complex reacts with bromine or ionizes directly in the rate-determining step has the advantage of picturing the total mechanism in a continuous fashion, with the fate of the initially formed complex depending on the ease of its breakdown in a given medium. The observation that an increase in polarity of the medium through addition of certain salts increases k_2 more than k_3,[6] and that in deuterium oxide–acetic acid k_2 is reduced more than k_3,[6] lends support to this view, but it is not a sufficient proof that the bimolecular reaction proceeds through a complex. The proton loss is for all mechanisms kinetically insignificant, which is supported by the absence, or near absence, of a significant deuterium isotope effect in aromatic bromination of hydrocarbons,[26] as well as by the absence of basic catalysis.

Partial Rate Factors.—The major product in the preparative bromination of fluorene is 2-bromofluorene.[27] The exact amount, formed under the kinetic conditions in 75% acetic acid, was determined by the isotopic dilution method with Br^{82}, as described before for other compounds.[15] From four independent determinations the amount of 2-bromofluorene was found to be 97.0 ± 0.8%. This value confirms, *inter alia*, that no appreciable free-radical bromination could have intervened, because free-radical bromination is known to attack the 9-position of fluorene.[28] In order to compare the reactivity of fluorene with that of other compounds, which had been measured in 50% acetic acid, naphthalene was brominated in 75% acetic acid at a 0.1 and 0.2 M sodium bromide concentration (at $\mu = 0.5$) and the rate constants compared with those for fluorene under the same conditions. The relative rate of fluorene to naphthalene was found to have an average value of 20.9. Assuming that a difference in solvent composition does not appreciably affect relative values of the second-order rate constants, fluorene is brominated 2.49×10^6 times faster than benzene, and the partial rate factor for bromination in the 2-position of fluorene is 7.25×10^6.[29] A value of 6.33×10^6, obtained by the technique of comparing reaction times, recently has been reported for bromination in glacial acetic acid[30]; the agreement is very satisfactory. In molecular chlorination the rate ratio of fluorene to benzene is 1.1×10^5,[31] and in nitration, which is much less selective than bromination or chlorination, it is considerably less.[32] The value for fluorene falls in an expected order of reactivity, and the partial rate factors for bromination, which have so far been obtained,[8,9] parallel data for the solvolysis of arylmethylcarbinyl chlorides[33] and aryldimethylcarbinyl chlorides.[34] The considerable increase in rate of fluorene over biphenyl (a factor of 2000) is due to forced planarity in the former compound,[35] in addition to the rate-enhancing effect of the methylene group.[30,31,32,36]

Acknowledgment.—This work was supported by National Science Foundation Grant G-4474, which is gratefully acknowledged. We also acknowledge many helpful discussions with Dr. George L. Zimmerman.

[26] L. Melander, *Arkiv. Kemi*, **2**, 213 (1950); P. B. D. de la Mare, T. M. Dunn and J. T. Harvey, *J. Chem. Soc.*, 923 (1957); E. Berliner, *Chemistry & Industry*, 177 (1960); E. Berliner and K. E. Schueller, *ibid.*, 1444 (1960); E. Baciocchi, G. Illuminati and G. Sleiter, *Tetrahedron Letters*, No. **23**, 30 (1960); R. Josephson, R. M. Keefer and L. J. Andrews, *J. Am. Chem. Soc.*, **83**, 3562 (1961). Somewhat larger isotope effects have been reported in the bromination of some compounds with functional groups; *i.e.*, H. Zollinger, *Experientia*, **12**, 165 (1956); P. G. Farrell and S. F. Mason, *Nature*, **183**, 250 (1959); F. M. Vainshtein and E. A. Shilov, *Doklady Akad. Nauk S.S.S.R.*, **133**, 581 (1960); P. C. Myhre, *Acta Chem. Scand.*, **14**, 219 (1960).

[27] Ch. Courtot and C. Vignati, *Bull. soc. chim. France*, [4] **41**, 58 (1927).

[28] For instance: G. Wittig and G. Felletschin, *Ann.*, **555**, 133 (1944); G. Wittig and F. Vidal, *Chem. Ber.*, **81**, 368 (1948); J. R. Sampey and E. E. Reid, *J. Am. Chem. Soc.*, **69**, 234 (1947).

[29] Because of the uncertainty in the relative rate, this value is about ±10%.

[30] H. C. Brown and L. M. Stock, *J. Am. Chem. Soc.*, **84**, 1238 (1962).

[31] P. B. D. de la Mare, D. M. Hall, M. M. Harris and M. Hassan, *Chemistry & Industry*, 1086 (1958).

[32] M. J. S. Dewar and D. S. Urch, *J. Chem. Soc.*, 3079 (1958), and footnote 58 in ref. 38.

[33] E. Berliner and N. Shieh, *J. Am. Chem. Soc.*, **79**, 3849 (1957).

[34] H. C. Brown and T. Inukai, *ibid.*, **83**, 4825 (1961); H. C. Brown, Y. Okamoto and T. Inukai, *ibid.*, **80**, 4964 (1958).

[35] D. M. Burns and J. Iball, *Nature*, **173**, 635 (1954); G. M. Brown and M. H. Bortner, *Acta Cryst.*, **7**, 139 (1954).

[36] For a more detailed discussion of this point, see L. M. Stock and H. C. Brown, *J. Am. Chem. Soc.*, **84**, 1242 (1962).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, DAVIS, CALIF.]

Intramolecular Nucleophilic Participation. II. Solvolysis of the 1- and 4-Carbomethoxy-9-bromofluorenes[1]

BY R. E. LOVINS, L. J. ANDREWS AND R. M. KEEFER

RECEIVED MAY 26, 1962

The relative reactivities of 1- and 4-carbomethoxy-9-bromofluorenes with respect to solvolysis in aqueous ethanol and with respect to hydrolysis in aqueous acetone in the presence of silver nitrate have been determined. In both media the 1-substituted compound is less reactive than its isomer. These results serve as the basis for a discussion of the geometric requirements for effective participation by a nucleophilic *ortho* substituent in the solvolysis of a benzhydryl-type halide.

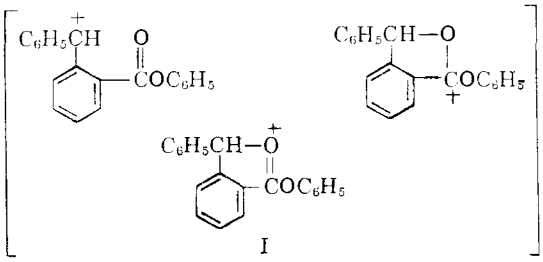
It has been shown previously that the rates of certain types of reactions at aromatic side chains are substantially enhanced when substituents which are nucleophilic in character are located *ortho* to the reaction centers.[1–3] The fact that a benzhydryl bromide bearing an *o*-carbophenoxy substit-

[1] For the first paper in this series see A. Singh, L. J. Andrews and R. M. Keefer, *J. Am. Chem. Soc.*, **84**, 1179 (1962).

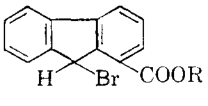
[2] M. L. Bender, *Chem. Revs.*, **60**, 53 (1960).

[3] (a) L. J. Andrews and R. M. Keefer, *J. Am. Chem. Soc.*, **81**, 4218 (1959); (b) R. M. Keefer and L. J. Andrews, *ibid.*, **81**, 5329 (1959).

uent is hydrolyzed much faster than its *p*-isomer has been explained on the assumption that the *o*-$COOC_6H_5$ group participates (structure I) in the activation process leading to the formation of the benzhydryl-type cation. To provide for maximum overlap of the *p*-orbital of the carbonyl oxygen with the vacant *p*-orbital at the reaction center in the transition state, the ring substituted with the *o*-carbophenoxy group should be oriented perpendicular to the plane of the trigonal valences of the exocyclic carbon atom. Actually a perpendicular orientation of the substituted ring relative to the unsubstituted one has been proposed as the favored conformation for the transition state for the hydrolysis of *o*-carbophenoxybenzhydryl bromide.


I

If the above argument concerning the geometric requirements for *o*-substituent participation in the hydrolysis of a benzhydryl halide is correct, it should follow that the cleavages of the C–Br bonds in the hydrolyses of esters (II) of 9-bromofluorene-1-carboxylic acid should not be subject to the influence, as nucleophilic participants, of the –COOR groups *ortho* to the reaction center. With this in mind, esters of 9-bromofluorene-1-carboxylic acid and of 9-bromofluorene-4-carboxylic acid have been prepared and their relative reactivities in solvolytic processes have been compared.


II

Experimental

The 9-Bromofluorene Derivatives.—Samples of 9-bromofluorene-1-carboxylic acid were prepared by two different procedures. In one case 10 g. of fluorene-1-carboxylic acid (Aldrich Chemical Co.) in 100 ml. of dry carbon tetrachloride was subjected to irradiation as it was treated dropwise with a solution of 7.63 g. of bromine in 80 ml. of carbon tetrachloride. The procedure was essentially the same as has been described previously.[4] The solvent was removed from the product under vacuum, and the residue was recrystallized from petroleum ether to provide 12.5 g. (91% yield) of the bromide, m.p. 238–240° (lit.[5] m.p. 242°).

Alternately, fluoranthene (Eastman Organic Chemicals) was used as starting material. It was subjected to reaction with chromium trioxide in acetic acid solution by a procedure similar to that reported elsewhere.[6] The acetic acid solution of the product was poured into a large volume of water. The crude 9-fluorenone-1-carboxylic acid which precipitated was dissolved in concentrated ammonium hydroxide solution and reprecipitated with mineral acid. It was then recrystallized from acetic acid to yield (57%) a product, m.p. 188–190° (lit.[6] m.p. 192–193°).

The keto acid was reduced to 9-fluorenol-1-carboxylic acid with magnesium in methanol.[5] The crude 9-fluorenol-1 carboxylic acid was recrystallized from acetic acid. A 31% yield of material, m.p. 190–192° (lit.[5] m.p. 196°), was obtained. The procedure of Forrest and Tucker[5] was used to convert the hydroxy acid to 9-bromofluorene-1-carboxylic acid in 64% yield, m.p. 237–240°.

A sample of 1-carbomethoxy-9-bromofluorene was prepared from the free acid as described by Forrest and Tucker.[5] The crude material was recrystallized from petroleum ether. A sample of m.p. 101–102°, which had an equivalent weight (based on bromine) of 308 (calcd. for $C_{15}H_{11}O_2Br$, 303), was obtained. A sample of 1-carbophenoxy-9-bromofluorene was prepared by refluxing 5 g. of the acid chloride of 9-bromofluorene-1-carboxylic acid[5] and 4 g. of phenol in 100 ml. of dry carbon tetrachloride for 5 hours. The crude product, isolated after removal of the solvent under vacuum, was recrystallized three times from petroleum ether to provide 2 g. (17% yield) of ester, m.p. 120–121°.

Anal. Calcd. for $C_{20}H_{13}O_2Br$: C, 65.94; H, 3.62; Br, 21.94. Found: C, 66.10; H, 3.72; Br, 21.53.

To prepare fluorene-4-carboxylic acid, diphenic acid (Eastman Organic Chemicals) was converted to 9-fluorenone-4-carboxylic acid by reaction with sulfuric acid,[7] and the keto acid was subjected to Wolff–Kishner reduction by methods described in detail elsewhere.[8] A 14-g. sample of fluorene-4-carboxylic acid was converted to the acid chloride by refluxing with 22 g. of phosphorus pentachloride in dry chloroform. After removal of the excess phosphorus pentachloride and the solvent, the product was added to 150 ml. of absolute methanol. The resultant solution was refluxed for 3 hours. The 4-carbomethoxyfluorene obtained after removing the methanol was recrystallized from petroleum ether; yield 10.2 g., m.p. 62–63° (lit.[9] m.p. 64°).

To prepare 4-carbomethoxy-9-bromofluorene, 10.2 g. of 4-carbomethoxyfluorene in 100 ml. of carbon tetrachloride was subjected to photobromination using much the same reaction conditions as were employed in the photobromination of fluorene-1-carboxylic acid. The solid product was recrystallized from petroleum ether; yield 9.5 g. (69%), m.p. 106–107°.

Anal. Calcd. for $C_{15}H_{11}O_2Br$: C, 59.42; H, 3.66; Br, 26.36. Found: C, 59.62; H, 3.74; Br, 26.15.

An attempt was made to prepare this compound by esterifying 9-bromofluorene-4-carboxylic acid (obtained by photobromination of fluorene-4-carboxylic acid) by essentially the same procedure which was used successfully in the preparation of 1-carbomethoxy-9-bromofluorene from 9-bromofluorene-1-carboxylic acid. The product, thus obtained, had a low melting point and analysis showed considerably less than the theoretical quantity of bromine. Attempts to purify it by recrystallization were unsuccessful. Apparently the bromide was partially solvolyzed during the esterification reaction.

A sample of unsubstituted 9-bromofluorene was obtained by photobromination of fluorene (Eastman Organic Chemicals) by a procedure analogous to that used in the photobrominations described above. A product, m.p. 103–104° (lit.[10] m.p. 104°), was obtained in 63% yield; equivalent weight based on Br, 249 (calcd. for $C_{13}H_9Br$, 245).

Benzhydryl bromide and *o*-carbophenoxybenzhydryl bromide were prepared by procedures used in an earlier investigation.[1]

The Kinetic Studies.—Acetone was purified for use as a solvent by the method of Conant and Kirner.[11] Commercially available absolute ethanol was used without further purification. Solvent mixtures described as $(100 - x)$% aqueous acetone or ethanol were prepared by mixing $(100 - x)$ volumes of acetone or ethanol and x volumes of water. The procedures used in initiating the rate runs and in conducting the analyses of rate samples were very similar to those of the previous study.[1] The solvolysis rate constants for reactions in 80% aqueous ethanol and 90% aqueous acetone, which are defined in eq. 1

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(4) E. L. Eliel and D. E. Rivard, *J. Org. Chem.*, **17**, 1252 (1952).

(5) J. Forrest and H. Tucker, *J. Chem. Soc.*, 1137 (1948).

(6) (a) E. Bergmann and M. Orchin, *J. Am. Chem. Soc.*, **71**, 1111 (1949); (b) L. Fieser and A. Seligman, *ibid.*, **57**, 2174 (1935).

(7) F. Bischoff and H. Adkins, *ibid.*, **45**, 1030 (1923).

(8) E. Weisburger and J. Weisburger, *J. Org. Chem.*, **20**, 1396 (1955).

(9) C. Grabe and C. Aubin, *Ann.*, **247**, 257 (1888).

(10) J. Sampey and E. Reid, *J. Am. Chem. Soc.*, **69**, 234 (1947).

(11) J. B. Conant and W. R. Kirner, *ibid.*, **46**, 232 (1924).

$$\ln([\mathrm{RBr}]_i/[\mathrm{RBr}]_t) = k_s t \qquad (1)$$

and the rate constants, k_{Ag^+}, for reactions in the presence of silver ion(eq. 2)

$$\frac{1}{[\mathrm{RBr}]_i - [\mathrm{Ag}^+]_i} \ln \frac{[\mathrm{Ag}^+]_i\,[\mathrm{RBr}]_t}{[\mathrm{RBr}]_i\,[\mathrm{Ag}^+]_t} = k_{\mathrm{Ag}^+} t \qquad (2)$$

were evaluated from the experimental data as described previously. The constants which are reported for the reactions with silver ion apply to the initial phases of the runs, since, as has been noted in other work on reactions of organic halides with silver ion,[1,12] the precipitating silver halide serves as a catalyst.

Results

The reaction conditions used in the previous investigation of the hydrolysis rates of substituted benzhydryl bromides were not suitable for the study of the relative reactivities of the 9-bromofluorene derivatives. In 90% aqueous acetone at 25° 1-carbophenoxy-9-bromofluorene undergoes no measurable reaction over a three-day period, whereas the half-life for hydrolysis of *o*-carbophenoxybenzhydryl bromide is approximately 4700 sec. under these same conditions. Unsubstituted 9-bromofluorene is not significantly hydrolyzed over a three-day period at 70° in this solvent. The remarkably low reactivities of the fluorene as compared to the diphenylmethane derivatives is presumed to be indicative of a substantial difference in delocalization energies of 9-fluorenyl and benzhydryl-type cations. Molecular orbital calculations are now being made to check this point.

The 9-bromofluorene derivatives were found to solvolyze at conveniently measurable rates in 80% aqueous ethanol in the region of 50–70°. The rate constants, k_s (see eq. 1), for reactions conducted under these conditions are summarized in Table I. There is no indication in the results of the rate experiments that the 1-$\mathrm{COOCH_3}$ substituent can participate in this reaction. Actually at both 58.7° and 70.2° 1-carbomethoxy-9-bromofluorene is only about one-third as reactive as the isomeric 4-carbomethoxy-9-bromofluorene. The rate constant for hydrolysis of *o*-carbophenoxybenzhydryl bromide in 90% aqueous acetone at 25°, a process which takes place with participation by the *o*-carbophenoxy group, is 86 times that for the reaction of *o*-carbophenoxybenzhydryl bromide. It is noteworthy in this regard that 1-carbomethoxy- and 1-carbophenoxy-9-bromofluorene solvolyze at approximately equal rates.

The 9-fluorenyl cation, like fluorene,[13] must have a planar carbon skeleton. The vacant *p*-orbital at the 9-position of this cation must be oriented with its long axis perpendicular to the plane of the fused ring system. The ineffectiveness of the 1-carbomethoxy substituent in functioning as a participating nucleophile in 9-bromofluorene solvolysis is ascribed to the rigidity of this ring system. For maximum overlap of a *p*-orbital of the carbonyl oxygen of the carbomethoxy group with a vacant *p*-orbital at the 9-position, the latter orbital and the ring bearing the carbomethoxy group should be coplanar. This, unlike the corresponding conformation for an *o*-substituted benzhydryl cation, is a geometrically impossible arrangement.

TABLE I

RATE CONSTANTS FOR SOLVOLYSIS OF 9-BROMOFLUORENE AND ITS SUBSTITUTION PRODUCTS IN 80% AQUEOUS ETHANOL

Substituent on 9-bromofluorene	Temp., °C.	Range[a] of $[\mathrm{RBr}]_i$, mole/l.	$10^4 k_s$, sec.$^{-1}$
4-$\mathrm{COOCH_3}$	58.7	0.0319–0.0568	0.458 ± 0.015
1-$\mathrm{COOCH_3}$	58.7	.0176– .0350	0.126 ± .003
4-$\mathrm{COOCH_3}$	70.2	.0254– .0405	1.40 ± .01
1-$\mathrm{COOCH_3}$	70.2	.0308– .0597	0.400 ± .002
1-$\mathrm{COOC_6H_5}$	70.2	.0230– .0301	0.348 ± .014
None[b]	58.7	.0195– .0534	1.39 ± .009
None[b]	70.2	.0436– .0686	4.91 ± .06[c]

[a] With each bromide two or more runs were made in which $[\mathrm{RBr}]_i$ was varied over the indicated range. [b] Reactions of unsubstituted 9-bromofluorene. [c] The half-life for this reaction is approximately 1400 sec. Benzhydryl bromide ($[\mathrm{RBr}]_i = 0.0685\ M$) is completely hydrolyzed in less than 30 sec. under the same reaction conditions.

The results of the rate studies in which 80% aqueous ethanol was used as a solvolyzing medium may not, however, serve rigorously to demonstrate the geometric requirements for *o*-substituent participation. The transition state for the solvolysis of 9-bromofluorene may not be sufficiently carbonium ion-like in character so that an *o*-substituent, even though it is properly oriented, can release electrons to the reaction site with maximum effectiveness. The fact that 9-bromofluorene is so much less reactive than benzhydryl bromide (Table I, footnote *c*) and the fact that the 4-carbomethoxy substituent has only a mildly deactivating effect on 9-bromofluorene reactivity are both significant in this regard.

The relative reactivities of the 1- and 4-carbomethoxy-9-bromofluorenes with silver nitrate in 80% aqueous acetone were also determined. It is assumed that under these conditions the carbon atoms at the reaction sites become appreciably electropositive in character as activation occurs. The bimolecular rate constants for the reactions with silver ion, k_{Ag^+} (eq. 2), are reported in Table II. Again the 4-substituted bromofluorene is more reactive (in this instance by a factor of about 13) than its 1-substituted isomer. That is, the argument concerning the preferred geometry for effective *o*-substituent participation is supported by this result.

TABLE II

RATE CONSTANTS FOR REACTIONS WITH SILVER NITRATE IN 80% AQUEOUS ACETONE (25.0°)

Substituent on 9-bromofluorene	$[\mathrm{RBr}]_i$, mole/l.	$[\mathrm{AgNO_3}]_i$, mole/l.	k_{Ag^+}, l. mole^{-1} sec.$^{-1}$
4-$\mathrm{COOCH_3}$	0.01193	0.0596	0.34
4-$\mathrm{COOCH_3}$	.01193	.02386	.29
4-$\mathrm{COOCH_3}$	.02387	.02386	.35[a]
1-$\mathrm{COOCH_3}$	.01191	.02387	.024
1-$\mathrm{COOCH_3}$	.02387	.02386	.025[a]
1-$\mathrm{COOCH_3}$	.02389	.01193	.027

[a] Values of k_{Ag^+} for these runs were calculated using the second-order rate law, $k_{\mathrm{Ag}^+} = \frac{1}{t}\frac{([\mathrm{RBr}]_i - [\mathrm{RBr}])}{[\mathrm{RBr}]_i\,[\mathrm{RBr}]}$.

The energies and entropies of activation for solvolyses in 80% aqueous ethanol have been calculated for those reactions for which the necessary data (Table I) are available. As indicated in

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(12) E. S. Gould, "Mechanism and Structure in Organic Chemistry," Henry Holt and Co., New York, N. Y., 1959, p. 274.

(13) G. M. Brown and M. H. Bortner, *Acta Cryst.*, **7**, 139 (1954).

TABLE III

HEATS AND ENTROPIES OF ACTIVATION FOR REACTIONS IN 80% AQUEOUS ETHANOL

Substituent on 9-bromofluorene	E_a, kcal./mole	$\Delta S^{\ddagger}$, e.u.
4-$COOCH_3$	22.1 ± 0.7	−14.3 ± 2.0
1-$COOCH_3$	22.9 ± .6	−14.3 ± 1.7
None[a]	24.9 ± 1.3	− 3.5 ± 3.8

[a] The constants reported in this case apply to the reaction of 9-bromofluorene.

Table III, the thermodynamic constants for the reactions of 1-carbomethoxy-9-bromofluorene are almost the same as those for the 4-carbomethoxy isomer. It is interesting to note that 9-bromofluorene is somewhat more reactive (Table I) than its 1- and 4-carbomethoxy derivatives because the activation entropy, rather than the activation energy, for solvolysis of the unsubstituted compound is lower than that for its derivatives. Additional evidence that the transition states in these reactions may not be highly ionic in character is to be found in the fact that the activation energy for 9-bromofluorene is more than for the bromofluorenes which have electron-withdrawing $-COOCH_3$ substituents.

Acknowledgment.—The authors are indebted to the National Science Foundation for a grant in support of this research.

COMMUNICATIONS TO THE EDITOR

MECHANISM OF CONVERSIONS OF *n*-PROPYL CARBONIUM ION TO CYCLOPROPANE. 1,3-HYDROGEN SHIFT

Sir:

It was reported recently that a fundamental reaction of carbonium ions is their conversion to cyclopropanes.[1,2] For example, nitrous acid deamination of *n*-propylamine and deoxideation of *n*-propoxide ion yield identical C_3H_6 fractions consisting of cyclopropane and propylene in 9:1 ratio.[1] The disconcerting coincidence that ethyl carbene, $CH_3CH_2\ddot{C}H$, produced by thermal decomposition of 1-diazopropane in aprotic media also yields a C_3H_6 fraction of the same composition,[3] raised the possibility that *n*-propyl carbonium ion is deprotonated to ethyl carbene and that cyclopropane and propylene are products of carbene rather than carbonium ion cyclization.

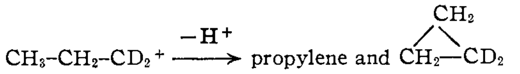
To distinguish between these mechanisms the deoxideation of 1,1-dideuterio-1-propanol was studied. The carbene mechanism, with intermediate $CH_3CH_2\ddot{C}D$, should lead to monodeuteriocyclopropane, while direct cyclization of carbonium ion $CH_3-CH_2-CD_2^+$ should yield dideuteriocyclopropane.

The 1,1-dideuterio-*n*-propyl alcohol was prepared by reduction of benzyl propionate with $LiAlD_4$. Its high isotopic purity was indicated by the failure to observe in the neat sample any proton magnetic resonance absorption characteristic of the $-CH_2-O-$ grouping. The deoxideation of this alcohol was carried out by refluxing with 50% aqueous potassium hydroxide and adding bromoform slowly. The gaseous products were trapped in a −140° trap and then analyzed and separated in pure condition by vapor phase chromatography. Since standards were not available for infrared spectroscopic identification of the deuterium labeled species, mass spectrometry was employed. It was assumed that the cracking probabilities for ordinary and deuterated cyclopropanes were identical. By this means it was found that the cyclopropanes from the deoxideation of $CH_3CH_2CD_2OH$ were $C_3H_4D_2$ (94 ± 2%) and C_3H_5D (5–6%).

Thus, $CH_3CH_2\ddot{C}D$ is not the intermediate in the major pathway to cyclopropane. The formation of cyclopropane is best explained as a 1,3 ring closure with loss of hydrogen ion.

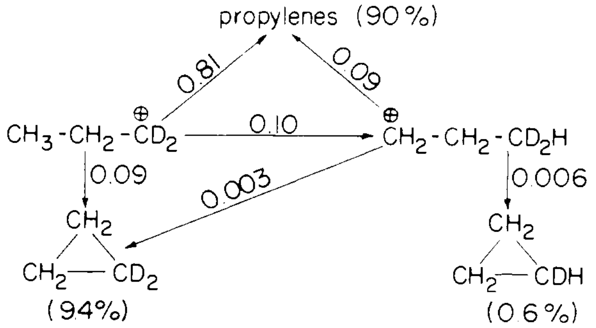
$$CH_3CH_2CD_2\text{–}O^- + \ddot{C}Br_2 \longrightarrow CH_3CH_2CD_2\text{–}O\text{–}\ddot{C}\text{–}Br^- + Br^-$$

$$CH_3\text{–}CH_2\text{–}CD_2\text{–}O\text{–}\ddot{C}\text{–}Br \longrightarrow CH_3\text{–}CH_2\text{–}CD_2^+ + CO + Br^-$$



$$CH_3\text{–}CH_2\text{–}CD_2^+ \xrightarrow{-H^+} \text{propylene and } \overset{CH_2}{CH_2\text{—}CD_2}$$

The monodeuteriocyclopropane could be attributed to a carbene intermediate, but more likely it results from a variation of the 1,3-interaction which does not involve proton loss, yielding $^+CH_2CH_2$-CHD_2, or 1,3 hydride shift. If this latter interpretation is correct, the partitioning among products (numbers over the arrows) follows from the assumption that on conversion of $^+CH_2CH_2CD_2H$ to cyclopropane, loss of D is twice as probable as loss of H.



Reutov and Shatkina[4] have reported that nitrous acid deamination of 1-propylamine-1-C^{14} leads to 92% 1-propanol-1-C^{14} and 8% 1-propanol-3-C^{14}. This evidence, taken with the published evidence and unpublished confirmations that 2-propyl cation

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(1) P. S. Skell and I. Starer, *J. Am. Chem. Soc.*, **82**, 2971 (1960).

(2) M. S. Silver, *ibid.*, **82**, 2971 (1960); **83**, 3482 (1961).

(3) L. Friedman and H. Shechter, *ibid.*, **81**, 5512 (1959).

(4) O. A. Reutov and T. N. Shatkina, *Tetrahedron*, **18**, 237 (1962).