Protonated Cyclopropanes. VIII. Trifluoroacetolysis of 1-Propyl-*1*-^{14}C-mercuric Perchlorate and of 1-Butyl-*1*-^{14}C Tosylate[1]

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Received March 9, 1973

Abstract: The trifluoroacetolysis of 1-propyl-*1*-^{14}C-mercuric perchlorate gave mainly 2-propyl trifluoroacetate, but the 1-propyl ester that was obtained showed more isotopic scrambling to C-3 than C-2. This finding suggests that at least some of the 1-propyl product was formed from edge-protonated cyclopropane. It is proposed that if corner-protonated cyclopropane were more stable, under the conditions of this reaction, kinetically controlled product formation from the edge-protonated species could compete significantly with conversion to the corner-protonated species. Trifluoroacetolysis of 1-butyl-*1*-^{14}C tosylate resulted in the formation of all four isomeric butyl esters. The chief product, 2-butyl trifluoroacetate, showed extensive isotopic scrambling, the mean ^{14}C distribution at C-1, C-2, C-3, and C-4 respectively being 48.1, 2.3, 3.3, and 46.3%. It is suggested that these results could be reasonably explained by involving the occurrence of two processes, the main pathway being the degenerate rearrangement interconverting the 2-butyl cations through hydride shifts, with the minor process involving protonated methylcyclopropanes as reaction intermediates.

Most of our previous isotopic scrambling studies on 1-propyl-*1*-^{14}C systems gave 1-propyl products with about equal amounts of the ^{14}C label rearranged from C-1 to C-2 and to C-3.[2] These results did not provide a differentiation between edge- and corner-protonated cyclopropanes as reaction intermediate. According to Collins,[3] in reactions with 1-propyl-*1*-^{14}C substrates, the 1-propyl product *can* show more isotopic scrambling to C-3 than C-2 if the mechanism were to involve equilibrating edge-protonated cyclopropane intermediates. On the other hand, products arising only from equilibrating corner-protonated species *can never* give more scrambling to C-3 than C-2. In the treatment of 1-chloropropane-*1*-^{14}C with $AlCl_3$,[4] more scrambling to C-3 than C-2 was observed in the recovered 1-chloropropane; however, reversible isomerization between 1- and 2-chloropropanes under these conditions rendered the results inapplicable to the conclusions of Collins. The present paper reports the finding that the trifluoroacetolysis of 1-propyl-*1*-^{14}C-mercuric perchlorate indeed gave a 1-propyl product with more scrambling to C-3 than C-2, which may be regarded as evidence for edge protonation, as well as the results from the trifluoroacetolysis of 1-butyl-*1*-^{14}C tosylate and the possible implication of protonated methylcyclopropanes in the reaction.

A solution of 1-propyl-*1*-^{14}C-mercuric perchlorate (**1**-$HgClO_4$-*1*-^{14}C) (~0.5 *M*) in F_3CCOOH was heated under reflux for 8 hr. The products, analyzed by vpc, consisted of 7 and 93%, respectively, of the 1- and 2-propyl trifluoroacetates (**1**-$OAcF_3$-^{14}C and **2**-$OAcF_3$-^{14}C). Degradation of the vpc purified **1**-OH-^{14}C[2c] and **2**-OH-^{14}C[4] derived from the product esters gave the results summarized in Tables I and II.

Table I. Isotopic Scrambling Data from Degradation of 1-Propanol-^{14}C Derived from 1-Propyl-^{14}C Trifluoroacetate

	Specific activity, cpm/mmol			^{14}C distribution, %		
Expt	CH_3CH_2-CH_2OH[a]	CH_3-COOH[b]	CH_3-NH_2[c]	C-1	C-2	C-3
1	97,400	24,500	14,500	74.8	10.3	14.9
2	83,100	21,000	12,300	74.7	10.5	14.8
3	108,000	28,200	15,500	73.9	11.7	14.4
4	107,000	26,100	15,600	75.6	9.8	14.6

[a] Assayed as the α-naphthylurethane. [b] Assayed as the *p*-toluidide. [c] Assayed as the *p*-toluenesulfonamide.

Table II. Isotopic Scrambling Data from Degradation of 2-Propanol-^{14}C Derived from 2-Propyl-^{14}C Trifluoroacetate

	Specific activity, cpm/mmol		^{14}C distribution, %	
Expt	$(CH_3)_2CHOH$[a]	PhCOOH[b]	C-1,3	C-2
1	1,102,000	12,500	98.9	1.1
2	1,076,000	12,500	98.8	1.2

[a] Assayed as the α-naphthylurethane. [b] Derived from C-2.

The data in Table I were obtained from two sets of duplicate experiments carried out by different workers at different times. Hence the finding of more scrambling to C-3 than C-2 has in effect been independently verified. When **1**-$OAcF_3$ and $HClO_4$ (0.5 *M*) in F_3CCOOH were heated as in the solvolysis, some conversion to **2**-$OAcF_3$ (about 5%) took place according to nmr analysis. Thus, the small extent of rearrangement of the ^{14}C label to C-2 in the **2**-OH-^{14}C, as shown in Table II, could be attributable to the conversion of some isotopically scrambled **1**-$OAcF_3$-^{14}C to **2**-$OAcF_3$-^{14}C. On the other hand, a similar treatment of equimolar quantities of **2**-$OAcF_3$ and $HClO_4$ in F_3CCOOH did not give any detectable amount of **1**-$OAcF_3$. Hence, reversible 1,2-hydride shifts did not occur and the finding of more scrambling of the ^{14}C from C-1 to C-3 than to C-2 (Table I) could be regarded as evidence in support of a mechanism involving equilibrating edge-protonated cyclopropanes.[3] Since the major product in this reaction is 2-propyl trifluoroacetate (**2**-$OAcF_3$-

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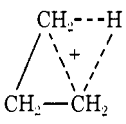
[1] Part of this work was reported as a communication to the Editor: C. C. Lee, S. Vassie, and E. C. F. Ko, *J. Amer. Chem. Soc.*, **94**, 8931 (1972).

[2] (a) C. C. Lee and K.-M. Wan, *J. Amer. Chem. Soc.*, **91**, 6416 (1969); (b) C. C. Lee and W. K.-Y. Chwang, *Can. J. Chem.*, **48**, 1025 (1970); (c) C. C. Lee and J. Law, *ibid.*, **49**, 2746 (1971).

[3] C. J. Collins, *Chem. Rev.*, **69**, 543 (1969).

[4] C. C. Lee and D. J. Woodcock, *J. Amer. Chem. Soc.*, **92**, 5992 (1970).

^{14}C), the major reaction route must have involved 1,2-hydride shifts *via* the 1-propyl cation or its equivalent. Equilibrating protonated cyclopropanes are invoked in explaining the isotopic scrambling in the minor product, **1**-OAcF$_3$-^{14}C. In accordance with the treatment of Collins,[3] the data in Table I would suggest that the scramblings in **1**-OAcF$_3$-^{14}C *cannot* arise *via* product formation only from equilibrating corner-protonated cyclopropanes, but *can* arise *via* product formation from equilibrating edge-protonated cyclopropanes or from both edge- and corner-protonated cyclopropanes. Recently, Radom, *et al.*,[5] have carried out *ab initio* calculations with optimization of geometry on the $C_3H_7^+$ ions and have obtained results indicating that edge-protonated cyclopropane **3** is less stable than the corner-protonated species **4** by about 10 kcal/mol. It was also concluded that besides the 2-propyl cation, the only stable intermediate may be the methyl eclipsed 1-propyl cation or distorted corner-protonated cyclopropane **5**, with **3** and **4** as transition states for the 1,3-hydride and 1,2-methyl shifts, respectively. These calculations predict that there should be more isotopic scrambling from C-1 to C-2 than to C-3 for reactions *via* protonated cyclopropanes from C-1 labeled 1-propyl substrates. It was suggested that discrepancies between this prediction and data obtained from reactions in solution might be the result of a solvent assistance for the 1,3-hydride shift, or a specific hydrogen bonding of the edge proton in transition state **3** for the 1,3 shift. Since F$_3$CCOOH is a solvent of extremely low nucleophilicity,[6] it is unlikely that F$_3$CCOOH would be especially efficient in providing solvent assistance or specific H-bonding to explain the scrambling data in Table I.[7] Interestingly, another set of recent calculations by Dewar, *et al.*,[8] using a modified version of the MINDO/2 method, has led to the entirely different finding that **3** is more stable than **4** or the 1-propyl cation, and that edge-protonated **3** is the only stable species besides the 2-propyl cation in the $C_3H_7^+$ potential surface.



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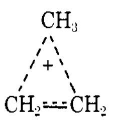

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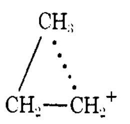

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Professor P. v. R. Schleyer (private communications) has pointed out to us that theoretical calculations are probably not yet capable of giving a definitive answer to the differentiation between edge- and corner-protonated cyclopropanes. Furthermore, because of the flatness of the energy surface, the distorted corner-protonated cyclopropane (**5**) may not survive as an energy minimum in a more sophisticated approach. Semiempirical calculations including the MINDO/2 type[8] tend to give too great a stability to structures containing small rings, while in *ab initio* calculations at the 4–31-G level,[5] small rings tend to come out too unstable. It was indicated that very recent modifications by Pople to correct for the latter defect by the inclusion of polarization functions still led to the conclusion that corner-protonated cyclopropane is more stable than the edge-protonated species by about 5 kcal/mol. Moreover, nmr studies by Saunders, *et al.*,[9] on the 2-propyl cation with simultaneous D and ^{13}C labels have led to the preliminary conclusion that in superacid, the stable species is corner protonated (**4**). Isotopic scramblings would take place through corner-to-corner migrations *via* the edge-protonated species either as a transition state or as an intermediate.

Thus, even if **4** were more stable than **3**, the involvement of **3** is not eliminated. There is strong experimental evidence that protonation of cyclopropanes takes place at the edge of the ring.[10] The edge-protonated **3** thus formed may then be converted smoothly to the more stable **4**. The present finding of more scrambling of the ^{14}C from C-1 to C-3 than to C-2 (Table I) may be attributable to the formation of some kinetically controlled product from **3** besides product formation from the more stable **4**. The situation may be comparable to behaviors in the norbornyl cationic system. In superacid, evidence has indicated that the stable species is the norbornonium ion (corner-protonated nortricyclene).[11] For reactions in solution, more complex processes may be involved; for example, the ^{14}C scrambling observed in the π-route formation of the norbornyl cation could be most readily explained by invoking product formation from the norbornonium ion as well as from edge-protonated nortricyclene.[12]

It is of interest to note that the deamination of **1**-NH$_2$-*1*-^{14}C,[2a] the trifluoroacetolysis of **1**-OTs-*1*-^{14}C,[2b] as well as the acetolysis and formolysis of **1**-HgClO$_4$-*1*-^{14}C[2c] gave 1-propyl products with essentially equal extents of ^{14}C scrambling to C-2 and C-3. The present finding of more scrambling to C-3 than C-2 in the trifluoroacetolysis of **1**-HgClO$_4$-*1*-^{14}C thus appears to be an unusual case. It may be suggested that the stability or lifetime of the cationic intermediates could play a significant role in determining the observed results. In the trifluoroacetolysis of **1**-OTs-*1*-^{14}C, the cationic intermediates generated in the reaction may form ion pairs with the tosylate counterion. Such ion pairing could provide the stabilization and give a longer lifetime to allow for the edge- and corner-protonated cyclopropane intermediates to equilibrate and thus giving rise to an equal distribution of the ^{14}C label in the 1-propyl product derived from these intermediates. The deamination and demercuration reactions will give cationic intermediates with no appropriate counterions to form ion pairs, and such ions have been considered as vibrationally excited or "hot." In the deamination of **1**-NH$_2$-*1*-^{14}C carried out in an aqueous medium, or in the acetolysis and formolysis of **1**-HgClO$_4$-*1*-^{14}C, the solvents are of sufficiently high nucleophilic character to provide some stabilization by solvation even of these hot cations and thus allowing again the protonated

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(5) L. Radom, J. A. Pople, V. Buss, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **94**, 311 (1972).

(6) P. E. Peterson and F. J. Waller, *ibid.*, **94**, 991 (1972); T. W. Bentley, F. L. Schadt, and P. v. R. Schleyer, *ibid.*, **94**, 992 (1972).

(7) Nmr evidence for a 1,3-hydride shift in the 2,4-dimethyl-2-pentyl cation has been reported very recently by M. Saunders and J. J. Stofko, Jr. [*ibid.*, **95**, 252 (1973)]. This process involves a hydride transfer between two tertiary centers. It is uncertain whether an analogous 1,3 shift could occur between two primary centers, as would be the case for such a process in the 1-propyl cation.

(8) N. Bodor, M. J. S. Dewar, and D. H. Lo, *ibid.*, **94**, 5303 (1972).

(9) M. Saunders, P. Vogel, E. L. Hagen, and J. Rosenfeld, *Accounts Chem. Res.*, **6**, 53 (1973). We thank Professor Saunders for supplying us with a copy of this manuscript prior to its publication.

(10) L. Joris, P. v. R. Schleyer, and R. Gleiter, *J. Amer. Chem. Soc.*, **90**, 327 (1968).

(11) G. A. Olah, A. M. White, J. R. DeMember, A. Commeyras, and C. Y. Lui, *ibid.*, **92**, 4627 (1970).

(12) C. C. Lee and B.-S. Hahn, *ibid.*, **91**, 6420 (1969).

Table III. Relative Yields (%) of Isomeric Butyl Alcohols Derived from the Ester Products in the Trifluoroacetolysis of 1-Butyl-*1*-^{14}C Tosylate

Expt	1-BuOH	2-BuOH	*t*-BuOH	*i*-BuOH
1	32.2	64.5	3.0	0.3
2	31.7	65.1	3.0	0.2

Table IV. ^{14}C Distribution in the 1-Butyl Product from Trifluoroacetolysis of 1-Butyl-*1*-^{14}C Tosylate

	Specific activity, cpm/mmol			^{14}C distribution, %		
Expt	1-BuOH[a]	CH_3-CH_2-COOH[b]	CH_3-COOH[c]	C-1	C-2	C-3,4
1	238,100	690	260	99.7	0.2	0.1
2	70,600	140	70	99.8	0.1	0.1

[a] Assayed as the α-naphthylurethane. [b] Assayed as the *S*-benzylisothiouronium salt. [c] Assayed as the *p*-nitrobenzyl ester.

Table V. ^{14}C Distribution in the 2-Butyl Product from Trifluoroacetolysis of 1-Butyl-*1*-^{14}C Tosylate

	Specific activity, cpm/mmol					^{14}C distribution, %			
Expt	2-BuOH[a]	CBr_4	CH_3CH_2-COOH[b]	CH_3-COOH[c]	CH_3NH_2[d]	C-1	C-2	C-3	C-4
1	511,400	245,800	266,100	254,200	237,400	48.1	2.3	3.3	46.4
2	247,500	118,400	129,100	122,900	114,800	47.8	2.5	3.3	46.4
3[e]	509,500	247,200	262,300	251,200	234,500	48.5	2.2	3.3	46.0
					Mean values	48.1	2.3	3.3	46.3

[a] Assayed as the α-naphthylurethane. [b] Assayed as the *S*-benzylisothiouronium salt. [c] Assayed as the *p*-nitrobenzyl ester. [d] Assayed as the *p*-toluenesulfonamide. [e] The heating of the reaction mixture in this experiment was extended from 7 to 9 days.

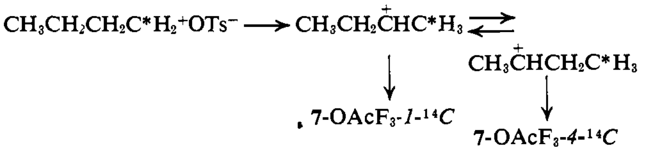
cyclopropane intermediates to equilibrate to give equal ^{14}C distributions in the 1-propyl products. On the other hand, in the trifluoroacetolysis of **1**-$HgClO_4$-*1*-^{14}C, the extremely low nucleophilic character of the solvent failed to provide such stabilization by solvation; thus kinetically controlled product formation from the edge-protonated species becomes significantly important, resulting in the net scrambling data as recorded in Table I.

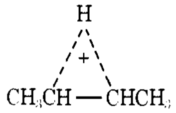
Recently, Lee and Zea Ponce[13] reported the observation of extensive isotopic scrambling in the 2-butyl-^{14}C chloride recovered from the treatment of 1-butyl-*1*-^{14}C chloride with $AlCl_3$. The data indicated the occurrence of complex scrambling processes, but no definitive evidence in support of protonated methylcyclopropane intermediates could be deduced. An extension of the work on the 1-butyl-*1*-^{14}C system to include the trifluoroacetolysis of 1-butyl-*1*-^{14}C tosylate (**6**-OTs-*1*-^{14}C) was carried out since such a study may provide information on whether protonated methylcyclopropanes would play a part under solvolytic conditions with the highly rearranging trifluoroacetic acid as solvent.

The reaction was carried out by heating a 20% solution of **6**-OTs-*1*-^{14}C in F_3CCOOH under reflux for 7 days. The products obtained were 1-butyl and 2-butyl trifluoroacetates (**6**-$OAcF_3$-^{14}C and **7**-$OAcF_3$-^{14}C) together with minor amounts of the *tert*-butyl and isobutyl esters. Given in Table III are the relative compositions of the product mixtures from duplicate experiments as measured by isotopic dilution.[13] After hydrolysis to give the corresponding alcohols followed by purification by preparative vpc, degradation[13] of the **6**-OH-^{14}C and **7**-OH-^{14}C showed only very minor scrambling of the ^{14}C label from C-1 to the other positions of the 1-butyl group (Table IV), while extensive isotopic scramblings were observed in the 2-butyl product (Table V).

The data in Table IV indicate that the almost completely unrearranged 1-butyl product from the trifluoroacetolysis of **6**-OTs-*1*-^{14}C likely arose almost entirely from direct displacement. Previous studies on the 1-butyl and 2-butyl systems, as discussed by Lee and Zea Ponce,[13] suggest that in accounting for the data in Table V, successive 1,2-hydride shifts must be a major pathway (Scheme I). However, the process will only scramble the ^{14}C label over the C-1 and C-4 positions in the 2-butyl product. Recently, Dannenberg, *et al.*,[14] have obtained evidence suggesting that in F_3CCOOH, the degenerate rearrangement interconverting the 2-butyl cations may involve H-bridged ion **8**, but the net result would still be the scrambling, of the label over C-1 and C-4.

Scheme I





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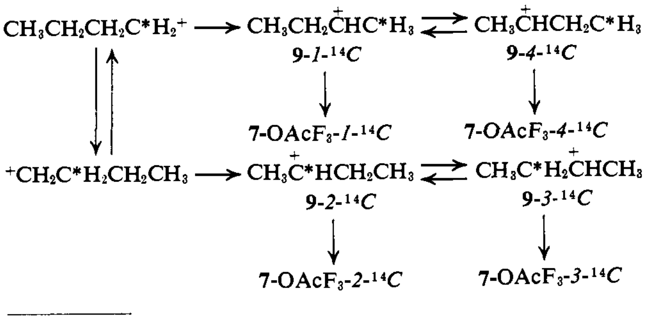
To account for the presence of ^{14}C in the C-2 and C-3 positions of the 2-butyl group (Table V), a mechanism as shown in Scheme II, involving classical ions in

Scheme II



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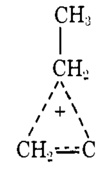
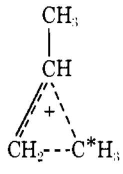
(13) C. C. Lee and I. Y. Zea Ponce, *Can. J. Chem.*, **50**, 3179 (1972).

(14) J. J. Dannenberg, D. H. Weinwurzel, K. Dill, and B. J. Goldberg, *Tetrahedron Lett.*, 1241 (1972).



10a



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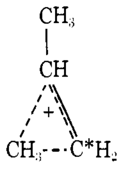
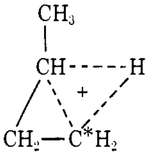


10c



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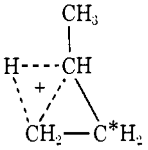

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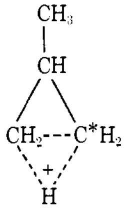
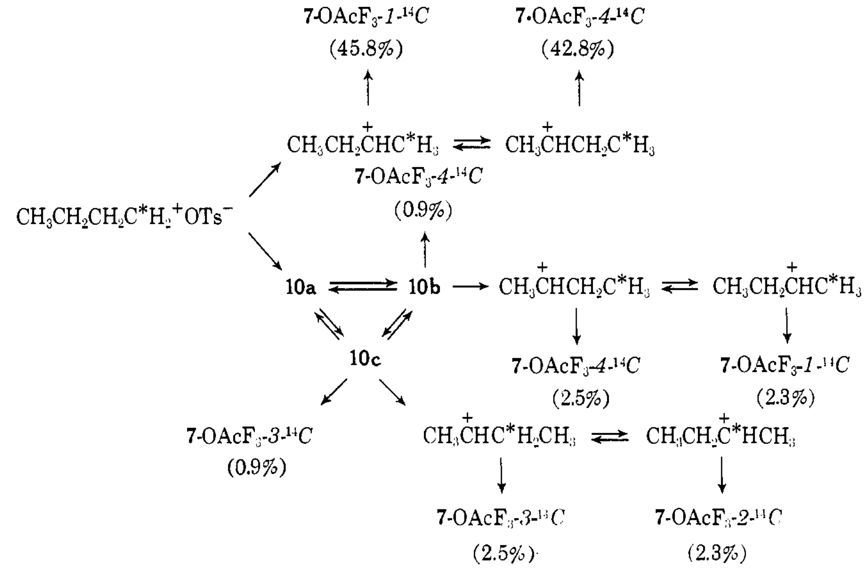


11c

which 1,2-ethyl shifts take place in the 1-butyl cation, may be considered. Since the 2-butyl cations **9**-*1*-^{14}C and **9**-*2*-^{14}C differ only in the position of the label, one would expect these ions to give the same subsequent reactions. Hence the ratio of 7-OAcF$_3$-*1*-^{14}C to 7-OAcF$_3$-*4*-^{14}C should be the same as the ratio of 7-OAcF$_3$-*2*-^{14}C to 7-OAcF$_3$-*3*-^{14}C.[15] We believe that the precision of the data in Table V is sufficiently good to indicate that this equality does not hold, the ratio of 7-OAcF$_3$-*1*-^{14}C/7-OAcF$_3$-*4*-^{14}C being greater than unity and the ratio of 7-OAcF$_3$-*2*-^{14}C/7-OAcF$_3$-*3*-^{14}C being less than unity.

Scheme III



An alternative route for locating the ^{14}C label at C-2 and C-3 of the 2-butyl product could involve protonated methylcyclopropanes. Deno, *et al.*,[16] have noted that the addition of DCl to methylcyclopropane gave 2-butyl-*4-d* chloride without isotopic scrambling. It was suggested that since the 2-butyl cation is more stable than protonated methylcyclopropane, the 2-butyl cation was formed directly and the protonated methylcyclopropane was by-passed in this reaction. On the other hand, examination of the 2-butyl cation in superacid by Saunders, *et al.*,[9] indicated that besides the degenerate rearrangement interconverting the 2-butyl cations by hydride shifts, there is another process which scrambles all the protons. The activation energy of this latter process was too low for a reversible rearrangement between 2-butyl and 1-butyl cations and it was suggested that the most probable mechanism would involve closure to corner-protonated methylcyclopropane, followed by degenerate corner-to-corner proton rearrangement and reopening to scrambled 2-butyl cation. The present data (Table V) might be explained in an analogous way. Besides the process of successive 1,2-hydride shifts as given in Scheme I, there is another process involving protonated methylcyclopropanes (corner protonated **10a–c** or edge-protonated **11a–c**). It is assumed that these protonated methylcyclopropanes could give ester products directly and also give rise to the more stable 2-butyl cation,[16] which subsequently would undergo degenerate hydride shifts. Given in Scheme III is a complete partitioning of the various routes (utilizing corner-protonated **10a–c**) leading to the ^{14}C scrambling in the 2-butyl product, 7-OAcF$_3$-^{14}C. In this scheme, the equality of the product ratios derived from equilibrating 2-butyl cations is maintained ($45.8/42.8 = 2.5/2.3$). The net ^{14}C contents at C-1, C-2, C-3, and C-4 respectively are $45.8 + 2.3$, 2.3, $2.5 + 0.9$, and $42.8 + 2.5 + 0.9$, or 48.1, 2.3, 3.4, and 46.2%, which agree very well with the mean values of 48.1, 2.3, 3.3, and 46.3% as given in Table V. Moreover, in this scheme, traces of scrambled 1-butyl product (Table IV) could arise from **10a**. From **10b** and **10c**, small amounts of the isobtuyl product could be formed and this subsequently could rearrange to *tert*-butyl trifluoroacetate (Table III). Thus the nature of the products from the trifluoroacetolysis of **6**-OTs-*1*-^{14}C and the isotopic scramblings in some of these products appear to be reasonably explicable by invoking some intervention of protonated methylcyclopropanes.

Experimental Section

Trifluoroacetolysis of 1-Propyl-*1*-^{14}C-mercuric Perchlorate (1-HgClO$_4$-*1*-^{14}C). The preparation of the starting material and the solvolysis reaction were carried out as in the previous acetolysis and formalysis of **1**-HgClO$_4$-*1*-^{14}C.[2c] The relative yields of 1-propyl and 2-propyl trifluoroacetates, as estimated by vpc analysis of a small portion of the reaction mixture, were about 7 and 93%, re-

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(15) This interpretation was first suggested to us by Professor Arthur Fry.

(16) N. C. Deno, D. LaVietes, J. Mockus, and P. C. Sholl, *J. Amer. Chem. Soc.*, **90**, 6457 (1968).

spectively. The ester products were hydrolyzed directly in the reaction mixture,[2c] and the overall yields of 1-propanol (**1**-OH-^{14}*C*) and 2-propanol (**2**-OH-^{14}*C*) ranged from 92 to 95% according to isotope dilution calculations. **1**-OH-^{14}*C* was degraded in the usual way through conversion to propionic acid, acetic acid, and methylamine,[17] and **2**-OH-^{14}*C* was degraded by conversion to acetone, dimethylphenylcarbinol, and benzoic acid as described by Lee and Woodcock.[4]

Trifluoroacetolysis of 1-Butyl-*1*-^{14}*C* Tosylate (6-OTs-*1*-^{14}*C*). A solution of 8.00 g (35 mmol) of **6**-OTs-*1*-^{14}*C* (prepared as previously described[13]) in 40 ml of F_3CCOOH was heated under reflux for 7 days. The reflux condenser was protected by a silica gel drying tube and was cooled by refrigerated water at 6–8°. The reaction time was chosen after preliminary nmr monitoring indicated that about 7 days were needed for the complete disappearance of the C-1 proton triplet of the **6**-OTs. In a third run, the reaction time was extended to 9 days and the isotopic scramblings in the recovered 2-butyl product were not significantly different (Table V).

At the completion of the period of refluxing, about 10% of the reaction mixture was removed for product analysis by isotopic dilution. Weighed quantities (about 3 g) of ordinary 1-butyl, 2-butyl, *tert*-butyl, and isobutyl trifluoroacetates were added as carriers. A sufficient amount of aqueous KOH solution was then added to neutralize the mixture and leave a final solution containing 20% KOH. This basic solution was refluxed for 2 hr to effect the hydrolysis of the esters to the isomeric butyl alcohols. The specific activities of these alcohols, recovered by preparative vpc,[13] were utilized to estimate the product yields by isotopic dilution as previously described.[13] The total yield of the isomeric butyl alcohols was about 50%, their relative composition being given in Table III. It should be noted that control experiments using their nmr spectra as an indicator showed that 1-butyl, 2-butyl, and isobutyl trifluoroacetates were stable under the trifluoroacetolysis conditions, while decomposition definitely took place with *tert*-butyl trifluoroacetate. Thus the relative yield of *tert*-butyl product as recorded in Table III represents only the surviving portion of the *tert*-butyl ester.

The remainder of the reaction mixture (about 90%) was also neutralized and then hydrolyzed in 20% KOH. 1-Butanol (**6**-OH) and 2-butanol (**7**-OH) (about 5 g each) were added as carriers and the **6**-OH-^{14}*C* and **7**-OH-^{14}*C* were recovered by preparative vpc and degraded as described by Lee and Zea Ponce[13] to give the ^{14}C distributions recorded in Tables IV and V.

Acknowledgment. We wish to express our sincere thanks to Professor P. v. R. Schleyer for valuable comments and to the National Research Council of Canada for financial support.

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A Study of the Biscyclooctatetraene and the Phenylcyclooctatetraene Anion Disproportionation Equilibria

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Abstract: The thermodynamic parameters controlling the disproportionation equilibrium ($\pi^{2-} + \pi \rightleftharpoons 2\pi\cdot^-$) constant for biscyclooctatetraene and phenylcyclooctatetraene have been studied in hexamethylphosphoramide. Upon comparing these thermodynamic parameters with those for cyclooctatetraene, we find that the enthalpy term increases with the degree of conjugation from the cyclooctatetraene ring system due to the decreased electron–electron repulsion in the dianion. However, the entropy term increases with extended conjugation of the ring system due to the formation of freer ions. Extended conjugation decreases ion pairing due to the dispersion of charge in the anion radical and dianion.

It is well known that solutions of cyclooctatetraene (COT) in hexamethylphosphoramide (HMPA)[1] or in ethereal solvents[2–4] will dissolve alkali metal to form the COT dianion and anion radical. The concentrations of these species are controlled by the disproportionation equilibrium (eq 1, where π = COT).

$$\pi^{2-} + \pi \rightleftharpoons 2\pi\cdot^- \qquad (1)$$

The thermodynamic parameters controlling this equilibrium are more sensitive functions of ion pairing than esr parameters and possibly conductivity measurements.[1] Based upon the effect of the alkali metal counterion upon these thermodynamic parameters, ion pairing was observed in HMPA[1] where previously only free ions were thought to exist.[5] HMPA is still recognized as one of the most powerful solvating agents for alkali metal cations.[6,7]

Here we wish to report the formation of the dianion and anion radical of biscyclooctatetraene (BCOT) and phenylcyclooctatetraene (PCOT) along with the thermodynamic parameters for their disproportionation equilibria in HMPA.

Experimental Section

X-Band esr spectra were recorded using a Varian E-3 esr spectrometer. The temperature was controlled using a Varian V-4557 variable-temperature controller. The sample preparation was exactly the same as previously described.[1]

BCOT was synthesized by the method of Cope and Marshall[8] and was recrystallized twice from ether to give a constant melting point of 125–126°. The mass spectrum and nmr were consistent with the pure compound. PCOT was synthesized by the method of

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