Solvolysis of β-Cyclopropylethyl p-Bromobenzenesulfonate

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Acetolysis and formolysis of β-cyclopropylethyl brosylate has been investigated. No rearranged products were found in the former case. In pyridine–formic acid, cyclopentanol (60%), methylallylcarbinol (19%), and crotylcarbinol (21%) were isolated and identified. From a consideration of the position of deuterium in the products of formolysis of α,α-dideuterio-β-cyclopropylethyl brosylate it was concluded that classical ions alone or a combination of reactions of classical and nonclassical ions could rationalize the results.

Nitrous acid deamination of β-cyclopropylethylamine was reported recently by Cartier and Bunce.[2] These workers were able to rationalize their results solely on the basis of reactions of the classical carbonium ion I. These results are of interest in view of the calculations by Winstein and co-workers,[3] which suggest that a nonclassical form of I—*i.e.*, II—has a delocalization energy of 2β. In view of the well-known differences between reactions of cations generated from amines and those generated from arenesulfonate solvolyses, it was of interest to reinvestigate this system, starting with the latter precursors.

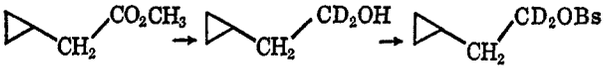
I II III

Results and Discussion

β-Cyclopropylethyl brosylate (III) was prepared and solvolyzed under a variety of conditions. The results are summarized in Table I.

The complete lack of rearrangement during acetolysis and the completeness of rearrangement with pyridine buffer suggest that a bimolecular displacement is responsible for any unrearranged products. This is further substantiated by the deuterium results discussed below. Also of interest is the absence of cyclopropylmethylcarbinol in the solvolysis products. That this is due primarily to the instability of the latter was shown by a control experiment. When cyclopropylmethylcarbinol was treated with formic acid under the reaction conditions, only methylallylcarbinol (72%) and crotylcarbinol (28%) were isolated.[4]

The results discussed at this point differ only in degree from those obtained on amine deamination.[2] In order to refine further any mechanistic interpretations, the solvolysis of α,α-dideuterio-β-cyclopropylethyl brosylate (VI) was also studied. This compound was readily prepared by reduction of methyl cyclopropyl acetate (IV) with lithium aluminum deuteride, followed by conversion to the brosylate VI.



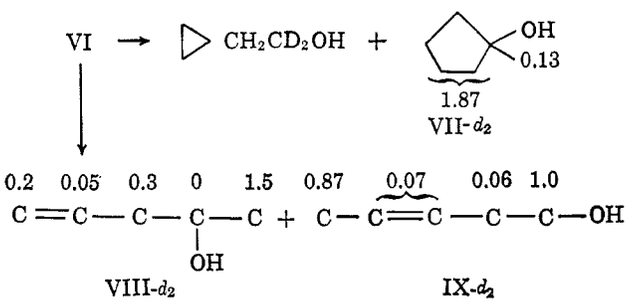
IV V VI

(1) NSF Undergraduate Research Fellow (GE 4048).
(2) G. E. Cartier and S. C. Bunce, *J. Am. Chem. Soc.*, **85**, 932 (1963).
(3) S. Winstein, P. Bruck, P. Radlick, and R. Baker, *ibid.*, **86**, 1867 (1964).
(4) K. L. Servis and J. D. Roberts, *ibid.*, **87**, 1331 (1965).

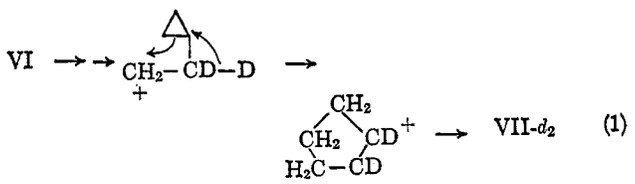
The formate ion buffered products of formolysis of VI were isolated and identified by standard methods and analyzed for deuterium content by examination of their integrated nmr spectra. The deuterium content found for the various positions for each of the products is shown in Chart I.

The lack of scrambling in the unrearranged β-cyclopropylethanol is in agreement with the bimolecular mechanism postulated for the formation of this product. It is significant that the cyclopentanol found cannot have been formed solely by a simple 1,3 shift or by solvent attack on a nonclassical ion as II-d_2.

CHART I

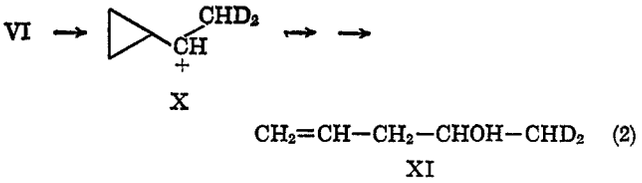


Only a deuteride shift at some stage allows entry of deuterium into the α-position of VII-d_2. This supports the mechanism advanced by Cartier and Bunce (eq 1), although it does not establish it.



(1)

The mechanisms for the formation of crotylcarbinol and methylallylcarbinol are intimately connected with the behavior of the methylcyclopropylcarbinyl cation.[4] It was originally anticipated that all of these alcohols would arise from partitioning of this cation. If this were true, the methylallylcarbinol would have the deuterium solely in the methyl group (see eq 2). In actual fact, using the data given in Chart I, it can be calculated that XI accounts for



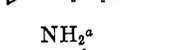
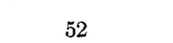
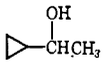
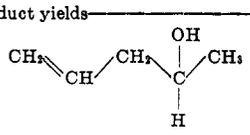
X

$CH_2{=}CH{-}CH_2{-}CHOH{-}CHD_2$ (2)

XI

TABLE I

CARBONIUM ION PRODUCTS FROM REACTIONS OF β-CYCLOPROPYLETHYL SYSTEMS

	Relative product yields				
					CH_3—CH=CH—CH_2CH_2OH
NH_2[a]	52	9	39	0	0
OBs[b]	100	0	0	0	0
OBs[c]	35	36	0	12	17
OBs[d]	0	60	0	19	21

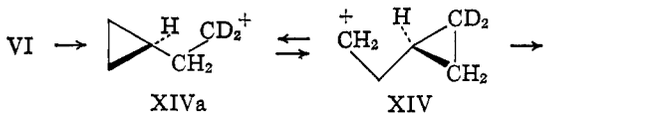
[a] See ref 2. [b] HOAc-NaOAc. [c] HCO_2H-NaO_2CH. [d] HCO_2H-C_5H_5N.

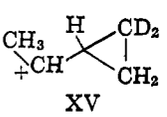
only 73% of the deuterated product. In addition to XI, there is formed about 16% of XII and 12% of XIII, assuming that these three products are the only ones formed.

CH_2=CH—CD_2—CHOH—CH_3
XII

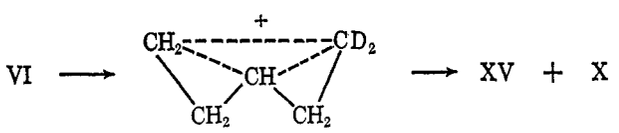
CD_2=CH—CH_2—CHOH—CH_3
XIII

These latter undoubtedly were formed by partitioning of ion XV which, in turn, could have been formed from XIV. Possibly, XIV is in rapid equilibrium with XIVa (see below), which goes on to form XV and X, respectively. Alternatively, the nonclassical ion, II-d_2, could also be invoked here. At




XV

best, this ion can account for only *ca.* 56% [2(12 + 16)] of the products,[5] the remainder coming from some other route (*e.g.*, eq 2).



It was expected that the crotylcarbinol would be formed from ions X and XV, in which case one would obtain the deuterated crotylcarbinols, XVI, XVII, and XVIII, in the approximate ratios 74:13:13. Assuming that the only deuterated species formed are

CHD_2—CH=CH—CH_2CH_2OH
XVI

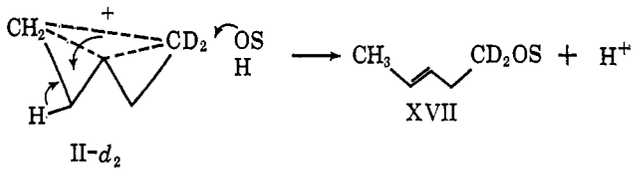
CH_3—CH=CH—CH_2CD_2OH
XVII

CH_3—CH=CH—CD_2CH_2OH
XVIII

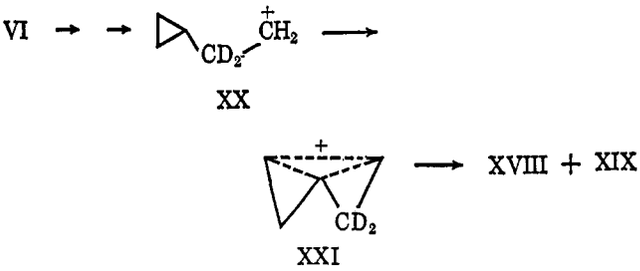
CH_2D—CD=CH—CH_2CH_2OH
XIX

XVI–XIX, one can calculate the following percentage distribution of products: XVI, 41; XVII, 50; XVIII, 3; XIX, 6. Thus, it is clear that, in contrast to the results of Servis and Roberts,[4] the methylallylcarbinols and the crotylcarbinols do not arise *via* partitioning of a common intermediate. Additional support for this comes from the results of the control experiment in which methylcyclopropylcarbinol was treated with formic acid. From this system, the ratio of these two alcohols was 72:28 compared with the 19:21 ratio obtained from the solvolysis.

One can envision highly concerted reactions of either the nonclassical ion II-d_2 or the classical counterparts as alternate modes of formation of the crotylcarbinols. Attack of solvent at one end of ion II-d_2 with concerted hydride shift at the other end, for example, would be expected to lead to approximately equal amounts of XVI and XVII.



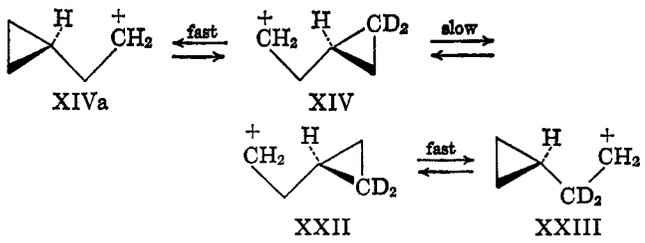
The small amounts of XVIII and XIX would have to arise from the isomeric ion XXI, which could arise by way of XX, the product of 1,2 cyclopropyl shift.



Attempts to utilize rapidly equilibrating classical ions to rationalize the deuterium results imposes some restrictions. The interconversion, XIV ⇌ XIVa, must not only be fast relative to direct collapse with solvent and hydride shifts but also must be rapid with respect to interconversion with XXII. In other words, there is a stereoelectronic factor involved such that the ring carbons can equilibrate only by rotation about the single bond from the ring.[6] Since XXII would be expected to equilibrate rapidly with XXIII, one has to assume that the rate constants for collapse

(5) It is impossible to estimate the effects of the isotopes on the product distributions in these reactions. Since no primary isotope effects are involved, they have been neglected. There are well-documented examples of the same type in the literature: *cf.* S. Winstein and J. Sonnenberg, *J. Am. Chem. Soc.*, **83**, 3244 (1961); K. Servis and J. D. Roberts, *ibid.*, **86**, 3773 (1964).

(6) P. S. Skell and R. J. Maxwell [*ibid.*, **84**, 3963 (1962)] have provided evidence concerning the rates of cationic rearrangements *vs.* solvent relaxations.



of these several ions to crotylcarbinols are intermediate in magnitude with respect to the two equilibrating processes.

In conclusion, we feel that both the product distributions and the deuterium-scrambling results can be explained without recourse to intermediates other than classical ones. If such intermediates are involved, they cannot be the sole intermediates.

Experimental Section

Nmr spectra were determined in carbon tetrachloride, unless otherwise noted, on a Varian Model A-60 spectrometer. Analytical gas chromatography was carried out on a 21 ft × 1/8 in. column at 5% γ-methyl-γ-nitropimelonitrile on 80–100 mesh Chromosorb G at 106°. Preparative gas chromatography utilized an 8 ft × 0.25 in. column of the same liquid phase (20%) on 35–80 mesh Chromosorb P. Areas were determined by triangulation and/or weighing the traces. No correction factors were used, since all of the compounds are isomers.

Methyl cyclopropylacetate was prepared from cyclopropanecarbonyl chloride and diazomethane according to a procedure given by Turnbull and Wallis.[7] A 71% yield was realized, bp 125–134° [lit.[7] 132° (745 mm)]. The nmr spectrum showed a sharp singlet (O–CH_3) at τ 6.4, a doublet (CH_2–C=O) at τ 7.8 (J = 7 cps), and complex absorption centered at τ 9.4 (relative areas, 2.8:2.0:5.1).

β-Cyclopropylethanol.—Methyl cyclopropyl acetate (10.0 g) was reduced with 5 g of lithium aluminum hydride to give 5.4 g (72%) of alcohol with bp 132–138°, $n^{25.5}$D 1.4319 (lit.[8] bp 135°, n^{25}D 1.4327).

The nmr spectrum showed a triplet at τ 6.4 (J = 6 cps) for the CH_2–O protons, a sharp singlet at τ 7.7 for the O–H proton, a quartet at τ 8.6 (J = 6 cps) for the β-CH_2 group, and complex absorption extending from τ 9 to 10 for the ring cyclopropyl protons. The relative peak areas were 2.1:1.0:1.95:4.95, respectively.

α,α-Dideuterio-β-cyclopropylethanol (V).—Methyl cyclopropylacetate (6.0 g) was reduced with 1.33 g of lithium aluminum deuteride (~96%) to give 2.7 g of alcohol V, bp 128–136°. The nmr spectrum showed essentially no absorption in the region about τ 6.4. The β-CH_2 group appeared as a doublet (J = 6 cps) at τ 8.6, and the remainder of the spectrum resembled that for the undeuterated analog. Relative peak areas were 2.0:5.0.

Brosylate Esters.—The p-bromobenzenesulfonate esters III and VI were prepared by reaction of the alcohols (0.012 mole) with brosyl chloride (0.012 mole) in pyridine (50 ml) at −20° over a period of 2 hr. The oily product (III) could be recrystallized in the cold from pentane at −70° and had mp 3–4°.

Anal. Calcd for $C_{11}H_{13}BrO_3S$: C, 43.28; H, 4.30. Found: C, 43.07; H, 4.20.

The nmr spectrum ($CHCl_3$) of the protio system showed, *inter alia*, a triplet at τ 5.9 (J = 7 cps) for the CH_2–O protons. This peak was absent in the deuterated analog.

Acetolysis of III.—A solution of 1 g (3.3 mmoles) of brosylate III in 10 ml of glacial acetic acid which contained 0.28 g of sodium acetate was heated at reflux for 20 hr. After cooling, the mixture was diluted with 50 ml of ice water followed by repeated pentane extractions. The combined extracts were washed with sodium carbonate solution, dried, and distilled. The infrared spectrum of this material showed no brosylate peaks. The residue was dissolved in ether and treated with 1 g of lithium aluminum hydride. After 1.5 hr, the reaction mixture was treated with water and processed in the usual way. Analysis of the crude product by gas chromatography indicated that β-cyclopropylethanol was the exclusive product (>99%).

Formolysis of III. A. With Sodium Formate.—A solution of 1.0 g of III and 0.48 g of sodium formate in 10 ml of 97–100% formic acid was kept at 100 ± 1° for 6 hr. Addition of water and extraction with pentane gave an oil which showed no peaks due to brosylate ester in the infrared spectrum. Reduction of the crude formates with lithium aluminum hydride gave a mixture of alcohols which was analyzed by gas chromatography. Four major components and one very minor one were observed. Each of the major peaks was identified by retention time and comparison of infrared or nmr spectrum of a collected sample with an authentic sample. From this experiment there was obtained a mixture which contained 35% of β-cyclopropylethanol, 36% of cyclopentanol, 17% of crotylcarbinol, and 12% of allylmethylcarbinol. No methylcyclopropylcarbinol was present.

B. With Pyridine.—Repetition of the formolysis for 7 hr using an equimolar amount of pyridine as a base gave an 85% yield of alcohols with the following composition: cyclopentanol (60%), crotylcarbinol (21%), and allylmethylcarbinol (19%). No low-boiling hydrocarbons were observed in the gas chromatograms.

Formolysis of Brosylate VI.—Brosylate VI was subjected to the formolysis conditions above, using both pyridine and sodium formate as buffers. The product alcohols were isolated in the same manner and analyzed in the same manner. Peaks were observed in the same ratios and at the same retention times as in the two runs with the protiated substrates. Each peak was collected on the preparative column and reanalyzed on the analytical column to check the homogeneity. Each sample proved to be greater than 99% pure. The amounts and positions of the deuterium were calculated from the integrated nmr spectra. The peak assignments could be made unambiguously from a consideration of the spectra of the protiated systems. Since small amounts of water invariably condensed in the collection tubes, the hydroxyl peaks were not considered in the calculations. Instead, the remaining area was set equal to seven protons and the individual peaks were evaluated accordingly. Table II lists the data which were used in the calculations.

TABLE II
NMR DATA[a]

Compd	Runs averaged	Proton distributions (±0.05) C-1	C-2	C-3	C-4	C-5
VII-d_2 (formate)	2	0.87		6.13		
		(5.8)		(8.4)		
(pyridine)	5	0.85		6.15		
VIII-d_2 (formate)	9	1.53	1.02	1.72	0.95	1.80
		(8.9)	(6.3)	(7.9)	(4.2)	(5.0)
(pyridine)	5	1.57	1.04	1.76	0.90	1.74
IX-d_2 (formate)	4	1.01	1.94	1.93		2.13
		(6.5)	(7.8)	(4.6)		(8.4)
(pyridine)	5	1.01	1.89	2.02		2.09

[a] The numbers in parentheses represent the mean chemical shifts of the multiplets integrated.

The product distributions were calculated by solving the appropriate sets of equations. It was necessary to assume that the only possible deuterated species present were those given in the text.

Control Experiments.—The stability of methylcyclopropylcarbinol under our conditions was checked by heating the alcohol with formic acid at 100° for 7 hr. After dilution with water and ether extraction, the crude formates (infrared) were reduced with lithium aluminum hydride. A 60% recovery of methylallylcarbinol and crotylcarbinol in the ratio 72:28 was obtained. These two alcohols themselves were shown to be stable to the reaction conditions in similar experiments.

(7) J. H. Turnbull and E. S. Wallis, *J. Org. Chem.*, **21**, 663 (1956).
(8) H. Hart and D. P. Wyman, *J. Am. Chem. Soc.*, **81**, 4891 (1959).