the aforementioned properties and was chosen for this purpose. The alcohols prepared for the investigation were  $\alpha$ -trifluoromethylallyl alcohol (Ia) and  $\gamma$ -trifluoromethylallyl alcohol (IIa), alcohols analogous to the butenyl

(4) R. H. De Wolfe and W. G. Young, *Chem. Revs.*, **56**, 753 (1956).