Fig. 3. This is a schematic representation based on average R_f values appearing in 7 different chromatographic runs. It is evident that the various antimycin A components were obtained in chromatographically homogeneous form. Further, from these results blastmycin appeared to consist mainly of antimycin A_3 with minor contamination by the A_4 component.

Paper chromatograms of the various antimycin complex preparations are also given in Fig. 3. It is apparent that the four antimycin preparations all contained at least the A_1, A_2 and A_3 components, although in somewhat varying proportions. Virosin was similar in composition but also contained a significant proportion of antimycin A_4. The other preparations may also have contained small amounts of A_4 as it certainly was present in the Harada sample but yet was not detected by the chromatogram.

Infrared spectra of various preparations as shown in Fig. 4 reveal extremely close similarity both of the individual components A_1 and A_3 to each other and to blastmycin and virosin. Antimycin A_2 and the antimycin complex also gave essentially the same infrared spectrum. The differences are too slight to be of much aid in establishing differences in the chemical structure. Evidently, the components differ from each other only in the alkyl side chains of the neutral portion of the molecule.[3] Such a relationship is also suggested by the molecular formulas of A_1, A_2 and A_3 which differ among themselves only by the equivalent of one to three methylene groups. The ultraviolet spectra of the individual components also were essentially identical.

The infrared tracing of blastmycin offers further evidence of its very close similarity with antimycin; furthermore, its melting point was close to that of antimycin A_3 and the mixed melting point showed no depression. These data taken together with the above paper chromatographic results establish quite conclusively that the major component of blastmycin is identical with antimycin A_3 and indicate that the minor component very probably is antimycin A_4.

All three of the isolated antimycin A components showed neutral equivalents appreciably lower than theory for their most probable molecular formulas. This discrepancy may be attributable to partial cleavage of the alkali-sensitive bond of the antimycin A structure.[13] The investigation of these and other aspects of the chemistry of antimycin A is being continued.

MADISON, WISCONSIN

[CONTRIBUTION NO. 2369 FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, AND THE DEPARTMENT OF CHEMISTRY AND LABORATORY FOR NUCLEAR SCIENCE AND ENGINEERING, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Small-ring Compounds. XXIII. The Nature of the Intermediates in Carbonium Ion-type Interconversion Reactions of Cyclopropylcarbinyl, Cyclobutyl and Allylcarbinyl Derivatives[1a]

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RECEIVED SEPTEMBER 4, 1958

Investigation of the extent of isotope-position rearrangement in carbonium ion-type reactions of ^{14}C-labeled cyclopropylcarbinyl derivatives has revealed that the three methylene groups of the starting material achieve a striking degree of equivalence between reactants and products. These results, taken in conjunction with the abnormally large solvolytic reactivities of cyclopropylcarbinyl and cyclobutyl halides and sulfonate esters, can best be accounted for by assuming rapid but not instantaneous equilibration of three isomeric non-classical unsymmetrical "bicyclobutonium" ion intermediates.

Considerable interest attends the question of how best to formulate the intermediate or intermediates involved in carbonium ion-type interconversion reactions of cyclopropylcarbinyl, cyclobutyl and allylcarbinyl derivatives.[2] The abnormally large solvolytic reactivities of cyclopropylcarbinyl and cyclobutyl halides[2] and sulfonate esters[3-5] are characteristic of reactions for which we believe that *non-classical* cationic intermediates have been well established.[6] Detailed information as to the structures of the intermediates was sought in the present research by measurement of the extent of isotope-position rearrangement in the reactions of cyclopropylcarbinylamine-α-^{14}C with nitrous acid[7] and cyclopropylcarbinol-α-^{14}C with Lucas reagent.

Synthetic and Degradative Methods

Cyclopropylcarbinylamine-α-^{14}C was obtained by lithium aluminum hydride reduction of the amide from cyclopropanecarboxylic-1-^{14}C acid. This acid was prepared by carbonation of the Gri-

(1) (a) Supported in part by the Petroleum Research Fund of the American Chemical Society and the U. S. Atomic Energy Commission. Grateful acknowledgment is hereby made to the Donors of the Petroleum Research Fund. Presented in part at the 75th Anniversary Meeting of the American Chemical Society, September 7, 1951; (b) National Research Council Postdoctoral Fellow, 1953-1954; (c) National Science Foundation Predoctoral Fellow, 1955-1958; (d) Gates and Crellin Laboratories, California Institute of Technology, Pasadena, Calif.

(2) J. D. Roberts and R. H. Mazur, THIS JOURNAL, **73**, 2509 (1951).

(3) J. D. Roberts and V. C. Chambers, *ibid.*, **73**, 5034 (1951).

(4) C. G. Bergstrom and S. Siegel, *ibid.*, **74**, 145 (1952).

(5) R. G. Pearson and S. H. Langer, *ibid.*, **75**, 1065 (1953).

(6) As leading references see (a) S. Winstein, B. K. Morse, E. Grunwald, H. W. Jones, J. Corse, D. Trifan and H. Marshall, *ibid.*, **74**, 1127 (1952); (b) J. D. Roberts, C. C. Lee and W. H. Saunders, Jr., *ibid.*, **76**, 4501 (1954).

(7) For a preliminary communication concerning this work, see J. D. Roberts and R. H. Mazur, *ibid.*, **73**, 3542 (1951).

gnard reagent from cyclopropyl bromide[8] with radioactive carbon dioxide.[9] A control degradation of the cyclopropanecarboxylic acid by the Schmidt reaction (see Fig. 1) showed that it contained $\leq 0.7\%$ of the total radioactivity in the ring carbon atoms.

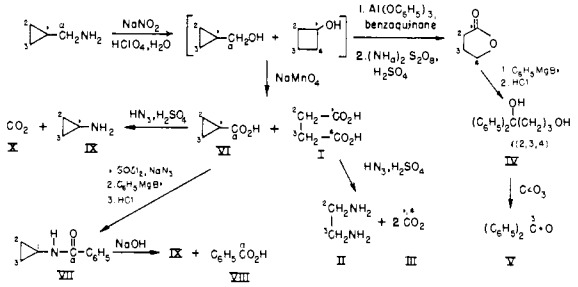


Fig. 1.

Treatment of cyclopropylcarbinylamine-α-^{14}C with sodium nitrite in aqueous perchloric acid solution gave a 60% yield of an alcohol mixture containing 48% cyclopropylcarbinol, 47% cyclobutanol and 5% allylcarbinol.[2] The small amount of allylcarbinol was removed by fractional distillation and the cyclopropylcarbinol and cyclobutanol were oxidized with permanganate to a mixture of cyclopropanecarboxylic and succinic acids. The acids were separated quantitatively by steam distillation and then further degraded as shown in Fig. 1.

Degradation of cyclobutanol-^{14}C (obtained by lithium aluminum hydride reduction of radioactive cyclobutanone[10] prepared from ketene and diazomethane-^{14}C) by the scheme shown in Fig. 1 gave a ^{14}C-distribution (C_1 = 0.0%, C_2 = C_4 = 37.1%, C_3 = 25.4%, total activity = 99.6%) which was in good agreement with that obtained by a second degradative scheme[10] (C_1 = 0.0%, C_2 = C_4 = 37.1%, C_3 = 25.8%, total activity = 100.0%) in which the activity of C_3 was measured directly. These results indicate the degree of reliability of the two methods of degradation.[11]

Degradation of cyclopropylcarbinol-α-^{14}C (obtained by lithium aluminum hydride reduction of cyclopropanecarboxylic-1-^{14}C acid) as per Fig. 1 gave cyclopropylamine (IX, $C_{1,2,3}$) containing 2.1% of the total radioactivity of the cyclopropanecarboxylic acid (VI, $C_{\alpha,1,2,3}$). The low activity of IX establishes that no extensive rearrangement occurs in the lithium aluminum hydride reduction of cyclopropanecarboxylic-1-^{14}C acid[12] nor during the degradation of cyclopropylcarbinol. It was further shown that cyclopropylcarbinol-α-^{14}C does not rearrange appreciably under the reaction and isolation conditions. We believe it safe to conclude by analogy that no extensive ^{14}C-rearrangement occurs in the preparation of cyclopropylcarbinylamine by lithium aluminum hydride reduction of cyclopropanecarboxamide-1-^{14}C.

Allylcarbinyl-^{14}C chloride, the only monochloride isolated from treatment of cyclopropylcarbinol-α-^{14}C with Lucas reagent,[2] was degraded by two procedures as outlined in Fig. 2. The results obtained by the two procedures were in good agreement.

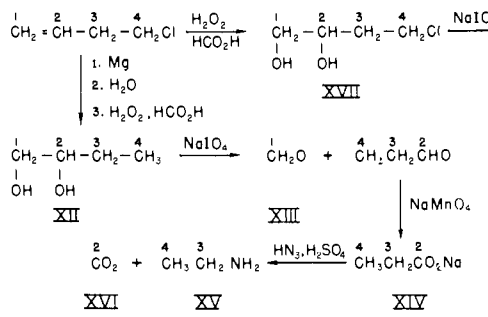


Fig. 2.

The ^{14}C-analyses for the various degradations are given in Tables I–III.

Discussion

A striking feature of most carbonium ion-type reactions of cyclopropylcarbinyl and cyclobutyl derivatives is that they give similar product mixtures and the compositions are essentially independent of whether one starts with a cyclopropylcarbinyl or a cyclobutyl compound. Thus, the reaction of cyclopropylcarbinylamine and cyclobutylamine with nitrous acid,[2] the solvolysis of cyclopropylcarbinyl and cyclobutyl derivatives,[2,3] the reactions of cyclopropylcarbinol and cyclobutanol with thionyl chloride, and cyclopropylcarbinol with hydrogen bromide or phosphorus tribromide[2] all give mixtures having closely similar relative amounts of products with the cyclopropylcarbinyl, cyclobutyl and allylcarbinyl structures.[12] This suggests that such reactions of cyclopropylcarbinyl and cyclobutyl compounds go through common cationic intermediates, and that the small observed variations in product composition are due to specific influences and not to drastic changes in mechanism.

A simple explanation of the product compositions is that classical cyclopropylcarbinyl and cyclobutyl cations are the intermediates and that they are very rapidly equilibrated. A possible test of such equilibration was provided by the reaction of cyclopropylcarbinol-α-^{14}C with Lucas reagent[2] since, under the reaction conditions, the small-

(8) J. D. Roberts and V. C. Chambers, THIS JOURNAL, **73**, 3176 (1951).

(9) The carbon dioxide was prepared from barium carbonate-^{14}C supplied by the Oak Ridge National Laboratory on allocation from the U. S. Atomic Energy Commission.

(10) D. A. Semenow, E. F. Cox and J. D. Roberts, THIS JOURNAL, **78**, 3221 (1956).

(11) Since the error in the C_3 activity due to ^{14}C–^{13}C isotope effects in the previously described scheme[10] is estimated to be approximately $\pm 0.25\%$, the error introduced by such isotope effects in the scheme of Fig. 1 is inferred to be negligible; for the general method of the isotope effect calculations, see E. F. Cox, Ph.D. thesis, California Institute of Technology, 1955.

(12) Professor H. C. Brown (Purdue) has questioned the validity of our earlier conclusions[2] regarding the ease of rearrangement of cyclopropylcarbinyl derivatives in carbonium ion-type reactions other than the deaminations with nitrous acid and the preparations of chlorides from alcohols with Lucas reagent. In particular, he has repeatedly alleged that there is no convincing evidence for the reported[2] formation of rearrangement products in the solvolysis of cyclopropylcarbinyl chloride in ethanol–water mixtures [see also H. C. Brown and M. Borkowski, THIS JOURNAL, **74**, 1894 (1952)]. These allegations will be discussed in detail in later papers—it should suffice for the present to report that they are not supported by the results of either the previous[2] or current experiments.

TABLE I

RADIOACTIVITY ANALYSES OF DEGRADATION PRODUCTS OF ALLYLCARBINYL-x-^{14}C CHLORIDE

Allylcarbinyl-x-^{14}C chloride		4-Chloro-1,2-butanediol (XVII)	Formaldehyde (XI)	1,2-Butanediol (XII)	Formaldehyde (XIII)	Sodium propionate (XIV)	Ethylamine (XV)	CO_2 (XVI)
From cyclopropylcarbinol-α-^{14}C[a] with Lucas reagent, 0°, 1 hr.	Meas. act.[b]	1926	156[d]	2704	214[d]	620[e]	700[f,g]	10.3[h]
	Cor. act.[c]	2660	881	3735	1258	2354	1936	3.6
	% total act.	(100.0)	33.1	(100.0)	33.7	63.0	51.8 (66)[g]	0.1

[a] This material was prepared by the method employed for cyclopropylcarbinol (B) in Table III and therefore contains $\leq 2.1\%$ of the radioactivity in the ring atoms. [b] Measured ^{14}C-activities in counts/min., determined with a windowless methane-filled counter (Nucleometer), of "infinitely thick" barium carbonate samples of cross-sectional area equal to 2.90 cm.^{2} and prepared as described by J. D. Roberts, W. Bennett, E. W. Holroyd, Jr., and C. H. Fugitt, *Anal. Chem.*, **20**, 904 (1948). The activities are corrected for background and have standard deviations of less than 2.2%. [c] ^{14}C-Activities in dis./min./mg. of barium carbonate, corrected for self-absorption and dilution by non-labeled carbon atoms as described by J. D. Roberts, R. E. McMahon and J. S. Hine, THIS JOURNAL, **72**, 4237 (1950). [d] Formaldehyde as dimethone. [e] Sodium propionate as *p*-bromophenacyl ester. [f] Ethylamine as *p*-bromobenzenesulfonamide. [g] Infrared spectra indicated that this material contained 76% N-ethyl- and 24% N-methyl-*p*-bromobenzenesulfonamide; the activity of the product *assuming pure* XV is 51.8% of XII and recalculation assuming 24% inactive N-methyl-*p*-bromobenzenesulfonamide corrects this value to 66%. [h] CO_2 as barium carbonate.

TABLE II

RADIOACTIVITY ANALYSES OF DEGRADATION PRODUCTS OF CYCLOBUTANOL-x-^{14}C

Cyclobutanol-x-^{14}C	Run		Succinic acid (I)	1,2-Diaminoethane (II)	$2CO_2$ (III)	1,1-Diphenylbutane-1,4-diol (IV)	Benzophenone (V)
From cyclobutanone from ketene and diazomethane-^{14}C	1	Meas. act.[a]	0.1236	0.07733[d]	0.04590[f]	....	....
		% total act.	(100.0)	62.56 ± 0.11	37.14 ± 0.29	....	....
	2	Meas. act.[a]	0.710	.....	.....	0.712	0.0000[i]
		% total act.	(100.0)	.....	.....	(100.0)	0.0
From cyclopropylcarbinylamine-α-^{14}C with HONO, 100°, 1 hr.	1	Meas. act.[a]	0.05665	0.03607[d]	0.02024[f]	....	....
		% total act.	(100.00)	63.67 ± 0.22	35.73 ± 0.26	....	....
	2	Meas. act.[b]	936, 981[e]	1200,[f] 1238[e,f]	670,[g] 668[g,h]	....	....
		Cor. act.[c]	1292, 1356	828, 854	462, 462	....	....
		% total act.	(100.0), (100.0)	64.1, 63.0	35.8, 34.1	....	....
	3	Meas. act.[a]	0.543	.....	.....	0.553	0.0036[j]
		% total act.	(100.0)	.....	.....	(100.0)	0.66 ± 0.03

[a] Activities in microcuries per millimole (μc./mmole); determined using the vibrating-reed electrometer method as described by O. K. Neville, THIS JOURNAL, **70**, 3499 (1948). [b,c] See corresponding footnotes for Table I. [d] 1,2-Diaminoethane as dibenzamide. [e] Repurified and recounted. [f] 1,2-Diaminoethane as dihydrobromide. [g] CO_2 as barium carbonate; activities are per 2 moles of barium carbonate. [h] Recounted. [i] Benzophenone as 2,4-dinitrophenylhydrazone. [j] Benzophenone as phenylhydrazone.

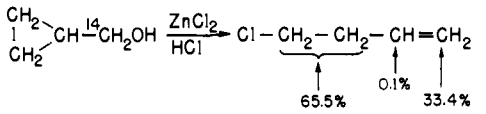
TABLE III

RADIOACTIVITY ANALYSES OF DEGRADATION PRODUCTS OF CYCLOPROPYLCARBINYL-x-^{14}C COMPOUNDS

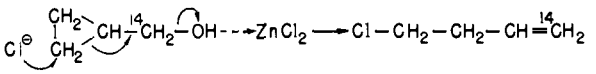
Cyclopropylcarbinyl-x-^{14}C compound		Cyclopropanecarboxylic acid (VI)	N-Cyclopropylbenzamide (VII)	Benzoic acid (VIII)	Cyclopropylamine (IX)	CO_2 (X)
Cyclopropanecarboxylic acid (A) from cyclopropylmagnesium bromide and $^{14}CO_2$	Meas. act.[b]	1313	.....	....	3.9[c]	4338[d]
	Cor. act.[c]	1812	.....	....	13	1498
	% total act.	(100.0)	.....	....	0.7	83[e]
Cyclopropylcarbinol (B) from $LiAlH_4$ reduction of cyclopropanecarboxylic acid (A)	Meas. act.[a]	0.693[d]	0.694	....	0.0145[f]	...
	% total act.	(100.0)	(100.0)	....	2.09	...
Cyclopropylcarbinol from treatment of cyclopropylcarbinol (B) with ethylamine and HONO, 60°, 20 min.	Meas. act.[a]	0.688[d]	0.688	0.679	0.0131[f]	...
	% total act.	(100.0)	(100.0)	98.7	1.90	...
Cyclopropylcarbinol from cyclopropylcarbinylamine-α-^{14}C with HONO, 60°, 20 min.	Meas. act.[a]	0.548[d]	0.550	0.292	0.265[f]	...
	% total act.	(100.0)	(100.0)	53.2	48.3[f]	...

[a] See corresponding footnote for Table II. [b,c] See corresponding footnotes for Table I. [d] Cyclopropanecarboxylic acid as anilide. [e] Cyclopropylamine as benzamide. [f] Degradation of the ring gave values of 6.3 and 20.9% of the total radioactivity for C_1 and $C_2 = C_3$, respectively; *however*, the ring degradation method employed was shown to be unreliable. Related experiments indicated that C_1 probably had <1% of the total activity of the cyclopropylcarbinol. [g] CO_2 as barium carbonate; activity probably low because of contamination with atmospheric CO_2.

ring chlorides appear to be in equilibrium with cationic intermediates but the final reaction product, allylcarbinyl chloride, is not. If equilibrium of the small-ring cations is complete before allylcarbinyl chloride is formed, then treatment of cyclopropylcarbinol-α-^{14}C with Lucas reagent should give allylcarbinyl chloride with the ^{14}C distributed equally between the three methylene groups, as Fig. 3 shows. The experimental results are entirely in accord with this prediction and elimi-



nate direct "push–pull" formation of allylcarbinyl chloride from cyclopropylcarbinol, since this would give a predominance of C_4-labeled chloride.



Although equilibrating classical cations can account for the course of the above rearrangement, the unusual solvolytic reactivity of both cyclopropylcarbinyl and cyclobutyl derivatives is hardly explicable on the basis of formation of such intermediates.[2,3] To be sure, the reactivity of the three-membered ring compounds might be explained by assuming relief of strain in the solvolysis transition state through direct formation of the cyclobutyl cation, but it seems impossible to use the same explanation for the reactivity of the four-membered ring compounds unless they directly

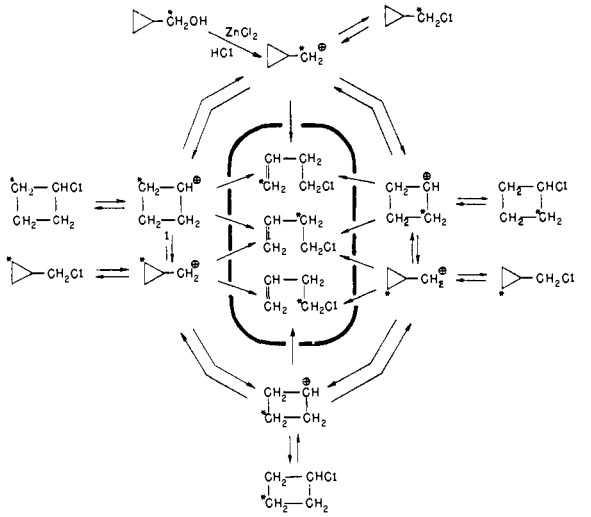
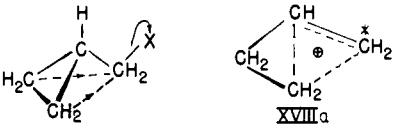


Fig. 3.

form allylcarbinyl cations. This latter possibility is ruled out by the failure to observe large amounts of allylcarbinyl derivatives as products in non-reversible reactions[2] and the great difficulty which attends efforts to obtain the allylcarbinyl cation in other ways.[2] While, presumably, separate explanations could be offered for the reactivities of three- and four-membered ring derivatives, all of the experimental data seem better accommodated by the assumption of a single common non-classical intermediate, or a rapidly equilibrating mixture of several such intermediates.[13] Indeed, the experimental observations are highly reminiscent of those obtained with the norbornyl system, a system which features enhanced reactivity and scrambling of ^{14}C that can only be reasonably accounted for by non-classical intermediates.[6] We proceed, therefore, to consider the kinds of non-classical intermediates which could be involved in carbonium ion-type interconversions of cyclopropylcarbinyl and cyclobutyl compounds. It should be realized that, although the discussion is detailed for the sake of clarity, the conclusions reached are tentative.

Pyramidal structures may be written as possible conformations for the cations derived from the cyclopropylcarbinyl system, and these might



XVIIIa

have either unsymmetric or symmetric shapes. A single unsymmetric cation (XVIIIa) is not a satisfactory representation because it would lead to allylcarbinyl chloride with ^{14}C located only in the methylene group of the double bond (*cf.* Fig. 4).

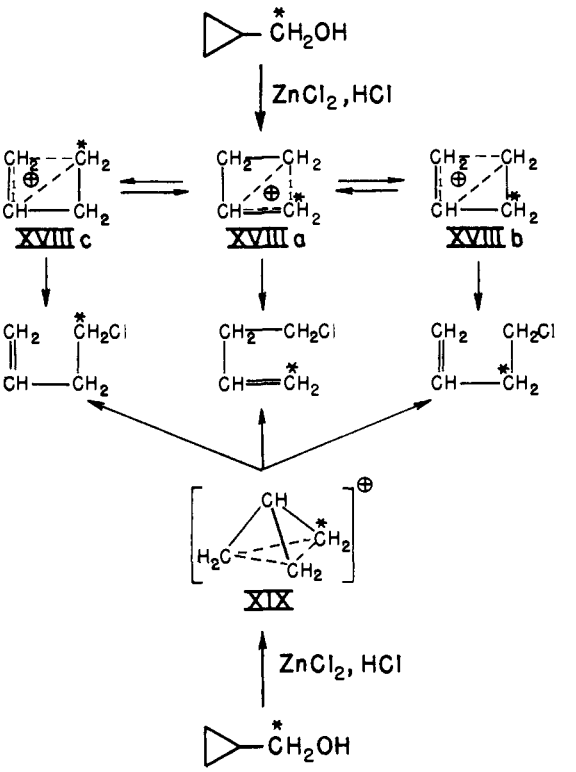
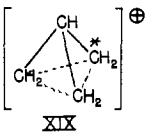


Fig. 4.

But, as Fig. 4 demonstrates, rapid equilibration of *three* unsymmetrical pyramidal cations, XVIIIa-c (each of which is a *d,l* pair), could account for the ^{14}C distribution in the allylcarbinyl chloride from cyclopropylcarbinol-α-^{14}C and Lucas reagent. Establishment of equilibrium between the ions XVIIIa-c is not hard to imagine, since they are so closely related that rather minor vibrations might suffice to interconvert them. If no barrier to inter-

(13) In a recent paper, H. Hart and J. M. Sandri, THIS JOURNAL, **81**, 320 (1959), imply that non-classical ion formation with cyclopropylcarbinyl derivatives must lead to rearrangement products if associated with enhanced solvolytic reactivity. However, as will be shown later with cyclopropylcarbinyl and cyclobutyl derivatives (and as is already well known with such substances as camphene hydrochloride or cyclocholesteryl compounds), overall rearrangement need not arise from non-classical intermediates formed in processes showing enhanced reactivities provided that the starting materials have certain predictably favorable structures.

conversion exists, a symmetric "tricyclobutonium" ion[4,7] (XIX) results, in which the three methylene groups are entirely equivalent.

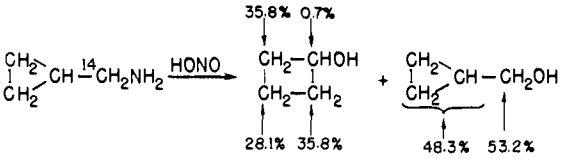


XIX

The isotopic distribution of the allylcarbinyl-^{14}C chloride from cyclopropylcarbinol-α-^{14}C and Lucas reagent does not permit differentiation between equilibrating ions XVIIIa-c and XIX since each pathway would lead to the same results for a reaction involving reversible intermediate stages. The only hope for differentiation between the two pathways appears to lie in a determination of the degree of equivalence achieved by the methylene groups during an irreversible process in a highly nucleophilic solvent. If cations XVIIIa-c are involved and they do not equilibrate much faster than they react with solvent to give the final products, then the degree of equivalence achieved by the methylene groups would be less than if the more symmetrical ion XIX were the sole intermediate. In the event that equilibration is essentially complete before reaction with solvent (implying a potential barrier of substantially less than 5 kcal. between the isotope-position isomers), the two formulations essentially merge for all practical purposes and it is almost a matter of taste to decide which to use.[14]

As a possible choice for an irreversible carbonium ion-type reaction, the deamination of cyclopropylcarbinylamine-α-^{14}C seemed most satisfactory. Loss of nitrogen from alkyldiazonium ions is amost certainly irreversible and the reaction is conveniently carried out in water, a solvent with excellent nucleophilic properties. Furthermore, the deamination conditions are customarily sufficiently mild to preclude undesirable rearrangements of the reaction products. However, these advantages have to be balanced against the considerable doubt which exists as to the exact nature of the carbonium ion formed by the loss of nitrogen from the diazonium ion.[15] Nonetheless, the product composition from the reaction of cyclopropylcarbinylamine with nitrous acid (48% cyclopropylcarbinol, 47% cyclobutanol, 5% allylcarbinol)[2] is rather typical for the carbonium ion reactions of this family of compounds, and, consequently, it was believed that the deamination of cyclopropylcarbinylamine-α-^{14}C might, in fact, contribute to an understanding of the normal carbonium ion reactions of cyclopropylcarbinyl and cyclobutyl derivatives.

The ^{14}C-distributions in the alcohols formed from cyclopropylcarbinylamine-α-^{14}C and nitrous acid provide strong evidence for behavior similar to that observed for the reaction of cyclopropylcarbinol-



α-^{14}C with Lucas reagent. Although the methylene groups do not attain complete equivalence, the extent of isotope-position rearrangement is truly striking. The points made earlier are still valid, and certainly the single unsymmetrical nonclassical ion XVIIIa insufficiently accounts for the results for, as Fig. 5 shows, it could not be expected to give rise to ^{14}C in the 3-position of cyclobutanol or the ring positions of cyclopropylcarbinol. However, formation and partial conversion of XVIIIa to XVIIIb and XVIIIc (84% of the equilibrium value) can account for the ^{14}C distribution in cyclobutanol but for only part of the excess ^{14}C in the α-position of cyclopropylcarbinol. The latter might arise from a non-rearranging SN2-type displacement at the α-carbon of the diazonium ion before XVIIIa is formed. Another possibility is that a "hot" classical cyclopropylcarbinyl cation is the first intermediate and it gives some non-rearranged alcohol by reaction with water before going over to XVIIIa.

Since symmetrical intermediate XIX would lead to complete equilibration of the methylene groups in the cyclobutanol at least, this intermediate seems to be ruled out unless some subordinate reaction path which gives a smaller degree of rearrangement also prevails. This is hardly the most economical explanation and it seems better to regard XIX not as the most stable non-classical intermediate but rather as a possible way point in the interconversion of XVIIIa-c (*vide infra*).

The most geometrically favorable conformation for the unsymmetrical "bicyclobutonium" ions XVIIIa-c would seem to be as in Fig. 6. For this arrangement, the degree of overlap of the three 2*p*-orbitals in which the two unsaturation electrons are delocalized could be very nearly the same as for the geometrically comparable and highly stabilized 7-dehydronorbornyl cation.[16,17] Reaction of a cation such as is shown in Fig. 6 with nucleophilic agents at positions 1, 2 and 4 would lead to cyclopropylcarbinyl, cyclobutyl or allylcarbinyl derivatives, respectively. The charge on the cation must be fairly evenly distributed between the 1-, 2- and 4-positions as judged by the fact that the proportions of the products corresponding to attack on

(14) A somewhat analogous situation has been encountered with respect to the intermediates involved in hydride ion migrations in norbornyl derivatives.[6b]

(15) See, for instance, A. Streitwieser, Jr., *J. Org. Chem.*, **22**, 861 (1957); D. J. Cram and J. E. McCarty, THIS JOURNAL, **79**, 2866 (1957), the discussion of ref. 6b, and also B. M. Benjamin, H. J. Schaeffer and C. J. Collins, *ibid.*, **79**, 6160 (1957).

(16) W. G. Woods, R. A. Carboni and J. D. Roberts, *ibid.*, **78**, 5653 (1956).

(17) The geometry here predicted for the cation formed from cyclopropylcarbinyl derivatives is not greatly different from our earliest proposal (J. D. Roberts, W. Bennett and R. Armstrong, *ibid.*, **72**, 3329 (1950)) except that the present formulation suggests that the nortricyclyl cation would be more favorable electronically than implied before. The earlier theorizing was based too heavily on π-type overlap of *p*-orbitals. The essential point of difference between the electronic stabilization envisioned for XVIII and a "hyperconjugated" cyclopropylcarbinyl cation (Roberts, Bennett and Armstrong, above) is that, for XVIII, substantial bonding is postulated between the carbinyl carbon and one of the ring methylene carbons. This bonding is particularly helpful in accounting for the ready formation of cyclobutyl derivatives which are not obviously expected to arise from a more or less highly hyperconjugated cyclopropylcarbinyl cation, irrespective of whether one or both of the C–C bonds of the ring were involved.

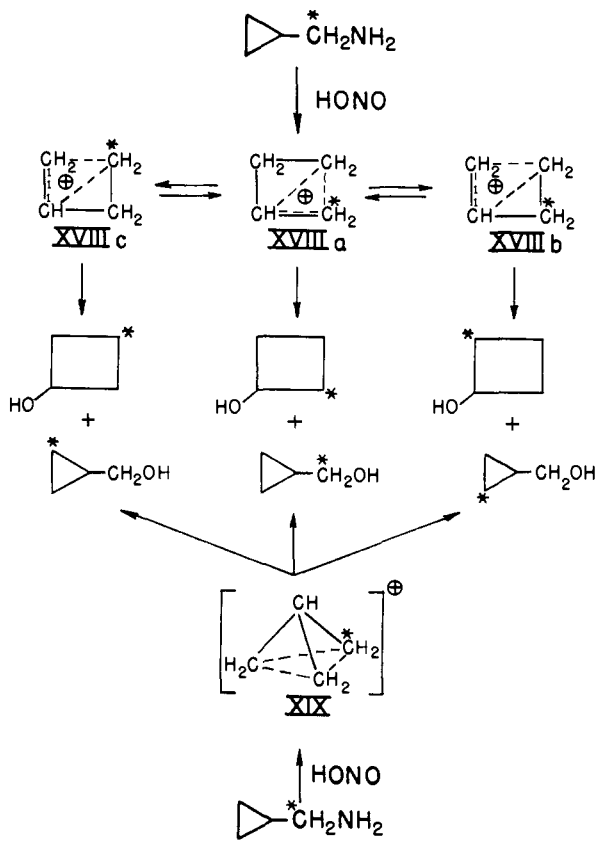


Fig. 5.

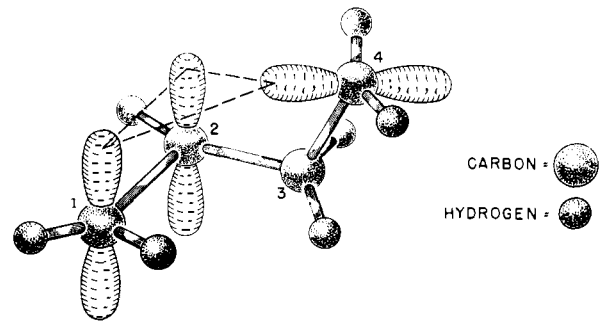


Fig. 6.

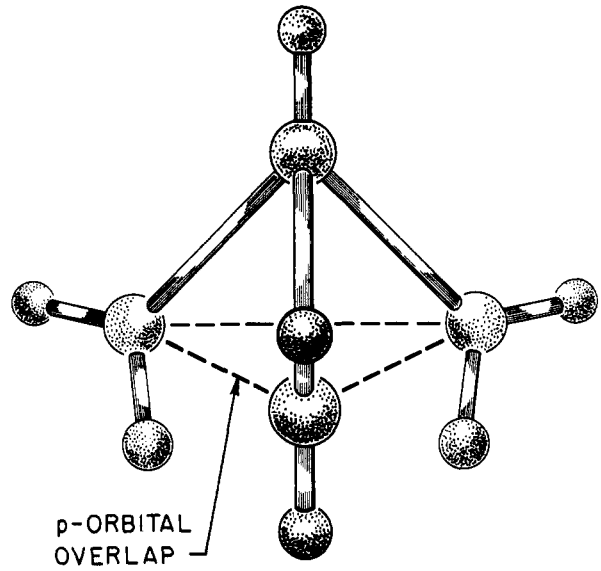


Fig. 7.

these positions are about 10:10:1. Since a very delicate balance between electrical and steric factors must be necessary to give such small differences in energy barriers for formation of the three products, it is to be expected that substitution of even a single methyl group on one of the carbons might alter the charge distribution sufficiently to change the product ratios drastically. Large effects of this type have been observed and will be discussed in detail in later papers. It suffices for the present to point out that these results substantiate the general correctness of the formulation presented above.

The mode of interconversion of the cations XVIIIa-c has only been briefly mentioned. If it is true that this interconversion takes place by way of XIX, the model for XVIIIa-c shown in Fig. 6 suggests that this may possibly be achieved with the least movement of atoms by passing through a conformation of XIX such as is shown in Fig. 7. It should be noted that in Fig. 7 the plane determined by the carbon and two hydrogens of each methylene group is *perpendicular* to the plane of the three methylene carbon atoms.

The atomic arrangement shown in Fig. 6 suggests another interesting possibility, namely that the barrier to the interconversion of XVIIIa and XVIIIb may be lower than the barrier for the conversion of either of these species to XVIIIc. If we now view the numbers of Fig. 6 as labeling specific carbon atoms, the models show that the transfer of carbon atom 4 from atom 3 to atom 1, with the resultant interchange in the roles of atoms 3 and 1, corresponds to the conversion XVIIIa to XVIIIb. This transfer might occur with a relatively slight movement of atoms. However, the change from either XVIIIa or XVIIIb to XVIIIc necessitates the formation of a bond between atoms 1 and 3, and might very well involve a pyramidal-type intermediate similar to XIX (which, of course, can open to any of the three unsymmetrical forms). Rearrangement of XVIIIc in correspondence to the interconversion of XVIIIa and XVIIIb results in no ^{14}C rearrangement but rather in the formation of the mirror image of XVIIIc.

As shown in Fig. 5, interconversion of XVIIIa and b would result in movement of ^{14}C into the cyclopropyl ring without introducing it into the 3-position of the cyclobutyl ring. If there is indeed an easier path than XIX for the XVIIIa-XVIIIb interconversion, a reaction may exist in which such a cyclopropylcarbinyl-α-^{14}C derivative may give ^{14}C rearrangement into the cyclopropyl ring but not to the 3-position of the cyclobutyl ring. The deamination of 1-methylcyclopropylcarbinylamine-α-^{14}C might well be expected to show such an effect, but unfortunately 1-methylcyclobutanol was the only product isolated.[11,18] However, the observation that only 2.6% of the total ^{14}C migrated to the 3-position of the cyclobutyl product is in accord with the above suggestions.[11,18]

(18) E. F. Cox, M. S. Silver and J. D. Roberts, THIS JOURNAL, unpublished.

Acknowledgment.—We are indebted to Miss Winifred Bennett for help with some of the radioactivity determinations.

Experimental

Starting Materials. Cyclopropylcarbinol-α-^{14}C.—Illustrative procedures are given. Cyclopropyl bromide[3] (0.60 g., 0.005 mole) was converted to the Grignard reagent and carbonated in an evacuated system at −20° with carbon dioxide generated from 0.7932 g. (0.00403 mole) of radioactive barium carbonate. The product was hydrolyzed with 2.0 g. of sulfuric acid in 12 ml. of water, about 10 g. of nonradioactive cyclopropanecarboxylic acid was added, and the mixture was continuously extracted with ether overnight. The ether was distilled, 10 ml. of benzene added, and the product dried by azeotropic distillation. Fractionation of the residue gave 9.43 g. (54% based on ^{14}C utilization) of cyclopropanecarboxylic-1-^{14}C acid, b.p. 100° (38 mm.). The acid was reduced with lithium aluminum hydride by the procedure previously described[19] to give cyclopropylcarbinol-α-^{14}C, b.p. 123°, n^{25}D 1.4300, in 78% yield.

Cyclopropylcarbinylamine-α-^{14}C.—A solution of 25.8 g. (0.30 mole) of cyclopropanecarboxylic-1-^{14}C acid in 44.1 g. (0.37 mole) of thionyl chloride was warmed to 30° over 0.5 hr., maintained at reflux for an additional hr., then fractionated through a 30-cm. column packed with a coil of tantalum wire to give 29.5 g. (94%) of cyclopropanecarbouyl-1-^{14}C chloride, b.p. 116.5–117.5° (lit.[20] b.p. 118–119° (739 mm.)).

The acid chloride (29.5 g., 0.282 mole), in 250 ml. of anhydrous ether, was cooled by an ice-bath and stirred vigorously while a rapid stream of dry ammonia was passed over it for 30 min. The ether was evaporated and the residue extracted with eight 75-ml. portions of boiling chloroform. The chloroform was evaporated to give 21.9 g. (91%) of colorless crystals of cyclopropanecarboxamide-1-^{14}C, m.p. 123.6–124.5° (lit.[21] m.p. 124.5–126.0°).

A mixture of the amide (3.74 g., 0.044 mole) (which is insoluble in solvents commonly used for lithium aluminum hydride reductions), 3.34 g. (0.088 mole) of lithium aluminum hydride and 100 ml. of anhydrous benzene was maintained at reflux and stirred under an atmosphere of nitrogen for 24 hr. The excess lithium aluminum hydride was decomposed by the addition of 25 ml. of 10 *N* sodium hydroxide. Most of the benzene was decanted, and the residue was boiled twice under reflux with 50 ml. of ether. The ether extracts and the benzene portion were combined and extracted with 2 *N* hydrochloric acid. The acidic extracts were evaporated to dryness to give cyclopropylcarbinylamine-α-^{14}C hydrochloride which, after recrystallization from ethanol–ether, had m.p. 201.5–203.5°. The hydrochloride, diluted with 6.00 g. (0.056 mole) of unlabeled cyclopropylcarbinylamine hydrochloride, was dissolved in 25 ml. of water and the solution made strongly basic by addition of ice-cold aqueous sodium hydroxide. The solution was steam distilled to give cyclopropylcarbinylamine-α-^{14}C, 0.090 mole (77%), as determined by titration with perchloric acid.

Reaction of Cyclopropylcarbinol-α-^{14}C with Lucas Reagent.—The procedure was as described previously.[2] From 6.6 g. (0.092 mole) of cyclopropylcarbinol-α-^{14}C and 66.0 g. of Lucas reagent was obtained 6.9 g. (84%) of crude allylcarbinyl-x-^{14}C chloride.

Degradation of Allylcarbinyl-x-^{14}C Chloride. Procedure 1.—To 6.9 g. (0.077 mole) of the crude chloride was added 50 ml. of 87% formic acid and 17.0 g. (0.15 mole) of 30% hydrogen peroxide. The temperature of the stirred mixture was maintained below 50° by intermittent cooling until a clear solution resulted (30 min.). Stirring was continued for 2 hr. and the formic acid was removed under reduced pressure. Methanolic hydrogen chloride (50 ml.) was added to the residue, the resulting solution was maintained at reflux for 1 hr., and the methyl formate and methanol were removed by distillation to give 6.1 g. (64%) of 4-chloro-1,2-butanediol-x-^{14}C (XVII), n^{25}D 1.4760. 4-Chloro-1,2-butanediol was found to be unstable to heat, some 3-hydroxytetrahydrofuran probably being formed through elimination of hydrogen chloride. Distillation of the crude chloroglycol gave material with b.p. 117° (0.8 mm.), n^{25}D 1.4735.

Anal. Calcd. for $C_4H_9O_2Cl$: C, 38.56; H, 7.28; Cl, 28.46. Found: C, 39.30; H, 7.34; Cl, 26.56.

Hydrolysis of the intermediate formate with aqueous potassium hydroxide in the usual manner[22] gave only 3-hydroxytetrahydrofuran, b.p. 61–62° (7 mm.), n^{25}D 1.4396 (lit.[23] b.p. 84–86° (16 mm.), n^{19}D 1.4431). The N-phenylcarbamate of 3-hydroxytetrahydrofuran, after crystallization from ethanol–water and recrystallization from hexane–benzene, had m.p. 117.2–117.6° (lit.[23] m.p. 120°).

Distilled 4-chloro-1,2-butanediol-x-^{14}C (0.66 g., 0.0053 mole) was mixed with a solution of 1.13 g. (0.0053 mole) of sodium metaperiodate in 50 ml. of water and allowed to stand for 2 hr. at room temperature. The solution was extracted with ether and the aqueous layer added to a filtered solution of a 0.74 g. (0.0053 mole) of methone in 200 ml. of water. The mixture was allowed to stand for 1 hr., the product removed by filtration and recrystallized from 95% ethanol to give 0.38 g. of formaldehyde-^{14}C (XI) dimethone, m.p. 191.6–192.6° (lit.[21] m.p. 191–191.5°), which was analyzed for ^{14}C.

Degradation of Allylcarbinyl-x-^{14}C Chloride. Procedure 2.—Allylcarbinyl-x-^{14}C chloride (4.66 g., 0.0521 mole) was converted to the Grignard reagent with 1.44 g. (0.06 mole) of magnesium turnings in 20 ml. of anhydrous di-*n*-butyl ether and the mixture was treated with 6.0 g. of sulfuric acid in 20 ml. of water. The evolved 1-butene was passed into a flask fitted with a Dry Ice condenser and containing 30 ml. of 87% formic acid and 11.3 g. (0.10 mole) of 30% hydrogen peroxide. The formic acid mixture was stirred for 4 hr. while the sulfuric acid–di-*n*-butyl ether mixture was heated to 110°, and then worked up as described above for 4-chloro-1,2-butanediol-x-^{14}C except that the crude glycol was dried by azeotropic distillation of the water present with benzene. The product was distilled through a semi-micro column packed with a platinum spiral to give 1.05 g. (23%) of 1,2-butanediol-x-^{14}C (XII), b.p. 90° (12 mm.), n^{25}D 1.4396; (lit. *levo*, b.p. 94–96° (12 mm.)[25]; *dextro*, b.p. 91–91.5° (13 mm.),[21] n^{20}D 1.435[26]).

The di-(N-phenylcarbamate), after recrystallization from hexane–benzene, had m.p. 116–117° (lit.[25] *levo*, m.p. 121–123°, *dextro*, m.p. 125–127°).

Anal. Calcd. for $C_{18}H_{20}O_4N_2$: C, 65.84; H, 6.14. Found: C, 65.92; H, 6.21.

Oxidation of 1,2-butanediol-x-^{14}C was carried out as described for 4-chloro-1,2-butanediol-x-^{14}C except that the reaction mixture was continuously extracted with ether for 2 hr. after the completion of the oxidation. The ether extract, containing propionaldehyde-x-^{14}C, was reserved for further degradation. From 0.516 g. (0.0056 mole) of 1,2-butanediol-x-^{14}C, 1.20 g. (0.0056 mole) of sodium metaperiodate and 1.57 g. (0.0112 mole) of methone was obtained 1.37 g. (84%) of formaldehyde (XIII) dimethone, m.p. 187–190°. After recrystallization from absolute ethanol, the dimethone had m.p. 190.2–191.0°; this material was analyzed for ^{14}C.

The ether extract containing propionaldehyde-x-^{14}C was stirred for 30 min. at 0° with a solution of 0.98 g. (0.005 mole) of sodium permanganate trihydrate and 0.12 g. (0.003 mole) of sodium hydroxide in 25 ml. of water. The manganese dioxide was removed by filtration, washed with 25 ml. of water, the combined filtrates decolorized with sodium bisulfite, and the ether separated. To the aqueous layer was added 30 g. of sodium sulfate and 3 g. of sulfuric acid, and the mixture was steam distilled until 300 ml. of distillate had been collected. The distillate was neutralized with carbonate-free sodium hydroxide and evaporated to dryness to give 0.87 g. of salt which probably contained some sodium bisulfite.

A portion of the salt XIV was converted to *p*-bromophenacyl propionate-x-^{14}C which, after recrystallization

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(20) N. Kishner, *Chem. Zentr.*, **76**, I, 1703 (1905).

(21) N. J. Demjanow and M. Dojarenko, *Ber.*, **56**, 2200 (1923).

(22) D. Swern, G. N. Billen and J. T. Scanlan, THIS JOURNAL, **68**, 1504 (1946).

(23) S. Olsen, *Acta Chem. Scand.*, **4**, 462 (1950).

(24) E. C. Horning and M. G. Horning, *J. Org. Chem.*, **11**, 95 (1946).

(25) P. A. Levene and H. L. Haller, *J. Biol. Chem.*, **74**, 343 (1927).

(26) D. V. Tischenko, *J. Gen. Chem.* (U.S.S.R.), **7**, 658 (1937).

from ethanol–water, had m.p. 62.4–62.8° (lit.[27] m.p. 63°) and was analyzed for ^{14}C.

The remainder of the sodium propionate-x-^{14}C was mixed with 0.6 ml. of concentrated sulfuric acid and treated with 0.0028 mole of hydrazoic acid in chloroform at 50°. The evolved gases were bubbled through carbonate-free sodium hydroxide and the system flushed with carbon dioxide-free nitrogen after completion of the reaction. To the sodium hydroxide was added a solution of 0.3 g. of barium chloride dihydrate in 5 ml. of boiled distilled water, the resulting precipitate was washed with boiled distilled water and acetone by centrifugation, and dried at 70° to give 0.194 g. of barium carbonate (XVI) which was analyzed for ^{14}C.[28]

The sulfuric acid–chloroform mixture was cooled to 0°, basified with cold dilute sodium hydroxide, and treated with a solution of 0.3 g. of *p*-bromobenzenesulfonyl chloride in 5 ml. of chloroform. The mixture was stirred for 15 min., the aqueous layer separated and heated to 100° to remove traces of chloroform, acidified with concentrated hydrochloric acid, and allowed to stand in the ice-box overnight to give, after 2 recrystallizations from hexane–benzene, a mixture of *p*-bromobenzenesulfonamides which had m.p. 74.5–75.0°. This material (XV), which was shown by infrared analysis to be a mixture containing 76% N-ethyl- and 24% N-methyl-*p*-bromobenzenesulfonamide, was analyzed for ^{14}C. Mixed melting points taken on authentic mixtures were slightly lower than the melting points of the pure components (N-methyl-*p*-bromobenzenesulfonamide, m.p. 77.2–77.8°, lit.[29] m.p. 77°; N-ethyl-*p*-bromobenzenesulfonamide, m.p. 80.6–81.2°, lit.[30] m.p. 81°) and the radioactivity analyses (Table I) checked if it was assumed that the mixture was 76% active N-ethyl- and 24% inactive N-methyl derivative. The N-methyl compound was probably derived from ethanol used as a preservative in chloroform.

Deamination of Cyclopropylcarbinylamine-α-^{14}C.—The cyclobutanol-x-^{14}C which was degraded was obtained from a deamination procedure similar to that previously described for crotylamine[2] except that the steam distillate was continuously extracted with ether for 10 hr. From 0.090 mole of cyclopropylcarbinylamine-α-^{14}C perchlorate and 20.7 g. (0.30 mole) of sodium nitrite heated at 100° for 1 hr. there was obtained, after fractionation through a center-tube column,[31] 0.32 g. of alcohols containing some allylcarbinol-x-^{14}C, b.p. 116–125°, and 3.60 g. of material containing no allylcarbinol, b.p. 125–126.5°, yield 3.92 g. (60%). The cyclopropylcarbinol-x-^{14}C which was degraded was obtained from a similar deamination procedure except that the reaction mixture was heated only to 55–60° for 20 min.

Degradation of Deamination Products. Oxidation of Mixture of Alicyclic-x-^{14}C Alcohols.—A warm solution of 36.5 g. (0.231 mole) of potassium permanganate in 300 ml. of water was added over a 15-min. period to a solution of 5.50 g. (0.0764 mole) of cyclic alcohol-x-^{14}C mixture and 1 pellet of potassium hydroxide in 10 ml. of water. The oxidation was quite exothermic. The reaction mixture was then heated on a steam-bath for 30 min., cooled, and treated with sodium formate solution to discharge the excess permanganate. The manganese dioxide was removed by filtration, and the filter cake was washed with 100 ml. of 2% sodium hydroxide. The filtrate was acidified with 120 ml. of 6 *N* sulfuric acid and distilled until 400 ml. of distillate (A) had been collected in a flask containing 25 ml. of 15% sodium hydroxide solution.

The acidic residue (75 ml.) from this distillation was continuously extracted with ether for 24 hr. The ether was removed by evaporation and the solid residue crystallized from water to give 2.23 g. (25%) of succinic-x-^{14}C acid (I), m.p. 184.0–185.0° (lit.[32] m.p. 184.5–185°). Four recrystallizations from water gave material of m.p. 186.5–187.0°, which was analyzed for ^{14}C.

The alkaline solution of steam distillate A was concentrated to 50 ml. and acidified with a solution of 7.5 ml. of concentrated sulfuric acid in 25 ml. of water. The resulting solution was continuously extracted with ether for 12 hr. The ether extract was dried over magnesium sulfate and the ether removed by evaporation. The high-boiling residue was distilled to give 2.92 g. (44%) of cyclopropanecarboxylic-x-^{14}C acid (VI), b.p. 160–180° (mainly 173–178°)(lit.[2] b.p. 97–98° (40 mm.)).

Cyclopropanecarboxylic-x-^{14}C acid (0.200 g., 0.00232 mole) was heated with 0.50 g. (0.0042 mole) of thionyl chloride for 5 min. at 50° and 10 ml. of anhydrous ether was added followed by 2.00 g. (0.0215 mole) of aniline in 10 ml. of anhydrous ether. The ethereal solution was washed with 50 ml. of 10% hydrochloric acid and the ether removed by evaporation. The solid residue was crystallized once from 80 ml. of water and twice from cyclohexane to give 0.163 g. (44%) of cyclopropanecarboxanilide-x-^{14}C, colorless needles, m.p. 108.8–109.7° (lit.[20] m.p. 110°), which was analyzed for ^{14}C to give the activity of VI.

Degradation of Cyclobutanol-x-^{14}C. Procedure 1.—Succinic-x-^{14}C acid (I) (prepared from the mixture of alicyclic alcohols as described above) was degraded by the Schmidt reaction as described previously for glutaric acid.[33,28] From 2.5 g. (0.21 mole) of succinic-x-^{14}C acid, 9.7 ml. of concentrated sulfuric acid and 0.049 mole of hydrazoic acid (1.61 *M* solution in chloroform which had been washed with sulfuric acid to remove any ethanol) there was obtained barium carbonate-^{14}C (from III) and 3.30 g. (60%) of crude ethylenediamine-^{14}C (II) dibenzamide. A small portion of the dibenzamide was recrystallized three times from absolute ethanol to give white needles, m.p. 250.9–251.3° (lit.[34] m.p. 249°). The pure dibenzamide and the barium carbonate were analyzed for ^{14}C.

Degradation of Cyclobutanol-x-^{14}C. Procedure 2.—The mixture of alicyclic alcohols (2.00 g., 0.0278 mole) from the cyclopropylcarbinylamine-α-^{14}C–nitrous acid reaction was combined with 1.0 g. of aluminum phenoxide, 6.48 g. (0.060 mole) of benzoquinone and 50 ml. of anhydrous toluene, heated on a steam-bath for 5 hr., and then distilled until 45 ml. of distillate had been collected. The distillate was shaken with a solution of 2 g. of sodium hydroxide and 3 g. of sodium sulfite in 20 ml. of water until the yellow color in the organic layer had disappeared, and this two-phase system was then distilled until 50 ml. of distillate was obtained. The aqueous layer of the distillate was saturated with sodium bisulfite and separated. The organic layer was washed five times with 10-ml. portions of saturated sodium bisulfite solution. The combined bisulfite solutions were made alkaline with solid potassium carbonate, diluted to 90 ml. with water and distilled until 45 ml. of distillate was collected. Ammonium persulfate (13 g., 0.057 mole) was dissolved in the distillate, and 20 ml. of concentrated sulfuric acid was added to the swirled solution while the temperature was kept below 10°. The solution was kept at 2° for 43 hr., and then continuously extracted with ether for 20 hr. during which time the solution being extracted was kept below 5°. The ethereal extract was dried over magnesium sulfate and the ether removed by evaporation. The residue was distilled to give 0.84 g. (35%) of slightly yellowish liquid, which was shown by its infrared spectrum to contain 75% γ-butyrolactone-x-^{14}C, b.p. 160–200° (lit.[35] γ-butyrolactone, b.p. 204° (756 mm.)). This material, in 30 ml. of anhydrous ether, was added during 10 min. to a stirred solution of phenylmagnesium bromide (prepared from 7.85 g. (0.050 mole) of bromobenzene, 1.25 g. (0.0514 g. atom) of magnesium and 75 ml. of anhydrous ether), the stirring was continued for 20 min. more and then 40 ml. of 10% hydrochloric acid was added cautiously. The ether layer was separated and the aqueous layer washed twice with 25-ml. portions of ether. The combined ether solutions were dried over potassium carbonate and the ether removed by evaporation. The solid residue was recrystallized three times from benzene to give 0.588 g. (9%) of 1,1-diphenylbutane-

(27) R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 3rd ed., 1948, p. 222.

(28) Since this work was completed an improved procedure for isolation of carbon dioxide from Schmidt reactions has been developed; J. D. Roberts, D. A. Semenow, H. E. Simmons, Jr., and L. A. Carlsmith, THIS JOURNAL, **78**, 601 (1956).

(29) C. S. Marvel and F. E. Smith, *ibid.*, **45**, 2696 (1923).

(30) W. Ssolonina, *J. Russ. Phys. Chem. Soc.*, **31**, 640 (1899); *Chem. Zentr.*, **70**, II, 867 (1899).

(31) E. A. Naragon and C. J. Lewis, *Ind. Eng. Chem., Anal Ed.*, **18**, 1448 (1946).

(32) M. T. Leffler and R. Adams, THIS JOURNAL, **58**, 1551 (1936).

(33) R. B. Loftfield, *ibid.*, **73**, 4713 (1951).

(34) N. D. Cheronis and J. B Entriken, "Semimicro Qualitative Organic Analysis," T. Y. Crowell Co., New York, N. Y., 1947, p. 402.

(35) P. Henry, *Z. physik. Chem.*, **10**, 96 (1892).

1,4-diol-x-^{14}C (IV), m.p. 105.5–106.4° (lit.[36] m.p. 108°), which was analyzed for ^{14}C.

To a solution of 0.26 g. (0.00107 mole) of 1,1-diphenylbutane-1,4-diol-x-^{14}C (IV) in 10 ml. of hot glacial acetic acid was added during 15 min. 1.50 g. (0.015 mole) of chromium trioxide. The reaction was vigorous. The mixture was heated on a steam-bath for 1 hr., then poured into 75 ml. of water. The aqueous solution was extracted five times with 10-ml. portions of ether. The combined ethereal solutions were washed with 30 ml. of water and twice with 30-ml. portions of 10% sodium bicarbonate solution, then dried over potassium carbonate. The ether was removed by evaporation and the residue heated with a solution of 1.50 g. (0.0104 mole) of phenylhydrazine hydrochloride in 6.0 ml. of ethanol and 3.0 ml. of water for 1 hr. on a steam-bath. The benzophenone-^{14}C (V) phenylhydrazone obtained upon cooling was filtered, washed twice with 3-ml. portions of ethanol, and recrystallized three times from ethanol to give 0.194 g. (67%) of slightly tan prisms, m.p. 135.4–136.0° (lit.[37] m.p. 137–138°), which were analyzed for ^{14}C.

Degradation of Cyclopropylcarbinol-x-^{14}C. Procedure 1.—The cyclopropylcarbinol-x-^{14}C was oxidized to cyclopropanecarboxylic-x-^{14}C acid (VI) by the method described above. The sodium salt was degraded by the Schmidt reaction as described for sodium propionate-x-^{14}C. From 0.581 g. (0.00539 mole) of cyclopropanecarboxylic-x-^{14}C acid (VI) was obtained 0.473 g. (45%) of barium carbonate-^{14}C (X) and 30% of cyclopropylamine-x-^{14}C (IX) isolated as the benzamide (0.255 g.) which, after two recrystallizations from hexane–benzene, had m.p. 97.6–98.0° (lit.[20] m.p. 98.5°) and was analyzed for ^{14}C.

Degradation of Cyclopropylcarbinol-x-^{14}C. Procedure 2.—To 0.80 g. (0.0093 mole) of cyclopropanecarboxylic-x-^{14}C acid (VI) (obtained as before) was added 1.30 g. (0.0109 mole) of thionyl chloride. The solution was heated at reflux for 45 min. and then cooled and dissolved in 15 ml. of cold tetrahydrofuran. To this solution was added an ice-cold solution of 3.25 g. (0.050 mole) of sodium azide in 15 ml. of water. The mixture, cooled in an ice-bath, was shaken for 15 min., then poured into 50 ml. of cold saturated sodium chloride solution, and extracted five times with 10-ml. portions of toluene. The combined extracts were dried over magnesium sulfate, then over Drierite, heated at reflux for 2 hr., cooled and added during 10 min. to a solution of phenylmagnesium bromide (prepared from 6.28 g. (0.040 mole) of bromobenzene, 1.00 g. (0.041 g. atom) of magnesium and 50 ml. of anhydrous ether). The reaction mixture was heated at reflux for 30 min., cooled, and cautiously treated with 40 ml. of 10% hydrochloric acid. The organic layer was separated and the aqueous layer washed twice with 20-ml. portions of ether. The combined organic phases were dried over potassium carbonate, and the solvents removed by evaporation, finally at reduced pressure. The residue was recrystallized three times from benzene–cyclohexane to give 0.886 g. (58%) of N-cyclopropylbenzamide-x-^{14}C (VII), slightly tan needles, m.p. 94.1–95.3°. Recrystallization of a portion of the benzamide once from water and once from cyclohexane gave colorless plates, m.p. 96.1–96.5°, which were analyzed for ^{14}C.

A mixture of 0.35 g. (0.0022 mole) of N-cyclopropylbenzamide-x-^{14}C (VII) and 20 ml. of 10% sodium hydroxide was heated at reflux for 15 hr. during which time the cyclopropylamine-x-^{14}C (IX) evolved was collected in a receiver cooled in a Dry Ice-bath. At the end of this time, a single phase was present and 15 ml. of water was added. The solution was distilled until 25 ml. of distillate had been collected in an ice-cooled flask containing 5.0 ml. of 10% hydrochloric acid. The contents of the Dry Ice-cooled receiver were washed into the distillate, and the solution washed three times with 10-ml. portions of ether (the washings were discarded). To the aqueous layer was added 1.00 g. (0.00715 mole) of benzoyl chloride and a solution of 2.00 g. (0.050 mole) of sodium hydroxide in 6.0 ml. of water. The N-cyclopropylbenzamide-x-^{14}C (from IX) was washed twice with 3-ml. portions of water and crystallized twice from water to give 0.226 g. (65%) of colorless plates, m.p. 96.0–96.5°, which were analyzed for ^{14}C.

The basic residue from the aqueous distillation was diluted to 25 ml. with water and washed three times with 10-ml. portions of ether (the ether washings were discarded). The basic solution was acidified with 40 ml. of 10% hydrochloric acid, and the liberated benzoic-^{14}C acid (VIII) extracted with four 10-ml. portions of ether. The ethereal extracts were combined, the ether removed by gentle evaporation, and the residue crystallized twice from water to give 0.200 g. (75%) of fine white needles, m.p. 120.6–121.2° (lit.[38] m.p. 122.38°), which were analyzed for ^{14}C.

Control Reaction of Cyclopropylcarbinol-α-^{14}C under Deamination Conditions.—To a solution of 2.30 g. (0.032 mole) cyclopropylcarbinol-α-^{14}C and 3.64 g. (0.081 mole) of ethylamine in 13.5 ml. of water were added, rapidly and consecutively, 85 ml. of 1.0 N perchloric acid and 15.53 g. (0.225 mole) of sodium nitrite in 50 ml. of water. The solution was maintained at 55–60° for 20 min., and then the excess acid was removed by the addition of 60 g. of potassium carbonate. The reaction mixture was worked up as before to give 1.80 g. (78%) of crude cyclopropylcarbinol, b.p. 118–124°. The product was degraded by the second procedure above and afforded an 84% yield of cyclopropanecarboxylic acid in the initial oxidation step. No significant rearrangement of ^{14}C was noted in the cyclopropylcarbinol (*cf.* Table III).

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