

of hexane added. The resulting precipitate was separated and extracted with three 250-ml. portions of hot hexane. Evaporation of hexane gave 4.0 g. of solid, which, after five recrystallizations from ethanol, afforded white crystals of XXXIII having m.p. 68.1–68.4°; ultraviolet spectrum:  $\lambda_{\text{max}}$  2740, 2800 and 2835 Å. ( $\epsilon$  1350, 1270 and 1520, resp.); infrared spectrum: bands at 1565, 1577 and 1600  $\text{cm}^{-1}$ .

*Anal.* Calcd. for  $\text{C}_{10}\text{H}_9\text{FCl}_2$ : C, 54.82; H, 4.14; Cl, 32.27; mol. wt., 203. Found: C, 54.88; H, 4.78; Cl, 33.54; mol. wt. (Rast), 227.

Further repeated extractions of crude reaction product eventually gave in all 10 g. (41%) of product; XXXIII did not decolorize bromine or potassium permanganate solutions and did not react with sodium iodide in acetone or ethanolic silver nitrate.

Similar results were obtained when 1,1-difluoro-2,4-dichloro-3-(cyclohex-1-enyl)-cyclobutene was substituted for XI.

**Isopropenylacetylene and Trifluorochloroethylene.**—To four heavy-walled Pyrex tubes (19 × 25 × 615 mm.), cooled in Dry Ice, were added 53.2 g. (75 ml., 0.81 mole) of isopropenylacetylene and 110 g. (75 ml., 0.9 mole) of trifluorochloroethylene. The tubes were sealed, heated at 95° for 20 hr., cooled in Dry Ice, vented, and the contents distilled. The low-boiling material was removed at water aspirator pressure, and the residue was separated by distillation through a 30-cm. Vigreux column into seven fractions.

Fraction 1 amounted to 30 g., b.p. 44–49° (35.3–36 mm.),  $n_{\text{D}}^{25}$  1.4039. The infrared spectrum had strong acetylenic carbon–hydrogen absorption at 3290  $\text{cm}^{-1}$  and weak carbon–carbon triple-bond absorption at 2100  $\text{cm}^{-1}$ . The material was assigned the structure 1,1,2-trifluoro-2-chloro-3-methyl-3-ethynylcyclobutane (XXXIX).

*Anal.* Calcd. for  $\text{C}_7\text{H}_5\text{F}_3\text{Cl}$ : C, 46.05; H, 3.31; Cl, 19.42. Found: C, 45.91; H, 3.42; Cl, 19.38.

Fractions 4 and 5 amounted to 27.2 g., b.p. 60–65° (32–37 mm.),  $n_{\text{D}}^{25}$  1.4288–1.4295, and were assigned the

structure 1,1,2-trifluoro-2-chloro-3-isopropenylcyclobutene (XXXVIII) on the basis of proton and fluorine magnetic resonance spectra and infrared absorptions at 1588 and 1635  $\text{cm}^{-1}$ .

*Anal.* Calcd. for  $\text{C}_7\text{H}_5\text{F}_3\text{Cl}$ : C, 46.05; H, 3.31; Cl, 19.42. Found: C, 45.93; H, 3.24; Cl, 19.37.

Fraction 7 amounted to 9.4 g., b.p. 51–53° (1 mm.),  $n_{\text{D}}^{25}$  1.4206, and was believed to be 1,1,2-trifluoro-2-chloro-3-methyl-3-(3,3,4-trifluoro-4-chlorocyclobutenyl)-cyclobutane (XL), by analogy with the course of the reaction of vinylacetylene and tetrafluoroethylene.<sup>21</sup>

**1,1,2-Trifluoro-2,3-dichloro-3-(cyclohex-1-enyl)-cyclobutane (XLI).**—The procedure was similar to that used for the preparation of IV. Trifluorochloroethylene (30 g., 0.258 mole) and 1-(1-chloroethenyl)-cyclohex-1-ene<sup>22</sup> (20.0 g., 0.14 mole) were heated at 125° for 18 hr. Distillation gave starting material (10 g.), b.p. 51–53° (2 mm.), and 10 g. of the pale-yellow adduct XLI, b.p. 91–94° (2 mm.),  $n_{\text{D}}^{25}$  1.4737.

*Anal.* Calcd. for  $\text{C}_{10}\text{H}_{11}\text{F}_3\text{Cl}_2$ : C, 46.35; H, 4.28; Cl, 27.37. Found: C, 46.47; H, 4.35; Cl, 27.17.

The infrared spectrum of XLI showed a single double-bond absorption at 1666  $\text{cm}^{-1}$ . There was no maximum in the ultraviolet spectrum above 2200 Å. With ethanolic silver nitrate, XLI formed a precipitate rapidly; however, XLI gave no reaction with sodium iodide in acetone. Microhydrogenation resulted in absorption of one mole-equivalent of hydrogen with apparent hydrogenolysis of the allylic chlorine. The structure XLI was indicated by the fact that dehydrochlorination with potassium hydroxide in *t*-butyl alcohol gave IV, identical in all respects with material prepared from trifluorochloroethylene and 1-ethynylcyclohex-1-ene.

(21) D. D. Coffman, P. L. Barrick, R. D. Cramer and M. S. Raasch, *J. Am. Chem. Soc.*, **71**, 490 (1949).

(22) Obtained as a side-reaction product from the preparation of 1-ethynylcyclohex-1-ene by phosphorus oxychloride dehydration of 1-ethynylcyclohexan-1-ol.

[CONTRIBUTION NO. 2628 FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, PASADENA, CALIF.]

## Small-Ring Compounds. XXXII. The Reaction of Allylcarbinylamine- $\alpha$ - $^{14}\text{C}$ (3-Butenyl-1- $^{14}\text{C}$ -amine) with Nitrous Acid<sup>1,2</sup>

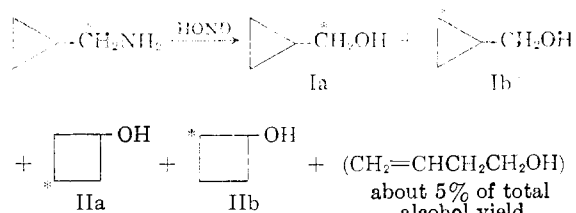
BY E. RENK AND JOHN D. ROBERTS

RECEIVED SEPTEMBER 27, 1960

The isotopic analysis of the cyclopropylcarbinol and cyclobutanol formed in the reaction of allylcarbinylamine- $\alpha$ - $^{14}\text{C}$  with nitrous acid has indicated that all of the possible methylene-labeled, isotope-position isomers are formed but not quite to the extent expected for statistical equilibrium. The compositions of the alcohols resulting from treatment of cyclopropylcarbinyl-, cyclobutyl- and allylcarbinylamines with nitrous acid have been measured accurately and correlated with the degree of isotope-position rearrangement obtained with  $^{14}\text{C}$ -labeled amines. The results are in agreement with the previously postulated interpretation of these reactions as involving rapid but not instantaneous equilibration of unsymmetrical non-classical cations.

Cyclopropylcarbinylamine- $\alpha$ - $^{14}\text{C}$  with nitrous acid has been reported to give a mixture of alcohols, with the isomers Ia and Ib being formed to the relative extents of 52 and 48%, respectively, and the isomers IIa and IIb being formed to the relative extents of 28 and 72%, respectively.<sup>3</sup>

The degree of isotope-position rearrangement in this reaction is extraordinarily high, and the ratios



(1) Supported in part by a grant from the Petroleum Research Fund of the American Chemical Society. Grateful acknowledgment is hereby made to the donors of this Fund.

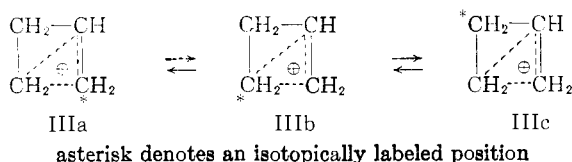
(2) Presented at the Sixteenth National Organic Chemistry Symposium of the American Chemical Society, Seattle, Wash., June, 1959.

(3) R. H. Mazur, W. N. White, D. A. Semenow, C. C. Lee, M. S. Silver and J. D. Roberts, *J. Am. Chem. Soc.*, **81**, 4390 (1959). The rearrangement figures used in the present paper are rounded values normalized to 100%.

of the methylene-labeled isomers Ia/Ib and IIa/IIb approach but do not reach the equilibrium values of  $1/2$ . These results, in conjunction with many other findings regarding carbonium ion-type interconversion reactions of cyclopropylcarbinyl, cyclobutyl and allylcarbinyl derivatives,<sup>4</sup> have led

(4) (a) J. D. Roberts and R. H. Mazur, *ibid.*, **73**, 2509 (1951);

to the suggestion<sup>8</sup> that such reactions involve rapidly equilibrating non-classical "bicyclobutonium" ion intermediates (IIIa-c).



Each of these is believed to be able to react with nucleophilic agents to give the same proportions of cyclopropylcarbinyl, cyclobutyl and allylcarbinyl derivatives with, of course, the possibility of the label winding up in different positions depending on whether or not the product arises from IIIa, IIIb or IIIc. To explain the observed  $^{14}\text{C}$  results it is necessary to assume that equilibration between IIIa-c is rapid but not instantaneous compared to the rate of reaction with solvent.

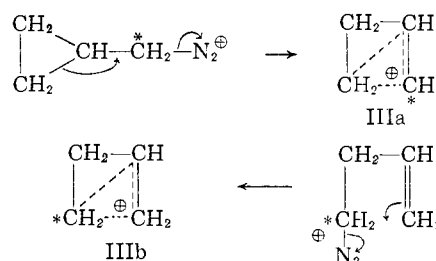
One possible objection to this interpretation is that the cumulative  $^{14}\text{C}$  kinetic-isotope in the degradation scheme used for location of the isotopic atoms<sup>8</sup> in the alcohols formed from cyclopropylcarbinylamine- $\alpha$ - $^{14}\text{C}$  might cause the observed distribution of the label to differ from the actual distribution, which could conceivably be that expected for statistical equilibrium. Another relatively unsatisfactory point is the fact that the observed distributions of the  $^{14}\text{C}$  in the cyclopropylcarbinol and cyclobutanol did not represent the same degree of shuffling of methylene groups. The cyclopropylcarbinol showed distinctly less rearrangement, and this was explained by postulation of some degree of non-rearranging (possibly  $\text{S}_{\text{N}}2$  or  $\text{S}_{\text{N}}2$ ) substitution in the reaction of the cyclopropylcarbinyl- $^{14}\text{C}$ -amine with nitrous acid. The idea was that some excess of cyclopropylcarbinol- $\alpha$ - $^{14}\text{C}$  could be formed by a noncarbonium process while the balance of the cyclopropylcarbinol and all of the cyclobutanol and allylcarbinol would arise from the equilibrating ions IIIa-c.

To clarify the above questions, it was desirable to produce the system of equilibrating ions starting from a different point, and for this purpose we chose to study the reaction of allylcarbinylamine- $\alpha$ - $^{14}\text{C}$  (3-butenyl-1- $^{14}\text{C}$ -amine, IV) with nitrous acid. With this starting material, there is no reasonable possibility of either cyclopropylcarbinol or cyclobutanol being formed by  $\text{S}_{\text{N}}2$ -type reactions. There is the further advantage of avoiding the "hot" carbonium ion imbroglio<sup>5</sup> currently associated with amine-nitrous acid reactions because it seems reasonable that any "hot" allylcarbinyl cations formed by ejection of nitrogen from the corresponding diazonium ions would lose most if not all of their sizzle by the time they undergo ring closure to yield the intermediate(s) that lead to cyclopropylcarbinol and cyclobutanol. Furthermore, the position of the  $^{14}\text{C}$  label in allylcarbinylamine- $\alpha$ - $^{14}\text{C}$  is such as to lead to expectation of IIIb as the first

(b) M. C. Caserio, W. H. Graham and J. D. Roberts, *Tetrahedron*, **11**, 171 (1961).

(5) See, for example, J. D. Roberts, C. C. Lee and W. H. Saunders, Jr., *J. Am. Chem. Soc.*, **76**, 4501 (1954); A. Streitwieser, Jr., *J. Org. Chem.*, **22**, 861 (1957); D. J. Cram and J. E. McCarty, *J. Am. Chem. Soc.*, **79**, 2866 (1957); B. M. Benjamin, H. J. Schaeffer and C. J. Collins, *ibid.*, **79**, 6160 (1957).

cyclic ion to be formed. This provides a different point of entry into the sequence IIIa-IIIc than cyclopropylcarbinyl- $^{14}\text{C}$ -amine, which would be expected to give IIIa first. Thus, equilibrium (if it occurs) can be approached starting from a different side.



### Results and Discussion

The suitability of the reaction of allylcarbinylamine with nitrous acid as a means of obtaining cations like IIIa-c was tested by a careful comparison of the distribution of isomeric alcohols arising from allylcarbinyl-, cyclopropylcarbinyl- and cyclobutylamines with nitrous acid under the same reaction conditions. The alcohol mixtures were analyzed by vapor-phase chromatography (v.p.c.) to a precision of about  $\pm 1\%$  (see Table I). In all cases, the product distributions are quite close to the approximate analyses reported by Mazur<sup>4a</sup> and support the contention that the rearrangements observed with these compounds involve common intermediates. One very important finding is the significantly greater ratio (1.39) of cyclopropylcarbinol to cyclobutanol obtained from cyclopropylcarbinylamine as compared to the values of 1.16 and 1.17 found for cyclobutyl- and allylcarbinylamines. The excess of cyclopropylcarbinol formed from cyclopropylcarbinylamine is in agreement both with the formulation of the reaction involving equilibrating classical cations and with our earlier conclusion based on the  $^{14}\text{C}$  results that this reaction is accompanied by some  $\text{S}_{\text{N}}2$ -like substitution. Indeed, in the latter connection, if we correct the amount of cyclopropylcarbinol- $\alpha$ - $^{14}\text{C}$  formed from cyclopropylcarbinylamine- $\alpha$ - $^{14}\text{C}$  for non-rearranging direct substitution on the basis of the product ratios (1.39 and 1.17)<sup>6</sup> cited above, we find that Ia and Ib are formed to the relative extents of 43 and 57%, respectively, from the equilibrating cations IIIa-c. This means that the isotopic label is  $(67-57)/67 \times 100 = 15\%$  short of being statistically distributed between the methylene groups. The relative extents of formation of  $^{14}\text{C}$ -position isomers of cyclobutanol (IIa and IIb) are 28 and 72%, which correspond  $(33-28)/33 \times 100 = 15\%$  short of statistical distribution of the isotope. Although the uncertainties are large because the calculations involve small differences between large numbers, we can reasonably conclude that the extent of isotopic equilibration is quite comparable for the cyclopropylcarbinol and cyclobutanol formed from free carbonium ion inter-

(6) The value of 1.17 obtained starting from allylcarbinylamine was used for the ratio of cyclopropylcarbinol to cyclobutanol expected for attack of water on the cationic intermediate(s) rather than the value of 1.16 found starting from cyclobutylamine because the latter value may be slightly low because of 1-2% of direct displacement.

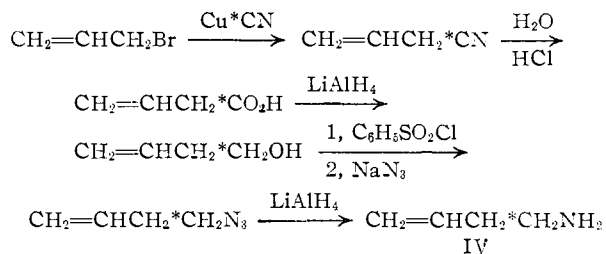
TABLE I  
 ANALYSIS OF ALCOHOLS FROM DEAMINATION REACTIONS<sup>a</sup>

	Cyclopropyl- carbinol, %	Cyclo- butanol, %	Allyl- carbinol, %	$\alpha$ -Methyl- allyl alcohol, %	Crotyl alcohol, %	Av. ratio $\triangleright\text{CH}_2\text{OH}/\square\text{OH}$
Cyclopropylcarbinylamine	56.3	41.1	4.1	..	..	1.39
	55.7	39.6	4.2	..	..	
Cyclobutylamine	51.2	44.8	3.9	..	..	1.16
	52.2	44.1	3.8	..	..	
Allylcarbinylamine	15.5	13.5	42	22	7.5	1.17
	14.3	12.0	45	21	7	
	(14) <sup>b</sup>	(13) <sup>b</sup>	(45) <sup>b</sup>	(18) <sup>b</sup>	(10) <sup>b</sup>	

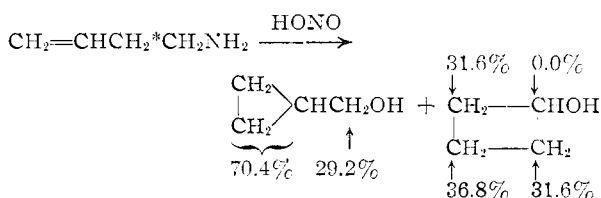
<sup>a</sup> Analyzed by Perkin-Elmer Vapor Fractometer using column A (diisodecyl phthalate) at 50°. <sup>b</sup> Previously reported analysis by Mazur<sup>16</sup> using a combination of refractive index, infrared and quantitative hydrogenation data.

mediates. This conclusion is in agreement with the earlier interpretation of these rearrangements.<sup>3</sup>

The preparation of allylcarbinylamine- $\alpha$ -<sup>14</sup>C for the tracer experiments might seem easily achievable by lithium aluminum hydride reduction of 3-butenonitrile-1-<sup>14</sup>C from allyl bromide and labeled cyanide. However, the reduction step proved unsatisfactory in many trials because of the activated  $\alpha$ -hydrogens of the nitrile, which appear to preclude the use of strongly basic reducing agents. The labeled amine was finally prepared satisfactorily by the following more roundabout but quite unambiguous route



The deamination reaction and degradation for location of the <sup>14</sup>C label were carried out essentially by the same procedures as described previously.<sup>3</sup> The radioactivity measurements are given in Table II and III and summarized in the equation



The results are unequivocal in supporting general validity of the degradation scheme used for location of the <sup>14</sup>C since it is obvious that statistical distribution of the isotope is being approached from a different side in the deamination of allylcarbinylamine- $\alpha$ -<sup>14</sup>C from that observed with cyclopropylcarbinyl- $\alpha$ -<sup>14</sup>C. The average extent of isotope-reposition rearrangement appears to be somewhat greater than found previously. Thus the cyclobutanol was calculated to be 5% and the cyclopropylcarbinol to be 11% short of statistical distribution of the <sup>14</sup>C between the methylene groups. The corresponding figures were 15% for both the cyclobutanol and the cyclopropylcarbinol<sup>7</sup> starting with cyclopropylcarbinylamine- $\alpha$ -<sup>14</sup>C. However, the calculation of these figures involves

(7) Corrected as described above for direct displacement.

TABLE II

 RADIOACTIVITY ANALYSIS OF DEGRADATION PRODUCTS OF  
 CYCLOPROPYL-CARBINOL- $\alpha$ -<sup>14</sup>C

	Cyclo- propane- carboxylic acid <sup>a</sup>	N-Cyclo- propyl- benzamide	Benzoic acid	Cyclo- propyl- amine <sup>b</sup>
Measd. act. <sup>c</sup>	0.1415	0.1378	0.0406	0.0973
	.1420	.1389	.0401	.0971
	.1432	.1378	.0405	.0972
Aver. act.	.1422	.1381	.0404	.0972
% total act.	(100.0)	29.2	70.4	

<sup>a</sup> Cyclopropanecarboxylic acid as anilide. These activities are consistently 3% higher than those found for the N-cyclopropylbenzamide given in the second column, possibly because of an intermolecular <sup>14</sup>C-kinetic isotope effect or traces of impurities. The activity of the N-cyclopropylbenzamide has been taken as probably the more reliable index of total activity. <sup>b</sup> Cyclopropylamine as benzamide. <sup>c</sup> Activities in microcuries per millimole ( $\mu\text{c./mmole}$ ) determined using the vibrating-reed electrometer method as described by O. K. Neville, *J. Am. Chem. Soc.*, **70**, 3499 (1948).

TABLE III

 RADIOACTIVITY ANALYSIS OF DEGRADATION PRODUCTS OF  
 CYCLOBUTANOL- $\alpha$ -<sup>14</sup>C

	Succinic acid	1,2-Di- amino- ethane <sup>a</sup>	2 CO <sub>2</sub> <sup>b</sup>	1,1-Di- phenyl- butane- 1,4-diol	Benzo- phenone <sup>c</sup>
Measd. act. <sup>d</sup>	0.1376	0.0943	0.0429	0.1383	
	.1374	.0944	.0440	.1389	
	.1383	.0940	.0432	.0280 <sup>e</sup>	0.0000 <sup>f</sup>
	.1392	.0944	.0438	.0289 <sup>e</sup>	.0000 <sup>f</sup>
Aver. act.	.1381	.0943	.0436	.0284 <sup>e</sup>	.0000 <sup>f</sup>
% total act.	(100.0)	68.2	31.6	(100.0)	0.0

<sup>a</sup> 1,2-Diaminoethane as dihydrobromide. <sup>b</sup> CO<sub>2</sub> as barium carbonate. <sup>c</sup> Benzophenone as 2,4-dinitrophenylhydrazones. <sup>d</sup> see footnote c of Table II. <sup>e</sup> After dilution with unlabeled 1,1-diphenylbutane-1,4-diol. <sup>f</sup> From diluted 1,1-diphenylbutane-1,4-diol.

taking quite small differences between large numbers and neglects any and all possible C<sup>12</sup>-C<sup>14</sup> kinetic isotope effects. Consequently, it seems undesirable to attempt to reach any conclusions regarding the nature of the intermediates or the sequence of their interconversion although a theoretical method has been sketched out for the purpose.<sup>8</sup> For the present, we note that the previous postulated intermediates IIIa-c, if interconverted by way of a "tricyclobutonium" cation or transition state, would lead to the expectation that the degree of isotopic equilibration would be the same in each product. Taking due account of the experimental uncertainties, we can say no more than that this is

(8) J. D. Roberts, Abstracts of the Sixteenth National Organic Chemistry Symposium of the American Chemical Society, Seattle, Wash., June, 1959, pp. 4-7.

approximately what is observed. Matters would be greatly helped by study of these interconversion reactions in bonafide carbonium processes in much more nucleophilic solvents so that the intermediates IIIa-c could be trapped before they become so extensively interconverted.

**Acknowledgment.**—E. R. is indebted to the Stiftung fuer Stipendien auf dem Gebiete der Chemie (Switzerland) for a fellowship in partial support of this research.

### Experimental

**Allylcarbinylamine-1- $^{14}\text{C}$ .**—3-Butenonitrile-1- $^{14}\text{C}$  (93.2 g.) was prepared from 190 g. (1.57 moles) of allyl bromide and 140 g. of cuprous cyanide- $^{14}\text{C}$ .<sup>9</sup> The latter was obtained by the following procedure, which, it should be noted, results in the loss of considerable of the  $^{14}\text{C}$  activity in starting material as cyanogen.

To a stirred solution of 325 g. of cupric sulfate in 1700 ml. of water at 80° was added a solution of 127.5 g. of sodium cyanide in 300 ml. of water over a period of 30 min. The resulting tan suspension was boiled for 5 min., the precipitate allowed to settle, the supernatant liquid decanted, and the precipitate washed with three 1-liter portions of water. Then 1.5 liters of water and 15 ml. of a solution of potassium cyanide- $^{14}\text{C}$  (3.0 mc.) were added to the wet solid and the suspension stirred for 7 days at room temperature. The precipitate was removed by filtration and washed successively with water, ethanol and ether. The filtrate was heated to 80°, stirred and part of 64 g. of sodium cyanide added. This was followed by addition of a concentrated aqueous solution of 163 g. of cupric sulfate. The remaining sodium cyanide was then added to the resulting suspension as a concentrated aqueous solution. After 10 min. at the boiling point, the precipitate was collected, washed as above, combined with the first batch, and dried at 110° for 10 hr. The yield was 140 g. of cuprous cyanide- $^{14}\text{C}$ .

3-Butenonitrile-1- $^{14}\text{C}$  (93.0 g.) was hydrolyzed to 3-butenic-1- $^{14}\text{C}$  acid with concentrated hydrochloric acid.<sup>10</sup> There was obtained 3.0 g., b.p. 51–60° (6 mm.), of 93% purity by v.p.c. and 88.1 g., b.p. 60–64° (6 mm.), of 95% purity. The radioactivity of the acid, analyzed as its anilide, was 1.10  $\mu\text{c./mmole}$ , which corresponds to a 37%  $^{14}\text{C}$  yield based on the starting potassium cyanide- $^{14}\text{C}$ .

A solution of 40.0 g. (0.465 mole) of 3-butenic-1- $^{14}\text{C}$  acid in 80 ml. of anhydrous ether was added to a stirred, ice-cooled suspension of 16.0 g. (0.42 mole) of lithium aluminum hydride in 350 ml. of anhydrous ether over a period of 1.25 hr. Stirring was continued for 2.5 hr. at room temperature and 0.5 hr. at the reflux temperature. The reaction mixture was then cooled in ice and the complexes decomposed by adding first 80 ml. of water and then 200 ml. of a solution of 50 ml. of concentrated sulfuric acid in 300 ml. of water. The ether layer was separated and the aqueous phase extracted with three 100-ml. portions of ether. The combined extracts were dried over sodium sulfate and the solvent fractionated with the aid of a 50-cm. Helipak column. The residue was combined with the reduction product of an additional 43.0 g. of 3-butenic-1- $^{14}\text{C}$  acid under identical conditions and distilled through a 50-cm. spiral wire-packed column. There was obtained 12.8 g., b.p. 85–110°, shown by v.p.c. to be a 1:1 mixture of allylcarbinol and water, and 43.0 g. of 95% pure allylcarbinol- $\alpha$ - $^{14}\text{C}$ , b.p. 110–111°.

Allylcarbinol- $\alpha$ - $^{14}\text{C}$  (43.0 g.) gave 102.7 g. of allylcarbinyl- $\alpha$ - $^{14}\text{C}$  benzenesulfonate, b.p. 132° (3 mm.), by the procedure of Bergstrom and Siegel.<sup>11</sup>

(9) "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 46.

(10) "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 851.

A solution of 53.0 g. (0.25 mole) of the benzenesulfonate and 27.0 g. (0.425 mole) of sodium azide in 60 ml. of water and 230 ml. of methanol was stirred in an oil-bath at 70° for 22 hr. The mixture was cooled and then added to a solution of 270 g. of calcium chloride in 650 ml. of water and extracted several times with a total of 500 ml. of pentane. The combined pentane extracts were dried over sodium sulfate and concentrated to a volume of about 30 ml. by distillation of the solvent through a 50-cm. Helipak column. The residual crude allylcarbinyl- $\alpha$ - $^{14}\text{C}$  azide was used in the following step.<sup>12</sup>

The crude azide was dissolved in 200 ml. of anhydrous ether and added to a stirred, water-cooled suspension of 9.0 g. of lithium aluminum hydride in 100 ml. of ether over 2.5 hr. The mixture was stirred for 1 hr. at room temperature, cooled in ice, and the complexes decomposed by the slow addition of 70 ml. of water. The evolved gases were passed through 5 ml. of 1 *N* hydrochloric acid to trap any amine that might have been entrained. A concentrated solution of potassium hydroxide was added and the ether layer separated. The aqueous suspension, combined with the contents of the trap, was extracted with four 100-ml. portions of ether. The combined ether extracts were dried over potassium carbonate and the solvent removed through a 50-cm. Helipak column. The residue was distilled through a 70-cm. spiral-wire packed column and gave 10.9 g. (61.5% based on allylcarbinyl benzenesulfonate) of allylcarbinylamine- $\alpha$ - $^{14}\text{C}$ , b.p. 75–77° (>98% purity by v.p.c.).

**Deamination of Allylcarbinylamine- $\alpha$ - $^{14}\text{C}$ .**—The procedure used was similar to the one described previously.<sup>4a</sup> To a stirred, ice-cooled solution of 10.83 g. (0.148 mole) of allylcarbinylamine- $\alpha$ - $^{14}\text{C}$  in 100 ml. of water was added 170 ml. of ice-cooled 1 *N* perchloric acid and then a solution of 35.9 g. (0.52 mole) of sodium nitrite in 100 ml. of water over 15 min. The yellow solution was heated to boiling, and a total of 100 ml. of distillate was collected in 30 min. The distillate was saturated with solid potassium carbonate and extracted continuously with ether for 7 hr. The ethereal extract was dried over sodium sulfate and the ether removed through a 50-cm. Helipak column. The residue was shown by v.p.c. to consist of 22%  $\alpha$ -methylallyl- $x$ - $^{14}\text{C}$  alcohol, 42% allylcarbinol- $x$ - $^{14}\text{C}$ , 7.5% crotyl- $x$ - $^{14}\text{C}$  alcohol, 15.5% cyclopropylcarbinol- $x$ - $^{14}\text{C}$ , and 13.5% cyclobutanol- $x$ - $^{14}\text{C}$ . Distillation through a 30-cm. spiral-wire packed column gave 5.60 g. of liquid, b.p. 87–122°. The residue in the distillation flask was mixed with 1.00 g. of unlabeled cyclopropylcarbinol and 1.00 g. of cyclobutanol, and further distillation gave 2.16 g. of distillate. The combined distillates were diluted with 5.00 g. each of unlabeled cyclopropylcarbinol and cyclobutanol and then fractionated through a center-tube column, the course of the distillation being followed by v.p.c. analysis. After several fractions consisting of mixtures of open-chain and cyclic alcohols, the following mixtures of cyclopropylcarbinol- $x$ - $^{14}\text{C}$  and cyclobutanol- $x$ - $^{14}\text{C}$  were collected: 0.757 g., b.p. 121.5° (92%); 0.491 g., b.p. 122° (94.5%); 1.669 g., b.p. 122° (99%); and 6.904 g., b.p. 122–122.5° (99%). The percentage figures in parentheses are the purities as indicated by v.p.c. analysis. These fractions were used for the degradations to locate the  $^{14}\text{C}$  atoms.

The degradation procedures involving oxidation of the cyclic alcohol- $x$ - $^{14}\text{C}$  mixtures to cyclopropanecarboxylic- $x$ - $^{14}\text{C}$  and succinic- $x$ - $^{14}\text{C}$  acid and further stepwise scission into smaller fragments were carried out as described earlier.<sup>3</sup> The Curtius reaction proved to give more consistent results than the Schmidt reaction for the degradation of succinic acid.

(11) C. Bergstrom and S. Siegel, *J. Am. Chem. Soc.*, **74**, 145, 254 (1952).

(12) The pure azide was obtained in a separate experiment as a colorless liquid of b.p. 102–106° (98% purity by v.p.c.), the infrared spectrum of which showed bands at 3.18, 5.35, 10.03 and 10.92  $\mu$ , indicative of the terminal vinyl group and, at 4.90  $\mu$ , indicative of the azide group. Distillation is not advisable as by-products are formed that may explode if the bath temperature is raised too high.