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Small-Ring Compounds. XXXIV. Carbonium Ion Reactions of 1-Methylcyclobutyl, (1-Methylcyclopropyl)-carbinyl and (β -Methylallyl)-carbinyl Derivatives¹

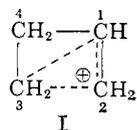
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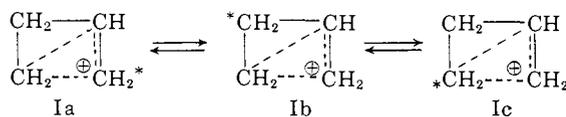
(1-Methylcyclopropyl)-carbinyl chloride was found to solvolyze in 50% aqueous ethanol *ca.* ten times faster than 1-methylcyclobutyl chloride and as fast as *t*-butyl chloride. Treatment of (1-methylcyclopropyl)-carbinylamine and 1-methylcyclobutylamine with nitrous acid gave only 1-methylcyclobutanol. (β -Methylallyl)-carbinylamine gave the same alcohol as the only cyclic product. About 3% of the ¹⁴C content of 1-methylcyclobutanol from the deamination of (1-methylcyclopropyl)-carbinyl- α -¹⁴C-amine was found at the 3-position. These results are interpretable in terms of classical carbonium ions and/or substituted "bicyclobutonium" ion intermediates with fairly localized positive charges.

Introduction

The striking facility with which cyclopropylcarbinyl, cyclobutyl and allylcarbinyl derivatives become interconverted in carbonium ion reactions, combined with the high solvolytic reactivity of cyclopropylcarbinyl and cyclobutyl derivatives, has aroused considerable interest as to the precise nature(s) of the intermediates involved. On the basis of the experimental evidence so far available³⁻⁹ we have proposed⁶⁻⁸ that unsymmetrical bicyclic cations of type I (referred to hereafter as "bicyclobutonium ions") are the important reaction intermediates.



Isotopic-labeling techniques have shown that a remarkably high degree of shuffling of methylene groups occurs in the deamination of cyclopropylcarbinyl⁶ and allylcarbinylamines,⁸ in the water-induced isomerization of cyclopropylcarbinyl chloride⁷ and in the reactions of thionyl chloride with cyclopropylcarbinol and cyclobutanol.⁷ To account for this, the three possible methylene-labeled bicyclobutonium ions Ia-c are considered to interconvert readily, thereby shuffling ¹⁴C or deuterium-labeled methylene groups between the 2-, 3- and 4-



(the asterisk denotes a labeled position)

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

(2) (a) U. S. Rubber Co. Fellow, 1954-1955; (b) National Science Foundation Predoctoral Fellow, 1955-1958.

(3) J. D. Roberts and R. H. Mazur, *J. Am. Chem. Soc.*, **73**, 2509 (1951).

(4) J. D. Roberts and R. H. Mazur, *ibid.*, **73**, 3542 (1951).

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

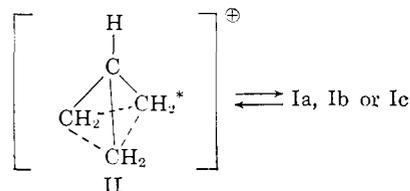
(6) R. H. Mazur, W. N. White, D. A. Semenow, C. C. Lee, M. S. Silver and J. D. Roberts, *ibid.*, **81**, 4390 (1959).

(7) M. C. Caserio, W. H. Graham and J. D. Roberts, *Tetrahedron*, **11**, 171 (1960).

(8) E. Renk and J. D. Roberts, *J. Am. Chem. Soc.*, **83**, 878 (1961).

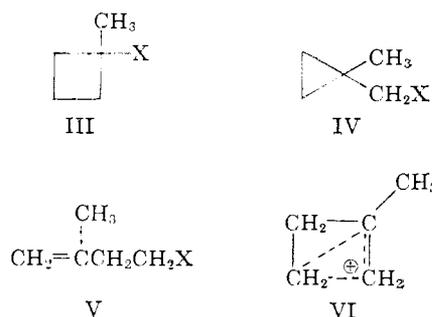
(9) C. G. Bergstrom and S. Siegel, *ibid.*, **74**, 145 (1952).

positions. A closer look at the possible structures of these ions⁶ shows that Ia and Ib could conceivably be interconverted with a relatively slight movement of atoms; however, the reversible conversion of either Ia or Ib to Ic would appear to require a more drastic rearrangement. Nonetheless, the rates of interconversion of Ia-c seem to be comparable.⁸ The precise way in which these changes occur is speculative, but an attractive path is by way of the pyramidal "tricyclobutonium" cation (or transition state) (II).^{4,6,9} Since II is symmetrical, it would collapse equally well to Ia, Ib or Ic.

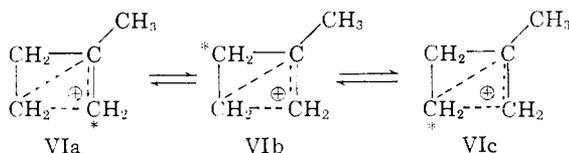


Any useful description of the structure of a bicyclobutonium ion (I) must include the disposition of the positive charge among the 1-, 2-, and 3-positions because the charge distribution is expected to be a dominant factor in controlling the product ratios. Attack of solvent at positions 1, 2 and 3 of I gives rise to cyclobutyl, cyclopropylcarbinyl and allylcarbinyl products, respectively. Since the proportions of these products obtained in irreversible carbonium-ion reactions are comparable,^{3,5-8} the positive charge in I seems likely to be fairly evenly distributed over C₁, C₂ and C₃. It is to be expected that any perturbation of this electrical balance, achieved for example by the substitution of a methyl group at any of these three positions, would seriously affect the product distribution. It is just this sort of perturbation of the bicyclobutonium structure with which we shall be concerned in this and later papers. Our procedure has been to compare the reactivities and product ratios in carbonium-ion reactions of methyl-substituted cyclopropylcarbinyl, cyclobutyl and allylcarbinyl derivatives to see if the results could be rationalized by the incidence of methyl analogs of the bicyclobutonium ions Ia-c.

The present paper deals with 1-methylcyclobutyl, (1-methylcyclopropyl)-carbinyl and (β -methylallyl)-carbinyl derivatives III, IV and V. In principle, at least, each of these substances could



lose X^- and form the bicyclobutonium cation VI. In the event that one of the methylene groups is labeled, one can formulate equilibration of the labeled cations (VIa-c) in a manner analogous to interconversion of Ia-c. The utility of the inter-



pretation of the reactions of III-V in terms of bicyclobutonium intermediates has been tested by a study of the solvolytic reactivities of the chlorides corresponding to III-V, the product distributions from nitrous acid deamination of the corresponding amines III-V and the degree of isotope-position rearrangement in the deamination of (1-methylcyclopropyl)-carbinyll- α - ^{14}C -amine.

First, we shall discuss the rates of solvolysis of chlorides III-V in aqueous ethanol relative to those of related substances. Second, the conclusions reached will be applied to interpretation of the products formed from the reaction of amines III-V with nitrous acid.

Results and Discussion

Solvolytic Rates.—Table I presents pertinent solvolytic rate data from the present work and from the literature for a number of halides in aqueous ethanol.

The solvolysis rates of cycloalkyl halides and some 1-methylcycloalkyl chlorides^{10,11} have been discussed in detail previously. The concept of I strain has been employed by Brown and co-workers^{10,11} as a rational explanation for the low reactivity of small ring halides. This explanation appears to be widely accepted; but I strain cannot be predominant in all cases. In particular, unsubstituted cyclobutyl derivatives have abnormally high solvolytic reactivities^{3,5} comparable, in fact, with cyclopentyl derivatives, which are recorded as *activated* in S_N1 solvolyses because of I strain. There must be then a driving force associated with the carbonium-ion formation in the four-membered ring that is strong enough to more than overcome any I strain resulting from the formation of a planar cyclobutyl carbonium ion. Observations of this kind are part of the cogent reasons for the proposed intervention of the non-classical intermediates Ia-c

(10) H. C. Brown, R. S. Fletcher and R. B. Johannesen, *J. Am. Chem. Soc.*, **73**, 212 (1951).

(11) H. C. Brown and M. Borkowski, *ibid.*, **74**, 1894 (1952).

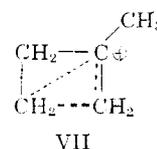
TABLE I
SOLVOLYSIS RATE CONSTANTS FOR ORGANIC HALIDES (RX)
IN AQUEOUS ETHANOL

R	X	Temp., °C.	$10^4 k_1$, sec. ⁻¹	% C ₂ H ₅ -OH	Ref.
Cyclopropyl	Br	130	0.26	50	^a
1-Methylcyclopropyl	Br	130	10.5	50	^a
Cyclobutyl	Cl	50	0.47	50	^b
1-Methylcyclobutyl	Cl	50	61.7	50	^a
1-Methylcyclobutyl	Cl	30	7.15	50	^a
Cyclopentyl	Cl	85	0.47	80	^d
1-Methylcyclopentyl	Cl	85	13,000	80	^d
Cyclohexyl	Cl	95	0.92	50	^e
1-Methylcyclohexyl	Cl	95	21,000	50	^f
Cyclopropylcarbonyl	Cl	50	12.5	50	^b
(1-Methylcyclopropyl)-carbonyl	Cl	30	69	50	^a
Allylcarbonyl	Cl	90	0.17	50	^b
(β -Methylallyl)-carbonyl	Cl	130	29	50	^a
<i>t</i> -Butyl	Cl	50	730	50	^g
<i>i</i> -Propyl	Cl	50	0.032	50	^h
<i>i</i> -Butyl	Br	95	1.13	50	ⁱ
<i>n</i> -Propyl	Br	95	8.03	50	ⁱ

^a This work. ^b Ref. 3. ^c J. D. Roberts, L. Urbanek and R. Armstrong, *J. Am. Chem. Soc.*, **71**, 3049 (1949). ^d Ref. 11, calculated from k_1 at 25° ($E_a = 20.8$ kcal. mole⁻¹). ^e Ref. 5. ^f Estimated from data of ref. *d*, using equation of E. Grunwald and S. Winstein, *ibid.*, **70**, 846 (1948). ^g Calculated from data of Grunwald and Winstein (*ref. f*), $E_a = 22.9$ kcal. mole⁻¹. ^h Calculated from data of J. D. Roberts, *ibid.*, **71**, 1880 (1949), $E_a = 22.8$ kcal. mole⁻¹. ⁱ I. Dostrovsky and E. D. Hughes, *J. Chem. Soc.*, 164 (1946).

in carbonium-ion reactions of cyclopropylcarbonyl and cyclobutyl derivatives.^{6,7}

If one now compares the effect of introducing a methyl group into the 1-position of the cycloalkyl halides, it is strikingly apparent that the rate enhancement in the cyclopropyl (~ 40 -fold) and cyclobutyl (~ 130 -fold) series is far less than in the cyclopentyl ($\sim 28,000$ -fold) and cyclohexyl ($\sim 23,000$ -fold) series.¹² At first acquaintance, it may seem surprising that 1-methyl substitution causes such a relatively small increase in the rate of solvolysis of cyclobutyl chloride; however, this can be understood from the difference in the distribution of charge (and thus the degree of participation of neighboring atoms) between the ionic intermediates I and VI. Substitution of a methyl group at the methinyl carbon atom will tend to localize the positive charge preferentially at this position, which confers tertiary carbonium-ion characteristics on the ions VI, so that they might well be better represented by the structure VII.¹³



(12) In unpublished work, Dr. Eugene I. Snyder has found similar behavior for phenyl as the 1-substituent.

(13) Die-hard exponents of the use of Occam's Razor might argue that postulation of VII is a needless complication when the classical 1-methylcyclobutyl cation might well suffice. Indeed, the rearrangements discussed in this paper *can* be explained by the incidence of classical carbonium ion intermediates. But, the failure of the I-strain

Consequently, in the solvolysis of 1-methylcyclobutyl chloride, the cationic intermediate is simultaneously subject to stabilization by the methyl group tending to localize the charge and destabilization by I strain (or its electrical equivalent⁵) in some proportion to the extent that the charge is localized. As a result, 1-methylcyclobutyl chloride is expected to and does show only a small increase in rate relative to cyclobutyl chloride. In direct contrast, but by similar reasoning, the reactivity of (1-methylcyclopropyl)-carbinyl chloride relative to cyclopropylcarbinyl chloride is predicted to be appreciable since the greater contribution of the cyclobutyl structure in intermediate VI relative to I constitutes a greater driving force for reaction. In fact, (1-methylcyclopropyl)-carbinyl chloride is some fifty times more reactive than cyclopropylcarbinyl chloride.^{14,15}

Amine-Nitrous Acid Reactions.—The evidence from reactivity data indicates that any bicyclobutonium intermediates VI formed in the solvolysis of 1-methylcyclobutyl and (1-methylcyclopropyl)-carbinyl chlorides are probably heavily weighted in favor of the 1-methylcyclobutyl structure as indicated by structure VII. In this situation, we should expect that the products of reaction of the intermediate cations with solvent would be 1-methylcyclobutyl derivatives; furthermore, that the rate of interconversion of the ions VIa-c would be

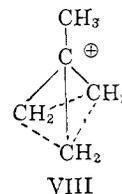
theory to account for the relatively small effect of 1-substituents on solvolysis rates of the cyclopropyl and cyclobutyl halides suggests (to us) that governing factors are more complicated. In particular, it seems probable that 1-methylcyclobutyl chloride is rather more reactive than would be expected if the classical 1-methylcyclobutyl cation were formed directly. We proceed therefore to show how the data are consistent with bicyclobutonium ion intermediates, but it should be remembered that a clear choice between classical and non-classical ions cannot be made from the present evidence.

(14) Winstein and co-workers have established that anchimeric assistance is decreased by stabilization of the unrearranged carbonium ion formed by loss of X⁻ from RX and is increased by stabilization of the carbonium ion that will result from the rearrangement of R⁺. For 1-methylcyclobutyl chloride the first consideration holds; for (1-methylcyclopropyl)-carbinyl chloride, the second holds. See S. Winstein and co-workers, *J. Am. Chem. Soc.*, **70**, 828 (1948); **74**, 1113 (1952); **75**, 147 (1953).

(15) In a recent communication, S. Borčić, M. Nikoletić and D. E. Sunko, *Chemistry & Industry*, 527 (1960), claim that the similarity in solvolysis rates of (C₂D₂)₂CHCH₂OSO₂C₆H₅ and (CH₂)₂CHCH₂OSO₂C₆H₅ indicates so little hybridization change of the ring carbons in the ionization of cyclopropylcarbinyl derivatives as to negate the postulation^{6,7} of the formation of bicyclobutonium ions such as I in the rate-determining step. We do not agree with this conclusion because it seems highly likely that bicyclobutonium ion formation from a cyclopropylcarbinyl derivative would not involve any substantial *net* hybridization changes except at the α -carbon. The argument takes cognizance [A. D. Walsh, *Trans. Faraday Soc.*, **45**, 179 (1949); C. A. Coulson and W. Moffitt, *Phil. Mag.*, **40**, 1 (1949)] that the carbons of cyclopropane rings are to be properly regarded as being hybridized to near *sp*³. This taken along with our current formulation of bicyclobutonium ions⁶ suggests that the following hybridization changes for the ring atoms will occur in going between a cyclopropylcarbinyl derivative and a transition state for formation of the corresponding bicyclobutonium ion. Two almost *sp*²-ring carbons tend to become more *sp*²; one almost *sp*²-ring carbon tends to become more *sp*³. Therefore it would hardly be surprising to have a negligibly small net hybridization change of the ring carbons in going to a bicyclobutonium transition state. The situation would be expected to be quite different for deuterium substitution at the α -carbon atom as is observed.

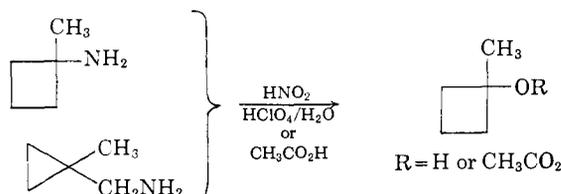
ADDED IN PROOF.—The above interpretation is supported by the kinetic isotope effect (~ 0.98) found by S. Borčić and D. E. Sunko, *J. Am. Chem. Soc.*, **83**, 2777 (1961), for solvolysis of C₂D₂CH₂CHCH₂OSO₂C₆H₅ in acetic acid and ethanol. We are indebted to these workers for communicating their results to us before publication.

diminished relative to that for Ia-c because the methyl-substituted pyramidal cation (or transition state VIII) would be less stable relative to VIa-c than II to Ia-c. This would be for the reason that

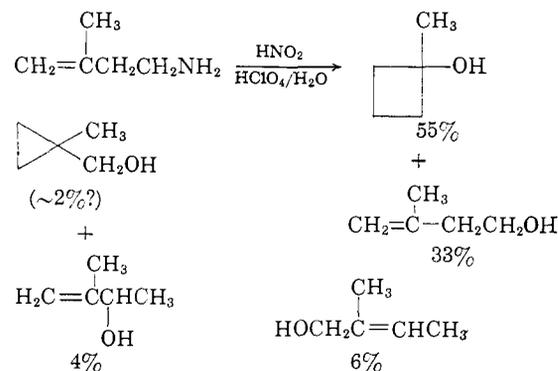


the methyl group of VIII would be located on a carbon carrying a rather small part of the cationic charge. The data from the amine-nitrous acid reactions are in agreement with these conclusions.

1-Methylcyclobutylamine and (1-methylcyclopropyl)-carbinylamine upon reaction with nitrous acid in both aqueous perchloric acid and in glacial acetic acid appear to give 1-methylcyclobutyl derivatives exclusively.



Deamination of (β -methylallylcarbinyl)-amine in aqueous perchloric acid gives a complex mixture of alcohols identified as 55% 1-methylcyclobutanol, 33% (β -methylallyl)-carbinol, 2% ($\pm 2\%$) (1-methylcyclopropyl)-carbinol, 4% α,β -dimethylallyl alcohol and 6% β,γ -dimethylallyl alcohol.



The product identities and distribution were determined by infrared analysis, and it was established that no more than 2% of (1-methylcyclopropyl)-carbinol or (β -methylallyl)-carbinol could have passed undetected. Furthermore, (1-methylcyclopropyl)-carbinol was shown to be stable under the reaction conditions.

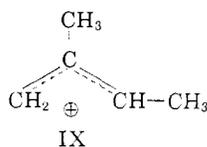
The rash of products from the deamination of (β -methylallyl)-carbinylamine indicates that several cationic intermediates are involved similar to the situation found for the deamination of allylcarbinylamine.^{3,8} The open-chain unsaturated alcohols are probably derived from the (β -methylallyl)-carbinyl cation. This can react with solvent to give unrearranged alcohol, or to a smaller extent

TABLE II
 RADIOACTIVITY ANALYSES OF DEGRADATION PRODUCTS OF 1-METHYLCYCLOBUTANOL-X-¹⁴C^a

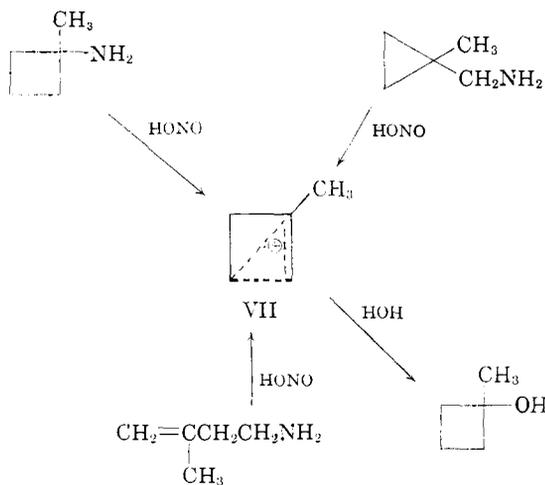
Deamination solvent		Methyl isopropyl ketone ^b (II) ^c	Iodoform (III) ^c	Acetaldehyde ^d (IV) ^c	Acetone ^b (V) ^c	Iodoform (VI) ^c
Water	Meas. act.	0.6156 ± 0.0033	0.0163 ± 0.0008	0.3197 ± 0.0051	0.2950 ± 0.0032	0.1509 ± 0.0004
	% total act.	100.0 ± 0.5	2.6 ± 0.1	51.9 ± 0.8	47.9 ± 0.5	24.5 ± 0.1
Acetic acid	Meas. act.	0.1486 ± 0.0016	0.00467 ± 0.00011	0.0735 ± 0.0027	0.0711 ± 0.0018	0.0350 ± 0.0004
	% total act.	100.0 ± 1.1	3.1 ± 0.1	49.5 ± 1.8	47.8 ± 1.2	23.6 ± 0.3

^a 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). ^b As 2,4-dinitrophenylhydrazones. ^c The degradation scheme was identical with that reported in ref. 16, and the same Roman numerals are used here to identify the degradation products. ^d As dimethone.

undergo a hydride shift to form the resonance stabilized α,β -dimethylallyl cation IX. Reaction of



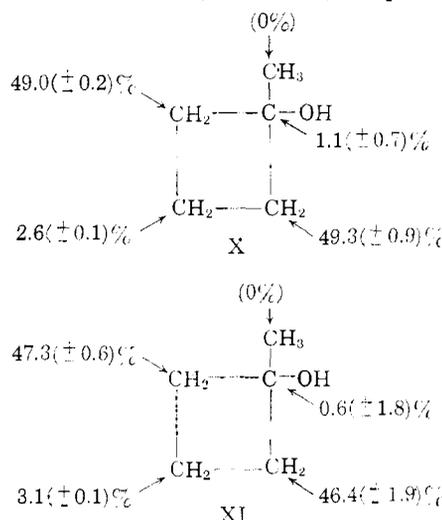
IX with water is expected to give both β,γ -dimethylallyl and α,β -dimethylallyl alcohols. The origin of the cyclic products is of more immediate interest and is considered to be the bicyclobutonium ion VI, which is also formed from 1-methylcyclobutylamine and (1-methylcyclopropyl)-carbonylamine on deamination. The overwhelming preponderance of 1-methylcyclobutanol in the products



clearly places most of the charge in the cation VI at the most heavily substituted position (C_1) and indicates as does the solvolytic reactivity data that the intermediate can be closely approximated by VII.

The ease of interconversion of intermediates VIa-c under the reaction conditions was determined from the ¹⁴C distribution in labeled 1-methylcyclobutanol obtained from the deamination of (1-methylcyclopropyl)-carbonyl- α -¹⁴C-amine. The synthetic and degradative procedures were similar to those described before.^{4,6,16} The deamination was carried out in both aqueous perchloric acid and glacial acetic acid. The ¹⁴C distributions in the re-

sulting alcohols (obtained either directly or by the reduction of the acetate with lithium aluminum hydride) may be derived from the data presented in Table II and are summarized in formulas X (perchloric acid) and XI (acetic acid), respectively.



The data reveal the interesting and significant fact that about 3% of the ¹⁴C is found in the 3-position, which contrasts to the 28% found in the 3-position of cyclobutanol formed in the deamination of cyclopropylcarbonyl- α -¹⁴C-amine.⁶ A small degree of equilibration of the non-classical cations VIa-c can satisfactorily account for this result. In our view, the ¹⁴C in the 3-position of the 1-methylcyclobutanol arises only from VIc. In turn, VIc can only arise from the initially formed ions VIa and VIb, possibly through the pyramidal structure VIII. As expected (*cf.* the earlier discussion), this process is considerably less facile than with the unsubstituted bicyclobutonium ions Ia-c, but occurs sufficiently to be easily measurable.

Experimental¹⁷

1-Methylcarbonylmethoxycyclopropane was prepared from diazomethane and methyl methacrylate in a modification of the procedure of Siegel and Bergstrom.¹⁸ The ester was added to a solution of diazomethane in ether at 0°. The pyrazoline formed in 99% yield and was decomposed in small quantities by heating. The combined crude product (520 g.) from several runs was distilled through a 11 × 1200-mm. glass helix-packed column and gave a middle fraction amounting to 316 g. (60%), b.p. 122.3–124.3°.

(17) All melting points are corrected and all boiling points are uncorrected. Analyses are by S. M. Nagy, Massachusetts Institute of Technology, and A. Elek, Los Angeles.

(18) S. Siegel and C. G. Bergstrom, *J. Am. Chem. Soc.*, **72**, 3815 (1950).

(16) D. A. Semenov, E. F. Cox and J. D. Roberts, *J. Am. Chem. Soc.*, **78**, 3221 (1956).

n_D^{25} 1.4180–1.4211, which contained some unsaturated material (permanganate test). This fraction was dissolved in 35–60° petroleum ether and washed with slightly alkaline 0.25 *M* sodium permanganate solution at 0° until the violet color persisted. The petroleum ether layer was separated, the aqueous layer extracted with petroleum ether and the combined organic layers dried over Drierite and fractionated. The product (35% based on methyl methacrylate) had b.p. 55.9–57.1° (60.4–65.6 mm.), n_D^{25} 1.4192–1.4193 [lit.¹⁸ b.p. 124.5–126.0° (760 mm.), n_D^{25} 1.4208].

1-Methylcyclopropanecarboxylic acid was prepared in 90% yield by hydrolysis of the corresponding methyl ester, m.p. 32.4–34.3° (lit.¹⁸ m.p. 29.5–32.0°), b.p. 111–112° (40.0–41.5 mm.).

The *p*-bromophenacyl ester was recrystallized from 50% aqueous ethanol; m.p. 64.1–65.0° (lit.¹⁸ 59–60°).

Anal. Calcd. for $C_{13}H_{13}O_3Br$: C, 52.52; H, 4.41; Br, 26.89. Found: C, 52.65; H, 4.57; Br, 26.59.

The anilide was prepared and recrystallized from 50% aqueous ethanol, m.p. 100.5–101.6°; from hexane, 100.6–101.3°.

Anal. Calcd. for $C_{11}H_{13}NO$: C, 75.40; H, 7.48; N, 8.00. Found: C, 75.37; H, 7.32; N, 7.89.

1-Methylcyclopropyl bromide was prepared¹⁹ in 71% yield through the reaction of the silver salt of 1-methylcyclopropanecarboxylic acid with bromine in Freon-12 and had b.p. 77.2–78.0° (740 mm.), n_D^{25} 1.4471–1.4474. A small amount of the bromide was converted to the Grignard reagent and when allowed to react with phenyl isocyanate gave 1-methylcyclopropanecarboxanilide, m.p. 99.2–100.1°, which when admixed with an authentic sample prepared directly from 1-methylcyclopropanecarboxylic acid gave m.p. 99.3–100.7°.

1-Methylcyclopropanecarboxamide was prepared in 72% yield from 1-methylcyclopropanecarboxylic acid following the procedure of Roberts, Moreland and Frazer²⁰ and had m.p. 145.7–146.9° after crystallization from benzene-cyclohexane.

Anal. Calcd. for C_5H_9ON : C, 60.58; H, 9.15; N, 14.13. Found: C, 59.74; H, 9.10; N, 14.31.

1-Methylcyclopropanecarbonitrile was prepared by the addition of α -methacrylonitrile²¹ to an ethereal solution of diazomethane in a procedure analogous to that used for 1-methylcarbomethoxycyclopropane. The pure nitrile had b.p. 127.7–128.5° (765 mm.), n_D^{25} 1.4128 [lit.²² b.p. 127–127.5° (761.5 mm.), n_D^{25} 1.41407].

(1-Methylcyclopropyl)-carbinol was prepared in 63% yield by the reduction of 1-methylcarbomethoxycyclopropane with lithium aluminum hydride¹⁸ and had b.p. 125.8–126.3° (739 mm.), n_D^{25} 1.4290–1.4292 [lit.¹⁸ b.p. 124.5–128.0° (760 mm.), n_D^{25} 1.4308]. The 3,5-dinitrobenzoate had m.p. 88.9–90.7° (lit.¹⁸ 85.5–85.7°) after crystallization from benzene-cyclohexane. A sample kindly supplied by Prof. S. Siegel,¹⁸ recrystallized from the same solvent, had m.p. 88.8–90.7° and when admixed with our material gave no m.p. depression.

Anal. Calcd. for $C_{12}H_{12}O_6N_2$: C, 51.43; H, 4.32; N, 10.00. Found: C, 51.08; H, 4.39; N, 9.96.

(1-Methylcyclopropyl)-carbinylamine was prepared in 56% yield by reduction of 1-methylcyclopropanecarbonitrile with sodium in ethanol, b.p. 95.0–96.8° (764 mm.), n_D^{25} 1.4269, and in 70% yield by the reduction of the nitrile with lithium aluminum hydride in ether, b.p. 94.3–96.1° (761 mm.), n_D^{25} 1.4267–1.4273.

N-Phenyl-*N'*-(1-methylcyclopropylcarbinyl)-thiourea had m.p. 112.7–113.5° after crystallization from 95% ethanol.

Anal. Calcd. for $C_{12}H_{16}N_2S$: C, 65.42; H, 7.29; N, 12.72. Found: C, 65.64; H, 7.38; N, 12.74.

1,1-Dimethylcyclopropane.—2,2-Dimethyl-1,3-propanediol was converted to the dibromide with phosphorus tribromide and cyclized according to Shortridge, *et al.*²³; b.p. 19.0–20.0° (738 mm.) [lit.²³ b.p. 20.63° (760 mm.)].

(19) J. D. Roberts and V. C. Chambers, *J. Am. Chem. Soc.*, **73**, 3176 (1951).

(20) J. D. Roberts, W. T. Moreland, Jr., and W. Frazer, *ibid.*, **75**, 637 (1953).

(21) Courtesy of Shell Chemical Co., b.p. 90.0–90.3° (759 mm.).

(22) D. Gotkis and J. B. Cloke, *ibid.*, **56**, 2711 (1934).

(23) R. W. Shortridge, R. A. Craig, K. W. Greenlee, J. M. Derfer, and C. E. Boord, *ibid.*, **70**, 946 (1948).

(1-Methylcyclopropyl)-carbinyl Chloride from the Chlorination of 1,1-Dimethylcyclopropane.—The apparatus and procedure were the same as those used by Roberts and Mazur³ for chlorination of methylcyclopropane. The crude product (113.2 g. from 74.5 g. of 1,1-dimethylcyclopropane) was rapidly distilled and the portion of b.p. 80–102° was taken as monochlorination product (102 g.). This material was dried over Drierite and carefully fractionated through a 12 × 500-mm. glass helix-packed column at 735 mm., 27 fractions being taken. The best values for the material on the plateau of the distillation curve [later shown to be rich in (1-methylcyclopropyl)-carbinyl chloride] were b.p. 83.0–83.9° (735 mm.), n_D^{25} 1.4045–1.4052. This center portion was redried and redistilled through the same column, a middle fraction having a micro b.p. of 85.4°.

The amount of (β -methylallyl)-carbinyl chloride in these mixtures could be reliably estimated from infrared spectra. The percentage of "reactive chloride" in a fraction was taken as the amount which solvolyzed in 50% aqueous ethanol at 50° for a time-period equivalent to 10 half-lives of 1-methylcyclobutyl chloride or about 100 half-lives of (1-methylcyclopropyl)-carbinyl chloride. The amount of 1-methylcyclobutyl chloride [and, by difference, the amount of (1-methylcyclopropyl)-carbinyl chloride] was estimated by (a) comparison with calculated reaction rate curves for various ratios of active chloride using the known rate constants, (b) the method of Brown and Fletcher²⁴ and (c) infrared spectra. The total mixture was thus estimated to have the composition 49% (1-methylcyclopropyl)-carbinyl chloride, 16% 1-methylcyclobutyl chloride, 14% (β -methylallyl)-chloride and 32% unreactive chloride. One of the more enriched fractions had 76%, 3%, 0% and 20% of these components, respectively.

Methylenecyclobutane was prepared according to Roberts and Sauer²⁵; b.p. 41.0–42.0° (739 mm.).

1-Methylcyclobutanol was prepared in three different ways. The method of Fischer²⁶ was followed in the sulfuric acid-catalyzed addition of water to methylenecyclobutane to give the alcohol in 68% yield, b.p. 117.8–118.3° (746 mm.), n_D^{25} 1.4332–1.4336 [lit.¹¹ b.p. 116–118° (742 mm.), n_D^{25} 1.4333]. The hydrolysis¹¹ of 1-methylcyclobutyl chloride gave a 40% yield of alcohol, b.p. 117.1–118.9° (756 mm.), n_D^{25} 1.4329. The reaction¹⁶ between cyclobutanone and methyl Grignard reagent gave a 67% yield of alcohol, b.p. 118.3° (765 mm.), n_D^{25} 1.4332. The products of all three methods had identical infrared spectra.

1-Methylcyclobutyl Chloride.—Hydrogen chloride was added to methylenecyclobutane by the procedure of Brown and Borkowski.¹¹ The yield was 81%, b.p. 90.8–91.3° (742 mm.), n_D^{25} 1.4283–1.4287 [lit.¹¹ b.p. 89.5–91.4° (744 mm.), n_D^{25} 1.4310].

1-Methylcyclobutylamine. A.—In a 500-ml. round-bottomed three-necked flask equipped with mechanical stirrer, dropping funnel and reflux condenser and immersed in an ice-salt-bath were placed 9.0 g. (0.22 mole) of acetonitrile, 100 ml. of glacial acetic acid and 20 g. of concentrated sulfuric acid. Methylenecyclobutane (13.6 g., 0.20 mole) was added slowly and stirring continued for 1 hr. at 20°. The solution was cooled, diluted with 300 ml. of water, basified with sodium carbonate and extracted with five 50-ml. portions of ether. The ethereal solution was dried, filtered and evaporated to give 17.7 g. (0.14 mole, 70%) of white crystal of *N*-(1-methylcyclobutyl)-acetamide. This material (10.0 g., 0.078 mole) and 400 ml. of 4 *N* potassium hydroxide in ethylene glycol were heated under reflux for 48 hr. Continuous ether extraction of the components boiling below 180°, followed by drying of the extracts over potassium hydroxide, and removal of the ether gave 3.1 g. (0.036 mole, 46%) of 1-methylcyclobutylamine, b.p. 85.5–86.0° (764 mm.), n_D^{25} 1.4200.

1-Methylcyclobutylamine. B.—A mixture of 11.0 g. (0.20 mole) of 90% sodium cyanide, 13.6 g. (0.20 mole) of methylenecyclobutane and 25 ml. of glacial acetic acid was placed in a 200-ml. round-bottomed three-necked flask equipped with stirrer, dropping funnel and Dry Ice condenser and cooled to 0°. An ice-cold solution of 25 ml. of glacial acetic acid and 50 g. of concentrated sulfuric acid was then added

(24) H. C. Brown and R. S. Fletcher, *ibid.*, **71**, 1845 (1949).

(25) J. D. Roberts and C. W. Sauer, *ibid.*, **71**, 3925 (1949).

(26) J. R. Fischer, Master's Thesis, California Institute of Technology, 1941.

dropwise with stirring over a period of 25 min. The solution was stirred for 3 hr. at 0°, 1 hr. at room temperature, 45 min. at 55° and then allowed to stand overnight at room temperature. An ice-cold solution of 120 g. of sodium hydroxide in 250 ml. of water was added slowly with stirring; the resulting solution was heated under reflux for 8 hr. and then steam distilled until 250 ml. of distillate was collected. The distillate was continuously extracted with ether for 18 hr., and the ether solution was dried over potassium hydroxide and distilled. The amine had b.p. 84.0–84.7° (745 mm.), n_D^{25} 1.4292–1.4293. The yield was 8.03 g. (47%).

N-Phenyl-N'-(1-methylcyclobutyl)-thiourea had m.p. 135.3–135.8° after crystallization from dilute ethanol.

Anal. Calcd. for $C_{12}H_{16}N_2S$: C, 65.42; H, 7.29; N, 12.72. Found: C, 65.23; H, 7.40; N, 12.97.

(β -Methylallyl)-carbinol was prepared from β -methylallyl chloride following the method of Kharasch and Fuchs²⁷ for the synthesis of allylcarbinol. The yield was 35%, b.p. 127.9–130.4° (741 mm.), n_D^{25} 1.4305–1.4312. The α -naphthylurethan had m.p. 66.7–67.3° after crystallization from petroleum ether.

Anal. Calcd. for $C_{16}H_{17}NO_2$: C, 75.28; H, 6.71; N, 5.49. Found: C, 75.26; H, 6.81; N, 5.23.

(β -Methylallyl)-carbinyl Chloride.—In a 100-ml. flask equipped with a dident, carrying a dropping funnel and drying tube, were placed 8.61 g. (0.10 mole) of (β -methylallyl)-carbinol, 25 ml. of anhydrous ether, 18.5 g. (0.10 mole) of tri-*n*-butylamine and a magnetic stirring bar. The solution was agitated magnetically at 0° while 11.9 g. (0.10 mole) of thionyl chloride was added dropwise over 3 hr. The product was washed with water, 5% sodium hydroxide and water and dried and distilled to give a middle fraction, b.p. 101.0–102.7° (739 mm.), n_D^{25} 1.4301–1.4305, amounting to 4.99 g. (48%) of β -methylallyl chloride.

(β -Methylallyl)-carbinylamine.—The method previously described³ for the preparation of allylcarbinylamine was used. N-1-(3-Methyl-3-butenyl)-phthalimide was obtained in 85% yield from (β -methylallyl)-carbinyl chloride and potassium phthalimide in dimethylformamide. The pure material had m.p. 51.2–52.8°.

Anal. Calcd. for $C_{13}H_{15}NO_2$: C, 72.61; H, 6.07. Found: C, 72.78; H, 5.73.

Hydrazinolysis of the phthalimide in perchloric acid gave a 26% yield of amine, b.p. 47.6–48.5° (101 mm.), n_D^{25} 1.4288.

α,β -Dimethylallyl alcohol was prepared in 16% yield by the addition of methyl Grignard reagent to α -methacrolein; b.p. 54.6–56.8° (59.9–60.4 mm.), n_D^{25} 1.4241–1.4242 (lit.²⁸ 112–113°, n_D^{25} 1.4296).

β,γ -Dimethylallyl Alcohol.—The high boiling fractions from the decomposition of 3-methyl-3-carbomethoxy-1-pyrazoline were redistilled to give methyl tiglate, b.p. 136.9–137.1° (740 mm.), n_D^{25} 1.4338 (lit.¹⁸ b.p. 138.0–139.2°, n_D^{25} 1.4338). The ester was reduced with lithium aluminum hydride in about 40% yield to give the pure alcohol, b.p. 137.6–137.9°, n_D^{25} 1.4386–1.4401 (lit.²⁹ b.p. 138.0°).

Amine-Nitrous Acid Reactions in Aqueous Media.—A typical procedure is given. A 500-ml. round-bottomed three-necked flask was equipped with dropping funnel, stirrer and Claisen head connected to a condenser positioned

for downward distillation. The receiver was connected through a Dry-Ice trap to a water aspirator via a calcium chloride drying tube. To 12.8 g. (0.150 mole) of (1-methylcyclopropyl)-carbinylamine in 50 ml. of water and 180 ml. of 1.0 *N* perchloric acid there was added, over 30 min. with stirring, a solution of 30 g. (0.44 mole) of sodium nitrite in 100 ml. of water. The temperature rose and gas was evolved. The pressure was reduced to 50–65 mm. for 1 hr. and then 100 ml. of steam distillate was collected. The layers of the distillate were separated and the aqueous layer was saturated with potassium carbonate and extracted with ether. The combined organic phases were dried over anhydrous magnesium sulfate and distilled. The Dry-Ice trap contained 2 ml. of dark liquid. It was warmed to 0°, and two layers remained; the top layer (alcohol), 0.72 g., was recovered. The infrared spectra of different fractions indicated that only 1-methylcyclobutanol was formed. The yield was 78%.

(1-Methylcyclopropyl)-carbinyl- α -¹⁴C-amine.—The Grignard reagent from 1-methylcyclopropyl bromide was carbonated in an evacuated system with carbon-¹⁴C dioxide, generated from barium carbonate-¹⁴C and sulfuric acid.³ Inactive 1-methylcyclopropanecarboxylic acid was added; and the 1-methylcyclopropanecarboxylic-¹⁴C acid was distilled, b.p. 96.6–97.4° (19.2–19.4 mm.). The recovery was 97% and the radioactivity yield from the barium carbonate-¹⁴C was 88%. The acid was converted to the amide as described earlier and the amide reduced to (1-methylcyclopropyl)-carbinyl- α -¹⁴C-amine by lithium aluminum hydride in 51% yield.

Treatment of (1-Methylcyclopropyl)-carbinyl- α -¹⁴C-amine with Nitrous Acid.—The reaction in aqueous media was carried out as described for the inactive compound.

The reaction in glacial acetic acid was essentially the same, the sodium nitrite being added in portions. The reaction solution was poured into 20% sodium hydroxide, extracted with ether, and the extract dried and distilled. With both inactive and active material in acetic acid, compounds with the 1-methylcyclobutyl structure (alcohol and acetate) were the only ones detected. The mixture of radioactive alcohol and acetate was reduced to 1-methylcyclobutanol- α -¹⁴C with lithium aluminum hydride before degradation. The procedure for the degradation has been published.¹⁵

(1-Methylcyclopropyl)-carbinol was shown to be stable under the reaction condition by substituting it for the amine in the deamination procedure and recovering it unchanged.

Confirmation of the structure of (1-methylcyclopropyl)-carbinyl- α -¹⁴C-amine was achieved by oxidizing its hydrobromide with alkaline permanganate. Part of the resultant acid was converted to the amide, which was shown to have a ¹⁴C content of 0.128 μ c./mmole. A Schmidt degradation³ on another portion of the acid gave 1-methylcyclopropylamine, which was converted to the benzamide, m.p. 161.7–163.0°.

Anal. Calcd. for $C_{11}H_{13}NO$: C, 75.47; H, 7.46; N, 7.97. Found: C, 76.08; H, 7.37; N, 8.14.

Radioactivity analysis of the benzamide showed it to have a ¹⁴C content of 0.00037 μ c./mmole, which corresponded to having 0.29% of the ¹⁴C-activity of the above 1-methylcyclopropanecarboxamide-¹⁴C in the ring carbons or at the methyl group.

Solvolysis Rate Determinations.—Conventional procedures were followed. There appeared to be some internal return to a less reactive species in the solvolysis of (1-methylcyclopropyl)-carbinyl chloride in 50% ethanol. Further details and discussion are given elsewhere.³⁰

(27) M. S. Kharasch and C. F. Fuchs, *J. Org. Chem.*, **9**, 359 (1944).

(28) A. Lauchenauer and H. Schinz, *Helv. Chim. Acta*, **34**, 1514 (1951).

(29) R. M. Keefer, L. J. Andrews and R. E. Kepner, *J. Am. Chem. Soc.*, **71**, 3906 (1949).

(30) E. F. Cox, Ph.D. Thesis, California Institute of Technology, 1955.