From the molecular weights obtained, it is evident that there is a decrease in molecular weight of nucleohistone from that in water to Santomerse D solution. The lack of agreement between the molecular weight in Santomerse D calculated from sedimentation and diffusion data as compared with that obtained from sedimentation and viscosity measurements is characteristic of polydisperse systems.

Although it has not been found possible to use the surface-active agents studied as agents for the extraction of tissue, information as to the mode of their combination with nucleohistone has been obtained.

Acknowledgment.—The authors wish to thank Dr. Harvey Walker, Jr., and Mr. David W. Einsel, Jr., of this Laboratory for technical assistance, and Mr. J. C. Harris, Central Research Dept. of Monsanto Chemical Co., for helpful suggestions.

COLUMBUS, OHIO RECEIVED JULY 24, 1950

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND LABORATORY FOR NUCLEAR SCIENCE AND ENGINEERING, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Small-Ring Compounds. IV. Interconversion Reactions of Cyclobutyl, Cyclopropylcarbinyl and Allylcarbinyl Derivatives

BY JOHN D. ROBERTS AND ROBERT H. MAZUR

A number of reactions have been investigated which lead to interconversion of cyclobutyl, cyclopropylcarbinyl and allylcarbinyl derivatives. Some degree of interconversion was observed in the following: vapor-phase light-catalyzed chlorination of methylcyclopropane; reaction of cyclopropylcarbinol with thionyl chloride, Lucas reagent, phosphorus tribromide and hydrobromic acid; cleavage of cyclopropylcarbinyl triethylsilyl ether with thionyl chloride; reaction of cyclobutanol with thionyl chloride and Lucas reagent; reaction of cyclopropylcarbinyl-, cyclobutyl- and allylcarbinylamines with nitrous acid; hydrolysis and acetolysis of cyclopropylcarbinyl and cyclobutyl chlorides; reaction of N-cyclopropylcarbinyl- and N-cyclobutylbenzamides with phosphorus pentabromide; and Grignard reactions of cyclopropylcarbinyl halides. No interconversion was observed in the following: reaction of allylcarbinol with thionyl chloride and phosphorus tribromide; vapor-phase light-catalyzed chlorination of cyclobutane; and Grignard reactions of allylcarbinyl and cyclobutyl halides. The products of those interconversion reactions which may reasonably be expected to involve carbonium ion intermediates have been correlated by consideration of carbonium ion stability and ease of interconversion, as well as the degree of reversibility of the reactions involved and the stabilities of the possible products. Cyclopropylcarbinyl halides have been shown to be unusually reactive in solvolysis reactions and, in fact, considerably more reactive than analogously constituted allylic halides.

Introduction

One of the principal limitations of carbonium-ion theory[1] as applied to rearrangement reactions occurring under the influence of polar catalysts or in polar media is the difficulty in deciding in advance which of several possible reaction paths should be most favorable. In no instance is this difficulty better exemplified than in the interconversion reactions of cyclobutyl, cyclopropylcarbinyl and allylcarbinyl derivatives where it has been reported that cyclobutyl- and cyclopropylcarbinylamines with nitrous acid give mixtures of cyclobutanol and cyclopropylcarbinol,[2] that cyclopropylcarbinol with phosphorus tribromide yields a bromide which on successive treatments with magnesium and carbon dioxide gives allylacetic acid,[3] and that cyclopropyldimethylcarbinol with hydrochloric acid forms (γ,γ-dimethylallyl)-carbinyl chloride which on hydrolysis with water regenerates cyclopropyldimethylcarbinol.[4] While simple *a posteriori* mechanistic interpretations of the above results may be made following the carbonium-ion theory of rearrangements, *prediction* of the product to be obtained from a given new carbonium-ion reaction must depend on a knowledge of some or all of several important factors such as: (1) the relative carbonium-ion stabilities, (2) the energy barriers to interconversion of the carbonium ions, (3) the relative reactivities of the carbonium ions toward nucleophilic substances (4) the reversibility of the reaction in question and (5) the thermodynamic stabilities of the possible products. It was of interest, therefore, to determine, insofar as possible, the importance of these factors in directing rearrangements under a variety of conditions in reactions of cyclobutyl, cyclopropylcarbinyl and allylcarbinyl derivatives.

Preparation and Characterization of Allylcarbinyl, Cyclobutyl and Cyclopropylcarbinyl Halides

In order to determine qualitatively the relative stabilities of the cyclobutyl, cyclopropylcarbinyl and allylcarbinyl cations, one of the first objectives of the work was to prepare the corresponding halides and study their solvolytic reactivities. Allylcarbinyl chloride was readily obtained by the reaction of thionyl chloride with allylcarbinol prepared by the partial hydrogenation of 3-butyn-1-ol over palladium on calcium carbonate catalyst. Allylcarbinyl bromide was similarly obtained from the reaction of allylcarbinol with phosphorus tribromide. No rearrangements were noted in these reactions. The infrared spectra of the allylcarbinyl halides are shown in Figs. 1 and 2.

Cyclobutyl chloride was obtained by a vapor-phase light-catalyzed chlorination of cyclobutane. No other monochloride appeared to be formed in this preparation. Pure cyclobutyl bromide was obtained from the reaction of silver cyclobutane-

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[1] (a) F. C. Whitmore, THIS JOURNAL, **54**, 3274 (1932); *Chem. Eng. News*, **20**, 668 (1947); (b) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, pp. 317-325.

[2] (a) N. J. Demjanow, *Ber.*, **40**, 4393 (1907); (b) N. J. Demjanow, *ibid.*, **40**, 4961 (1907); (c) R. Skrabal, *Monatsh.*, **70**, 420 (1937).

[3] L. I. Smith and S. McKenzie, Jr., *J. Org. Chem.*, **15**, 74 (1950).

[4] (a) P. Bruylants and A. Dewael, *Bull. classe Sci. Acad. roy. Belg.*, [5] **14**, 140 (1928); *Chem. Zentr.*, **99**, I, 2708 (1928); (b) T. A. Favorskaya and S. A. Fridman, *J. Gen. Chem.* (*U. S. S. R.*), **15**, 421 (1945).

carboxylate with bromine.[5] The infrared spectra of the cyclobutyl halides are given in Figs. 1 and 2.

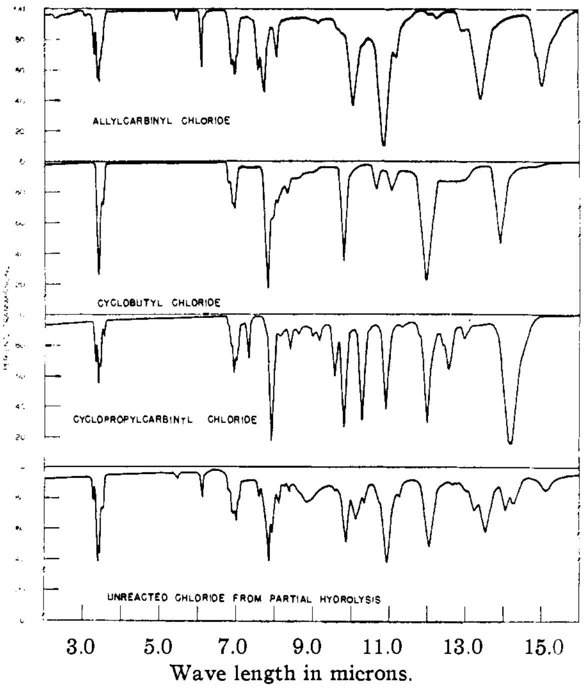
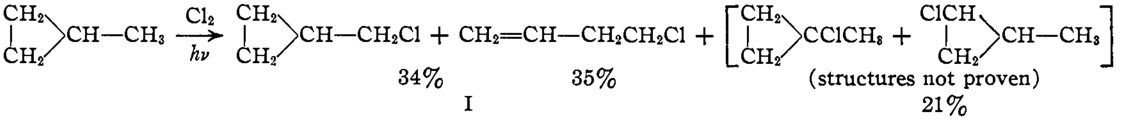


Fig. 1.—Infrared spectra: Baird spectrograph with NaCl prism, solutions of 50 mg. of compounds in 0.50 ml. of carbon disulfide except in the regions 4.2–5.0 μ and 6.2–7.2 μ where carbon tetrachloride was used as solvent.

Synthesis of pure cyclopropylcarbinyl chloride proved to be difficult. The reaction of the alcohol with thionyl chloride was unsatisfactory as was the cleavage of triethylsilyl cyclopropylcarbinyl ether with thionyl chloride,[6] both giving mixtures containing some cyclobutyl chloride. Chlorination of methylcyclopropane by the procedure used for cyclobutane gave a mixture of monochlorides which on fractional distillation yielded 21% of a mixture apparently comprised of 1- and 2-chloro-1-methylcyclopropane, 35% of allylcarbinyl chloride and 34% of a chloride (I), b.p. 87–89°, which from its properties and reactions (*vide infra*) was assigned the cyclopropylcarbinyl chloride structure.



$$\mathrm{\underset{CH_2}{\overset{CH_2}{|}}\!\!>CH-CH_3 \xrightarrow[h\nu]{Cl_2} \underset{CH_2}{\overset{CH_2}{|}}\!\!>CH-CH_2Cl + CH_2{=}CH-CH_2CH_2Cl + \left[\underset{CH_2}{\overset{CH_2}{|}}\!\!>CClCH_3 + \underset{CH_2}{\overset{ClCH}{|}}\!\!>CH-CH_3\right]}$$

34% I 35% (structures not proven) 21%

I was saturated and its infrared spectrum (Fig. 1) showed none of the characteristic bands of cyclobutyl chloride although a small proportion (less than 5%) of cyclobutyl chloride might have remained undetected. However, analysis of the rate of solvolysis of I in 50% ethanol–50% water (by volume) at 50° indicated the presence of about

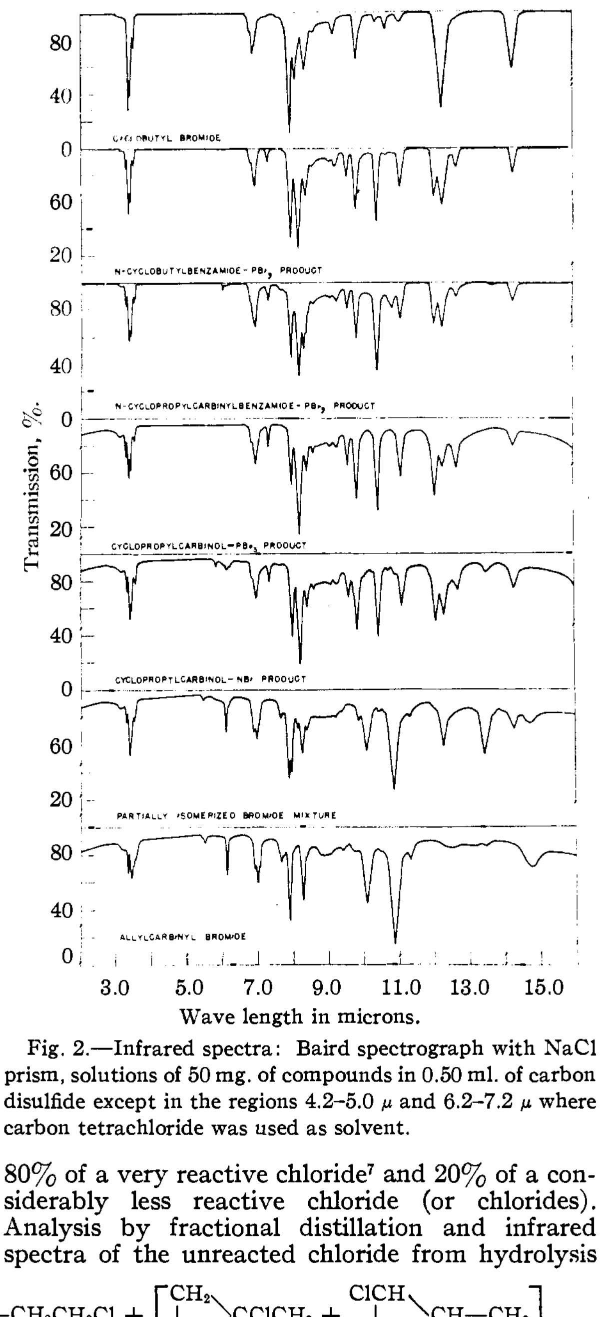


Fig. 2.—Infrared spectra: Baird spectrograph with NaCl prism, solutions of 50 mg. of compounds in 0.50 ml. of carbon disulfide except in the regions 4.2–5.0 μ and 6.2–7.2 μ where carbon tetrachloride was used as solvent.

80% of a very reactive chloride[7] and 20% of a considerably less reactive chloride (or chlorides). Analysis by fractional distillation and infrared spectra of the unreacted chloride from hydrolysis of I with boiling water showed about 45% allylcarbinyl chloride, 45% cyclobutyl chloride and 10% cyclopropylcarbinyl chloride. The infrared spectrum of the largest fraction which contains all three chlorides is shown in Fig. 1. The product (II) of the reaction of cyclopropylcarbinyl triethylsilyl ether with thionyl chloride which appeared to contain no allylcarbinyl chloride and about 15% of cyclobutyl chloride gave a similar

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(5) This reaction was carried out by Dr. V. C. Chambers using a modification of the procedure of J. Cason and R. L. Way, *J. Org. Chem.*, **14**, 31 (1949).

(6) This reaction was suggested by the work of Dr. L. H. Sommer of Pennsylvania State College who has found that the cleavage of triethylsilyl alkyl ethers with thionyl chloride produces alkyl chlorides without rearrangement in other cases. We are indebted to Dr. Sommer for information about this reaction in advance of publication.

(7) It is unlikely that the reactive chloride could be either 1-chloro-1-methylcyclopropane or 1-chloro-2-methylcyclopropane since cyclopropyl chloride has been found by G. Gustavson, *J. prakt. Chem.*, [2] **43**, 396 (1891), and in unpublished experiments to be an exceptionally unreactive halide.

solvolysis rate curve in aqueous ethanol which indicated the presence of about 30% of a less reactive chloride. The fact that both I and II on solvolysis appeared to contain considerably more less-reactive chloride than was consistent with their infrared spectra indicates that the solvolysis reaction is accompanied by a rearrangement process similar to that discovered by Young, Winstein and Goering[8] for α,α-dimethylallyl chloride in acetic acid. It was possible to calculate the over-all solvolysis rates of I and II to about the experimental error (Fig. 3) by assuming a unimolecular solvolysis with rate constant k_1 equal to 0.47 hr.$^{-1}$ competing with a unimolecular rearrangement having a rate constant k_1', equal to 0.14 hr.$^{-1}$ and yielding unreactive products. If, as indicated by the infrared spectra, the rearrangement results in cyclobutyl chloride with a k_1 of 0.017 hr.$^{-1}$ at 50° or allylcarbinyl chloride with $k_1 < 0.0005$ hr.$^{-1}$ at 50°, then only a slight error is introduced by assuming the rearrangement products to be unreactive.

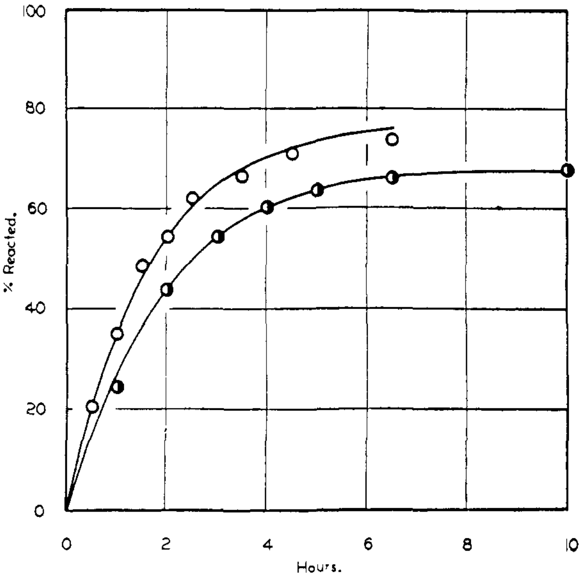

Fig. 3.—Solvolysis rates of chlorides I, ○ and II, ◑ in 50% ethanol–50% water (by volume) at 50°. Solid lines represent calculated reaction rate curves.

The rearrangement reaction was considerably faster than solvolysis in acetic acid in the presence of acetate ion at 100°, and I was essentially completely converted to cyclobutyl and allylcarbinyl chlorides by the time that 30% of the theoretical amount of chloride ion was formed (*cf.* Fig. 4). The ratio of formation of cyclobutyl chloride to allylcarbinyl chloride was about 1.7 as calculated from the rate of formation of unsaturated material in the reaction mixture (*cf.* Fig. 4) and confirmed by isolation and fractionation of the unreacted chloride. Cyclobutyl chloride was found to rearrange to allylcarbinyl chloride at about the same rate as it solvolyzed in acetic acid at 100°. In 50% ethanol–50% water at 70°, the solvolysis rate curve of cyclobutyl chloride deviated slightly from the first-order law in the later stages of the reaction. This result could be explained on the basis of (1) the presence of about 5% of inert chloride in the original material or (2) the occurrence of a first-order rearrangement with k_1' equal to about a tenth of k_1.

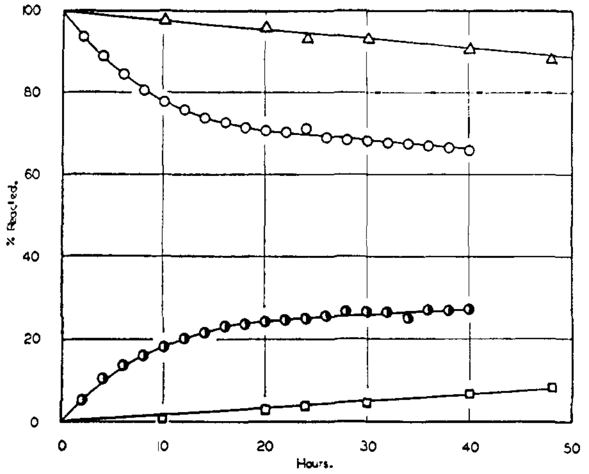

Fig. 4.—Solvolysis and isomerization (to allylcarbinyl chloride) rates of cyclopropylcarbinyl and cyclobutyl chlorides in acetic acid at 100°: ○, solvolysis; ◑, isomerization for cyclopropylcarbinyl chloride. △, solvolysis; □, isomerization for cyclobutyl chloride.

The formation of allylcarbinyl chloride in the chlorination of methylcyclopropane appears to be a unique example of a carbon skeleton rearrangement occurring in a vapor-phase chlorination reaction. Similar results were obtained in three runs and since only one product was obtained in the chlorination of cyclobutane it appears unlikely that the abnormal products resulted from rearrangements in the isolation or distillation procedures.

Cyclopropylcarbinyl bromide has not as yet been prepared in purity comparable to that of the chloride. The reaction of cyclopropylcarbinol with phosphorus tribromide was found to give a mixture of cyclic bromides containing only a few per cent. of allylcarbinyl bromide. The b.p. of the bulk of the product (111–112°) agreed only fairly well with that (105–108°) previously reported[3] for material obtained from this reaction and inferred to be allylcarbinyl bromide. The b.p. of pure allylcarbinyl bromide obtained from allylcarbinol and phosphorus tribromide was 99–100°. The non-identity of the bromide mixture with allylcarbinyl bromide was confirmed by its saturated character and by infrared spectra (Fig. 2). Solvolysis rate data on the bromide indicated 65% of a very reactive bromide (presumably cyclopropylcarbinyl bromide). The presence of only about 20% of cyclobutyl bromide was indicated by the infrared spectrum (Fig. 2) and it is possible that here, also, solvolysis was accompanied by a rearrangement reaction although this has not yet

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(8) W. G. Young, S. Winstein and H. L. Goering, paper presented at the Philadelphia meeting of the American Chemical Society, April 12, 1950. Dr. S. Siegel of the Illinois Institute of Technology has kindly informed us that the solvolysis of cyclopropylcarbinyl benzenesulfonate in acetic acid competes with a similar rearrangement which yields a mixture of cyclobutyl and allylcarbinyl benzenesulfonates. Analogous behavior has been noted in this Laboratory for the corresponding *p*-toluenesulfonate as well as other *p*-toluenesulfonates in acetic acid.

been definitely established. Cyclopropylcarbinol and constant-boiling hydrobromic acid gave a mixture of bromides similar to that obtained in the phosphorus tribromide reaction (*cf.* infrared spectra in Fig. 2). The complexity of this reaction has been recognized previously by Demjanow and Demjanow.[9]

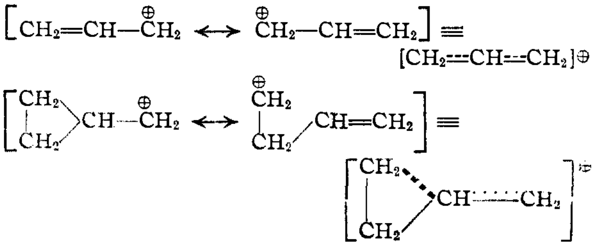
Attempts to characterize the pure halides by reaction of the corresponding Grignard reagents with phenyl isocyanate to yield the anilides of the next higher carboxylic acids were not completely successful. Cyclobutyl and allylcarbinyl halides reacted normally to give cyclobutylcarboxanilide and allylacetanilide, respectively. However, cyclopropylcarbinyl chloride appeared to give no cyclopropylacetanilide but only allylacetanilide. This behavior was observed repeatedly and, when mixtures of chlorides or bromides which contained cyclopropylcarbinyl, but not allylcarbinyl halides, were employed, allylacetanilide was formed in amount corresponding roughly to the proportion to cyclopropylcarbinyl halide present. The lack of rearrangement with cyclobutyl halides is surprising since in many other reactions, rearrangements are observed with *both* cyclobutyl and cyclopropylcarbinyl derivatives. It is not yet known at which step of the Grignard sequence rearrangement occurs. An attempt to induce an abnormal reaction with cyclobutyl bromide by isomerizing the halide with magnesium bromide in ether solution prior to formation of the Grignard reagent was unsuccessful.

A further point of interest in connection with the abnormal Grignard reactions of cyclopropylcarbinyl halides is the fact that they represent a rearrangement *opposite* in direction to that previously observed[10] in the Grignard reactions of *endo*-dehydronorbornyl halides which result with formation of cyclopropane ring-containing nortricyclene derivatives. Also in contrast is the finding[10] that nortricyclyl halides form Grignard reagents which react *without* rearrangements.

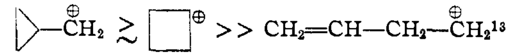
Solvolytic Reactivities of Halides

The relative solvolytic reactivities of cyclopropylcarbinyl, cyclobutyl and allylcarbinyl halides in 50% ethanol–50% water (by volume) are of particular interest (*cf.* Table I). The rate constant of cyclopropylcarbinyl chloride as calculated from the solvolysis rate of the high-boiling monochlorination product of methylcyclopropane was *27 times* that of cyclobutyl chloride and *40 times* that of β-methylallyl chloride at 50°. At the same temperature, allylcarbinyl chloride did not react at a measurable rate. Similarly cyclopropylcarbinyl bromide was found to be about 20 times more reactive than cyclobutyl bromide and 30 times more reactive than allyl bromide at 25°.

The high reactivity of cyclopropylcarbinyl halides is perhaps unexpected. Cyclobutyl halides could be anticipated to be more reactive than cyclopropylcarbinyl halides since secondary halides are customarily more reactive than primary halides in solvolytic reactions. However, since the cyclopropane ring has many of the physical and chemical characteristics[11] of the carbon–carbon double bond it can also be expected that a cyclopropylcarbinyl cation should be stabilized to some degree, at least, by resonance similar to that which stabilizes an allyl cation. The resonance forms here written for the cyclopropylcarbinyl cation are not considered to be energetically equivalent as are those of the allyl cation and this difference is indicated in the representation of the hybrid structure, where the cyclopropylcarbinyl form is weighted more heavily.[12] The considerable reactivity of cyclopropylcarbinyl chloride as compared to β-methylallyl chloride is unexpected and it will be interesting to see if cyclopropylcarbinyl derivatives are generally more reactive than analogously constituted allyl compounds.



It is possible to conclude from the relative solvolytic reactivities of cyclobutyl, cyclopropylcarbinyl and allylcarbinyl halides in aqueous ethanol that the order of stability of the carbonium ions corresponding to these substances is probably



Irreversible Carbonium Ion Reactions

The major difficulty in obtaining information on the behavior of carbonium ions under conditions

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[9] N. Demjanow and J. Demjanow, *J. Russ. Phys.-Chem. Soc.*, **46**, 42 (1914); *Chem. Zentr.*, **85**, I, 1998 (1914).

[10] J. D. Roberts, E. R. Trumbull, Jr., R. Armstrong and W. Bennett, THIS JOURNAL, **72**, 3116 (1950).

[11] (a) E. P. Carr and C. P. Burt, *ibid.*, **40**, 1590 (1918); (b) I. M. Klotz, *ibid.*, **66**, 88 (1944); (c) J. D. Roberts and C. Green, *ibid.*, **68**, 214 (1946); (d) M. T. Rogers and J. D. Roberts, *ibid.*, **68**, 843 (1946); (e) M. T. Rogers, *ibid.*, **69**, 2544 (1947); (f) G. Gustavson, *J. prakt. Chem.*, [2] **62**, 273 (1900); (g) E. P. Kohler and J. B. Conant, THIS JOURNAL, **39**, 1404 (1917); (h) W. A. Bone and W. H. Perkin, *J. Chem. Soc.*, **67**, 108 (1895); (i) R. C. Fuson and F. N. Baumgartner, THIS JOURNAL, **70**, 3255 (1948); (j) C. A. Coulsen and W. E. Moffitt, *Phil. Mag.*, [7] **40**, 1 (1949); (k) A. D. Walsh, *Trans. Faraday Soc.*, **45**, 179 (1949).

[12] The reasons for writing only one bond of the cyclopropane ring as participating in the resonance stabilization of the carbonium ion have been given by J. D. Roberts, W. Bennett and R. Armstrong, THIS JOURNAL, **72**, 3329 (1950).

[13] It must be recognized that this sequence is purely qualitative since the solvolytic reactivities measure, at best, only the tendency toward partial ionization in the solvolysis transition state. Furthermore, under the conditions of our experiments, it is possible that part of the reactions involved a direct (non-ionization) replacement mechanism between solvent and halide. This latter complication is probably not of considerable importance with cyclopropylcarbinyl or cyclobutyl halides since, in common with many other carbonium ion processes, the solvolyses of these substances result in extensive rearrangement as will be shown later. A further complexity is introduced by the fact that the reaction rates do not depend on the absolute free energies of the solvolysis transition states but rather on the difference in free energy ($(\Delta F)^{\ddagger}$) between the ground and transition states. As a result, relative carbonium ion stabilities may be safely inferred from solvolytic reactivities only if there is reasonable assurance that the substances being solvolyzed have rather similar thermodynamic stabilities. In the present series of compounds, the order of increasing solvolytic reactivity corresponds to *decreasing* thermodynamic stability as will be shown later. Although this fact considerably weakens the basis for assignment of the sequence of carbonium ion stabilities, nonetheless, the sequence is useful in correlating the products of a number of interconversion reactions.

where the ions can rearrange or react irreversibly with nucleophilic substances is the paucity of reactions which can be used to generate unstable primary as well as secondary and tertiary carbonium ions. The most generally suitable reactions seem to be the reaction of aliphatic primary amines with nitrous acid. Whitmore and others[14] have offered compelling evidence for the carbonium ion character of this reaction with amines such as *n*-propyl-, *n*-butyl- and neopentylamines. The characteristic nitrogen evolution and relatively mild conditions under which the reaction is usually run ensure complete irreversibility and freedom from rearrangements of the starting materials or products except during the reaction proper.

TABLE I

SOLVOLYSIS RATE CONSTANTS OF HALIDES IN 50% ETHANOL–50% WATER (BY VOLUME)

Halide	Temp., °C. (± 0.1°)	k_1 (hr.$^{-1}$)
Allylcarbinyl chloride	90	0.0060
Cyclobutyl chloride	50	.017
	70	.15
Cyclopropylcarbinyl chloride (I)	50	.45[a]
β-Methylallyl chloride	50	.011
Cyclobutyl bromide	25	.015
Cyclopropylcarbinyl bromide	25	.34[b]
Allyl bromide	25	.013

[a] Obtained from the initial slope of the rate curve of Fig. 3. [b] The value given is computed for a mixture containing 65% cyclopropylcarbinyl bromide and 35% cyclobutyl bromide. If the material contained 20% cyclobutyl bromide as indicated by the infrared spectrum and rearrangement accompanied solvolysis, the corrected k_1 would be about 0.27 hr.$^{-1}$.

We have utilized the amine–nitrous acid reaction to generate cyclopropylcarbinyl, cyclobutyl and allylcarbinyl cations in aqueous solution and, as a test of the reliability of the reaction for this purpose, crotyl- and α-methylallylamines were also studied. To avoid complications resulting from the formation of halides, the reactions were carried out by adding sodium nitrite solution to dilute aqueous solutions of the amines in perchloric acid. Crotylamine gave a mixture of alcohols which was found by fractional distillation to contain 47% of crotyl alcohol and 53% of α-methylallyl alcohol.[15] The over-all yield was 62%. α-Methylallylamine gave a similar but not identical mixture (73% yield) containing 31% of crotyl alcohol and 69% of α-methylallyl alcohol. The compositions of the alcohol mixtures correspond within our experimental error to those reported by Young and Andrews[16] for the products of the carbonium ion type reactions of crotyl and α-methylallyl chlorides with silver hydroxide in aqueous media.

It has been reported previously[2] that the reaction of cyclopropylcarbinyl- and cyclobutylamines with nitrous acid gives mixtures of cyclopropyl carbinol and cyclobutanol. However, in earlier work[17] it was not possible to reproduce the melting points given[2a,18] for the N-phenylcarbamates which were used to separate and identify the cyclobutanol and cyclopropylcarbinol present in the reaction mixtures and reinvestigation of these reactions seemed desirable. Treatment of cyclopropylcarbinyl- and cyclobutylamines with sodium nitrite in dilute aqueous perchloric acid solution was found to give essentially identical mixtures of four-carbon alcohols from each amine. The total yields of alcohols ranged from 35–57%. The principal components of the mixtures were cyclobutanol (~47%) and cyclopropylcarbinol (~48%). The presence of about 5% of allylcarbinol was indicated by the infrared spectra. No crotyl or α-methylallyl alcohols were detected.

The reaction of allylcarbinylamine with sodium nitrite in dilute aqueous perchloric acid solution gave a complex mixture of alcohols which was analyzed partly by fractional distillation and partly by infrared spectra. The mixture (64% yield of alcohols) had approximately the following composition: 45% allylcarbinol, 18% α-methylallyl alcohol, 10% crotyl alcohol, 14% cyclopropylcarbinol and 13% cyclobutanol. The presence of α-methylallyl and crotyl alcohols among the products is particularly significant since it shows that the allylcarbinyl cation, when actually (or incipiently) formed, tends to undergo a hydride shift to the resonance-stabilized α-methylallyl-crotyl cation, as well as to undergo ring closure and form the cyclobutyl or cyclopropylcarbinyl cations. This fact appears to provide a useful diagnostic test for the free allylcarbinyl cation based on the formation or non-formation in a given reaction involving allylcarbinyl compounds of crotyl or α-methylallyl derivatives.

The results of the amine–nitrous acid reactions provide a qualitative idea of what is to be expected from carbonium ions in irreversible (or essentially irreversible) reactions with nucleophilic substances. The amounts of the various products appear to correspond roughly with relative carbonium ion stabilities. The energy barrier to the interconversion of the cyclobutyl and cyclopropylcarbinyl cations seems to be quite small since, starting with substances corresponding to either ion, the same mixture of final products is obtained.[19] The energy barrier to conversion of these ions to the allylcarbinyl cation seems to be high while that of the reverse process, as judged from the nearly equal ratio of allylcarbinol to cyclopropylcarbinol and cyclobutanol formed in the allylcarbinylamine–nitrous acid reaction, seems to have an intermediate value.

The information so far obtained is applicable to other irreversible carbonium ion reactions of cyclobutyl, cyclopropylcarbinyl and allylcarbinyl derivatives. For example, the solvolysis of the

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[14] (a) F. C. Whitmore and D. P. Langlois, THIS JOURNAL, **54**, 3441 (1932); (b) F. C. Whitmore and R. S. Thorpe, *ibid.*, **63**, 1118 (1941); (c) M. Freund and F. Lenze, *Ber.*, **24**, 2150 (1891).

[15] E. Galand, *Bull. soc. chim. Belg.*, **39**, 529 (1930), has reported that the reaction of crotylamine with nitrous acid gives only crotyl alcohol.

[16] W. G. Young and L. J. Andrews, THIS JOURNAL, **66**, 421 (1944).

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

[18] N. J. Demjanow and K. Fortunatow, *Ber.*, **40**, 4397 (1907).

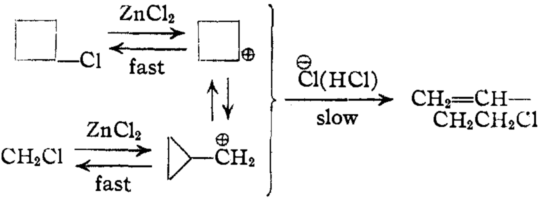
[19] The possibility is being investigated that the cyclobutyl and cyclopropylcarbinyl cations have effectively no separate existence but are converted to an intermediate ion of the type suggested by T. P. Nevell, E. de Salas and C. L. Wilson, *J. Chem. Soc.*, 1188 (1939), for the camphanyl cation.

chlorides in neutral or slightly alkaline aqueous media could reasonably be expected to be such a process, and it is not surprising to find that cyclopropylcarbinyl chloride and cyclobutyl chloride produce mixtures of alcohols of similar compositions to those formed from the corresponding amines with nitrous acid. Allylcarbinyl chloride was very unreactive and, in an attempt to speed the reaction by boiling with an aqueous suspension of silver carbonate, almost no alcohol was formed.

Reversible Carbonium Ion Reactions

In a reversible reaction, the relative stabilities of the possible products are of particular importance. It is perhaps surprising that, of the cyclopropylcarbinyl, cyclobutyl and allylcarbinyl halides, the last is most stable. This is strikingly demonstrated by complete conversion of a roughly equivalent mixture of cyclopropylcarbinyl and cyclobutyl chlorides or bromides at, or below, room temperature by Lucas reagent (a solution of zinc chloride in concentrated hydrochloric acid) or its bromide analog into allylcarbinyl halides. Allylcarbinyl chloride was also apparently the sole product of the reaction at room temperature between cyclopropylcarbinol or cyclobutanol with Lucas reagent. As expected from the estimates of the relative carbonium ion stabilities, allylcarbinol was by far the least reactive alcohol toward Lucas reagent. No reaction occurred below, or at, room temperature and, on boiling, extensive decomposition resulted. Cyclobutyl chloride is intermediate in stability between allylcarbinyl and cyclopropylcarbinyl chlorides, and it was found that a 2:1 mixture of cyclopropylcarbinyl and cyclobutyl chlorides was isomerized to a 1:1 mixture of allylcarbinyl and cyclobutyl chlorides by using a shorter reaction time and less Lucas reagent than was employed for complete isomerization to allylcarbinyl chloride.

The rearrangements of the chlorides and the reactions of the alcohols with Lucas reagent may be interpreted in several ways. The function of the zinc chloride is to facilitate the formation of carbonium ions from cyclobutanol, cyclopropylcarbinol and their respective chlorides. As one possibility, an equilibrium might be postulated between the various cations with a slow irreversible reaction between the allylcarbinyl cation and chloride ion or, to obviate the necessity of assuming a slow reaction of the allylcarbinyl cation, this entity could be considered to be formed slowly and to react rapidly and essentially irreversibly with chloride ion. An alternative and somewhat more attractive interpretation is similar to that proposed[20] for the analogous formation of isobornyl chloride from camphene hydrochloride. Here, the cyclobutyl and cyclopropylcarbinyl cations are postulated to be essentially in equilibrium with each other as well as with the respective chlorides. Allylcarbinyl chloride is formed by a direct and essentially irreversible slow reaction between either or both of the cations and chloride ion or hydrogen chloride as shown in the equations



This formulation is favored since, if the allylcarbinyl cation were actually an intermediate, some formation of crotyl and α-methylallyl chlorides would be expected, in accordance with the modes of reaction of the allylcarbinyl cation observed in the allylcarbinylamine–nitrous acid reaction.

Direct evidence that the rearrangement is not an intramolecular process was obtained by measurement of the extent of chlorine exchange between allylcarbinyl chloride and a mixture of cyclopropylcarbinyl and cyclobutyl chlorides with Lucas reagent containing Cl^{38}. Under conditions where the mixture of cyclopropylcarbinyl and cyclobutyl chlorides was 77% isomerized to allylcarbinyl chloride, 107%[21] of the theoretical chlorine exchange took place. However, under the same conditions, allylcarbinyl chloride showed but 13% exchange indicating that allylcarbinyl chloride is not readily converted to the corresponding carbonium ion in the presence of Lucas reagent.

Regardless of the mechanisms involved, the reactions of cyclopropylcarbinol and cyclobutanol with Lucas reagent to give allylcarbinyl chloride are obviously controlled by the relative stabilities of the possible products. It is likely that the same effects are operative in the formation of (γ,γ-dimethylallyl)-carbinyl chloride from dimethylcyclopropylcarbinol and hydrochloric acid.[4] In the hydrolysis of the chloride, where dimethylcyclopropylcarbinol is formed,[4] an irreversible carbonium ion type reaction is probably involved and the relative carbonium ion stabilities are the important factor in determining the reaction products.

Applications to Other Reactions

The reactions of alcohols with thionyl chloride do not generally seem to be considered[22] carbonium ion type reactions and, as pointed out earlier, allylcarbinol reacts with thionyl chloride (and also phosphorus tribromide) without rearrangement. Nonetheless, in some cases (as with isopropylmethylcarbinol[23a] and 2-methyl-2-phenyl-1-butanol[23b]) rearrangements occur which are characteristic of carbonium ion reactions. We find that cyclobutanol and cyclopropylcarbinol react with thionyl chloride to give mixtures of chlorides. Similar mixtures were obtained from each alcohol, with compositions on the order of cyclobutyl chloride (30%), cyclopropylcarbinyl chloride (67%) and allylcarbinyl chloride (3%). The compositions of the products were not altered by carrying out the

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(20) (a) P. D. Bartlett and I. Pöckel, This Journal, **60**, 1585 (1938). (b) W. E. Doering, Abstracts of 113th (Chicago) Meeting of the American Chemical Society, April 19 to 23, 1948, p. 41L.

(21) The difference between this figure and 100% may be due to experimental error or else some addition of HCl^{38} to the double bond with Lucas reagent may have occurred.

(22) *Cf.* W. Gerrard, *J. Chem. Soc.*, 688 (1936); 99 (1939); 218 (1940); 85 (1944); W. Gerrard and K. H. V. French, *Nature*, **159**, 263 (1947).

(23) (a) F. C. Whitmore and F. Johnston, This Journal, **60**, 2265 (1938); (b) E. S. Wallis and P. I. Bowman, *J. Org. Chem.*, **1**, 383 (1936).

reaction in the presence of a mole of pyridine for each mole of thionyl chloride used. The results indicate an irreversible carbonium ion type mechanism in the reaction of thionyl chloride with cyclobutanol and cyclopropylcarbinol. Presumably, similar considerations apply to the reaction of cyclopropylcarbinol with phosphorus tribromide.

Leonard and Nommensen[24] have shown that the von Braun synthesis of alkyl halides from N-substituted benzamides has some of the characteristics of a carbonium ion reaction and on this basis it is not unexpected that N-cyclobutyl- and N-cyclopropylcarbinylbenzamides give similar mixtures of bromides on treatment with phosphorus pentabromide.[25] The bromide mixtures are seen by their infrared spectra (Fig. 2) to be similar to cyclopropylcarbinol–phosphorus tribromide product.

Acknowledgment.—The radioactive exchange experiments were supported in part by the joint program of the Office of Naval Research and the Atomic Energy Commission.

Experimental

Cyclopropanecarboxylic Acid.—A procedure similar to that described by Jeffery and Vogel[26] was found to be more convenient than other large-scale preparations.[27] The yields in runs involving as much as 5 moles of ketone were 70–85% of material having b.p. 97–98° (40 mm.).

Cyclopropylcarbinol.—Lithium aluminum hydride reduction of cyclopropanecarboxylic acid and ethyl cyclopropanecarboxylate by the procedures of Nystrom and Brown[28] gave cyclopropylcarbinol, b.p. 123° (lit.[3] 122–123°), n^{25}D 1.4300 in 68 and 54% yield, respectively. The N-phenylcarbamate had m.p. 76.6–77.0° (lit. 100–104°,[18] 75.5–76°[3]) after crystallization from hexane.

Anal. Calcd. for $C_{11}H_{12}O_2N$: C, 69.11; H, 6.81. Found: C, 68.88; H, 6.77.

The **3,5-dinitrobenzoate** had m.p. 101.2–101.4° after crystallization from hexane–benzene.

Anal. Calcd. for $C_{11}H_{10}O_6N_2$: C, 49.62; H, 3.76. Found: C, 49.96; H, 3.83.

Cyclobutanol was prepared from cyclobutanone as described previously.[17]

Allylcarbinol.—The starting material for the preparation of allylcarbinol was 3-butyne-1-ol which was obtained by distillation of commercial material (Farchan); b.p. 128°, n^{25}D 1.4388. The **N-α-naphthylcarbamate** of 3-butyn-1-ol was prepared and had m.p. 98.5–98.8° after crystallization from hexane–benzene.

Anal. Calcd. for $C_{15}H_{13}O_2N$: C, 75.29; H, 5.48. Found: C, 75.15; H, 5.52.

Hydrogenation of 3-butyn-1-ol mixed with an equal volume of methanol at 30 p.s.i. over 2% palladium-on-calcium carbonate catalyst was carried out in a water-cooled jacketed bottle until one mole of hydrogen per mole of butynol was absorbed. The catalyst which was too finely divided to be separated by filtration was removed by distillation of the organic material under reduced pressure into a Dry Ice-cooled trap. Fractional distillation through a glass-helix packed column gave allylcarbinol, b.p. 115° (770 mm.), 47.5° (41 mm.), n^{25}D 1.4182 (lit.[29] b.p. 112.5–113.5° (748 mm.), n^{20}D 1.4224). The yields averaged 65% in several preparations of varying size.

The **N-α-naphthylcarbamate** of allylcarbinol had m.p. 75.2–75.6° after crystallization from hexane–benzene.

Anal. Calcd. for $C_{15}H_{15}O_2N$: C, 74.69; H, 6.22. Found: C, 74.34; H, 6.29.

Allylcarbinyl Chloride.—A mixture of 8.0 g. (0.11 mole) of allylcarbinol with five drops of pyridine was cooled in an ice-bath and 13.2 g. (0.11 mole) of thionyl chloride added dropwise. The flask was shaken occasionally during the addition of the thionyl chloride and, after the addition was complete, the mixture was heated under reflux for 30 minutes. Fractional distillation of the products gave 7.3 g. (73%) of allylcarbinyl chloride, b.p. 73–74°, n^{25}D 1.4192 (lit.[29] b.p. 75.0°, n^{20}D 1.4233). The infrared spectrum of the product is given in Fig. 1.

Treatment of allylcarbinylmagnesium chloride with phenyl isocyanate gave allylacetanilide which had m.p. 91.4–91.8° (lit.[30] 91°) after crystallization from benzene–hexane.

Allylcarbinyl bromide was prepared in 43% yield from allylcarbinol by the method of Juvala[29]; b.p. 99–100°, n^{25}D 1.4573 (lit.[29] b.p. 98.5–99°, n^{20}D 1.4622). The infrared spectrum of the product is given in Fig. 2.

Cyclobutyl Chloride from the Chlorination of Cyclobutane.—Part of the apparatus used for the vapor-phase chlorination of cyclobutane is shown in Fig. 5. Joint A was connected to the top of a short vacuum-jacketed Vigreux column, a Dry Ice condenser was mounted on B and chlorine was passed in at C. The apparatus was covered with asbestos paper except for the glass spiral which was irradiated with an RS type G. E. Sunlamp at 5–10 cm.

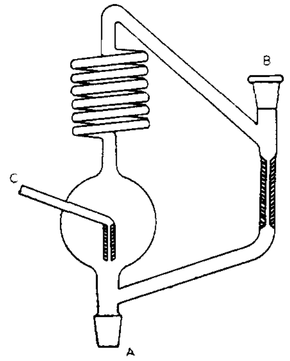

Fig. 5.—Chlorination apparatus.

Cyclobutane[17] (8.4 g., 0.15 mole) was placed in the boiler of the Vigreux column and heated so that a rapid stream of reflux was evident at B. After allowing a few minutes for displacement of air from the system, chlorine was admitted at C from a gas buret at about 500 ml./hr. When 3700 ml. (measured at atmospheric pressure over saturated salt solution at room temperature) of chlorine had been run in, the thermometer in the head of the Vigreux column reached 60°. Distillation of the chlorination product gave 9.9 g. (73%) of cyclobutyl chloride; b.p. 82–83°, n^{25}D 1.4332. A middle fraction of b.p. 82.7–82.9° had d^{25}_4 0.991; MRD 23.75 (the calculated value of MRD was 23.66 using 0.32 for the exaltation of the cyclobutane ring[26]).[31]

Anal. Calcd. for C_4H_7Cl: C, 53.05; H, 7.79. Found: C, 53.35; H, 7.73.

Treatment of the Grignard reagent prepared from cyclobutyl chloride with phenyl isocyanate gave cyclobutanecarboxanilide, m.p. 109.0–110.6° after crystallization from benzene–hexane. This material did not depress the m.p. (113.8–114.0°) of an authentic sample prepared from the acid chloride of cyclobutanecarboxylic acid and aniline. The reported[32] m.p. for cyclobutanecarboxanilide is 111°. In some instances, particularly when the phenyl isocyanate was added to ice-cooled ethereal solutions of cyclobutylmagnesium chloride, a product of m.p. 99.6–100.2°, after crystallization from hexane, was isolated. This substance had the correct elemental analysis for N-cyclobutanecarboxyl-N,N′-diphenylurea which could reasonably arise through reaction between phenyl isocyanate and the chloromagnesium salt of cyclobutanecarboxanilide. Attempts to

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(24) N. J. Leonard and E. W. Nommensen, THIS JOURNAL, **71**, 2808 (1949).

(25) The reaction of N-cyclopropylcarbinyl benzamide with phosphorus pentabromide has been reported previously by J. A. Arvin and R. Adams, *ibid.*, **50**, 1983 (1928), and J. von Braun, R. Fuszgänger and M. Kühn, *Ann.*, **445**, 201 (1925), to give cyclopropylcarbinyl bromide. The purity of the earlier preparations is questionable.

(26) G. H. Jeffery and A. I. Vogel, *J. Chem. Soc.*, 1804 (1948).

(27) (a) M. J. Schlatter, THIS JOURNAL, **63**, 1733 (1941); (b) C. M. McCloskey and G. H. Coleman, *Org. Syn.*, **24**, 36 (1944).

(28) R. F. Nystrom and W. G. Brown, THIS JOURNAL, **69**, 1197, 2548 (1947).

(29) A. Juvala, *Ber.*, **63**, 1989 (1930).

(30) R. P. Linstead and H. N. Rydon, *J. Chem. Soc.*, 1995 (1934).

(31) Cyclobutyl chloride has previously been reported by W. H. Perkin, Jr., *ibid.*, **65**, 950 (1894), from the reaction of "cyclobutanol" (prepared from cyclobutylamine hydrochloride and silver nitrite) with phosphorus pentachloride. In view of the possibilities for rearrangement in these reactions the purity of Perkin's preparation is questionable.

(32) M. Freund and E. Gudeman, *Ber.*, **21**, 2697 (1888).

prepare authentic material by reaction of cyclobutanecarboxanilide with phenyl isocyanate for 24 hours in refluxing dry xylene[33] or by successive treatments of cyclobutanecarboxanilide with one equivalent of methylmagnesium iodide and phenyl isocyanate were unsuccessful. The substance depressed the m.p. (100°) of cyclopropylacetanilide prepared as described below.

Anal. Calcd. for $C_{18}H_{18}O_2N_2$: C, 73.44; H, 6.16; N, 9.52. Found: C, 73.74; H, 6.27; N, 9.37.

Isobutyl Triethylsilyl Ether and Cyclopropylcarbinyl Triethylsilyl Ether.—In a 500-ml. three-necked flask equipped with stirrer, dropping funnel, reflux condenser and nitrogen inlet tube was placed 4.8 g. (0.20 mole) of sodium hydride and 100 ml. of dry ether and the air in the flask displaced by dry nitrogen. Isobutyl alcohol (13.0 g., 0.175 mole) was added dropwise to the stirred suspension and the mixture was then heated under reflux for two hours. Triethylbromosilane[34] (39.0 g., 0.20 mole) was added to the rapidly stirred mixture at such a rate as to keep the ether refluxing gently. After the addition was complete, the mixture was refluxed for two hours and then treated with 100 ml. of water. The ether layer was separated, the aqueous layer extracted with ether and the combined extracts dried over magnesium sulfate. The ether was distilled and the residue fractionated under reduced pressure. The forerun included 2.8 g. of triethylsilane, b.p. 42° (50 mm.). The yield of isobutyl triethylsilyl ether was 30.3 g. (92%); b.p. 76° (21 mm.); n^{25}D 1.4169.

Anal. Calcd. for $C_{10}H_{24}OSi$: C, 63.76; H, 12.84. Found: C, 63.73; H, 12.86.

Cyclopropylcarbinyl triethylsilyl ether was prepared in a similar manner except that the treatment of the reaction mixture with water was omitted and instead the solids were filtered and the filtrate distilled. From 5.8 g. (0.080 mole) of cyclopropylcarbinol was obtained 7.0 g. (47%) of cyclopropylcarbinyl triethylsilyl ether; b.p. 90–91° (22 mm.), n^{25}D 1.4334.

Anal. Calcd. for $C_{10}H_{22}OSi$; C, 65.45; H, 11.90. Found: C, 64.32; H, 12.10.

Reaction of Silyl Ethers with Thionyl Chloride.—The cleavage of isobutyl triethylsilyl ether by thionyl chloride was found to give diisobutyl sulfite in the absence of pyridine and a low yield of isobutyl chloride in the presence of pyridine.

A.—To 23.5 g. (0.125 mole) of isobutyl triethylsilyl ether contained in a flask equipped with a reflux condenser was added 15.3 g. (0.13 mole) of thionyl chloride. A spontaneous reaction occurred after which the mixture was heated under reflux for six hours. Fractionation under reduced pressure gave 17.6 g. (94%) of triethylchlorosilane, b.p. 60° (40 mm.) and 4.3 g. (40%) of diisobutyl sulfite, b.p. 89–90° (10 mm.), n^{25}D 1.4253. An authentic sample of diisobutyl sulfite prepared by the method of Voss and Blanke[35] had b.p. 92–93° (12 mm.) and n^{25}D 1.4242.

B.—A mixture of 5.5 g. (0.046 mole) of thionyl chloride and 0.8 g. of pyridine was heated to reflux and 8.7 g. (0.046 mole) of isobutyl triethylsilyl ether added dropwise. A vigorous reaction ensued with liberation of sulfur dioxide. The mixture was refluxed for one-half hour and then distilled. The crude low-boiling material, 3 g., was washed with sodium bicarbonate solution to remove thionyl chloride, dried over calcium chloride and distilled. The yield of isobutyl chloride was 0.6 g. (15%); b.p. 69.5°, n^{25}D 1.3953 (lit.,[36] b.p. 68.9°, n^{25}D 1.3958).

C.—The reaction of cyclopropylcarbinyl triethylsilyl ether with thionyl chloride was carried out in the presence of pyridine as described in the preceding preparation except that the reflux period was 1.5 hours. From 10.0 g. (0.084 mole) of thionyl chloride, 0.8 g. of pyridine and 15.5 g. (0.083 mole) of cyclopropylcarbinyl triethylsilyl ether there was obtained 6.1 g. of crude product, b.p. 84–86°, which on fractionation through an efficient center-tube column[37] gave 4.6 g. (61%) of material; b.p. 87–88.5°, n^{25}D 1.4310–1.4323. A middle fraction had an infrared spectrum virtually identical with that of the product of cyclopropylcarbinol with thionyl chloride. The solvolysis rate curve at 50° in aqueous alcohol indicated 63% of cyclopropylcarbinyl chloride (assuming no rearrangement).

Chlorination of Methylcyclopropane.—The methylcyclopropane used in these experiments was prepared starting from 1,3-butyleneglycol by the procedures employed in the synthesis of 1,1-dimethylcyclopropane.[38] The over-all yield of methylcyclopropane, b.p. 2° (lit.[39] 4–5°), was 67%.

The chlorination procedure was similar to that described above for cyclobutane; 24.3 g. (0.43 mole) of methylcyclopropane and 4900 ml. of chlorine were used and, at the conclusion of the reaction, the column head temperature was 50°. The crude chlorination product was distilled rapidly through a short Vigreux column and the monochlorinated material which amounted to 31 g. (80%), b.p. 60–95°, was then carefully fractionated through an efficient center-tube column.[37] The following fractions were taken: b.p. 64–74°, n^{25}D 1.4009–1.4045, 5.4 g. (21%), probably a mixture of 1- and 2-chloro-1-methylcyclopropane; b.p. 75–76°, n^{25}D 1.4180–1.4198, 8.8 g. (35%), identified as allylcarbinyl chloride by its infrared spectrum; and b.p. 87–89°, n^{25}D 1.4310–1.4328, 8.6 g. (34%) shown by its infrared spectrum (Fig. 1) to contain no cyclobutyl or allylcarbinyl chlorides and inferred to be cyclopropylcarbinyl chloride. Intermediate fractions amounted to 2.2 g. (10%). The purest cyclopropylcarbinyl chloride had n^{25}D 1.4328 and d^{25}_{4} 0.980, corresponding to MRD 24.00 (the calculated value of MRD was 23.94 using 0.60 for the exaltation of the cyclopropane ring).[26]

Conversion of the material of b.p. 87–89° to the Grignard reagent and treatment with phenyl isocyanate gave allylacetanilide, m.p. 88.8–90.2°, after recrystallization from hexane–benzene. This material did not depress the m.p. of an authentic sample having m.p. 91.4–91.8°. The crude anilide (before recrystallization) absorbed 99% of the theoretical amount of hydrogen calculated for allylacetanilide on quantitative hydrogenation in methanol over platinum oxide.

Authentic **cyclopropylacetanilide** was obtained by treatment of cyclopropylacetic acid[40] with thionyl chloride in dry ether and reaction of the crude acid chloride with aniline. The material so obtained had m.p. 98.8–99.6° after crystallization from benzene–hexane.

Anal. Calcd. for $C_{11}H_{13}ON$: C, 75.40; H, 7.48. Found: C, 75.26; H, 7.46.

Reaction of Cyclopropylcarbinol with Phosphorus Tribromide.—Cyclopropylcarbinol (4.2 g., 0.059 mole) was added dropwise to 7.0 g. (0.026 mole) of stirred ice-cooled phosphorus tribromide. Ten ml. of methylene chloride was added, the mixture was stirred for 30 minutes, and then the excess phosphorus tribromide was decomposed by addition of ice. The methylene chloride layer was separated, washed with water, dried over calcium chloride and fractionated through a center-tube column.[37] Three fractions were taken: 0.66 g., b.p. 102–110°, n^{25}D 1.4568; 3.89 g., b.p. 110.8–111.6°, n^{25}D 1.4750 and 0.97 g., b.p. 111.6–112.0°, n^{25}D 1.4740. The total yield of bromide was 5.5 g. (70%).

The infrared spectra indicated that the first fraction contained about 50% allylcarbinyl bromide while the later fractions contained no allylcarbinyl bromide. The amount of allylcarbinyl bromide formed on this basis was 6% of the total yield. The spectrum of the middle fraction is shown in Fig. 2.

Solvolysis rate studies on the middle fraction in 50% ethanol–50% water (by volume) indicated the presence of a very reactive bromide to the extent of about 65%.

Conversion of 1.33 g. of the middle fraction to the Grignard reagent followed by treatment with 0.98 g. of phenyl isocyanate gave 1.03 g. of a mixture of anilides. Fractional crystallization of the anilide mixture from benzene–hexane yielded allylacetanilide, m.p. 90.2–90.6°, which did not depress the m.p. of authentic material. Quantitative hydro-

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[33] P. F. Wiley, THIS JOURNAL, **71**, 3746 (1949).

[34] This substance, b.p. 56-59° (23 mm.), was prepared in 64% yield by the method used by P. A. DiGiorgio, W. A. Strong, L. H. Sommer and F. C. Whitmore, *ibid.*, **68**, 1380 (1946), for triethylchlorosilane employing ammonium bromide in place of ammonium chloride.

[35] W. Voss and E. Blanke, *Ann.*, **485**, 258 (1931).

[36] J. Timmermans and F. Martin, *J. chim. phys.*, **23**, 747 (1926).

[37] The fractionating section of this column was similar to that described by E. A. Naragon and C. J. Lewis, *Ind. Eng. Chem., Anal. Ed.*, **18**, 448 (1946).

[38] R. W. Shortridge, R. A. Craig, K. W. Greenlee, J. M. Derfer and C. E. Boord, THIS JOURNAL, **70**, 946 (1948).

[39] W. A. Lott, W. G. Christiansen and L. F. Shackell, *J. Am. Pharm. Assoc.*, **27**, 125 (1938).

[40] The cyclopropylacetic acid was prepared by the procedure of Smith and McKenzie.[3] The diethyl cyclopropylmalonate was kindly furnished by Mr. Malcolm Chamberlain.

genation of a sample of the anilide mixture in methanol over platinum resulted with absorption of 58% of the theoretical quantity of hydrogen calculated for pure allylacetanilide. The presence of cyclobutanecarboxanilide in the anilide mixture was demonstrated by oxidation of the unsaturated material with potassium permanganate in acetone followed by removal of the manganese dioxide with sulfur dioxide and purification of the unoxidized anilide. The material so obtained had m.p. 112.0–112.6° and did not depress the m.p. (113.8–114.0°) of an authentic sample of cyclobutanecarboxanilide.

Cyclopropylcarbinol with Hydrobromic Acid.—A mixture of 4.1 g. (0.057 mole) of cyclopropylcarbinol and 51 g. (0.3 mole) of 48% hydrobromic acid was stirred in an ice-bath for 30 minutes and then extracted with methylene chloride. The extract was dried over calcium chloride and distilled. Two fractions were taken; 0.35 g., b.p. 102–110°, $n^{25}\mathrm{D}$ 1.4520 and 1.93 g., b.p. 110.5–112.0°, $n^{25}\mathrm{D}$ 1.4710. The total yield was 2.3 g. (28%) and assuming half of the first fraction to be allylcarbinyl bromide the extent of formation of this material was about 8%. The infrared spectrum of the second fraction (Fig. 2) indicates this material to be cyclopropylcarbinyl and cyclobutyl bromides in a ratio of about 2:1.

Attempted Isomerization of Cyclobutyl Bromide by Magnesium Bromide.—This experiment was designed to determine whether cyclobutyl bromide might be isomerized by magnesium bromide to allylcarbinyl bromide in a Grignard solution and thus give the over-all effect of an abnormal Grignard reaction such as was obtained with cyclopropylcarbinyl bromide.

The magnesium bromide was prepared by adding 0.59 g. (0.0037 mole) of bromine to 0.089 g. (0.0037 mole) of well-stirred magnesium turnings in 10 ml. of anhydrous ether. When the bromine color disappeared, 0.56 g. (0.0041 mole) of cyclobutyl bromide was added and the mixture heated under reflux for four hours. Additional magnesium (0.10 g., 0.0041 mole) was added and, after formation of the Grignard reagent was complete, 0.48 g. (0.0040 mole) of phenyl isocyanate was run in. The yield of crude anilide was 0.66 g. (94%). The product contained no allylacetanilide since no hydrogen was absorbed over platinum in methanol. Some of the by-product obtained in the cyclobutylmagnesium chloride reaction appeared to be present and pure cyclobutanecarboxanilide, m.p. 113.0–113.6°, was obtained only after sublimation and several crystallizations from hexane–benzene.

Solvolysis Rate Determinations.—The solvolysis rate experiments were carried out in 50% ethanol–50% water (by volume) using the procedure described previously.[41] The rate curve of the cyclopropylcarbinyl–cyclobutyl bromide mixture was treated by the procedure of Brown and Fletcher.[42]

The rate expression used for the calculated curves of Fig. 3 is

$$-(k_1 + k_1')t = \log \frac{k_1(a - b) - (k_1 + k_1')x}{k_1(a - b)}$$

where a = starting total concentration of chloride
b = starting concentration of unreactive chloride
x = concentration of hydrochloric acid formed by solvolysis
t = time
k_1 = first-order solvolysis constant
k_1' = first-order rearrangement constant

The value of 0.47 hr.$^{-1}$ for k_1 was obtained from the initial slope of the solvolysis rate curve of I. The value of 0.14 hr.$^{-1}$ for k_1' was obtained by successive approximations.

The solvolyses of cyclopropylcarbinyl, cyclobutyl and allylcarbinyl chlorides in acetic acid were followed by titration of the excess potassium acetate as described earlier.[43] With cyclopropylcarbinyl and cyclobutyl chlorides, the extent of formation of unsaturated material was determined by bromide–bromate titration. It was assumed that the unsaturated material was exclusively allylcarbinyl chloride formed by rearrangement (and not a solvolysis product) since other solvolysis reactions of cyclopropylcarbinyl and cyclobutyl derivatives yield almost no unsaturated substances. The rate data are shown in Fig. 4. The rate constants computed from the slopes of the rate curves are given in Table II.

TABLE II

RATE CONSTANTS FOR SOLVOLYSIS AND REARRANGEMENT OF CHLORIDES IN ACETIC ACID IN THE PRESENCE OF ACETATE ION AT 100°

Chloride	RCl, mole/l.[a]	KOAc, mole/l.[a]	k_1, hr.$^{-1}$	k_1', hr.$^{-1}$
Cyclopropylcarbinyl	0.0267	0.0213	0.032	0.027[b] .045[c]
Cyclobutyl	.0334	.0323	.0024 (.004)[d]	.0018[b] (.002)[b,d]
Allylcarbinyl	.0252	.0213	<.0002	.....

[a] Initial concentrations. [b] For rearrangement to allylcarbinyl chloride. [c] For rearrangement to cyclobutyl chloride. [d] Calculated from the final slopes of the cyclopropylcarbinyl chloride rate curves.

Isolation of Solvolysis Products of Cyclopropylcarbinyl Chloride in Acetic Acid.—A solution of 5.94 g. (0.066 mole) of cyclopropylcarbinyl chloride and 2.13 g. (0.022 mole) of potassium acetate in 40 ml. of dry acetic acid was heated for 24 hours in a thermostat at 100°. It was calculated from the rate constants that the chloride should have been about 30% solvolyzed and 70% rearranged at the end of the heating period. The solution was cooled, neutralized with aqueous potassium hydroxide and extracted with ether. The extract was dried over magnesium sulfate and the ether distilled. The residue was fractionated through a center-tube column.[37] The chloride fractions, b.p. 76–88°, $n^{25}\mathrm{D}$ 1.4187–1.4232, amounted to 3.3 g. and were shown by their infrared spectra to contain cyclobutyl and allylcarbinyl chlorides in a ratio of about 1.7:1. The ratio calculated from the rate constants is 1.6:1. None of the characteristic infrared absorption bands of cyclopropylcarbinyl chloride were present in the chloride spectra. After an intermediate fraction of b.p. 88–120° amounting to 0.3 g., there was obtained 1.9 g. of a mixture of esters, b.p. 126–133° and $n^{25}\mathrm{D}$ 1.4050–1.4100. The infrared spectra of the ester mixture indicated the presence of cyclopropylcarbinyl and cyclobutyl acetates in a ratio of about 2.6:1. Little, if any, allylcarbinyl acetate appeared to be present. Infrared spectra of pure cyclopropylcarbinyl, cyclobutyl and allylcarbinyl acetates were obtained by Dr. Vaughan C. Chambers as part of a separate investigation and will be published later.

Crotylamine.—The procedure was based on those used by Sheehan and co-workers[44] for preparation of amino acids. A mixture of 35 g. (0.38 mole) of crotyl chloride, b.p. 43–45° (190 mm.), 74 g. (0.40 mole) of potassium phthalimide and 150 ml. of dimethylformamide was heated at 120° for 30 minutes and then at 160° for an additional 30 minutes. The hot mixture was poured over 200 g. of ice and extracted with four 50-ml. portions of chloroform. The combined extracts were washed successively with 1 *N* potassium hydroxide, water, 0.5 *N* hydrochloric acid and again with water. The chloroform solution was dried over magnesium sulfate and the chloroform distilled. The residual crude solid N-crotylphthalimide amounted to 70.4 g. (92%). A sample recrystallized from 95% ethanol had m.p. 75.2–75.8° (lit.[45] 76°).

A mixture of 69.2 g. (0.34 mole) of crude N-crotylphthalimide, 200 ml. of 95% ethanol and 21.9 g. (0.37 mole) of 85% hydrazine hydrate was heated under reflux for one hour, cooled, treated with 37 ml. of 10 *N* hydrochloric acid and filtered. The collected phthalhydrazide was triturated with 200 ml. of water, filtered and the combined filtrates evaporated to dryness under reduced pressure. The residue was treated with a solution of 26 g. (0.4 mole) of 85% potassium hydroxide in 50 ml. of water and then extracted with three 20-ml. portions of ether. The combined extracts were dried over potassium hydroxide and fractionated through a glass-helix packed column. The yield of crotylamine was 17 g. (70%); b.p. 81–82°, $n^{25}\mathrm{D}$ 1.4304 (lit.[15] b.p. 81–84°, $n^{20}\mathrm{D}$ 1.428–1.432).

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[41] J. D. Roberts, L. Urbanek and R. Armstrong, THIS JOURNAL, **71**, 3049 (1949).

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

[43] J. Steigman and L. P. Hammett, *ibid.*, **59**, 2536 (1937); J. D. Roberts, W. G. Young and S. Winstein, *ibid.*, **64**, 2157 (1942).

[44] (a) J. C. Sheehan and V. S. Frank, *ibid.*, **71**, 1856 (1949); (b) J. C. Sheehan and W. A. Bolhofer, *ibid.*, **72**, 2786 (1950).

[45] K. H. Slotta and R. Tschesche, *Ber.*, **62**, 1398 (1929).

α-Methylallylamine.—The preparation of N-α-methylallylphthalimide paralleled that of N-crotylphthalimide except that the α-methylallyl chloride-potassium phthalimide reaction mixture was refluxed for three hours. The yield of crude N-α-methylallylphthalimide from 41 g. (0.45 mole) of α-methylallyl chloride, b.p. 28–29° (190 mm.), 88.8 g. (0.48 mole) of potassium phthalimide and 150 ml. of dimethylformamide was 70 g. (77%). A small sample recrystallized several times from 95% ethanol had m.p. 85.0–85.6° (lit.[46] 87–88°).

Treatment of 69 g. (0.34 mole) of N-α-methylallylphthalimide with 27 g. (0.45 mole) of 85% hydrazine hydrate in 300 ml. of 95% ethanol as described for the preparation of crotylamine gave 10.5 g. (44%) of α-methylallylamine; b.p. 62–64°, n^{25}_{D} 1.4090 (lit.[47] b.p. 62.3°, n^{20}_{D} 1.4150).

Allylcarbinylamine.—N-Allylcarbinylphthalimide was prepared in the same manner as N-crotylphthalimide except that potassium iodide was used as a catalyst and the reaction time was one hour. From 13 g. (0.14 mole) of allylcarbinyl chloride, 28 g. (0.15 mole) of potassium phthalimide, 0.2 g. of potassium iodide and 100 ml. of dimethylformamide there was obtained 23 g. (82%) of crude **N-allylcarbinylphthalimide**. A small sample was recrystallized twice from 95% ethanol and had m.p. 51.1–51.5°.

Anal. Calcd. for $C_{12}H_{11}O_2N$: C, 71.62; H, 5.51. Found: C, 71.51; H, 5.60.

Treatment of 27 g. (0.13 mole) of crude N-allylcarbinylphthalimide with 10 g. (0.17 mole) of 85% hydrazine hydrate in 125 ml. of 95% ethanol as described for the preparation of crotylamine yielded 6.4 g. (67%) of allylcarbinylamine; b.p. 75–77°, n^{25}_{D} 1.4191 (lit.[15] b.p. 81–82.5°, n^{20}_{D} 1.4273). Since the properties of the amine were quite different than those previously reported[15] the material was carefully characterized.

N-Allylcarbinyl-N′-phenylthiourea was obtained from the reaction of the amine with phenyl isothiocyanate and had m.p. 44.5–44.9° after crystallization from ethanol–water (lit.[15] m.p. 91°).

Anal. Calcd. for $C_{11}H_{14}N_2S$: C, 64.04; H, 6.84. Found: C, 63.93; H, 6.85.

N-Allylcarbinyl-N′-phenylurea from allylcarbinylamine and phenyl isocyanate had m.p. 94–95° after recrystallization from ethanol–water.

Anal. Calcd. for $C_{11}H_{14}ON_2$: C, 69.44; H, 7.42. Found: C, 69.39; H, 7.28.

The carbon-skeleton of the N-allylcarbinyl-N′-phenylurea was established by hydrogenation of a 0.14-g. sample over platinum at atmospheric pressure in methanol solution. The catalyst was removed by filtration, the filtrate concentrated to small volume and the product precipitated with water. Recrystallization from ethanol–water gave 0.097 g. (65%) of N-*n*-butyl-N′-phenylurea, m.p. 129.2–129.8° (lit.[48] 129–130°).

Cyclobutylamine.—The procedure of Zelinsky and Gutt[49] was used for the conversion of cyclobutanecarboxylic acid[50] to cyclobutylamine.

N-Cyclobutylbenzamide was obtained from the reaction of cyclobutylamine with benzoyl chloride by the Schotten–Baumann procedure. The product after crystallization from benzene–hexane had m.p. 120.6–121.6°.

Anal. Calcd. for $C_{11}H_{13}ON$: C, 75.41; H, 7.48. Found: C, 75.91; H, 7.53.

Cyclopropylcarbinylamine.—A solution of 27 g. (0.40 mole) of cyclopropyl cyanide[51] in 600 ml. of anhydrous ethanol[52] was treated with 46 g. (2.0 g.-atom) of sodium metal at such a rate as to maintain gentle refluxing of the solvent. After the sodium had dissolved, the solution was cooled and 240 ml. of 10 *N* hydrochloric acid added slowly. The precipitated sodium chloride was collected by filtration and washed with two portions of 95% ethanol. The filtrate and washings were combined and evaporated under reduced pressure on a steam cone. The residue was made up to 100 ml. with water and 27 ml. of the solution was used to make N-cyclopropylcarbinylbenzamide as described above for N-cyclobutylbenzamide. The yield of N-cyclopropylcarbinylbenzamide was 17.7 g. (94%); m.p. 67–70°, after evaporative distillation at 0.9–1.5 mm. Sublimation of a small sample gave material of m.p. 72.5–74.5° (lit.[25] 74–75°).

The remainder of the cyclopropylcarbinylamine hydrochloride solution was basified and steam-distilled into a receiver containing 28 ml. of 10 *N* hydrochloric acid. After 100 ml. of distillate had been collected, the solution was evaporated to dryness under reduced pressure on a steam cone. Benzene (50 ml.) was added, and the mixture again evaporated to dryness. The residue was taken up in 150 ml. of warm absolute ethanol, the solution filtered and the filtrate concentrated to 80 ml. Dry ether (50 ml.) was added and the mixture allowed to stand in a refrigerator for several hours. Three crops of **cyclopropylcarbinylamine hydrochloride** were obtained which amounted to 27.9 g. (89%) and had m.p. 203–204°. A small sample was recrystallized for analysis; m.p. 206–207.5°.

Anal. Calcd. for $C_4H_{10}NCl$: C, 44.65; H, 9.37. Found: C, 44.47; H, 9.23.

In one preparation, the free amine was isolated by treatment of the hydrochloride solution with potassium hydroxide and saturation with potassium carbonate. The crude product was dried over potassium hydroxide and distilled; b.p. 83.5°, n^{25}_{D} 1.4300 (lit.[53] b.p. 86°, n^{19}_{D} 1.4251).

Reactions of Amines with Nitrous Acid.—Similar procedures were used throughout and only the details of a single reaction will be given.

A. **Crotylamine.**—In a 500-ml. three-necked flask equipped with stirrer and a condenser set for downward distillation was placed an ice-cold solution of 9.3 g. (0.13 mole) of crotylamine in 50 ml. of water, 150 ml. of ice-cold 1 *N* perchloric acid and an ice-cold solution of 27.6 g. (0.40 mole) of sodium nitrite in 100 ml. of water. The stirrer was started, the solution was heated to boiling and the mixture distilled until about 50 ml. of distillate was collected. A Dry Ice-cooled trap was connected to the outlet of the receiver but no significant quantity of material was collected in the trap and it was concluded that no butadiene was formed in the reaction. The distillate was saturated with potassium carbonate and extracted with two 15-ml. portions of ether. The combined extracts were dried over magnesium sulfate, the ether distilled and the residue fractionated through a center-tube column.[37] The total yield of a mixture of α-methylallyl and crotyl alcohols was 5.8 g. (62%). The composition of the mixture as determined from the distillation and refractive index data was 53% α-methylallyl alcohol and 47% crotyl alcohol. The materials collected on the plateaus of the distillation curve had b.p. 98–99°, n^{25}_{D} 1.4120 (lit. for α-methylallyl alcohol,[16] b.p. 97°, n^{25}_{D} 1.4125) and b.p. 122–124°, n^{25}_{D} 1.4270 (lit. for *trans*-crotyl alcohol,[16] b.p. 121°, n^{25}_{D} 1.4270).

B. **α-Methylallylamine.**—From 10.5 g. (0.15 mole) of α-methylallylamine by a similar procedure was obtained 7.7 g. (73%) of a mixture of 69% α-methylallyl and 31% crotyl alcohols. The properties of the materials obtained on the distillation plateaus were in good agreement with those given above.

C. **Cyclopropylcarbinylamine.**—The cyclopropylcarbinylamine was generated from the hydrochloride (28 g., 0.26 mole) by shaking with freshly precipitated silver oxide prepared from 51 g. (0.30 mole) of silver nitrate and 12 g. (0.30 mole) of sodium hydroxide. The silver chloride was removed by filtration and the solution neutralized with 1 *N* perchloric acid. The procedure was not completely successful in that some silver chloride seemed to be carried along as an amine complex and precipitated on acidification with perchloric acid. The remainder of the procedure was similar to that used for crotylamine and 6.4 g. (35%) of a mixture of cyclobutanol and cyclopropylcarbinol of b.p. 57° (42 mm.) and n^{25}_{D} 1.4316 was obtained. Analysis of the mixture by its infrared spectrum indicated approximately 47% cyclobutanol, 48% cyclopropylcarbinol and 5% of allylcarbinol. No crotyl or α-methylallyl alcohol was detected.

D. **Cyclobutylamine.**—From 5.6 g. (0.08 mole) of cyclobutylamine was obtained 3.6 g. (64%) of alcohol mix-

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(46) O. Mumm and H. Richter, *Ber.*, **73**, 843 (1940).

(47) J. Krueger and M. Schwarcz, THIS JOURNAL, **63**, 2512 (1941).

(48) T. L. Davis and N. D. Constan, *ibid.*, **58**, 1800 (1936).

(49) N. Zelinsky and J. Gutt, *Ber.*, **40**, 4744 (1907).

(50) J. Cason and C. F. Allen, *J. Org. Chem.*, **14**, 1036 (1949).

(51) M. J. Schlatter, *Org. Syntheses*, **23**, 20 (1943).

(52) The ethanol was dried by the method of E. L. Smith, *J. Chem. Soc.*, 1288 (1927).

(53) P. Dalle, *Rec. trav. chim.*, **21**, 123 (1902).

ture in two fractions; 1.3 g., b.p. 124-126°, n^{25}D 1.4310 and 2.3 g., b.p. 126°, n^{25}D 1.4319. The infrared spectra indicated 12% allylcarbinol in the first fraction and none in the second. Approximately equal amounts of cyclobutanol and cyclopropylcarbinol were present in each and the calculated composition of the over-all mixture was 48% cyclopropylcarbinol, 48% cyclobutanol and 4% allylcarbinol. No crotyl or α-methylallyl alcohol was detected.

E. Allylcarbinylamine.—From 8.9 g. (0.12 mole) of allylcarbinylamine was obtained 5.1 g. (57%) of a mixture of alcohols; b.p. 100-126°, n^{25}D 1.4110-1.4300. The mixture was found from distillation, refractive index, infrared and hydrogenation data to contain approximately 18% α-methylallyl alcohol, 10% crotyl alcohol, 45% allylcarbinol, 13% cyclobutanol and 14% cyclopropylcarbinol.

Since particular interest was attached to the formation of cyclobutanol and cyclopropylcarbinol in the reaction, an attempt was made to identify these substances more positively than possible by infrared spectra. The latter fractions, which amounted to 2.0 g. and had b.p. 123-126°, n^{25}D 1.4290-1.4300, were shown by infrared and quantitative hydrogenation data to contain about 10% allylcarbinol, 20% crotyl alcohol, and 35% each of cyclobutanol and cyclopropylcarbinol. One and one-half grams of the combined material was converted to a mixture of N-phenylcarbamates with 2.5 g. of phenyl isocyanate. The crude mixture was dissolved in 25 ml. of methylene chloride and stirred at room temperature for an hour with a solution of 4 g. of sodium permanganate trihydrate in 50 ml. of water. The mixture was cooled, the manganese dioxide destroyed by passing in sulfur dioxide, the methylene chloride layer separated, washed with water, washed with dilute potassium hydroxide solution and dried over magnesium sulfate. The residue obtained after removal of the methylene chloride was shown by its infrared spectrum (Fig. 6) to consist of approximately equal amounts of cyclopropylcarbinyl and cyclobutyl N-phenylcarbamates. No unsaturated material was present. Fractional crystallization of the material yielded the pure cyclobutyl compound, m.p. 130.2-130.8° which did not depress the m.p. of material previously prepared.[17] Attempts to separate the pure cyclopropylcarbinyl derivative from the mixture by fractional crystallization from several solvents, fractional sublimation and chromatographic adsorption were uniformly unsuccessful and the identification of this material in the mixture rests on the infrared spectra.

Hydrolysis of Chlorides. A. Cyclobutyl Chloride.—A mixture of 3.0 g. (0.033 mole) of cyclobutyl chloride, 1.2 g. (0.016 mole) of lithium carbonate and 10 ml. of water was refluxed for 30 hours, then saturated with potassium carbonate and extracted with ether. The ether extracts were dried over magnesium sulfate, the ether was distilled and the residue fractionated through a center-tube column.[37] The yield of a mixture of alcohols having an infrared spectrum practically identical with the spectra of the cyclobutylamine and cyclopropylcarbinylamine-nitrous acid products was 0.69 g. (29%); b.p. 125-127°, n^{25}D 1.4295-1.4329.

B. Cyclopropylcarbinyl Chloride.—Since cyclopropylcarbinyl chloride was found to rearrange to cyclobutyl and allylcarbinyl chlorides on solvolysis, complication in the interpretation of the reaction products by extensive hydrolysis of the cyclobutyl chloride was avoided by carrying the reaction only to 80% of completion. Under these conditions only a few per cent. of cyclobutyl chloride should have been hydrolyzed because of its relatively slow hydrolysis reaction rate compared to cyclopropylcarbinyl chloride.

A mixture of 10.2 g. (0.113 mole) of cyclopropylcarbinyl chloride, 3.3 g. (0.045 mole) of lithium carbonate and 40 ml. of water was refluxed until the lithium carbonate dissolved. The reaction mixture was extracted continuously with methylene chloride, the methylene chloride extract dried over magnesium sulfate and the methylene chloride distilled. The residue was fractionated through a center-tube column[37] giving 0.13 g., b.p. 73.5-77°, n^{25}D 1.4238; 0.65 g., b.p. 77-84.5°, n^{25}D 1.4264, and 0.38 g., b.p. 84.5-85°, n^{25}D 1.4297, of unreacted chlorides as well as 4.5 g. (69%) of a mixture of alcohols, b.p. 42-43° (31 mm.), n^{25}D 1.4324, which was shown by its infrared spectrum to have approximately the same composition as the products of the cyclobutylamine and cyclopropylcarbinylamine-nitrous acid reactions. Analysis of the chloride fractions by means of their refractive indexes and infrared spectra indicated 45% allylcarbinyl chloride, 45% cyclobutyl chloride and 10% cyclopropylcarbinyl chloride. The infrared spectrum of the largest fraction clearly shows the presence of all three halides (*cf.* Fig. 1).

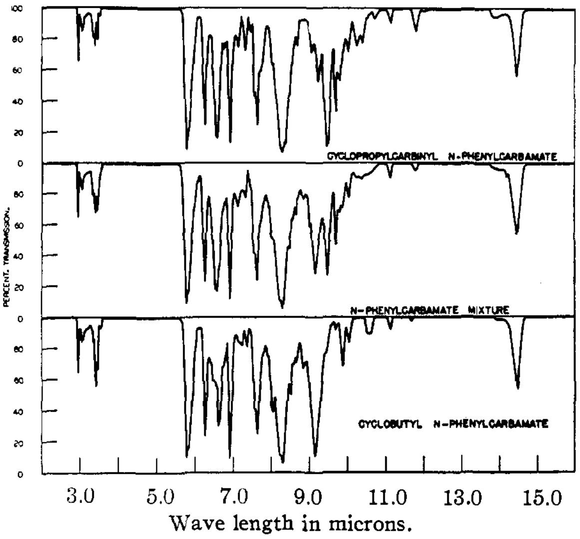

Fig. 6.—Infrared spectra: Baird spectrograph with NaCl prism, solutions of 50 mg. of compounds in 0.50 ml. of carbon disulfide except in the regions 4.2-4.0 μ and 6.2-7.2 μ where carbon tetrachloride was used as solvent.

C. Allylcarbinyl Chloride.—The reaction of allylcarbinyl chloride with water is extremely slow and an attempt was made to achieve a useful reaction rate by carrying out the reaction rate with silver carbonate instead of lithium carbonate. A reflux period of nine days was required for disappearance of the chloride layer. During the reaction a slight odor of 1,3-butadiene was apparent at the top of the reflux condenser and a silver mirror formed on the sides of the flask. A trace of starting material was the only organic product which could be isolated.

Reaction of Alcohols with Lucas Reagent.—The following experiment with cyclopropylcarbinol is illustrative of the procedure. Cyclopropylcarbinol (10.0 g., 0.14 mole) was added dropwise to 100 g. of ice-cooled stirred Lucas[54] reagent. An immiscible layer formed immediately. After the addition was complete the mixture was stirred at ice-bath temperature for an hour and then at room temperature for an additional hour. Ice water (100 ml.) was added, the upper layer was separated and the lower layer extracted with ether. The crude product and ethereal extracts were combined and dried over magnesium sulfate. After distillation of the ether the residue was distilled through a short Vigreux column. The yield of allylcarbinyl chloride, b.p. 75-75.4°, n^{25}D 1.4191, was 7.41 g. (59%). The only other products were high-boiling polymeric materials.

Cyclobutanol (2.54 g., 0.035 mole) was stirred with 25 g. of Lucas reagent at room temperature for two hours. The yield of allylcarbinyl chloride was 1.46 g. (46%); b.p. 75-76°, n^{25}D 1.4185.

Allylcarbinol did not appear to react with Lucas reagent at room temperature and, on heating, decomposition with formation of dark-colored products occurred.

Isomerization of Chlorides with Lucas Reagent.—Treatment of 11.0 g. of a mixture containing approximately 65% cyclopropylcarbinyl chloride and 35% cyclobutyl chloride with 80 g. of Lucas reagent for one hour at 0° and one hour at room temperature gave 5.1 g. (46%) of allylcarbinyl chloride; b.p. 75°, n^{25}D 1.4186.

With 2.8 g. of a similar mixture of cyclopropylcarbinyl and cyclobutyl chlorides and 2.8 g. of Lucas reagent and a reaction time of one hour at room temperature, there was obtained on fractionation through an efficient center-tube column[37] 0.62 g. of allylcarbinyl chloride, b.p. 77-78°, n^{25}D 1.4202 and 0.68 g. of material, b.p. 84-84.5°, n^{25}D 1.4329. Intermediate fractions amounted to 0.52 g., n^{25}D 1.4269. The material of b.p. 84-84.5° was shown by its infrared spectrum to contain 93% cyclobutyl chloride and 7% cyclopropylcarbinyl chloride.

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(54) H. J. Lucas, THIS JOURNAL, **52**, 802 (1930).

TABLE III

RESULTS OF EXCHANGE EXPERIMENTS USING Cl^{38}-CONTAINING LUCAS REAGENT AND ORGANIC CHLORIDES

Chloride	Wt., g.	G.-eq. of Cl	Layer	Elapsed time,[d] min.	Counts/ min.[e]	Counts/ min., cor. to zero time[f]	Fraction of layer counted[g]	Total counts/ min.	Calcd. total counts at exchange equilibrium	Exchange, %
Mixture of cyclopropylcarbinyl and cyclobutyl	6.36 LR[a]	0.077[c]	H_2O	0	4579	4579	0.420	10950	11200	107
	2.11 RCl[b]	.023	CH_2Cl_2	2.0	1618	1679	.452	3650	3400	
Allylcarbinyl	6.34 LR[a]	.077[c]	H_2O	3.5	5534	5905	.421	14100	11100	13
	2.19 RCl[b]	.024	CH_2Cl_2	5.0	212	233	.451	460	3500	
Blank	6.11 LR[a]	.074[c]	H_2O	7.0	4951	5637	.423	13300	13400	0.4
	.. RCl[b]	....	CH_2Cl_2	8.5	21	27	.500	54	...	

[a] LR = Lucas reagent. [b] RCl = organic chloride. [c] The Lucas reagent contained 0.0121 g.-eq. of Cl/g. [d] Elapsed time from beginning of counting period. [e] Corrected for background. [f] Using 37.4 min. for Cl^{38} half-life. [g] Calculated using d^{30} for Lucas reagent of 1.68, for cyclobutyl chloride of 0.99 and for allylcarbinyl chloride of 0.92.

Bromide Isomerizations with Zinc Bromide–Hydrobromic Acid Solutions.—The reagent was prepared by dissolving anhydrous zinc bromide in an equimolar amount of cold 48% hydrobromic acid. Isomerization of 2.0 g. of a mixture of about 2:1 cyclopropylcarbinyl and cyclobutyl bromides with 35 g. of zinc bromide–hydrobromic acid solution at 0° for one hour yielded 0.60 g. (29%) of bromides; b.p. 100–102° n^{25}D 1.4600. The infrared spectrum of the product (Fig. 2) indicates the product to contain about 30% of cyclobutyl bromide and 70% of allylcarbinyl bromide.

A similar experiment with 4.6 g. of the same bromide mixture and 25 g. of zinc bromide–hydrobromic acid solution at room temperature for one hour resulted in the formation of a bromide, b.p. 99–101°, n^{25}D 1.4600 which had an infrared spectrum which was identical with that of authentic allylcarbinyl bromide. The yield was 3.1 g. (67%).

Exchange Experiments Using Radioactive Chlorine (Cl^{38}).—One gram of potassium chloride was bombarded with deuterons in the M.I.T. cyclotron for ten minutes.[55] The target was allowed to stand for 30 minutes, and then the potassium chloride was transferred to an all-glass distillation apparatus. An excess of concentrated sulfuric acid was added and the resulting hydrogen chloride swept with a stream of carbon dioxide into a receiver containing 1 ml. of water. The radioactive hydrochloric acid so formed was then added to 30 g. of ordinary Lucas reagent.

The exchange reactions were carried out by stirring a halide sample with about three times its weight of radioactive Lucas reagent for one hour at room temperature. Twenty ml. each of water and methylene chloride was pipetted in, the mixtures shaken and the layers separated. The aqueous and methylene chloride layers were washed with methylene chloride and water, respectively, and the methylene chloride layer was dried over sodium sulfate. The washings were discarded. Ten-ml. aliquots were taken from each layer, placed in test-tubes and counted with a G–M counter at a standard distance. Appropriate corrections were made for the decay of the Cl^{38} (half-life, 37 min.) during the counting period.

A mixture of cyclopropylcarbinyl (~ 65%) and cyclobutyl (~ 35%) chlorides was used in one of the exchange experiments and under the conditions (1 part of chloride to 3 parts of Lucas reagent for one hour at room temperature) about 80% of the material was isomerized to allylcarbinyl chloride. In the other exchange experiment, allylcarbinyl chloride was used. The results along with those obtained in a blank are given in Table III.

Reaction of Cyclopropylcarbinol and Cyclobutanol with Thionyl Chloride.—The procedure was similar to that used for the preparation of allylcarbinyl chloride.

Cyclopropylcarbinol (15.0 g., 0.21 mole) with 24.8 g. (0.21 mole) of thionyl chloride yielded 13.7 g. (73%) of a mixture of chlorides, b.p. 84–86°, n^{25}D 1.4314–1.4324. Infrared spectra of the various fractions indicated the presence of 3% allylcarbinyl chloride, 67% cyclopropylcarbinyl chloride and 30% of cyclobutyl chloride. All of the allylcarbinyl chloride appeared in the first fraction which amounted to 2.08 g.

Treatment of the Grignard reagent prepared from a fraction containing no unsaturated material with phenyl isocyanate gave a mixture from which an anilide was isolated of m.p. 88.2–89.0° after crystallization from benzene–hexane. This material did not depress the m.p. of allylacetanilide.

A similar chloride mixture was obtained when equimolar amounts of pyridine, alcohol and thionyl chloride were used. Cyclobutanol (9.4 g., 0.13 mole) with 15.7 g. (0.13 mole) of thionyl chloride in the absence of pyridine gave 5.9 g. (50%) of chlorides, b.p. 83.5–84.8°. The infrared spectra of this material and that obtained in a similar preparation using an equimolar quantity of pyridine were almost identical with the spectrum of the products of the thionyl chloride–cyclopropylcarbinol reaction.

Reaction of Benzamides with Phosphorus Pentabromide. A. N-Cyclopropylcarbinylbenzamide.—A mixture of 32 g. (0.18 mole) of N-cyclopropylcarbinylbenzamide and 51.5 g. (0.19 mole) of phosphorus tribromide was warmed until the amide dissolved and then cooled to 0°. Bromine (30.4 g., 0.19 mole) was added dropwise with shaking to the ice-cooled mixture. The crude products were distilled from the reaction mixture into a Dry Ice-cooled trap under reduced pressure. The organic layer was decanted and fractionated. The yield of material, b.p. 104°, n^{25}D 1.4759 (lit.,[25] b.p. 106°) was 4.3 g. (17%). The product was shown to contain about 30% of cyclobutyl bromide by its infrared spectrum (Fig. 2). Treatment of the Grignard reagent from the bromide with phenyl isocyanate gave a mixture of anilides, m.p. 70–77°, which after several recrystallizations yielded allylacetanilide, m.p. 88.8–89.6°. Since the bromide was saturated to permanganate and cyclobutyl bromide yields cyclobutanecarboxyanilide in the Grignard reaction, the allylacetanilide must have been formed from cyclopropylcarbinyl bromide.

B. **N-Cyclobutylbenzamide.**—A similar reaction using 41 g. (0.23 mole) of N-cyclobutylbenzamide, 63.5 g. (0.23 mole) of phosphorus tribromide and 37 g. (0.23 mole) of bromine yielded 18.5 g. (59%) of bromide mixture, b.p. 106–108°; n^{25}D 1.4760–1.4784. The infrared spectrum of this material (Fig. 2) indicated somewhat more (about 40%) cyclobutyl bromide than was formed in the preceding reaction.

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(55) We are indebted to the M.I.T. cyclotron crew for the preparation and bombardment of the sample.