methanol, and petroleum ether and dried under vacuum at 60°. Polymer prepared with hydrogen peroxide as initiator showed an O—H band at 2.85 and a strong $C\equiv N$ band at 4.45 μ.

Polymer prepared with compound I as initiator showed a very weak OH absorption at 2.8–3.0, a very weak $C=O$ band at 6.0, characteristic monosubstituted phenyl band at 13.2 and 14.2, and a strong $C\equiv N$ band at 4.45 μ. The ultraviolet spectrum showed a band at 235 and a broad band at 330–360 $m\mu$. The infrared spectra of polyacrylonitrile prepared with N,N′-dibenzoyldiimide as initiator in both the H^+ and Fe^{3+} series showed an O—H band at 2.8–3.0, a strong $C=O$ band at 5.95, characteristic monosubstituted phenyl bands at 13.2 and 14.4, and the strong $C\equiv N$ band at 4.45 μ. The infrared spectra of polyacrylonitrile prepared with diethyl azodicarboxylate as initiator in both the H^+ and Fe^{3+} series showed O—H band at 2.8–3.0, strong $C=O$ band at 5.78, and the strong $C\equiv N$ band at 4.45 μ. All samples of polymer were extracted with petroleum ether for 48 hr to remove occluded methanol and initiator fragments. Combustion of the polyacrylonitrile formed by the ferric-induced methanolysis of I, N,N′-dibenzoyldiimide, and diethyl azodicarboxylate left no residue.

The Electrolytic Decarboxylation of *cis*- and *trans*-Bicyclo[3.1.0]hexane-3-carboxylic Acids

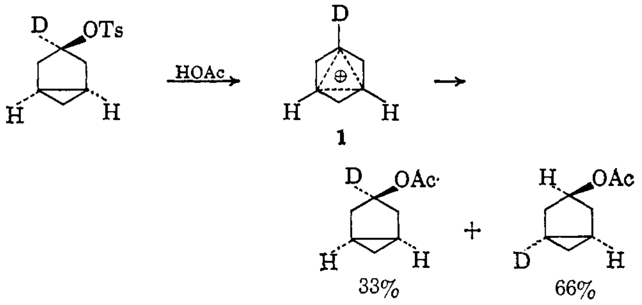
P. G. Gassman and F. V. Zalar[1]

Contribution from the Department of Chemistry, The Ohio State University, Columbus Ohio 43210. *Received December 8, 1965*

Abstract: The electrolytic oxidative decarboxylation of *cis*- and *trans*-bicyclo[3.1.0]hexane-3-carboxylic acid was investigated. When the electrolysis was run in pyridine–water the predominant products were *cis*- and *trans*-bicyclo[3.1.0]hexan-2-ols. These rearranged alcohols are explained on the basis of cationic intermediates. The reactions are stereospecific insofar as the *trans* acid yields mostly *trans* alcohol while the *cis* acid yields *cis* alcohol as the major product. Bicyclo[3.1.0]hexane-3-carboxylic acid labeled with deuterium at C-6 was converted to bicyclo[3.1.0]hexan-2-ols with no deuterium shift. These results are discussed in relation to the question of the existence of trishomocyclopropenyl cations.

The nature of the 3-bicyclo[3.1.0]hexyl cation has been the topic of numerous recent publications.[2-8] The synthesis of this cation has been approached by three different research groups from three different directions. Winstein and co-workers were the first to investigate the 3-bicyclo[3.1.0]hexyl cation.[2,4,5] They found that acetolysis of both *cis*- and *trans*-3-bicyclo[3.1.0]hexyl toluenesulfonate afforded *cis*-3-bicyclo[3.1.0]hexyl acetate as the major solvolysis product. In addition it was shown that the *cis* toluenesulfonate solvolyzed about ten times faster than the *trans* isomer to give a quantitative yield of *cis* acetate. The *cis* toluenesulfonate showed a "special salt effect" while the *trans* toluenesulfonate failed to act similarly. Finally, Winstein and co-workers investigated the acetolysis of the epimeric 3-deuterio-3-bicyclo[3.1.0]hexyl toluenesulfonates. The *cis* toluenesulfonate yielded *cis* acetate with the deuterium statistically distributed between the 1, 3, and 5 positions while the *trans* toluenesulfonate gave *cis* acetate with no deuterium scrambling. On the basis of these data, Winstein postulated the existence of the unique nonclassical ion (**1**) for which he coined the name "trishomocyclopropenyl cation."

Corey and Dawson[6] generated a 3-bicyclo[3.1.0]hexyl cation by deamination of the epimeric 3-aminobicyclo[3.1.0]hexanes. Their results differed drastically from those obtained in solvolysis studies. In contrast to Winstein's acetolysis, deamination of either epimer of 3-aminobicyclo[3.1.0]hexane yielded both epimeric 3-alcohols and also both epimeric 2-alcohols (probably *via* a C-2 to C-3 hydride shift). In addition, these workers deaminated 3-deuterio-*cis*-3-aminobicyclo[3.1.0]hexane and found less than 50% deuterium scrambling in the resulting *cis*-3-alcohol. The *trans*-3-alcohol isolated from the same reaction showed no deuterium shift. These results were interpreted as evidence for the absence of a trishomocyclopropenyl cationic intermediate in the deaminations.



A third approach to the 3-bicyclo[3.1.0]hexyl cation was that of Freeman and co-workers.[9] They reasoned that if the trishomocyclopropenyl cation was an unusually stable intermediate, as might be expected, protonation of bicyclo[3.1.0]hex-2-ene (**2**) followed by addition of the nucleophile X might yield **3**. However, they found no evidence for the formation of a trishomocyclopropenyl cation.

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[1] Sinclair Oil Corporation Foundation Fellow, 1964–1965.

[2] S. Winstein, J. Sonnenberg, and L. de Vries, *J. Am. Chem. Soc.*, **81**, 6523 (1959).

[3] S. Winstein, *ibid.*, **81**, 6524 (1959).

[4] S. Winstein and J. Sonnenberg, *ibid.*, **83**, 3235 (1961).

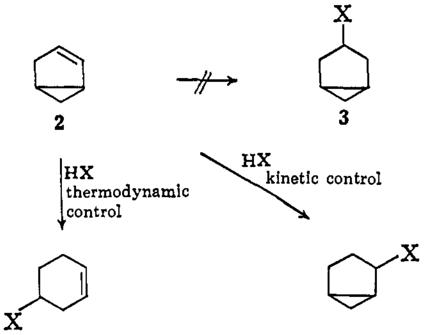
[5] S. Winstein and J. Sonnenberg, *ibid.*, **83**, 3244 (1961).

[6] E. J. Corey and R. L. Dawson, *ibid.*, **85**, 1782 (1963).

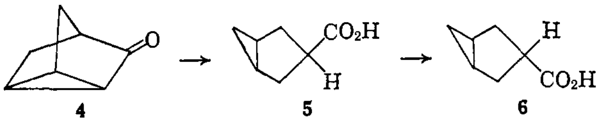
[7] E. J. Corey and H. Uda, *ibid.*, **85**, 1788 (1963).

[8] T. Norin, *Tetrahedron Letters*, **1**, 37 (1964).

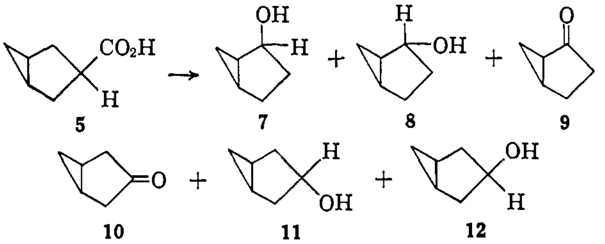
[9] P. K. Freeman, M. F. Grostic, and F. A. Raymond, *J. Org. Chem.*, **30**, 771 (1965).



As part of our continuing interest in the postulated existence of nonclassical bicyclic cations,[10] we decided to investigate the electrolytic oxidative decarboxylation of the epimeric bicyclo[3.1.0]hexane-3-carboxylic acids.[11] These acids were conveniently available from the basic cleavage of nortricyclanone[12] (**4**). This cleavage yields *cis*-bicyclo[3.1.0]hexane-3-carboxylic acid (**5**) which underwent facile epimerization to *trans*-bicyclo[3.1.0]hexane-3-carboxylic acid (**6**) when heated to 60° in a mixture of dimethyl sulfoxide, potassium *t*-butoxide, and water.[12] The *cis* and *trans* acids or their esters could not be separated *via* vapor phase chromatography on several columns. Analysis for isomer purity was achieved by initial reduction of the acids to the corresponding carbinols followed by vpc separation of these reduction products (see the Experimental Section for details.).

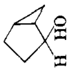
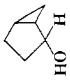
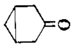
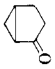
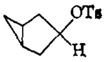
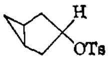
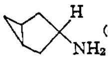
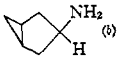
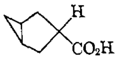
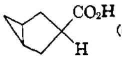


The electrolytic decarboxylation of the epimeric bicyclo[3.1.0]hexane-3-carboxylic acids was carried out in a pyridine–water solution at 80° utilizing smooth platinum electrodes with a current of about 0.6 amp at 35 v. The electrolysis reaction mixture was considerably more complex than anticipated. The *cis* acid yielded *cis*-bicyclo[3.1.0]hexan-2-ol (**7**), *trans*-bicyclo[3.1.0]hexan-2-ol (**8**), bicyclo[3.1.0]hexan-2-one (**9**), bicyclo[3.1.0]hexan-3-one (**10**), *trans*-bicyclo[3.1.0]hexan-3-ol (**11**), and *cis*-bicyclo[3.1.0]hexan-3-ol (**12**) in order of decreasing yield. Similar products were obtained from the electrolysis of the *trans* acid (**6**). However, the product ratios were significantly changed.



Comparisons of electrolytically generated carbonium ions with carbonium ions generated *via* other methods have been made on several occasions.[11] In the case of the bicyclo[3.1.0]hexyl system, the products obtained in tosylate solvolyses, amine deaminations, and electrolytic decarboxylations differ considerably, both in the types of products formed and in the stereochemistry of the products formed.[13] These results are contrasted in Table I.

Table I

		Composition of oxygenated products, %					
Compd	Ref						
	4,5	100					
	4,5	98.5	1.5				
 [a]	6	41	14	9	36		
 [b]	6	5	30.5	27.5	37		
		4.3	2.0	34.5	41	7.1	11.1
 [c]		4.3	4.6	37	30.8	10.7	12.6

[a] Values corrected to compensate for 6% *cis* amine in the starting *trans* amine. [b] Values corrected to compensate for 7% *trans* amine in the starting *cis* amine. [c] Percentages adjusted for the presence of 8% *trans* acid in the starting *cis* acid.

The electrolytic decarboxylation of the epimeric bicyclo[3.1.0]hexane-3-carboxylic acids gave a product mixture which was quite different from the results obtained in the aforementioned deaminations and solvolyses. Most important, the electrolyses yielded a negligible amount of 3-alcohols whereas even the deamination of the *trans*-3-amine yielded greater than 50% 3-alcohols. A second significant point is that *trans* acid (**6**) gave *trans*-2-alcohol as the major product while the *cis* acid (**5**) yielded primarily *cis*-2-alcohol.

Our results can be interpreted in several ways. We shall discuss the mechanistic implications of our data by considering two possible sets of circumstances. The first is that all reactions other than electron transfers occur in homogeneous solution. The second possibility is that product formation occurs on the surface of the electrode and thus the stereochemical results are determined in a heterogeneous reaction.

The minor components, the ketones and the 3-alcohols, are not pertinent to the mechanistic discussion. The ketones **9** and **10** undoubtedly arise from oxidation of the corresponding alcohols. There is ample precedent for this type of electrolytic oxidation.[11,14] It is likely that the oxidation of these bicyclic

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(10) P. G. Gassman and J. L. Marshall, *J. Am. Chem. Soc.*, **87**, 4648 (1965); P. G. Gassman and J. L. Marshall, *Tetrahedron Letters*, **46**, 4073 (1965).

(11) For recent references to the generation of carbonium ions *via* electrolytic decarboxylation see: (a) E. J. Corey, N. L. Bauld, R. T. La Londe, J. Casanova, Jr., and E. T. Kaiser, *J. Am. Chem. Soc.*, **82**, 2645 (1960); (b) E. J. Corey and J. Casanova, Jr., *ibid.*, **85**, 165 (1963); (c) W. J. Koehl, Jr., *ibid.*, **86**, 4686 (1964).

(12) P. G. Gassman and F. V. Zalar, *Tetrahedron Letters*, **40**, 3031 (1964); **44**, 3251 (1964). A detailed account of the mechanism and experimental parameters of the cleavage of nonenolizable ketones will be presented in a forthcoming publication from this laboratory.

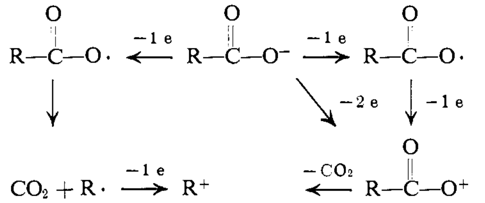
(13) Although the stereochemistry of the products shows considerable dependence on the mode of generation of the parent carbonium ion, it should be stressed that differences in energy between the transition states leading to the stereoisomers of the various products are quite small.

(14) G. Giacomello and A. Mayer, *Gazz. Chim. Ital.*, **65**, 546 (1935).

alcohols to the corresponding ketones would have little effect on the isomer ratio since the oxidation potential of the epimers should be quite similar.

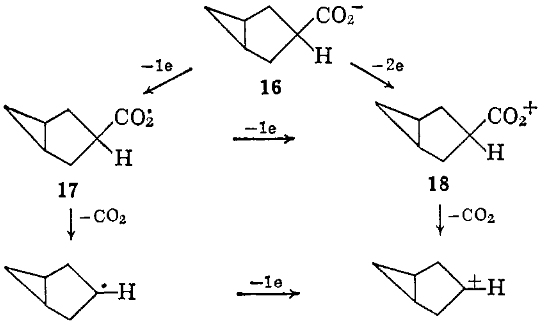
The ratio of *cis*-3-alcohol to *trans*-3-alcohol indicated little, if any, preference for steric control of the product ratio in our electrolytic reactions. Since the per cent composition was determined by vpc analysis it is doubtful whether the results are accurate to better than ±1%. Thus, any significance which might be attributed to the very small relative amounts of *cis*- and *trans*-3-alcohols should be questioned.

The bicyclo[3.1.0]hexan-2-ols present a very different situation. It was felt that these alcohols were obtained *via* cationic intermediates. Two different mechanisms have been postulated for the oxidative decarboxylation of carboxylic acids. These have been discussed in great detail[11,15–17] both with reference to anodic decarboxylations[11] and to the oxidative decarboxylation effected by lead tetraacetate.[15–17] The diverse reaction schemes are depicted below. The essential difference in these two pathways is the stage at which carbon dioxide is eliminated from the acid.



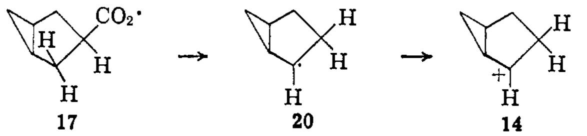
At present the available data do not warrant a firm acceptance of either mechanism in the case of anodic decarboxylation. In light of these proposed mechanisms the partial retention of stereochemistry in the bicyclo[3.1.0]hexan-2-ols poses some unique problems.

Initially the *cis*-carboxylate anion, **16**, might undergo a one-electron transfer to the *cis*-acyloxy radical, **17**, or a two-electron transfer to produce the *cis*-acyloxonium ion, **18**. The positively charged intermediate **18**

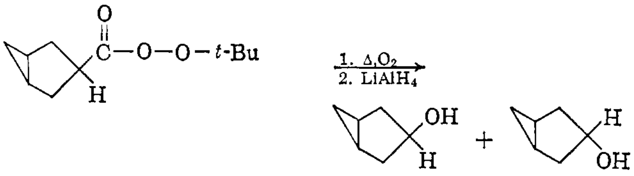


could also arise from **17** *via* a one-electron transfer. Either **17** or **18** could be converted to **13** as shown above. If **13** were a critical intermediate in the electrolytic conversion of *cis* acid to epimeric 2-alcohols, it should play the same role in the transformation of *trans* acid to 2-alcohols. Since the *cis*- and *trans*-3-acids yield different ratios of *cis*- to *trans*-2-alcohols a carbonium ion such as **13** cannot be a keystone in the mechanistic bridge which connects starting materials to products in a stereospecific manner if all reactions other than electron transfer occur in homogeneous solution.

In order to rationalize the partial stereospecificity observed in the formation of the isomeric bicyclo[3.1.0]hexan-2-ols it becomes necessary to invoke a concerted reaction mechanism. Since in homogeneous solution neither the radical (**19**) nor the cation (**13**) can differentiate whether they were derived from the *cis* or *trans* acids, they cannot account for the control of product stereospecificity. Thus, any concerted migration must start with either the acyloxy radical (**17**) or the acyloxonium ion (**18**). The acyloxy radical is unlikely to undergo conversion to **20** *via* a concerted

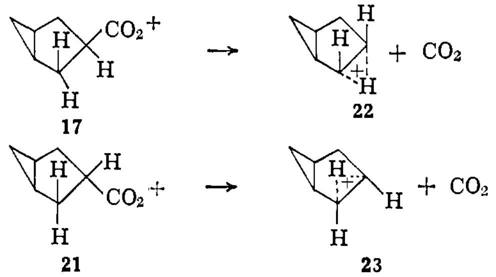


hydrogen migration since the majority of evidence indicates that 1,2-shifts of hydrogen do not occur to a detectable extent during the lifetime of radicals.[18] To obtain some indication that our system was not a unique exception we investigated the thermal decomposition of the *t*-butyl perester of *cis*-bicyclo[3.1.0]hexane-3-carboxylic acid in the presence of oxygen.[19] This gave



both *cis*- and *trans*-3-alcohols but no trace of either *cis*- or *trans*-2-alcohols. In addition if **20** were formed there is precedent[20] for opening of the cyclopropyl ring. However, the anticipated product of such ring opening, Δ^3-cyclohexenol, was not observed in either the *t*-butyl perester decomposition or in the electrolysis experiment.

Thus, the partial stereospecificity of our electrolysis may emanate from the epimeric acyloxonium ions **17** and **21**. These intermediates could undergo a con-



certed hydrogen-bridging, carbon dioxide loss. This would result in the formation of the hydrogen-bridged species **22** from the *cis* acid and the hydrogen-bridged intermediate **23** from the *trans* acid. It has been well established that the 2-bicyclo[3.1.0]hexyl cation is more stable than the 3-bicyclo[3.1.0]hexyl cation.[21] Thus the

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(15) J. K. Kochi, *J. Am. Chem. Soc.*, **87**, 3609 (1965).

(16) W. H. Starnes, *ibid.*, **86**, 5603 (1964).

(17) W. A. Mosher and C. L. Kehr, *ibid.*, **75**, 3172 (1953); **82**, 5342 (1960); W. A. Mosher, C. L. Kehr, and L. W. Wright, *J. Org. Chem.*, **26**, 1044 (1961).

(18) For a recent review on free radical rearrangements see C. Walling in "Molecular Rearrangements," P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, p 407.

(19) P. D. Bartlett, R. E. Pincock, J. H. Rolston, W. G. Schindel, and L. A. Singer, *J. Am. Chem. Soc.*, **87**, 2590 (1965).

(20) D. C. Neckers, *Tetrahedron Letters*, **23**, 1889 (1965).

(21) See ref 9, and references contained therein.

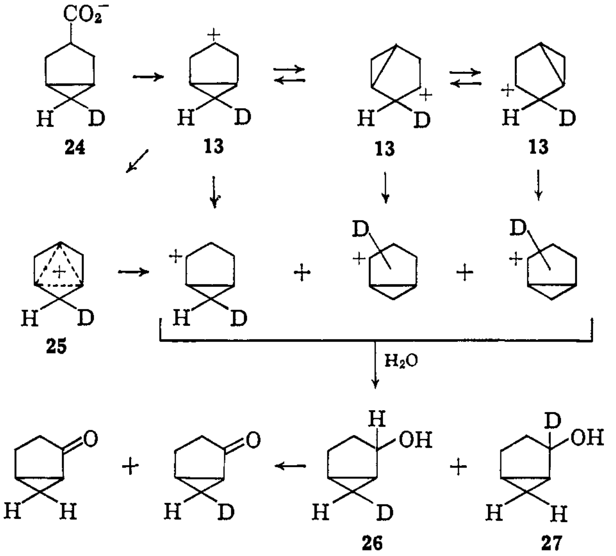
positive charge at C-2 seems to be stabilized in preference to a positive charge at C-3. This being the case, nucleophilic attack by solvent on the hydrogen-bridged species, **22** or **23**, would occur from the side opposite the hydrogen bridge and would preferentially take place at C-2. This would account for the observed stereospecificity.[22] An alternate possibility would be a completely concerted loss of carbon dioxide, hydride shift, and solvent addition. This cannot be ruled out.

It should be stressed at this time that the major portion of the 2-alcohols could be derived from **14** in a nonstereospecific manner. Unfortunately, the available evidence was insufficient for a determination of whether **14** was derived from **17** *via* **13**, from **18** *via* **13**, or directly from **22** or **23**.

The discussion thus far has been based on the premise that the reactions of the carbonium ions are occurring in a homogeneous environment. The alternate possibility that the reaction is occurring on the electrode surface also merits consideration. It has been shown that the electrode plays a part in determining whether the electrolysis of an acid follows the classical Kolbe route (*i.e.*, proceeds only to the radical stage) or whether carbonium ions are formed.[11c] The question of whether or not the stereochemistry of the products is a function of reactions (other than electron transfer) occurring on the surface of the electrode has not been answered.

If the formation of *cis*- and *trans*-2-alcohols occurred on the surface of the electrode, a hydride shift from C-2 to C-3 would still be required since the initially generated carbonium ion must be at C-3. Transfer of solvent from the surface of the electrode to the side of the molecule from which the carbon dioxide was lost (presumably the side nearest the electrode) would then give some stereospecific product formation. Although this possibility cannot be ruled out, it seems unlikely in view of the fact that in the electrolysis of the epimeric *exo*- and *endo*-norbornane-2-carboxylic acids and in the electrolysis of *exo*- and *endo*-5-norbornene-2-carboxylic acids only a single product is obtained.[11a] This product is identical with the product obtained from carbonium ion generation in a homogeneous reaction. Furthermore, no *endo* products were observed as might have been expected had solvent added from the electrode in a manner similar to that discussed for the bicyclo[3.1.0]hexyl system.

The question of the intermediacy of **13** exists regardless of whether the reaction of the C-2 cation occurs in solution or on the surface of the electode. In order to obtain some indication as to the intermediacy of **13** in the formation of the 2-alcohols, we electrolyzed 6-deuterio-*cis*-bicyclo[3.1.0]hexane-3-carboxylic acid (**24**). Both Winstein[4,5] and Corey[6] have shown that products arising from **13** (or some analogous nonclassical ion) give deuterium scrambling. Thus, if **13** were an intermediate in the formation of the 2-alcohols, one would expect to find some deuterium scrambling in the electrolysis experiments. Deuterium scrambling *via* **13** or the trishomocyclopropenyl cation, **25**, could occur as shown. The resulting alcohols, **26** and **27**, would suffer loss of deuterium from **27** on oxidation to the corresponding ketone. Mass spectral analysis showed no loss of deuterium in the ketones obtained from the procedure described. Thus, it seems probable that an ion such as **13** (or the trishomocyclopropenyl cation) is not an intermediate in the electrolytic formation of the 2-alcohols (which account for over 80% of the electrolysis product).



Experimental Section

Elemental analyses were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark. Mass spectral analyses were obtained on an AEI MS-9 mass spectrophotometer. Vapor phase chromatographic work was performed with an Aerograph Hy-Fi Model 600 and an Autoprep Model A-700. The electrolyses were performed using a 2.25 in. high × 1.5 in. diameter platinum cathode and a 2.25 in. high × 0.5 in. diameter platinum anode, both of 45 mesh wire gauze.

***cis*-Bicyclo[3.1.0]hexane-3-carboxylic Acid (5).** In a drybox under nitrogen pressure, 16 g (0.13 mole) of sublimed potassium *t*-butoxide (M. S. A. Research Corp., Callery, Pa.) was weighed in a 250-ml, side-arm, round-bottom flask equipped with a magnetic stirring bar. The stoppered flask was immersed in an ice bath and 50 ml of anhydrous diethyl ether (distilled from lithium aluminum hydride) was injected from a syringe through a rubber septum in the side arm of the flask. To the rapidly stirred suspension was slowly injected 0.77 ml of water (0.043 mole, butoxide to water ratio of 10:3). The ice bath was removed and 2.0 g of nortricyclanone (0.0185 mole) was slowly injected with a syringe. The suspension was stirred at room temperature for 2 hr, the flask was again immersed in an ice bath, and ice was slowly added until the mixture separated into two clear phases. The aqueous phase was separated from the ether and diluted with an additional 50 ml of water, acidified with concentrated hydrochloric acid, and extracted with three 50-ml portions of ether. The ether extracts were combined, dried over anhydrous magnesium sulfate, and filtered, and the

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(22) Although Corey and Dawson discuss the deamination of the epimeric 3-aminobicyclo[3.1.0]hexanes in detail and draw comparisons with the solvolysis results of the Winstein group,[2,4,5] they fail to account for the differences in product ratios of the 2-alcohols obtained from the deaminations of the *cis* and *trans* amines. The stereochemistry of the epimeric 3-alcohols was rationalized on the assumption that these alcohols were derived from the classical ion **13** "with an additional proviso, *viz.*, that the reaction with nucleophilic solvent be sufficiently fast so that the shielding effect of the detached nitrogen molecule is of some consequence." It was further postulated[6] that the epimeric 2-alcohols were derived from the classical ion **14** or the delocalized ion **15**. This postulate fails to explain the different ratio of *cis*- to *trans*-2-alcohols obtained from the deamination of the *cis*- and *trans*-3-amines. It would be anticipated that either **14** or **15** would yield a given product ratio which would not depend on the stereochemistry of the amine from which it was derived. Hydrogen-bridged species similar to those discussed for the electrolysis could also account for the partial stereospecificity observed by Corey and Dawson.

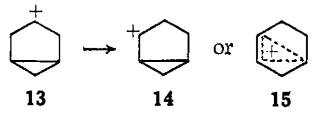

Table II

Acid (moles)	Time, hr	Compn, % *cis*-3-ol	*trans*-3-ol	*cis*-2-ol	*trans*-2-ol	3-keto	2-keto	Over-all yield
cis (0.0159)	17.5	4.3	4.9	35.2	31.8	10.0	13.8	34.6
cis (0.0175)	21.5	3.8	3.9	38.6	33.0	10.2	10.5	63.3
cis (0.0213)	26	4.8	4.6	36.5	30.0	10.9	13.2	27.2
trans (0.0112)	12	3.3	2.2	34.5	41.4	6.5	11.2	35.6
trans (0.0103)	19	5.3	1.8	33.6	40.5	7.7	11.1	50.5

Table III

Acid	Source	Compd	Mass numbers 96	97	139	140	141	142	% D (±1)
	Standard	2-one	100	7.5					
cis	*cis*-2-ol	2-one	61	100					61.0
cis	*trans*-2-ol	2-one	55	100					63.5
trans	*cis*- and *trans*-2-ol	2-one	57	100					62.7
trans	Standard	Methyl ester			48	100	11	1	
trans	Deuterated	Methyl ester			26	83	100	12	61.0

ether was distilled through a 1-ft column packed with glass helices. The residue was distilled *in vacuo* to give 2.07 g (89%), bp 69–70° (0.25 mm), of the bicyclo[3.1.0]hexane-3-carboxylic acid. Repeated recrystallization from pentane gave an analytical sample, mp 30–31°.

Anal. Calcd for $C_7H_{10}O_2$ (126.15): C, 66.64; H, 7.99. Found: C, 66.87; H, 8.05.

A portion of the original liquid distillate was reduced with lithium aluminum hydride in ether and gave two components in a ratio of 92:8 by vpc on a 4 ft × 1/8 in. 15% β,β′-oxydipropionitrile column at 80°. The larger fraction was collected by preparative vpc on a 6 ft × 0.25 in. 10% β,β′-oxydipropionitrile column to give an analytical sample of the *cis*-bicyclo[3.1.0]hexyl-3-carbinol, $n^{25}D$ 1.4784.

Anal. Calcd for $C_7H_{12}O$ (112.17): C, 74.95; H, 10.78. Found: C, 74.47; H, 10.68.

The smaller alcohol fraction was found to be identical with the *trans* carbinol. This 92:8 mixture of *cis* and *trans* acids was used in electrolysis experiments to determine the electrolysis results on the *cis* acid.

***trans*-Bicyclo[3.1.0]hexane-3-carboxylic Acid (6).** A mixture of potassium *t*-butoxide, dimethyl sulfoxide (distilled from calcium hydride and stored over molecular sieves), and water was prepared using the same relative proportions of reagents and solvent and the same technique as outlined above for cleavage of **4** to the *cis* acid. The mixture was magnetically stirred and heated to 60° in an oil bath, 2 g of the 92:8 mixture of *cis* and *trans* acids was added, and the epimerization was run for 48 hr. The solution was quenched with about 150 ml of water, acidified with concentrated hydrochloric acid, and extracted with three 50-ml portions of pentane. The extracts were combined, dried over anhydrous magnesium sulfate, filtered, and distilled through a short column packed with glass helices. The residue was recrystallized from pentane and sublimed *in vacuo* (45° (0.01 mm)) to give an analytical sample of **6**, mp 58–59°.

Anal. Calcd for $C_7H_{10}O_2$ (126.15): C, 66.64; H, 7.99. Found: C, 66.76; H, 8.00.

A portion of this *trans* acid was reduced with lithium aluminum hydride in ether to an alcohol which was homogeneous by vpc. The *trans*-bicyclo[3.1.0]hexyl-3-carbinol was collected by preparative vapor phase chromatography to give an analytical sample, $n^{25}D$ 1.4752.

Anal. Calcd for $C_7H_{12}O$ (112.17): C, 74.95; H, 10.78. Found: C, 74.65; H, 10.78.

This *trans* carbinol was identical with the minor component from reduction of the *cis* acid mixture.

***cis*- and *trans*-Bicyclo[3.1.0]hexane-3-carboxylic Acids-6-d_1 (24).** The *cis* acid with excess deuterium at C-6 was prepared as previously described for the undeuterated compound with the additional requirement that deuterium oxide is used in place of water. That deuterium incorporation occurs stereospecifically at C-6 was confirmed by nmr and comparison with the previously reported compound.[12] The *trans* acid with excess deuterium at C-6 was obtained from epimerization of the deuterated *cis* acid as outlined above.

Electrolysis of *cis*- and *trans*-Bicyclo[3.1.0]hexane-3-carboxylic Acids. In a typical experiment, 100 ml of pyridine and 300 ml of water were mixed in a 1-l., round-bottom flask equipped with smooth platinum electrodes, reflux condenser, gas inlet tube, and magnetic stirring bar. The solution was vigorously stirred at an applied voltage of 35, and 2.0 g (0.0150 mole) of the *cis* acid in 10 ml of pyridine and 1 ml of triethylamine was slowly added. The temperature rose to 80° during the first hour and remained fairly constant. A slow stream of nitrogen flushed the reaction vessel during the 17.5-hr period of electrolysis. The amperage remained fairly constant at 0.6 after the initial addition of acid. The dark mixture was cooled in an ice bath and a 1:1 aqueous solution of concentrated hydrochloric acid was slowly added with stirring until the excess pyridine was converted to the hydrochloride. The aqueous solution was saturated with sodium chloride and continuously extracted with ether for 24 hr. (Alternatively, the reaction mixture was extracted with about 1 l. of ether and the ether was washed free of pyridine with aqueous acid. Either method gave essentially the same ratio of products.) The ether extract was dried over anhydrous magnesium sulfate, filtered, and distilled through a short column of glass helices. The residue was quantitatively transferred to a standard amount of *n*-hexyl alcohol and the yields were determined by integration of the vpc traces.

The *cis*-3-alcohol and *trans*-2-alcohol could be cleanly separated by vpc with a 10 ft × 0.25 in. 10% β,β′-oxydipropionitrile on firebrick column at 85° as previously reported.[6] Although the 2- and 3-ketones were also well separated, the *trans*-3- and *cis*-2-alcohols could not be completely separated from one another on this column. Fortunately, the *cis*-2-alcohol could be separated from all other products with a 5 ft × 1/8 in. 19% Carbowax 20M Chromosorb W column at 100°. Both of these columns were used in the product analysis. The retention times of all products corresponded to those of authentic samples. In addition, oxidation of the electrolysis mixture with chromic acid in acetone at 0° gave only two components which were collected using a 10 ft × 3/8 in. 20% SE30 on Chromosorb W column at 100° and shown to be the 2- and 3-ketones by comparison with authentic samples.

Table II illustrates the rough data obtained by vpc for varying time intervals of electrolysis. The values obtained in successive runs for any one product vary by at most 3%.

Mass Spectral Analysis. The *cis*- and *trans*-2-alcohols obtained from electrolysis of *cis*-bicyclo[3.1.0]hexane-3-carboxylic acid-6-d_1, were separately collected by vpc, oxidized with chromic acid in acetone to the 2-ketones, and analyzed for deuterium content by mass spectra. The mixture of alcohols obtained from electrolysis of the deuterated *trans* acid was oxidized in the same manner. The 2-ketone was collected by vpc and similarly analyzed. The *trans*-bicyclo[3.1.0]hexane-3-carboxylic acid-6-d_1 methyl ester was also analyzed by mass spectra to determine the amount of deuterium incorporation at C-6 for both epimeric acids. Samples of the undeuterated 2-ketone and *trans*-methyl ester were run as standards. The raw data from the mass spectra of the ketones and esters (Table III) were the relative peak heights, after suitable amplification, of the parent ions in question. The excess deuterium content of the ketones was determined by assuming that the peak heights at mass numbers 96 and 97 are in the same ratio as the number of molecules of these approximate molecular weights in the ketone sample. There is no measurable peak at mass number 95. An equation has been derived (eq 1) for the determination of excess deuterium content in the bicyclo[3.1.0]hexan-3-one where R_0 is the ratio of peak heights at mass numbers 96 to that of 97 for ketone with normal isotopic distribution, R is the ratio of these same peaks for the sample under consideration, and P_d is the percentage of deuterated molecules in the sample.[6] Utilization of this equation produced the results listed in Table III. The analysis of

$$P_d = \frac{R - R_0}{1 + R - R_0} \times 100 \qquad (1)$$

the methyl ester was complicated by the formation of a substantial peak at mass number 139 due to the loss of one hydrogen. It was assumed that the fragmentation leading to this ion would not involve the abstraction of a proton from the methylene carbon of the cyclopropane ring which is substituted by deuterium in the ester under consideration. An equation can be derived (eq 2) involving the same reasoning as indicated above for the ketone where R_0 is the ratio of peak heights for mass numbers, 140 and 139, respectively, for the deuterated ester and R_4 is the same ratio for the undeuterated ester; R_1 is the ratio of peak heights for mass numbers, 141 and 139, respectively, for the deuterated species and R_3 is the same ratio for the standard ester; finally, R_2 is the ratio of peak heights for mass numbers, 142 and 139, respectively, for the deuterated methyl ester. The calculated percentage of deuterated

$$P_d = \frac{R_0 + R_1 + R_2 - R_3 - R_4}{1 + R_0 + R_1 + R_2} \times 100 \qquad (2)$$

methyl ester obtained from mass spectral data is in good agreement with a value of 64 ± 2% obtained from nmr analysis. A variation of ±1% from duplicate mass spectra of the compounds in question indicates no loss of deuterium in the rearranged alcohols obtained from electrolysis of *cis*- or *trans*-bicyclo[3.1.0]hexane-3-carboxylic acids-6-d_1.

***cis*-Bicyclo[3.1.0]hexane 3-*t*-Butyl Perester Synthesis and Decomposition.** To a solution of 1.8 g (0.016 mole) of sodium *t*-butyl peroxide in 20 ml of ether at 0° was slowly added 1.1 g (0.0076 mole) of *cis*-bicyclo[3.1.0]hexane-3 acid chloride, bp 79° (17 mm), dissolved in 10 ml of ether. The suspension was stirred for 3 hr at room temperature, then 5 ml of water was added and the solution was vigorously stirred for 15 min followed by extraction with 25 ml of pentane. The organic phase was successively washed with 10% cold sulfuric acid, 10% cold sodium bicarbonate, and cold water, dried over anhydrous magnesium sulfate, filtered, and concentrated in the cold. An infrared spectrum of the residue indicated the presence of residual *t*-butyl peroxide. The concentrate was redissolved in pentane, washed successively with cold water, and concentrated to a colorless, sweet-smelling liquid, the infrared spectrum of which contained a strong, sharp peak at 5.6 μ and no absorption in the hydroxyl region. The ester was dissolved in 20 ml of monoglyme (distilled from calcium hydride) and heated to reflux in a steady flow of oxygen for 30 hr. The solution was cooled to room temperature and slowly added to 0.8 g (0.021 mole) of lithium aluminum hydride in ether at 0°, stirred at room temperature for 2 hr, and slowly hydrolyzed with 3.2 ml of water. Additional stirring for 1 hr followed by filtration and concentration with a short column of glass helices gave a colorless liquid residue which was analyzed by vpc on a β,β′-oxydipropionitrile column at 80°. The chromatogram indicated the epimeric 3-alcohols were present but none of the rearranged 2-alcohols could be detected. The epimeric bicyclo[3.1.0]hexyl-3-carbinols were also present.

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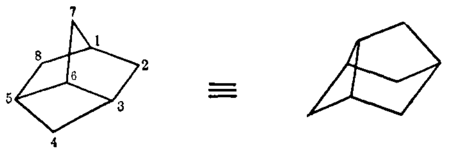
Synthesis and Chemistry of the Tricyclo[3.2.1.$0^{3,6}$]octane System

R. R. Sauers, R. A. Parent, and S. B. Damle

Contribution from the School of Chemistry, Rutgers, The State University, New Brunswick, New Jersey 08903. *Received January 19, 1966*

Abstract: The tricyclo[3.2.1.$0^{3,6}$]octane system (I) and several of its derivatives have been synthesized by a novel ring closure reaction. A study of reactions involving cationic intermediates at C_2 has revealed a remarkable resistance to rearrangement.

The chemistry of bridged polycyclic carbon systems has attracted the attention of innumerable investigators. In addition to the many challenging synthetic problems involved, many of these systems have exhibited interesting physical and chemical properties as well. We wish to expand and detail our earlier results on the synthesis and chemistry of the tricyclo[3.2.1.$0^{3,6}$]-octane system (I)[1,2] and some of its derivatives.



I

The key synthetic step in which the cyclobutyl ring is constructed is noteworthy owing to the potential generality of this procedure for the preparation of other strained ring systems. Additionally, the reactivity of strained systems is not well understood and data obtained in this study provide further insights and suggest other experimentation.

Synthesis. The basic starting materials for the successful synthesis of this tricyclic system were the readily available 5-halomethylnorbornenes (IIa and IIb). Treatment of the olefins with buffered peracetic acid led to epoxides IIIa and IIIb.[3]

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