above the plane of the conjugated system, and that the α-C atom is the central part of the π system. The lithium resonance of benzyllithium, being only slightly upfield from inorganic lithium, might then follow if the C–Li interaction is presumed to be stronger[17] and the average lithium position (as indicated by Hückel charge density) is near the perimeter of the aromatic moiety.

It is noteworthy that the lithium resonance of triphenylmethyllithium is sharp like that of inorganic lithium and ethyllithium.[15] On the other hand the lithium resonances of diphenylmethyllithium and benzyllithium are extremely broad. A broad resonance line could arise through quadrupole broadening which requires the Li to be in an unsymmetrical electric field gradient,[9] or *via* a slow lithium exchange process.[14] A sharp resonance line can be indicative of a spherically symmetrical environment[15] or a more rapid lithium exchange. A study of these and other lithium resonances is in progress.

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[17] R. Waack and M. A. Doran, *J. Phys. Chem.*, **69**, 148 (1963), and subsequent paper: R. Waack and M. A. Doran, *J. Am. Chem. Soc.*, in press.

Carbanions. VIII. Products and Mechanisms of Reaction of Allyl- and Cyclopropyltrimethylammonium Halides and of Ally Chloride, Alcohol, and *p*-Tolyl Sulfide with Sodium in Liquid Ammonia[1]

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Abstract: Allyltrimethylammonium chloride and cyclopropyltrimethylammonium iodide are readily cleaved by sodium in liquid ammonia to hydrocarbons and tertiary amines. Whereas the relative rate of cleavage of the cyclopropyl group *vs.* the methyl group in cyclopropyltrimethylammonium iodide was variable with the mode of mixing of the reactants and the concentration of sodium employed, the relative rate of cleavage of the allyl group *vs.* the methyl group in allyltrimethylammonium chloride was invariable under similar conditions. These results indicate that allyl and methyl groups cleave from quaternary nitrogen by two-electron addition as carbanions while cyclopropyl groups cleave by one-electron addition as free radicals. Allyl chloride, allyltrimethylammonium chloride, and allyl *p*-tolyl sulfide react with sodium in liquid ammonia to produce, besides propylene, biallyl and a mixture of isomeric hexenes. With allyl alcohol propylene, but no biallyl or hexenes, is formed. If ammonium chloride is present during these cleavages, the yield of biallyl relative to propylene is greatly reduced and formation of hexenes is prevented. Hexenes appear to be produced by isomerization of biallyl by strong bases to conjugated dienes which in turn are reduced by sodium to hexenes. Reductive cleavage of the corresponding allyl-1-C^{14} compounds and of allyl-1,3-C^{14}-trimethylammonium chloride in presence of excess of an acid such as ammonium chloride gave propylene having $6.4 \pm 1.5\%$ greater radioactivity at C-1 than at C-3. These results are most simply interpreted on the basis of formation of a symmetrically solvated, kinetically free allyl anion. The distribution of carbon-14 in biallyl formed from reaction of allyl-1-C^{14} chloride with sodium in liquid ammonia is in agreement with formation of biallyl primarily through attack of allyl anion upon allyl chloride by the normal mechanism of bimolecular nucleophilic substitution (SN2).

In previous papers in this series[2] it was shown that quaternary ammonium halides of the type $R_n(CH_3)_{4-n}NX$ are rapidly cleaved by sodium in liquid ammonia at −33° to give hydrocarbons, RH and CH_4, and tertiary amines; in an accompanying reaction with sodamide, alkene and tertiary amine also are formed. The ratio of hydrocarbon (RH) to methane, after statistical correction for unequal numbers of groups, provides a convenient measure of the relative rates of cleavage of different groups from quaternary nitrogen. To account for the observed relative rates it was proposed that methyl and higher primary alkyl groups cleave from nitrogen as carbanions, by consecutive or simultaneous two-electron addition (eq 1), while secondary and tertiary alkyl groups predominantly cleave as free radicals, by one-electron addition (eq 2).

$$RZ + 2e^- \longrightarrow R:^- + :Z^- \qquad (1)$$

$$RZ + e^- \longrightarrow R\cdot + :Z^- \qquad (2)$$

The radicals then are reduced readily to carbanions and the latter, upon protonation by the solvent (or added acids), yield the observed hydrocarbons.

Although the contrary has sometimes been implied, it is not clear, *a priori*, that reductive cleavage of alcohols, ethers, sulfides, halides, quaternary ammonium salts, or like compounds (RZ) bearing identical alkyl or aryl groups (R) must proceed by similar mechanisms. In particular, cleavage by one-electron addi-

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[1] Abstracted in part from the following theses at the Georgia Institute of Technology: S. Chandra, Ph.D. Thesis, March 1961; C. E. Collum, M.S. Thesis, Sept 1964. These theses should be consulted for more complete experimental details.

[2] E. Grovenstein, Jr., and R. W. Stevenson, *J. Am. Chem. Soc.*, **81**, 4850 (1959); E. Grovenstein, Jr., and L. C. Rogers, *ibid.*, **86**, 854 (1964).

tion might also occur[3] to give a carbanion (eq 3).

$$RZ + e^- \longrightarrow R:^- + \cdot Z \qquad (3)$$

The course of the reaction should be determined not only by the relative stability of the group R as a carbanion or radical but also by the related stability of Z. A sufficient charge in the nature of Z (such as in the electronegativity of Z) might change the mechanism of reductive cleavage.

The present work was undertaken in order to deduce the mechanism of reductive cleavage of the allyl group from oxygen, sulfur, chlorine, and quaternary nitrogen by alkali metals in liquid ammonia solution. Allyl alcohol is reported to be cleaved by sodium in liquid ammonia to give about equal amounts of propylene and sodium allyloxide.[4] Diallyl sulfide is cleaved by sodium and lithium in liquid ammonia in presence of ammonium sulfate to yield allyl mercaptan (85–92%) and hydrogen sulfide (8–15%).[5] Allyl *t*-butyl sulfide with lithium in methylamine gives a mixture of *n*-propyl mercaptan (67%) and *t*-butyl mercaptan (33%).[6] Allyl chloride and bromide have been briefly reported to react with sodium in liquid ammonia to give "considerable quantities of biallyl."[7] Allyltrimethylammonium chloride is cleaved to propylene (22.3%), methane (6.4%), and trimethylamine (29.6%) by molten sodium in dioxane.[8]

While the detailed mechanism of reductive cleavage of most of these allyl derivatives is largely a matter of conjecture or dispute, Birch[9] has presented a fairly convincing argument for the cleavage of allylic alcohols by way of two-electron addition with cleavage as an allylic anion. His chief evidence was that alkyl groups at the α or γ position of allyl alcohol derivatives retard cleavage, that allylic rearrangements occur (*e.g.*, 1-vinylcyclohexanol yields ethylidenecyclohexane) as expected for the final product being formed by protonation of a mesomeric allylic anion, and that no dimerization products are produced (a fact which was regarded as providing "some evidence against the formation of radicals"). On the basis that the lithium–ethylamine reduction of (+)-*cis*-carvotanacetol methyl ether yields racemic *p*-menthene, Hallsworth, *et al.*,[10] have concluded that the reduction proceeds *via* a symmetrical intermediate, probably the mesomeric carbanion resulting from addition of two electrons to the ether; also the lithium–ethylamine reduction[10] of 4β-acetoxycholest-5-ene and of 6β-acetoxycholest-4-ene likely proceeds by a similar mechanism since this reduction gives about the same mixture (from either acetate) of cholest-4-ene and cholest-5-ene. The allyl compounds in the present investigation have in some experiments been labeled with carbon-14 at position 1 of the allyl group in order to deduce the symmetry of the intermediates and/or transition states in the reductive cleavages.

Results and Discussion

Products from Allyl Compounds under Various Reaction Conditions. Allyl chloride, allyltrimethylammonium chloride, and allyl *p*-tolyl sulfide were allowed to react with sodium in liquid ammonia solution under various reaction conditions and the products analyzed by vapor phase chromatography on a dimethylsulfolane column with the results shown in Table I. In addition to propylene, biallyl and hexenes were observed under some conditions. The source of the hexenes is of interest. Although unconjugated olefins are not ordinarily reduced by sodium in liquid ammonia,[11] the conjugated diolefin 2,4-hexadiene (of unspecified composition of geometrical isomers) has been reported[12] to be reduced by this reagent to a mixture of 2-hexene (~60–65%) and 3-hexene (~35–40%), each hexene being formed in a ratio of *cis/trans* isomers of about 30/70. It seems likely, therefore, that the hexenes in the present work are formed by reduction of conjugated hexadienes. The conjugated hexadienes are in turn likely formed by isomerization of biallyl by strong bases. In fact biallyl has been isomerized to 2,4-hexadiene by potassium amide[13] upon heating in liquid ammonia solution (detailed conditions not specified) and by calcium amide[14] upon heating in absence of solvent at reflux temperature.

To test for the feasibility of isomerization of biallyl and reduction under the conditions of the reductive cleavages of Table I, the experiments of Table II were performed.[15] In order to simulate as nearly as possible the general conditions of Table I, sodium amide was prepared *in situ* from sodium metal in presence of a little ferric nitrate, added to catalyze the conversion to sodium amide. At −33° in experiments 1 and 2 of Table II all of the possible hexadienes, save those having cumulative double bonds, were identified in the reaction product, though *trans,trans*- and *cis,trans*-2,4-hexadiene were most prevalent. Moreover considerable reduction to hexenes also was observed. In an experiment which was run like experiment 2 of Table II but with potassium in place of sodium, similar products of reduction and isomerization were obtained and the most striking difference was that only 2.5% of the recovered hydrocarbon was biallyl. When, however, ammonium chloride was added to destroy potassium amide before evaporation of the liquid ammonia, 87% of the recovered hydrocarbon was biallyl. These results show that potassium amide is a somewhat more effective catalyst than sodium amide doubtlessly because of the greater solubility[16] and more highly dissociated character[17] of potassium amide than of sodium amide in liquid ammonia. Also these data indicate that most of the isomerization with potassium amide (and likely also with sodium amide) took place at the higher concentrations and higher temperatures which

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(3) Such possibilities have also been briefly considered by H. E. Zimmerman, *Tetrahedron*, **16**, 175 (1961).

(4) E. Chablay, *Ann. Chim.* (Paris), [9] **8**, 188 (1917); *Compt. Rend.*, **143**, 123 (1906).

(5) R. C. Krug and S. Tocker, *J. Org. Chem.*, **20**, 1 (1955).

(6) W. E. Truce and J. J. Breiter, *J. Am. Chem. Soc.*, **84**, 1621 (1962).

(7) A. Beverloo, M. C. Dieleman, K. S. deVries, and B. M. Wepster, *Konikl. Ned. Akad. Wetenschap., Proc. Ser. B*, **59**, 445 (1956).

(8) E. Grovenstein, Jr., E. P. Blanchard, Jr., D. A. Gordon, and R. W. Stevenson, *J. Am. Chem. Soc.*, **81**, 4842 (1959).

(9) A. J. Birch, *Quart. Rev.* (London), **4**, 69 (1950).

(10) A. S. Hallsworth, H. B. Henbest, and T. J. Wrigley, *J. Chem. Soc.*, 1969 (1957).

(11) See H. Greenfield, A. A. Friedel, and M. Orchin, *J. Am. Chem. Soc.*, **76**, 1258 (1954), and references therein.

(12) R. Ya. Levina, V. R. Skvarchenko, V. M. Tatevsky, and E. G. Treshchova, *J. Gen. Chem. USSR*, **20**, 721 (1950).

(13) A. I. Shatenshteĭn, L. N. Vasil'eva, and N. M. Dykhno, *Zh. Fiz. Khim.*, **28**, 193 (1954); *Chem. Abstr.*, **49**, 59366 (1955).

(14) I. V. Gostunskaya and B. A. Kazansky, *J. Gen. Chem. USSR*, **25**, 1943 (1955).

(15) We are indebted to Mr. Stephen Peng for the preliminary experiments on isomerization of biallyl and for preparation of 1,4-hexadiene.

(16) F. W. Bergstrom and W. C. Fernelius, *Chem. Rev.*, **20**, 413 (1937); **12**, 43 (1933).

(17) W. W. Hawes, *J. Am. Chem. Soc.*, **55**, 4422 (1933).

Table I. Products from Various Allyl Compounds with Sodium in Liquid Ammonia Solution[a]

Allyl compd, mmoles	Sodium, mg-atoms	NH_4Cl,[d] mmoles	Temp, °C	Yield of products, %[b] Propylene	Biallyl	Hexenes[c] A	B
			Allyl Chloride				
10.0	15.0	None	−72	11.0	57	11	1.9
10.0	15.0	30.0	−72	31.0	6.1	None[e]	None[e]
36.8[f]	60.2	63[g]	−72	. . .[h]	65	6.9	1.1[i]
			Allyltrimethylammonium Chloride				
7.1	21.3	None	−33	86	3.9	2.4	0.3
6.4	19.6	None	−72	72	9.5	2.7	0.6
7.1	23.4	32.0	−33	58	2.2	None[e]	None[e]
			Allyl *p*-Tolyl Sulfide				
6.1	15.2	None	−33	85[j]	6.0	1.4	0.2
			Allyl Alcohol				
10.0	23.5	None	−33	47	None[e]	None[e]	None[e]

[a] The volume of liquid ammonia used was 50 ± 10 ml unless otherwise specified. [b] The yields are calculated on the basis of the amount of allyl compound taken for reaction. [c] Hexene B was *cis*-2-hexene; hexene A was a mixture of the remaining hexenes but contained little, if any, 1-hexene. [d] The ammonium chloride was added prior to addition of sodium unless otherwise specified. [e] The yield of this product, if any, was less than 0.3%. [f] The volume of liquid ammonia used was 100 ± 5 ml. [g] The ammonium chloride was added *after* completion of the reaction with sodium. [h] Yield not determined. [i] In addition 2,4-hexadienes were observed in a combined yield of about 2%. [j] A small amount of propane, 0.9%, was also produced in this reaction.

Table II. Isomerization of Biallyl in Liquid Ammonia Solution[a]

Expt no.	Biallyl, mmoles	Na, mg-atoms	$Fe(NO_3)_3 \cdot 9H_2O$, mmoles	NH_4Cl, mmoles	Temp, °C	Time,[c] hr	Product composition,[d] % Biallyl	Hexenes[b] A	B	Hexadienes[b,g] C	D	E	F	G	H
1[e]	3.6	5.1	0.0061	None	−33	3.3	38	21	4.1	0.01	0.02	0.57	16	18	2.1
2[f]	2.5	4.3	0.0036	None	−33	4	12	3.0	0.6	0.0	0.0	0.7	40	41	3.3
3	11.8[j]	31.2	0.020[h]	36.8	−72	11[i]	99	0.36	0.03	0.0	0.0	0.0	0.0	0.0	0.0

[a] The volume of liquid ammonia used in each run was 50 ± 5 ml. [b] The hexenes are: B, *cis*-2-hexene; A, the remaining hexenes but with little or no 1-hexene. The hexadienes are: C, *trans*-1,4-hexadiene; D, *cis*-1,4-hexadiene; E, both *cis*- and *trans*-1,3-hexadiene; F, *trans*,-*trans*-2,4-hexadiene; G, *cis*,*trans*-2,4-hexadiene; H, *cis*,*cis*-2,4-hexadiene. [c] After the reactions were allowed to proceed with stirring for the recorded time, the liquid ammonia was allowed to evaporate over a period of 2 to 3 hr. [d] The products recovered accounted for about 84% of the starting biallyl. [e] The solution changed from the deep blue color of sodium to red after some 2 hr. [f] The blue color of sodium disappeared in 25 min and the solution then slowly acquired a deep red color. [g] The number 0.0 means less than 0,1%, if any, was present. [h] Added in three portions after 0, 2.5, and 3.5 hr. [i] Stirring was continued at −72° for 4.6 hr; the still dark blue solution was stored for the remaining time without stirring at −72 to −78°. The now pale yellow solution, was then decomposed with addition of the ammonium chloride before evaporation of the ammonia. [j] About 3.8 mmoles of biallyl will dissolve in 50 ml of ammonia at −72°.

developed during evaporation of the liquid ammonia. It is not surprising, therefore, that in experiment 3 of Table II, which was run at −72° for 11 hr before addition of excess ammonium chloride and allowing the solution to warm to its boiling point, at least 99% of the recovered hydrocarbon consisted of biallyl.

If sodium amide is an ineffective agent in isomerization of biallyl at −72°, then it is at first hand surprising that 10% yield of hexenes and isomers of biallyl were obtained in the third run with allyl chloride in Table I where excess ammonium chloride was added to the reaction mixture at −72° some 20 min after addition of sodium metal. Moreover ammonium chloride was demonstrated to be effective in destroying the reagent responsible for the isomerization since in the two runs in Table I in which excess ammonium chloride was present throughout the reaction with sodium no hexenes were observed. It is postulated that the powerful reagent which isomerizes biallyl even at −72° is allylsodium.

In summary the following reactions are suggested to account for the products of Table I; in principle eq 6, 7, and 8 in addition to 9 are reversible. The detailed mechanism whereby 1,3- and 2,4-hexadienes are reduced to hexenes will not be considered here. It is thought that eq 6 is the slow step in the isomerization of biallyl to conjugated dienes and that the chief, and, at −72°, probably sole effective base (B:⁻) is allylsodium. The ionization of eq 8 probably can be brought about by weaker bases such as sodium amide. The ion (I) in eq 9 which upon protonation gives 1,3- and 2,4-hexadienes is thought to be responsible for the red color of many of the final liquid ammonia solutions of Table II.

$$CH_2{=}CH{-}CH_2Z + 2e^- \longrightarrow (CH_2{\overset{\cdots}{-}}CH{\overset{\cdots}{-}}CH_2)^- + Z^- \quad (4)$$

$$(CH_2{\overset{\cdots}{-}}CH{\overset{\cdots}{-}}CH_2)^- + CH_2{=}CH{-}CH_2Z \longrightarrow CH_2{=}CHCH_2CH_2CH{=}CH_2 + Z^- \quad (5)$$

$$CH_2{=}CHCH_2CH_2CH{=}CH_2 + B{:}^- \longrightarrow (CH_2{\overset{\cdots}{-}}CH{\overset{\cdots}{-}}CHCH_2CH{=}CH_2)^- + BH \quad (6)$$

$$(CH_2{\overset{\cdots}{-}}CH{\overset{\cdots}{-}}CHCH_2CH{=}CH_2)^- + NH_3 \longrightarrow CH_3{-}CH{=}CH{-}CH_2CH{=}CH_2 + {}^-NH_2 \quad (7)$$

$$CH_3{-}CH{=}CHCH_2CH{=}CH_2 + B{:}^- \longrightarrow (CH_3CH{\overset{\cdots}{-}}CH{\overset{\cdots}{-}}CH{\overset{\cdots}{-}}CH{\overset{\cdots}{-}}CH_2)^- + BH \quad (8)$$

$$\underset{\mathbf{I}}{(CH_3CH{\overset{\cdots}{-}}CH{\overset{\cdots}{-}}CH{\overset{\cdots}{-}}CH{\overset{\cdots}{-}}CH_2)^-} + NH_3 \rightleftharpoons NH_2^- + CH_3CH_2CH{=}CHCH{=}CH_2 \text{ and } CH_3CH{=}CHCH{=}CHCH_3 \quad (9)$$

The influence of ammonium chloride on the product composition from the cleavage reactions can be interpreted on the basis of the above equations and the additional eq 10 and 11. The yield of all organic

Table III. Reaction of Allyltrimethylammonium Chloride with Sodium in Liquid Ammonia at −33°

Sodium, mg-atoms	Quaternary salt, mmoles	Yield of products,[d] % Methane	Propylene	Biallyl	Hexenes[e]	Molar ratio[a] $(C_3H_6 + C_6H_{12} + C_6H_{10})/CH_4$
		Sodium Metal (Solid) Added to Solution of Quaternary Salt in Liquid Ammonia				
3.67	1.65	0.034	67.5	3.6	0.5	2040
4.90	2.11	0.029	65.4	3.0	1.2	2320
7.39[c]	1.72	0.030	77.8	3.9	1.2	2680
		Crystalline Quaternary Salt Added to Solution of Sodium in Liquid Ammonia				
7.16	1.30	0.046	74.6	2.2	0.4	1650
6.11[c]	1.93	0.037	82.1	...[b]	...[b]	2220
33.9	1.57	0.045	74.2	2.5	0.6	1680
140	2.35	0.048	73.9	5.5	0.3	1600
						2000 ± 300

[a] Calculated as the yield of propylene plus one half the combined yields of biallyl and hexenes all divided by the yield of methane. [b] Yield not determined. [c] Run in 50 ml of liquid ammonia; in other runs 100 ml of liquid ammonia was used. [d] The likely errors are propylene, ±1%; methane, ±10%; biallyl and hexenes, ±10% of the recorded values. [e] The hexenes are identified as chiefly 2- and 3-hexenes.

$$(CH_2{\cdots}CH{\cdots}CH_2)^- + NH_4^+ \longrightarrow CH_2{=}CH{-}CH_3 + NH_3 \quad (10)$$

$$2NH_4^+ + Na \longrightarrow H_2 + 2NH_3 + 2Na^+ \quad (11)$$

products is lower in presence of ammonium ion because of loss of sodium by reaction with ammonium ion (eq 11); however, the *relative* yield of propylene to biallyl plus hexenes is *larger* in presence of ammonium ion. This result is interpreted on the basis that ammonium ion readily and irreversibly protonates allyl anion (eq 10) before extensive reaction with allylic starting material can occur to give biallyl (eq 5). For the same reason and because the yield of biallyl is so low in presence of ammonium ion, subsequent isomerization of biallyl by allyl anion is negligible.

The yield of biallyl varies in an interesting manner with the nature of the group Z in the allyl compound, $CH_2{=}CHCH_2Z$. Allyl alcohol with lithium or sodium metal in liquid ammonia at −33° gave propylene, but no biallyl or hexenes; in addition with lithium, but not sodium, about one part of propane to three parts of propylene was obtained.[18] Allyltrimethylammonium chloride and allyl *p*-tolyl sulfide gave small amounts of biallyl and hexenes, while allyl chloride gave chiefly biallyl and hexenes (see Table I). Thus the yield of biallyl (and hexenes derived therefrom) increases with the expected increase in SN2 reactivity of the starting allyl compound just as would be expected if biallyl resulted from SN2 attack of allyl anion upon the allylic compound (eq 5).

While the products from the present reductive cleavages can be satisfactorily accounted for by eq 4–11, it must be borne in mind that a rigorous mechanistic argument has not been presented for all of the reactions. Additional evidence will be presented in the discussion which follows.

Relative Rate of Cleavage of Allyl and Methyl Groups from Allyltrimethylammonium Chloride. This quaternary salt was found to be readily soluble in liquid ammonia. In the first three reactions recorded in Table III, solutions of the quaternary salt were allowed to react with sodium metal by addition of small pieces of the metal to the solution; in all other runs, crystalline quaternary salt was added to the deep blue solutions of sodium in liquid ammonia. In either case reaction was extremely rapid and almost violent. The hydrocarbon products were identified qualitatively and quantitatively by vapor phase chromatography as chiefly propylene, some biallyl, and traces of 2- and 3-hexene and methane. In other runs qualitative identification of propylene was made by infrared spectroscopy, and quantitative measurements at 5.98 μ revealed comparable yields of propylene.

The quantity of greatest interest in the present table is the relative rate of cleavage of allyl and methyl groups from quaternary nitrogen. This quantity is approximately given by the ratio of the per cent yield of propylene to that of methane. Since, as is indicated by other work, biallyl apparently results from combination of allyl carbanion with allyltrimethylammonium ion and the hexenes come from isomerization of biallyl followed by reduction, each mole of biallyl and hexene comes by way of reductive cleavage of 1 mole of allylmethylammonium ion. The molar ratio of propylene plus biallyl plus hexene to methane, therefore, corresponds to the relative rate of cleavage of allyl *vs.* methyl. This ratio is given in the right-hand column of Table III and has an average value of 2000 ± 300. The ratio appears, within these limits of error, to be independent of the concentration of sodium. Such a result is to be expected if both methyl and allyl groups cleave from quaternary nitrogen by the same mechanism. Since methyl appears to cleave as a carbanion,[2] the present results imply that allyl also cleaves from quaternary nitrogen as a carbanion. This argument is strengthened (see below) by contrary results obtained with cyclopropyltrimethylammonium ion. The present argument, while strongly suggestive, is not as firm as might be desired since the yield of methane is so low that it might have come from a trace impurity or a minor side reaction.

The high selectivity in cleavage of the allyl group is striking. After statistical correction for unequal numbers of groups, allyl is seen to cleave 6000 ± 900 times faster than methyl. Thus allyl cleaves almost as readily from quaternary nitrogen as does the 2,2,2-triphenylethyl group[2] and a vinyl group is, therefore, about as effective as a triphenylmethyl group in promoting cleavage. Both the inductive and mesomeric effect of the vinyl group should stabilize the transition state for cleavage of allyl as an anion.

Relative Rate of Cleavage of Cyclopropyl and Methyl Groups from Cyclopropyltrimethylammonium Iodide.

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(18) We are indebted to Mr. Lynn C. Rogers for this study of the reaction of allyl alcohol with alkali metals and for the reaction of allyl *p*-tolyl sulfide given in Table I.

The reductive cleavage of cyclopropyltrimethylammonium ion was studied for comparison with isomeric allyltrimethylammonium ion. Cyclopropyltrimethylammonium iodide was found to be completely soluble in liquid ammonia at the concentrations used in the present work. Reactions with sodium in liquid ammonia were run according to the two modes of addition used for allyltrimethylammonium chloride. The products were identified qualitatively and quantitatively by vapor phase chromatography and are reported in Table IV. The only major hydrocarbons found were cyclopropane and methane; minor amounts of propane (0.12%) and propylene (0.019%) were identified in the first reaction recorded in the table and presumably were formed also in the other reactions. The significance of these minor hydrocarbons is open to question, but in any event the results rule out any appreciable isomerization of cyclopropyl anion or free radical to allyl anion or free radical under the conditions of the present experiment.

Table IV. Reaction of Cyclopropyltrimethylammonium Iodide with Sodium in Liquid Ammonia at −33°

Sodium, mg-atoms	Quaternary salt, mmoles	Yield of product, % Cyclopropane	Yield of product, % Methane	Molar ratio C_3H_6/CH_4
Sodium Metal (Solid) Added to Solution of Quaternary Salt in Liquid Ammonia				
3.07	1.00	66.0 ± 0.7	12.0 ± 0.6	5.5 ± 0.3
5.00	1.07	(16.0 ± 0.8)[a]	(2.69 ± 0.3)[a]	6.0 ± 1.0
9.36	1.53	61.0 ± 1.2	15.6 ± 0.8	3.9 ± 0.3
Crystalline Quaternary Salt Added to Solution of Sodium in Liquid Ammonia				
6.86	1.27	46.8 ± 0.5	27.4 ± 0.8	1.71 ± 0.07
9.55	1.61	48.7 ± 1.0	30.7 ± 0.9	1.58 ± 0.08
21.2	1.52[b]	39.1 ± 1.2	42.3 ± 0.5	0.92 ± 0.03

[a] The products were diluted with air to an unknown extent before analysis; therefore, only the relative yield of cyclopropane to methane is of significance. [b] This run was in 65 ml of liquid ammonia; in all other runs 50 ml of ammonia was used as solvent.

The ratio of cyclopropane to methane is given in the right-hand column of Table IV. Surprisingly this ratio is found to vary with the mode of mixing of the reactants. In the first mode of addition (sodium metal added to a solution of the quaternary salt) the ratio was somewhat irregular; however, the ratio was always higher by this mode than by the second mode (quaternary salt added to a solution of sodium). The ratio of cyclopropane to methane formed by the second mode of addition decreased regularly as the concentration of sodium metal increased. Since the effective concentration of sodium metal in the first mode of addition is likely lower than the corresponding concentration in the second mode, all the results in Table IV are summarized by the conclusion that the ratio of cyclopropane to methane decreases as the concentration of sodium in the liquid ammonia solution increases. Because of the hetereogeneous nature of the present reactions, a more exact statement concerning the variation of this ratio with the concentration of sodium cannot be made.[19]

The observed variation in the ratio of cyclopropane to methane with sodium concentration can be explained by the mechanisms (eq 1 and 2) presented earlier if it is assumed that cyclopropyl cleaves from quaternary nitrogen as a free radical while methyl cleaves as a carbanion. If in liquid ammonia solution the effective concentration of electrons can be equated to the stoichiometric concentration of sodium[20] [Na], then the rate of cleavage of cyclopropyl and methyl groups is likely given by the equations

$$d[C_3H_6]/dt = k_c[Na][C_3H_5N(CH_3)_3^+] \tag{12}$$

$$d[CH_4]/dt = k_m[Na]^2[C_3H_5N(CH_3)_3^+] \tag{13}$$

where the symbols enclosed in brackets refer to the concentration of the species indicated and t is time. The ratio of cyclopropane to methane produced at any particular concentration of sodium is then given by the relation

$$d[C_3H_6]/d[CH_4] = k_c/k_m[Na] \tag{14}$$

Equation 14 is found to be in at least qualitative accord with the experimental results reported in Table IV. The present conclusion, that methyl cleaves from quaternary nitrogen by a process which is of higher kinetic order with respect to sodium concentration than cleavage of cyclopropyl, provides the first experimental confirmation of the view[2] that methyl cleaves as a carbanion according to the mechanism indicated by eq 1 rather than that of eq 3.

According to Table IV cyclopropyl cleaves some 15 ± 2 times more readily than methyl if statistical corrections are made for unequal numbers of groups and if the mode of mixing is that of addition of sodium metal to the liquid ammonia solution of the quaternary salt. By a similar technique isopropyl cleaves 0.14 and *sec*-butyl 0.44 times as readily as methyl.[2] Cyclopropyl, therefore, appears to cleave more readily than isopropyl or *sec*-butyl.[21] Since all three of these groups are believed to cleave as free radicals, the observed relative reactivities imply that cyclopropyl radical cleaves more readily from quaternary nitrogen than isopropyl or *sec*-butyl radical. This observation is at first hand surprising since the statistically corrected rate of attack of a CD_3 radical upon a secondary hydrogen atom of *n*-butane at 249° is some 29 times faster than upon a hydrogen atom of cyclopropane and this difference in reactivity should be greater still at −33° since the difference in reactivity is due almost entirely to a difference in energy of activation of 3.8 kcal/mole.[22] This apparent contradiction can be rationalized on the basis that the solvated electron in liquid ammonia solution should be a much better electron-donor "radical" than the CD_3 radical and moreover the cyclopropyl radical should be a better electron-acceptor radical than the *sec*-butyl radical (because of the ex-

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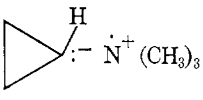
[19] It is obviously desirable to study this and related reactions under completely homogeneous conditions. We hope to be able to do this by use of flow techniques.

[20] In solutions of sodium as concentrated as the present this assumption and the accompanying argument are likely to be only qualitatively accurate because of the complex equilibria involved. For the nature of these equilibria see M. Gold, W. L. Jolly, and K. S. Pitzer, *J. Am. Chem. Soc.*, **84**, 2264 (1962).

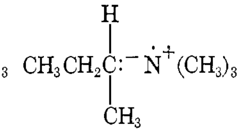
[21] Since these three groups appear to cleave as free radicals and methyl as a carbanion, then the rates of cleavage relative to methyl should be dependent on the effective concentration of sodium as is illustrated for cyclopropyl in Table IV. For reactions which are all run by the technique of adding solid sodium to a liquid ammonia solution of the quaternary salt, it is uncertain that the effective concentration of the sodium is the same from one salt to another and thus the present comparisons are probably only qualitatively meaningful.

[22] J. R. McNesby and A. S. Gordon, *J. Am. Chem. Soc.*, **79**, 825 (1957); **78**, 3570 (1956).

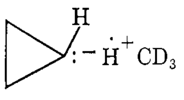
pected greater amount of s character in the orbital linking cyclopropyl[23] to nitrogen or hydrogen than in the corresponding orbital for *sec*-butyl). The change in relative rates of formation of *sec*-butyl and cyclopropyl radicals with the nature of the reaction therefore is attributable to a more favorable polar effect[24] for cleavage of cyclopropyl in the reaction with sodium in liquid ammonia than in the reaction with CD_3 radical. The arguments here are summarized by the statement that structures like II contribute more toward stabilization of the transition state for cleavage of cyclopropyl by electrons from sodium than structures like III in similar cleavage of *sec*-butyl or structures like IV in formation of cyclopropyl radical by attack of CD_3 radical upon cyclopropane.



II



III



IV

The present conclusion that cyclopropyl free radical is formed as an initial product of cleavage of cyclopropyltrimethylammonium ion by sodium in liquid ammonia receives some support from work in the related area of the mechanism of the formation of Grignard reagents where it was concluded, on the basis of optical activity studies,[25] that much or all of the reaction of 1-methyl-2,2-diphenylcyclopropyl halides with magnesium in ethereal solvents occurs by way of the 1-methyl-2,2-diphenylcyclopropyl radical, which is further reduced by magnesium metal to give the corresponding Grignard reagent.

As far as we are aware, the present work on cleavage of cyclopropyltrimethylammonium iodide constitutes the *first demonstration* that *product composition* in competitive reductive cleavages *can vary with the concentration of alkali metal employed* where two groups are cleaved by *different mechanisms.* This observation may account for some of the inconsistencies reported in the literature for relative ease of cleavage of some groups, especially secondary or tertiary alkyl groups *vs.* primary alkyl groups. Finally the demonstration of such variation of cleavage ratios with concentration of alkali metal would appear to be an *important criterion of reaction mechanism.*

Syntheses of Carbon-14-Labeled Reactants. Allyl-1-C^{14} alcohol was synthesized from radioactive sodium cyanide by a procedure similar to that of Leak.[26] Allyl-1-C^{14} chloride was synthesized from allyl-1-C^{14} alcohol by the procedure of Sharman, *et al.*,[27] and was converted into allyl-1-C^{14}-trimethylammonium chloride, containing only 1.2% of allyl-3-C^{14}-trimethylammonium chloride, by reaction with trimethylamine in acetone. Reaction of allyl-1-C^{14} alcohol with Lucas reagent gave allyl chloride which upon reaction with trimethylamine in acetone gave a product containing 50.8% allyl-1-C^{14}- and 49.2% allyl-3-C^{14}-trimethylammonium chloride. It is concluded from these results that reaction of allyl-1-C^{14} alcohol with Lucas reagent gives allyl chloride having its radioactivity distributed about equally at carbon 1 and carbon 3. Reaction of allyl-1-C^{14} chloride (containing 1.1% of allyl-3-C^{14} chloride) with the sodium salt of *p*-thiocresol in absolute alcohol at about −10° gave 33.4% of allyl-3-C^{14} and 66.6% of allyl-1-C^{14} *p*-tolyl sulfide. Since it was deemed desirable to have a sample of this sulfide which was more specifically labeled, the reaction was repeated in acetone as solvent at 20°. Under these conditions the product contained 3.8% of allyl-3-C^{14} and 96.2% of allyl-1-C^{14} *p*-tolyl sulfide. For the related reaction of sodium thiophenoxide with 3,3-dichloroprop-1-ene in ethanol, de la Mare and Vernon[28] have demonstrated that the reaction is second order with 38% of the thioether being of rearranged structure, *i.e.*, $PhSCH_2CH{=}CHCl$, formed by mechanism S_N2'. It seems likely that most of the allyl-3-C^{14} *p*-tolyl sulfide in our products is formed by mechanism S_N2'. However, de la Mare and Vernon[29] found that on going from 75% ethanol–25% water to 100% ethanol the amount of S_N2' reaction increased somewhat relative to the S_N2 reaction, while in our case on going from a more polar solvent (ethanol) to a less polar solvent (acetone) the amount of S_N2' reaction decreased relative to the S_N2 reaction. No simple theory of solvent effects seems able to account for these contrary results.

Distribution of Carbon-14 in Propylene from Cleavages in Presence of Excess Acid. Propylene from reductive cleavages of radioactive reactants was assayed for distribution of carbon-14 by ozonolysis in chloroform solution followed by reduction of the ozonide with zinc in aqueous acetic acid. The resulting formaldehyde and acetaldehyde were converted to their dimethone derivatives which were separated by a modification of the procedure of Vorländer.[30] The radiochemical assays upon propylene obtained from reductive cleavage of various allyl-C^{14} compounds in the presence of excess weak acids such as ammonium chloride, alcohols, or acetic acid are summarized in Table V.

The most striking qualitative observation concerning this table is that despite the diversity of allyl compounds, reducing agents (lithium, sodium, or zinc), solvents (liquid ammonia, isopropyl alcohol, or acetic acid), and temperatures (−78 to 50°), the propylene produced had almost equal radioactivity in its methylene and methyl groups as indicated by the molar activities of the formaldehyde and acetaldehyde derivatives.[31] Closer examination of the data in Table V reveals that in every instance the formaldehyde had a slightly greater activity than the corresponding acetaldehyde. The average value of the ratio of the molar activity of the formaldimethone to that of acetaldimethone anhydride from

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(23) See K. B. Wiberg, "Physical Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1964, pp 123–127.

(24) For a discussion of polar effects in free-radical reactions see J. Hine, "Physical Organic Chemistry," 2nd ed, McGraw-Hill Book Co., Inc., New York, N. Y., 1962, pp 420–434.

(25) H. M. Walborsky and A. E. Young, *J. Am. Chem. Soc.*, **86**, 3288 (1964).

(26) J. C. Leak, Ph.D. Thesis, University of Illinois, Urbana, Ill., 1954; *Dissertation Abstr.*, 14, 1543 (1954).

(27) S. H. Sharman, F. F. Casserio, R. F. Nystrom, J. C. Leak, and W. C. Young, *J. Am. Chem. Soc.*, 80, 5965 (1958).

(28) P. B. D. de la Mare and C. A. Vernon, *J. Chem. Soc.*, 3331 (1952).

(29) P. B. D. de la Mare and C. A. Vernon, *ibid.*, 3679 (1954).

(30) D. Vorländer, C. Ihle, and H. Volkholz, *Z. Anal. Chem.*, 77, 321 (1929).

(31) It will be assumed in the present paper that all of the activity of the acetaldehyde resides in the methyl group. It should be borne in mind that this is an unproved though reasonable assumption. Had the radioactivity become completely randomly distributed in the propylene, then the resultant acetaldehyde would have possessed twice the molar activity of the formaldehyde.

Table V. Distribution of Carbon-14 in Propylene from Cleavages in the Presence of Excess Acid

Allyl compd, mmoles	Metal, mg-atoms	Added reagent, mmoles	Solvent	Temp, °C	Propylene, % yield[a]	Formaldimethone,[b] molar activity = F (μcuries/mmole) $\times 10^4$	Acetaldimethone,[b,c] molar activity = A (μcuries/mmole) $\times 10^4$	Ratio[b] F/A
Allyl-1-C^{14}-trimethylammonium Chloride[d]								
7.16	Na, 23.0	NH$_4$Cl, 32.9	NH$_3$	−72	45	1857 ± 7	1779 ± 10	1.044 ± 0.010
5.09	Na, 18.9	CH$_3$OH, 22.3	NH$_3$	−33	58	1873 ± 22	1813 ± 44	1.033 ± 0.037
6.49	Li, 19.3	NH$_4$Cl, 23.8	NH$_3$	−78	44	1804 ± 34	1711 ± 11	1.054 ± 0.027
6.65	Li, 25.7	NH$_4$Cl, 32.7	NH$_3$	−33	...	1804 ± 6	1739 ± 9	1.037 ± 0.009
5.16	Na, 45.0	...	(CH$_3$)$_2$CHOH	28	...	1786 ± 10	1680 ± 26	1.063 ± 0.022
Allyl-1,3-C^{14}-trimethylammonium Chloride[f]								
7.08	Na, 23.4	NH$_4$Cl, 32.0	NH$_3$	−33	58	1795 ± 10	1711 ± 14	1.049 ± 0.014[h]
Allyl-1-C^{14} Alcohol[e]								
15.0	Li, 30.0	NH$_4$Cl, 40.0	NH$_3$	−33	28	1694 ± 6	1587 ± 3	1.067 ± 0.006
Allyl-1-C^{14} Chloride[g]								
8.00	Na, 23.0	NH$_4$Cl, 24.0	NH$_3$	−72	54	2050 ± 15	1902 ± 14	1.078 ± 0.016[h]
8.00	Zn, 21.4	NaI, 8.0	CH$_3$CO$_2$H	35-50	54	2028 ± 13	1887 ± 8	1.075 ± 0.011[h]
Allyl-1-C^{14} *p*-Tolyl Sulfide[i]								
7.32	Li, 22.9	NH$_4$Cl, 36.1	NH$_3$	−33	49	2076 ± 7	1976 ± 4	1.051 ± 0.006

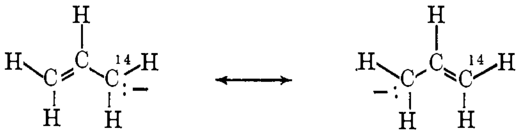
[a] Yields are based on the amount of starting allyl compound. [b] The number following the symbol ± is the average deviation of the reported value from the individual values. [c] Separated and assayed for radioactivity as the corresponding anhydride. [d] This sample of allyl-1-C^{14}-trimethylammonium chloride had an activity of 0.368 ± 0.004 μcurie/mmole and contained 1.2% of allyl-3-C^{14}-trimethylammonium chloride. [e] This sample of allyl-1-C^{14} alcohol had an activity of 0.334 ± 0.001 μcurie/mmole and contained 1.1% or less allyl-3-C^{14} alcohol. [f] This sample of allyl-1,3-C^{14}-trimethylammonium chloride had an activity of 0.3547 ± 0.0023 μcurie/mmole and consisted of 50.8% allyl-1-C^{14}- and 49.2% of allyl-3-C^{14}-trimethylammonium chloride. [g] The allyl-1-C^{14} chloride had an activity of 0.396 ± 0.004 μcurie/mmole and contained 1.1% of allyl-3-C^{14} chloride. [h] Allyl chloride and/or biallyl was removed from the propylene before ozonization by passing the gases back and forth through a U tube cooled in a bath at −49 to −60°. [i] The allyl-1-C^{14} *p*-tolyl sulfide had an activity of 0.406 ± 0.009 μcurie/mmole and contained 3.8% of allyl-3-C^{14} *p*-tolyl sulfide.

each sample of propylene for the ten reactions recorded is 1.055 ± 0.016. This ratio may show a slight variation with temperature, but the change is too small to be certain. All of the allyl compounds cleaved as reported in Table V were essentially pure allyl-1-C^{14} compounds save for the case of allyl-1,3-C^{14}-trimethylammonium chloride. It is of considerable interest that this allyl-1,3-C^{14}-trimethylammonium chloride gave propylene at −33° having about the same distribution of carbon-14, as exemplified by the ratio of activities of formaldehyde to acetaldehyde of 1.049 ± 0.014, as obtained on the average from the other compounds.

Before discussion of likely interpretations of these data, we will consider possible complications and sources of error. In the first place the possibility of rearrangement of products or reactants under the conditions of reductive cleavage needs to be considered. For the reactions reported with alkali metals in Table V, it is not thought that significant amounts of rearrangement are probable because of the short reaction times, the low temperatures, and especially the presence of excess weak acid (such as ammonium chloride) which should readily destroy any strongly basic catalysts (such as amide ion and allyl anion) which are produced. The possibility of rearrangements in the absence of excess acid will be taken up in the next section.

Another complication is the formation of biallyl in most of the present reactions. This complication was not appreciated until nearly all the reactions reported in the table were completed. Biallyl was formed in 2.2% yield in the reaction reported for allyl-1,3-C^{14}-trimethylammonium chloride in Table V. If comparable yields of biallyl relative to propylene are obtained in the other reactions with this quaternary salt, if all of this biallyl is present as a contaminant in the propylene, and if the biallyl has a distribution of carbon-14 such as that found in the biallyl from reaction of allyl-1-C^{14} chloride with sodium in liquid ammonia (see later section), it can be calculated that the ratio of the activity of formaldehyde to that of acetaldehyde will be reduced about 3%. About the same per cent reduction is estimated for the reaction of allyl-1-C^{14} *p*-tolyl sulfide in Table V. On the other hand no biallyl was found in the reaction of allyl alcohol with lithium, no appreciable amount of biallyl is expected for the reaction of allyl-1-C^{14}-trimethylammonium chloride with sodium in isopropyl alcohol as solvent, and for the reactions of allyl-1-C^{14} chloride and allyl-1,3-C^{14}-trimethylammonium chloride, the biallyl was removed before ozonization of the propylene. The average ratio of the activity of formaldehyde to that of acetaldehyde for these four reactions with sodium and lithium is 1.064 ± 0.015. The ratios for the other reactions reported in Table V are seen to be close to this average value if corrections of the order of magnitude estimated for presence of biallyl are applied.

The question now remains to be answered as to why propylene from all of these reductive cleavages contains the indicated distribution of carbon-14. An important preliminary conclusion is that addition of electrons with fission of bonds and addition of protons occur in separate and distinct steps. If this were not so, it would be hard to understand why cleavage of an unsymmetrical compound such as allyl-1-C^{14}-trimethylammonium ion could give an essentially even distribution of radioactivity at the ends of the allyl system in the product propylene. Moreover it would be even harder to understand why this distribution should remain constant in going from the quaternary salt to allyl alcohol, chloride, and *p*-tolyl sulfide. The obvious answer to the question, then, is that either an intermediate is formed of such symmetry that positions 1 and 3 of the allyl group become equivalent or else there is a dynamic equilibrium between unsymmetrical species which results in effective equilibration of the ends of the allylic system before protonation can occur. A likely symmetrical intermediate, which is suggested also by previous work, is the allyl anion V, for which the indicated delocalization of electrons brings about equivalence of the terminal methylene groups. Since, however, according to conductivity measurements,[32] sodium and lithium acetylides behave as comparatively weak electrolytes in liquid ammonia, it is possible that allyllithium and allylsodium in liquid ammonia solution exist as ion pairs or even covalent molecules. Indeed the nmr spectrum[33] of allyllithium in ethyl ether solution suggests that there is a very rapid equilibrium between two covalent forms such as VIa and VIb. In

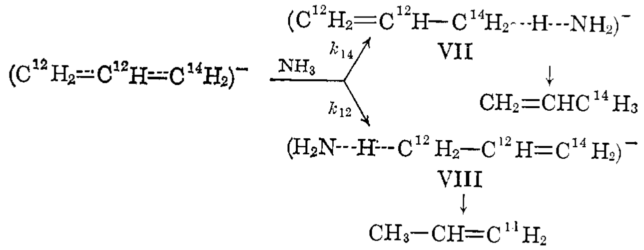

Va Vb

$$\underset{\text{VIa}}{CH_2{=}CH{-}C^{14}H_2M} \rightleftarrows \underset{\text{VIb}}{MCH_2{-}CH{=}C^{14}H_2} \qquad (15)$$

our opinion, the nmr spectrum does not exclude the simultaneous presence of some of the allyl anion V but this too must be in dynamic equilibrium with VIa and VIb. Such an equilibrium as expressed by eq 15 can account for the present carbon-14 distribution in the product propylene if it is assumed that the equilibrium is rapid compared to the rate of protonation. For simplicity and because lithium, sodium, and even zinc give propylene with the same carbon-14 distribution, and because liquid ammonia is a better ionizing solvent than ethyl ether, we prefer the interpretation involving the allyl anion.

It is to be noted that the allyl radical possesses the same symmetry as the allyl anion and cannot be excluded as an intermediate on the basis of the present tracer experiments; however, the previous results on the cleavage of allyltrimethylammonium ion by sodium in liquid ammonia strongly implied that allyl anion rather than allyl radical is the primary product from this reductive cleavage. Finally allyllithium can be synthesized by reaction of lithium metal with allyl bromide in ethyl ether[34a] or with allyl phenyl ether in tetrahydrofuran,[34b] and allylsodium by reaction of sodium with diallyl ether in hexane.[34c] It seems logical to infer, therefore, that allyllithium and allylsodium are formed in the present cleavages in liquid ammonia but are destroyed rapidly by protonation by ammonia or added acids to yield propylene.

Why does the terminal methylene group of propylene from the present reductive cleavages have a greater activity than the methyl group of the propylene? The possibility that a minor side reaction occurs with preferential protonation at the terminal methylene group of the allyl derivative is rendered unlikely by the very similar distribution in activity between allyl-1,3-C^{14}-trimethylammonium chloride and the various allyl-1-C^{14} compounds. The most likely explanation for the 6.4 ± 1.5% greater activity of the methylene than the methyl group of propylene is that an isotope effect of this magnitude exists in protonation of the allyl anion. Thus on protonation at the terminal positions allyl anion gives transition states which are approximately represented by structures VII and VIII. The double bond, $C^{12}{=}C^{14}$, in structure VIII is expected to be more stable than the double bond, $C^{12}{=}C^{12}$, in structure VII because bonds with heavier isotopes have lower zero point vibrational energies than those with lighter isotopes. Similarly the $C^{12}{-}C^{14}$ single bond of structure VII should be more stable than the $C^{12}{-}C^{12}$ single bond of structure VIII. However, the effect due to the double bond may reasonably be expected to outweigh the effect due to the single bond (because double bonds have larger force constants than single bonds of similar type) with the result that transition state VIII is slightly more stable than transition state VII and hence that k_{12} is slightly larger than k_{14} or the amount of propylene-1-C^{14} is slightly larger than the amount of propylene-3-C^{14}.



Finally the present results imply that allyl anions in liquid ammonia solution have sufficient lifetime to become symmetrically solvated before protonation occurs. With such a comparatively long-lived intermediate, other chemical reactions should be observable which could compete with protonation by the solvent ammonia. Two which have been observed in the present work are isomerization of biallyl promoted by allyl anion (see earlier discussion) and the reaction of allyl chloride with allyl anion to give biallyl (see especially later discussion).

Distribution of Carbon-14 in Propylene from Cleavages in Absence of Excess Acid. When reductive cleavages were run with sodium and lithium in liquid ammonia solution in absence of added acids, the propylene from allyl-1-C^{14} compounds generally gave a higher ratio of the activity of formaldimethone to that of acetaldimethone anhydride than was obtained in presence of excess acid and, moreover, this ratio was more erratic. The available data are reported in Table VI. The ratios from allyl-1-C^{14} *p*-tolyl sulfide and allyl-1-C^{14}-tri-

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(32) E. Masdupuy and F. Gallais, *Compt. Rend.*, **232**, 1935 (1951).

(33) C. S. Johnson, Jr., M. A. Weiner, J. S. Waugh, and D. Seyferth, *J. Am. Chem. Soc.*, **83**, 1306 (1961); however, an infrared study of Nujol mulls of allylic sodium, potassium, lithium, and magnesium compounds suggested that these were largely ionic: E. J. Lanpher, *ibid.*, **79**, 5578 (1957).

(34) (a) W. Kawai and S. Tsutsumi, *Nippon Kaguku Zasshi*, **81**, 109 (1960); *Chem. Abstr.*, **56**, 7339 (1962); (b) J. J. Eisch and A. M. Jacobs, *J. Org. Chem.*, **28**, 2145 (1963); (c) R. L. Letsinger and J. G. Traynham, *J. Am. Chem. Soc.*, 70, 3342 (1948).

Table VI.[a–i] Distribution of Carbon-14 in Propylene from Cleavages in Absence of Excess Acid

Allyl compd, mmoles	Metal, mg-atoms	Added reagent, mmoles	Solvent	Temp, °C	Propylene, % yield[a]	Formaldimethone,[b] molar activity = *F* (μcuries/mmole) × 10^4	Acetaldimethone,[b,c] molar activity = *A* (μcuries/mmole) × 10^4	Ratio[b] *F*/*A*
Allyl-1-C^{14}-trimethylammonium Chloride								
5.61[d]	Na, 14.2	. . .	NH_3	−33	70	1855 ± 27	1730 ± 22	1.072 ± 0.029
5.46[d]	Na, 15.2	$(NH_4)_2SO_4$, 2.9	NH_3	−33	40	1868 ± 9	1743 ± 16	1.072 ± 0.015
4.43[d]	Li, 25.7	. . .	NH_3	−33	64	1822 ± 15[j]	1642 ± 8[j]	1.110 ± 0.015
10.6[k]	Na, 17.5	KNH_2, 4.55[l]	NH_3	−72	. . .	2008 ± 23	1476 ± 20	1.360 ± 0.034[m]
Allyl-1-C^{14} Alcohol[e]								
10.0	Li, 18.6	. . .	NH_3	−33	50.6	1726 ± 16	1588 ± 5	1.087 ± 0.014
Allyl-1-C^{14} Chloride[n]								
27.1	Na, 49.5	. . .	NH_3[o]	−70	. . .	1866 ± 13	1825 ± 31	1.022 ± 0.025[m]
Allyl-1-C^{14} *p*-Tolyl Sulfide[i]								
6.1	Na, 15.2	. . .	NH_3	−33	64	2150 ± 26	1931 ± 23	1.113 ± 0.027
6.1	Li, 14.3	. . .	NH_3	−33	42	2184 ± 13	1722 ± 19	1.268 ± 0.022
7.3	Li, 15.7	. . .	NH_3	−33	57	2121 ± 6	1932 ± 12	1.098 ± 0.010

[a–i] The footnotes are the same as *a–i* for Table V. [j] The ionization chamber used was different from that used for assaying the starting quaternary salt. [k] The allyl-1-C^{14}-trimethylammonium chloride used in this run had a molar activity of 0.348 ± 0.004 μcurie/mmole and contained 1.2% of allyl-3-C^{14}-trimethylammonium chloride. [l] The quaternary ammonium salt was allowed to react with the KNH_2 for 27 min at −72° before addition of 4.90 mmoles of NH_4Cl to destroy any remaining KNH_2 before addition of sodium. [m] Biallyl was separated from propylene before ozonization by sweeping gases with He through a trap cooled with liquid nitrogen. [n] The allyl-1-C^{14} chloride was prepared from alcohol of activity 0.381 ± 0.007 μcurie/mmole and contained 1.2% of allyl-3-C^{14} chloride. In this run 25 min after completion of addition of sodium 54.2 mmoles of NH_4Cl was added before removal of the cooling bath. [o] The volume of liquid ammonia used was 100 ± 10 ml.

methylammonium chloride would possibly have been some 1 to 4% higher[35] than the recorded values had biallyl and hexenes been removed from the propylene before ozonization (these substances were removed from the propylene in the run with KNH_2). It is thought that those ratios in Table VI which are significantly higher than the value of 1.064 ± 0.015 obtained from analysis of Table V are high because of isomerization of allyl to propenyl compounds by strong bases prior to reductive cleavage. The likely reactions involved are summarized by eq 16–19. In

$$CH_2{=}CH{-}C^{14}H_2Z + B{:}^- \rightleftharpoons [CH_2\overset{\cdots}{-}CH\overset{\cdots}{-}C^{14}HZ]^- + B\text{-}H \quad (16)$$

$$[CH_2\overset{\cdots}{-}CH\overset{\cdots}{-}C^{14}HZ]^- + B{:}H \longrightarrow CH_3CH{=}C^{14}HZ + B{:}^- \quad (17)$$

$$CH_3CH{=}C^{14}HZ + 2e^- \longrightarrow CH_3CH{=}\underset{\cdot\cdot\,-}{C^{14}}H + {:}Z^- \quad (18)$$

$$CH_3CH{=}\underset{\cdot\cdot\,-}{C^{14}}H + NH_3 \longrightarrow CH_3CH{=}C^{14}H_2 + {:}NH_2^- \quad (19)$$

eq 16, $B{:}^-$ is a strong base such as the amide ion or allyl anion. For allyltrimethylammonium chloride the product of eq 16 is an ylide like that postulated as an intermediate[36] in the Stevens rearrangement of certain quaternary allylammonium salts brought about by sodium amide in liquid ammonia solution. This ylide on protonation can regenerate the starting allyl compound (reversal of eq 16) or give the isomeric propenyl compound (eq 17). Reductive cleavage of the propenyl compound gives a vinyl anion with localized charge (eq 18) which upon protonation gives propylene-1-C^{14} (eq 19).

As a test of this proposed mechanism allyl-1-C^{14}-trimethylammonium chloride was treated with about 0.4 equiv of potassium amide at −72° for 27 min and then the potassium amide was destroyed by ammonium chloride before reductive cleavage by sodium. The results (Table VI) show that the propylene produced gave a ratio of activity of formaldehyde to acetaldehyde considerably greater than that obtained from any of the other reductive cleavages of this quaternary salt, as expected for the proposed mechanism. It is of interest to note that Rothstein[37] states that allyltrimethylammonium halide and propenyltrimethylammonium halide are not interconverted in alkoxide solution. On the other hand, alkoxide ions have been reported to catalyze the rearrangement of allyl to propenyl ethers,[38a] allyl to propenyl sulfides,[38b] and 1-chloro-2-methylpropene-2 to 1-chloro-2-methylpropene-1.[38c] Whereas the reductive cleavage of alkyl vinyl ethers and of quaternary vinylammonium salts appears to be unknown, vinyl aryl sulfides[39a] and vinyl halides[39b] are readily cleaved by alkali metals in liquid ammonia solution.

Besides the complication that allyl compounds may be isomerized to propenyl prior to cleavage for reactions run in the absence of excess acid, there is also the possibility that the product, propylene, may suffer base-catalyzed rearrangement of the location of the carbon-14 label. Shatenshtein, *et al.*,[40] have studied the rate of exchange of hydrogen in propylene and other olefins for deuterium in deuterated ammonia containing potassium amide. Extrapolation of these results to the temperature and conditions of the present cleavages leads to the conclusion that hydrogen exchange upon

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(35) These estimates are made like the previous estimates for Table V with an added correction for presence of hexenes.

(36) H. Hellmann and G. M. Scheytt, *Ann.*, **654**, 39 (1962).

(37) E. Rothstein, *J. Chem. Soc.*, 1560 (1940).

(38) (a) T. J. Prosser, *J. Am. Chem. Soc.*, **83**, 1701 (1961); C. C. Price and W. H. Snyder, *ibid.*, **83**, 1773 (1961); (b) D. S. Tarbell and W. E. Lovett, *ibid.*, **78**, 2259 (1956); C. C. Price and W. H. Snyder, *J. Org. Chem.*, **27**, 4639 (1962); (c) M. Tanabe and R. A. Walsh, *J. Am. Chem. Soc.*, **85**, 3522 (1963).

(39) (a) W. E. Truce and J. J. Breitner, *ibid.*, **84**, 1623 (1962); (b) M. C. Hoff, K. W. Greenlee, and C. E. Board, *ibid.*, **73**, 3329 (1951).

(40) A. I. Shatenshtein, L. N. Vasil'eva, N. M. Dykhno, and E. A. Izrailevich, *Dokl. Akad. Nauk SSSR*, **85**, 381 (1952); *Chem. Abstr.*, **46**, 9954*d* (1952).

Table VII. Distribution of Carbon-14 in Biallyl from Allyl-1-C^{14} Chloride with Sodium in Liquid Ammonia Solution at −72°

		Allyl chloride				Biallyl		
			Molar activity, μcurie/mmole × 10^3			Molar activity, μcurie/mmole × 10^3		Ratio of molar activities, succinic acid/ allyl chloride
	Sodium,		Ozonization products[a]			Ozonization products[a]		
Run no.	mg-atoms	mmoles	CH_2O	CH_3CHO	Total activity	CH_2O	Succinic acid	
1	51.9	22.7	7.6 ± 0.2	. . .	242 ± 18[b]	. . .	364 ± 2	1.50 ± 0.12
2[d]	49.5	27.1	4.5 ± 0.2	. . .	381 ± 7[c]	142 ± 3	495 ± 9	1.30 ± 0.05
3	38.6	33.2	0.9 ± 0.1[e]	100.5 ± 1.0[e]	101.4 ± 1.1[f]	33.0 ± 0.5	140.0 ± 0.9	1.39 ± 0.02
4[g]	13.2	30.7	0.9 ± 0.1	100.5 ± 1.0	101.4 ± 1.1[f]	. . .	. . .	. . .
								Av 1.40 ± 0.07

[a] Formaldehyde and acetaldehyde were assayed as formaldimethone and acetaldimethone anhydride derivatives. [b] Based on assay of allyl-1-C^{14}-trimethylammonium chloride prepared from the present sample of allyl chloride. The uncertainty in activity arises chiefly from uncertainty in dilution of the sample before reaction with sodium. [c] Based on assay of the allyl-1-C^{14} alcohol which was used without further dilution in preparation of the allyl chloride. [d] Ozonization of the propylene produced in this run gave formaldimethone and acetaldimethone anhydride of activity of 187 ± 1 and 183 ± 3 × 10^{-3} μcurie/mmole, respectively. [e] The activity cited was determined upon another batch of allyl chloride (that of run no. 4) prepared from the same batch of allyl alcohol. [f] The total activity is calculated as the sum of the activities of the products of ozonization of allyl chloride. [g] The recovered, unreacted allyl chloride from this run gave after ozonization formaldimethone and acetaldimethone anhydride of activity 3.1 ± 0.1 and 91.0 ± 1.0 × 10^{-3} μcuries/mmole, respectively.

propylene as catalyzed by sodium and lithium amide is unlikely to be of importance in the present work; therefore, appreciable isomerization of propylene-1-C^{14} to propylene-3-C^{14} or *vice versa* by amide ion is also almost certainly not of importance either. The possibility that such isomerization may be promoted by allyl anions cannot be eliminated however, especially for reactions run near −70° where all the propylene produced remains until completion of the reaction.

Distribution of Carbon-14 in Biallyl from Allyl-1-C^{14} Chloride. The distribution of carbon-14 in biallyl formed during the present reactions was deemed of interest since it provides a criterion of reaction mechanism for formation of this Wurtz[41] coupling product in liquid ammonia solution. The distribution of carbon-14 was determined by ozonization of the biallyl, followed by reduction of a portion of the ozonide to give formaldehyde (isolated as formaldimethone) and oxidation of the remainder with hydrogen peroxide in formic acid solution to give succinic acid. According to the present analytical method, C-1 and C-6 of biallyl appear as formaldehyde and the remainder of the carbon atoms of biallyl appear as succinic acid as is shown in eq 20. For formation of biallyl by

$$CH_2{\vdots}{=}CHCH_2CH_2CH{=}{\vdots}CH_2 \xrightarrow{[O]}$$

$$CH_2O + HO_2CCH_2CH_2CO_2H + CH_2O \qquad (20)$$

combination of two allyl free radicals, in view of the expected symmetry of the allyl free radical, allyl-1-C^{14} chloride should lead to biallyl with carbon-14 evenly distributed at C-1, C-3, C-4, and C-6, or the resultant formaldehyde and succinic acid should have exactly one half and equal molar activity respectively to that of the starting allyl chloride. The same carbon-14 distribution would be obtained if biallyl were formed by the (unlikely) union of allyl cation with allyl anion. On the other hand if biallyl were formed by SN2 displacement of allyl anion upon allyl-1-C^{14} chloride, the product would consist of equal amounts of the two isotopically labeled biallyls shown in eq 21. The resultant formaldehyde and succinic acid would, therefore, have, respectively, 0.25 and 1.50 times the molar activity of the starting allyl-1-C^{14} chloride. If, however, biallyl were formed by an SN2′ displacement of allyl anion upon allyl chloride, the two isotopically labeled biallyls shown in eq 22 would be expected in equal amounts. The resultant formaldehyde and succinic acid would then have, respectively, 0.75 and 0.50 times the molar activity of the starting allyl-1-C^{14} chloride. Obviously a 50/50 mixture of reaction by mechanisms SN2 and SN2′ would lead to biallyl with the same distribution of radioactivity as expected for combination of free radicals. All of these estimates ignore isotope effects, assume that the starting material was pure allyl-1-C^{14} chloride uncontaminated by allyl-3-C^{14} chloride, and presume that the postulated allyl cation, radical, or anion is a kinetically free entity which reacts with equal velocity at either methylene group.

$$\begin{aligned}(CH_2{\overset{\dots}{=}}CH{\overset{\dots}{=}}C^{14}H_2)^- + CH_2{=}CH{-}C^{14}H_2Cl \longrightarrow&\\ CH_2{=}CH{-}C^{14}H_2C^{14}H_2CH{=}CH_2&\\ \text{and}&\qquad(21)\\ C^{14}H_2{=}CH{-}CH_2C^{14}H_2CH{=}CH_2&\end{aligned}$$

$$\begin{aligned}(CH_2{\overset{\dots}{=}}CH{\overset{\dots}{=}}C^{14}H_2)^- + CH_2{=}CH{-}C^{14}H_2Cl \longrightarrow&\\ CH_2{=}CH{-}C^{14}H_2CH_2{-}CH{=}C^{14}H_2&\\ \text{and}&\qquad(22)\\ C^{14}H_2{=}CH{-}CH_2CH_2{-}CH{=}C^{14}H_2&\end{aligned}$$

The available data on the distribution of carbon-14 in the product biallyl and in the starting allyl chloride is summarized in Table VII along with the average deviation of each molar activity. The activities of the products are in general agreement with the activity of the starting allyl chloride. For brevity we will consider only the ratio of activity of succinic acid to activity of starting allyl chloride in the following discussion; however, the same conclusion could be drawn from the independent measurement of the ratio of the activity of formaldimethone (from biallyl) to the activity of starting allyl chloride.

The measured ratio of the molar activity of succinic acid to the molar activity of the starting allyl chloride is given in the right-hand column of Table VII. The

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(41) For discussions of the mechanism of the Wurtz reaction see J. Hine, "Physical Organic Chemistry," 2nd ed, McGraw-Hill Book Co., Inc., New York, N. Y., 1962, pp 245,246; P. E. Verkade, K. S. de Vries, and B. M. Wepster, *Rec. Trav. Chim.*, **83**, 367 (1964); A. A. Morton, "Solid Organoalkali Metal Reagents, A New Chemical Theory for Ionic Aggregates," Gordon and Breach Science Publishers, New York, N. Y., 1964, pp 87–107.

average value of this ratio (1.40 ± 0.07) for the three runs reported is in close agreement with the most precisely measured value of run 3; however, there do appear to be small variations in this ratio from run to run which are outside of the range of expected experimental error. Before interpretation of the numerical value of the observed ratio, it is proper to inquire whether or not the starting allyl-1-C^{14} chloride and the product biallyl are stable toward isotope-position rearrangement under the conditions of reaction and product isolation. In run no. 4 enough sodium was added to combine with only some 43% of the starting allyl chloride. The unreacted allyl chloride was separated from the product biallyl by preparative vapor phase chromatography; however, the more difficult separation of allyl chloride from 2,4-hexadienes or propenyl-1-C^{14} chloride was evidently incomplete as judged by the low combined molar activities of the products of ozonization. Nevertheless these impurities should effect only the activity of the acetaldehyde resulting from ozonization. The activity of the formaldehyde increased from 0.9 to 3.1×10^{-3} μcurie/mmole; this small increase in activity indicates the maximum amount (2%) of isomerization of allyl-1-C^{14} chloride to allyl-3-C^{14} chloride which could have taken place during the reaction with sodium in liquid ammonia. Actually this small amount of isomerization may have occurred during isolation of the unreacted allyl chloride or the apparent isomerization may arise from some other cause such as failure to separate all of the diallyl from the unreacted allyl chloride. The important conclusion here is that little if any isomerization of allyl-1-C^{14} chloride occurs under the conditions of the present reaction with sodium in liquid ammonia.

The next question pertains to the stability of the product biallyl. While as discussed earlier biallyl is isomerized in part under the conditions of the present reaction, such isomerizations as have been observed involve shifting the location of double bonds but do not appear to involve skeletonal rearrangement. Although examples of skeletonal rearrangements of carbanions of hydrocarbons are known, such rearrangements are comparatively rare and do not appear to be likely under the conditions of the present experiments. To test the possibility of rearrangement during vapor phase chromatography, in run 3 of Table VII the crude biallyl was subjected to ozonolysis without prior purification by vapor phase chromatography. The impurities (chiefly hexenes and 2,4-hexadienes) which are expected to be present in the crude biallyl should not disturb the analysis by ozonization since, on the one hand, none of these can give succinic acid on oxidation and, on the other hand, those which yield formaldehyde should give formaldehyde of the same isotopic composition as biallyl. While the ratio of the molar activity of succinic acid/allyl chloride was somewhat higher in this run than in run 2, it agreed closely with the average of runs 1 and 2; moreover since it was demonstrated that allyl-1-C^{14} chloride could be put through the gas chromatographic apparatus under similar conditions without appreciable rearrangement of the location of carbon-14, it is believed that rearrangements did not occur under the conditions of the present experiments. In conclusion it is thought that little, if any, rearrangement of the carbon skeleton of biallyl occurred under the conditions of Table VII.

The results of Table VII and previous considerations lead to the conclusion that the majority of the biallyl in the present experiments is formed by the mechanism of S_N2 attack of allyl anion upon allyl chloride (eq 21). For run no. 3 since about 1% of the starting allyl chloride was allyl-3-C^{14} chloride, the expected ratio of molar activities of succinic acid/starting allyl chloride is 1.49; in addition, if 2% isomerization of allyl-1-C^{14} chloride to allyl-3-C^{14} chloride occurred before reaction (*cf.* run no. 4), the calculated ratio of activities is 1.47. Since previous work has shown that an isotope effect of 6.4 ± 1.5% exists during protonation of allyl anion (larger rate of protonation at C-12 than at C-14), it seems likely that an isotope effect of this order of magnitude exists also for allylation of allyl anion. If a 6% isotope effect is assumed along with 2% isomerization, the calculated ratio of molar activities of succinic acid/starting allyl chloride is 1.45. This calculated value is possibly to be regarded as in satisfactory agreement with the experimentally measured ratio. The experimental results, however, clearly do not exclude a small amount of biallyl formation by combination of allyl radicals or by the S_N2′ reaction of allyl anion upon allyl chloride (eq 22); thus if, in addition to 2% isomerization and 6% isotope effect, 6% of reaction occurs by mechanism S_N2′ the calculated ratio of molar activities of succinic acid/allyl chloride is 1.39. If the major path of biallyl formation is by mechanism S_N2, we think that it is more logical to assume that the remainder of the reaction is by the closely related mechanism S_N2′ rather by the entirely different route of coupling of free radicals.

In retrospect the present results are seen to be similar to those of Young, *et al.*,[42] who found that the sodium salt of allylbenzene (3-phenylallylsodium) reacts with α-methylallyl chloride and with γ-methylallyl chloride in liquid ammonia solution to give products of alkylation as expected for mechanism S_N2, while no products of alkylation by mechanism S_N2′ were detected. In contrast reaction of phenyllithium in ethyl ether solution with both α- and γ-methylallyl chloride gives substantially identical mixtures of crotylbenzene and α-methylallylbenzene from each of the two chlorides; these results were interpreted by Cristol and coworkers[43] in terms of a carbonium ion process.

Conclusion

All of the present reactions of allyl compounds with sodium in liquid ammonia solution can be explained without invoking the formation of allyl free radicals. Allyltrimethylammonium ion undergoes cleavage with sodium in liquid ammonia solution by the process of two-electron addition with direct cleavage of the allyl group from nitrogen as the allyl anion. It seems likely that allyl chloride under similar conditions is also directly cleaved to allyl anion without prior formation of allyl radical. The intermediate formed in reductive cleavage of various allyl-1-C^{14} compounds has the symmetry expected for a symmetrically solvated, kinetically free allyl anion. This intermediate in part

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[42] W. G. Young, M. Kosmin, R. Y. Mixer, and T. W. Campbell, *J. Am. Chem. Soc.*, 74, 608 (1952).

[43] S. J. Cristol, W. C. Overhults, and J. S. Meek, *ibid.*, 73, 813 (1951); see also S. E. Ulrich and J. F. Lane, *ibid.*, 72, 5130 (1950).

undergoes protonation by the solvent to give propylene and is alkylated by allyl chloride to give biallyl predominantly by mechanism S_N2.

While under the present conditions in liquid ammonia solution allyl chloride appears to react with sodium to give allyl anions but no appreciable amount of allyl radical, in the vapor phase sodium reacts with allyl chloride or other alkyl halides primarily with formation of allyl or alkyl free radicals.[44] This dichotomy of reaction mechanism should not be surprising since the reaction conditions are vastly different. An idea of the difference is provided by the ionization energy of gaseous sodium atoms which is 5.14 ev; in contrast dilute solutions of sodium in liquid ammonia are already ionized and the binding energy (heat of solution) of the electron in liquid ammonia is estimated[45] to be only 1.7 ± 0.7 ev. Chiefly for this reason and because the concentration of sodium in the liquid ammonia reactions is greater than in the vapor phase reactions (where the volatility of sodium limited the concentration[44] to about 10^{-7} *M*), electrons are much more readily available in the liquid ammonia reactions than in the vapor phase reactions. Two-electron reduction (to give carbanions) is expected to increase in rate relative to one-electron reduction (to give free radicals) in proportion to the availability of electrons. Also on proceeding from reactants to the transition state, charge is being more concentrated in the transition state for the process of two-electron reduction (eq 23) than that for one-electron reduction; therefore

$$\mathrm{R{:}Cl} + 2e^- \text{——} [\mathrm{R{:}^-\,^-{:}Cl}] \longrightarrow \mathrm{R{:}^-} + \mathrm{Cl^-} \qquad (23)$$

solvation should accelerate two-electron reduction more than one-electron reduction on going from the vapor phase into liquid ammonia solution.

An interesting question arises as to where electrons are added to a saturated alkyl halide during a reduction such as that of eq 23. The most obvious answer is that, in or near the transition state, the electrons are in an antibonding orbital, presumably the σ^* orbital between carbon and halogen.

Experimental Section

Vapor phase chromatography was performed on a Perkin-Elmer vapor fractometer, Model 154-C. Proton magnetic resonance spectra were obtained on a Varian Associates, Model A-60 spectrometer. Infrared spectra were measured with a Perkin-Elmer Model 21 spectrophotometer with rock salt prisms.

Reagents. Cyclopropyltrimethylammonium iodide, from K & K Laboratories, Inc., and allyltrimethylammonium chloride[8] were recrystallized from *t*-butyl alcohol and dried thoroughly *in vacuo* at 80 and 56°, respectively. Their purity was checked by Volhard titration. Propane, propylene, and cyclopropane were of 99.0% minimum purity and were most commonly from Matheson Co., Inc. Methane was Phillips Petroleum Co. research grade (99.5% purity). Biallyl (1,5-hexadiene) was from Columbia Organic Chemicals Co. and was of 99.8% minimum purity according to analysis by vapor phase chromatography. Hexene-1 and hexene-2 were from Matheson Coleman and Bell. 1-, 2-, and 3-Hexynes were from Columbia Organic Chemical Co., Inc. Allyl chloride and allyl alcohol were commercial samples which were distilled before use. The anhydrous ammonia was from Matheson Co., Inc., 99.9% minimum purity, and was dried further by passage through a tube, 60 cm in length, packed with barium oxide, before condensation in the reaction tube. Allyl-1-C^{14} alcohol was prepared by a method[1] similar to that of Leak[26] or, in later stages of this work, purchased from Isotope Specialties Co. (Division of Nuclear Corp. of America, Inc.) and Volk Radiochemical Co. Allyl *p*-tolyl sulfide was prepared according to the first procedure described below for allyl-1-C^{14} *p*-tolyl sulfide.

1,4-Hexadiene was prepared by coupling allyl chloride with the Grignard reagent of 1-bromopropene in tetrahydrofuran solution according to the procedure of Normant[46] for the same coupling but with allyl bromide. The 1-bromopropene was obtained from Columbia Organic Chemical Co., Inc., and distilled at 60–64.5° (uncorrected). Final purification of the product (especially separation from accompanying biallyl) was by preparative gas chromatography (on Perkin-Elmer column E, 3.0 m × 2.5 cm, operated at 34° in Perkin-Elmer vapor fractometer Model 154-C). The final product contained some 3% biallyl and consisted of a mixture of *cis* and *trans* isomers of 1,4-hexadiene in a ratio of 1.6:1, respectively (according to gas chromatography on a Perkin-Elmer column E, 2.0 m × 0.63 cm column at 34°, the assumption being made that the *cis* isomer has a longer retention time than the *trans* isomer in analogy with similar geometrical isomers[47]). The product in the vapor phase had intense infrared absorption at 3.27, 3.34, 3.44, 6.08, 6.95, 7.09, *ca.* 10.1, *ca.* 10.3 (assignment *trans* -CH=CH-), 11.0, and 14.4 μ (assignment *cis* -CH=CH-). The nuclear magnetic resonance absorption spectrum in CCl_4 solution had complex multiplets centered at τ 4.5 (-CH=C<), 5.0 (CH_2=C<), 7.3 $[\mathrm{CH_2}(-\overset{|}{\mathrm{C}}=\mathrm{C}<)_2]$, and 8.4 ($CH_3$–) in relative peak areas of 3.0, 2.1, 2.0, and 2.9, respectively.

Allyl-C^{14} chloride was prepared from allyl-1-C^{14} alcohol by the procedure of Sharman, *et al.*,[27] in 78% yield of purified product; tri-*n*-propylamine could replace tri-*n*-butylamine in this preparation without noticeable change in the results. In five preparations, the allyl chloride or allyltrimethylammonium chloride prepared therefrom consisted, according to the results from ozonization, of 0.9–1.2% of allyl-3-C^{14} and 99.1–98.8% of allyl-1-C^{14} derivative starting in two cases with our preparation and in the remainder with commercial preparations of allyl-1-C^{14} alcohol; a sixth preparation contained 3.1% of allyl-3-C^{14} chloride in the product.

Allyl-1-C^{14}-trimethylammonium Chloride. Allyl-1-C^{14} alcohol (7.5 g, 0.129 mole) was converted to allyl chloride by the above procedure; the crude product after distillation from the reaction vessel at 150–160 mm was added while cold to a solution of 17.1 g (0.29 mole) of trimethylamine in 110 ml of anhydrous acetone at −78°. After standing for 6 hr at −78°, 24 hr at 0°, and 2 hr at room temperature, the reaction solution was diluted with 300 ml of anhydrous ethyl ether and allowed to stand for 2 hr with occasional shaking. The crystalline product was separated by filtration, washed with ether, and dried *in vacuo* at 71° for 2 days. The yield was 15.1 g or 86.4% based on allyl-1-C^{14} alcohol. Ozonization of this salt and that from a similar preparation indicated that each consisted of 98.8% of allyl-1-C^{14}- and 1.2% of allyl-3-C^{14}-trimethylammonium chloride. The radioactivity of this salt (0.365 μcurie/mmole) was essentially the same as that of its corresponding picrate (0.374 μcurie/mmole).

Anal. Calcd for $C_6H_{14}NCl$: Cl, 26.14. Found: Cl, 26.36 (by Volhard titration).

Allyl-1,3-C^{14}-trimethylammonium Chloride. Allyl-1-C^{14} alcohol (9.6 ml, 141 mmoles) was mixed with 50 ml of Lucas reagent (from a portion freshly prepared from 171 g of fused zinc chloride and 110 ml of concentrated hydrochloric acid). On standing for 5 min a separate layer appeared; the mixture was stirred with a magnetic stirrer for 48 hr at 20 to 25°. The red-brown solution was extracted with a little *n*-butyl ether. The ether phase was washed with cold, aqueous sodium carbonate solution, dried overnight with Drierite, and distilled through a short Vigreux column. The allyl chloride upon reaction with excess trimethylamine in anhydrous acetone by the previous procedure gave 7.2 g (38% yield based on allyl alcohol) of quaternary salt. Assay of the radioactivity of this salt and of the formaldehyde obtained therefrom by ozonization indicated that it consisted of 50.8% allyl-1-C^{14}- and 49.2% allyl-3-C^{14}-trimethylammonium chloride.

Allyl-1-C^{14} *p*-Tolyl Sulfide. To the freshly prepared sodium salt of *p*-thiocresol (7.7 mmoles) dissolved in 120 ml of acetone was added dropwise with stirring at 20° a solution of 4.2 g (5.5 mmoles)

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[44] E. Warhurst, *Quart. Rev.* (London), **5**, (1951).

[45] J. Jortner, S. A. Rice, and E. G. Wilson in "Metal-Ammonia Solutions," G. Lepoutre and M. J. Sienko, Ed., W. A. Benjamin, Inc., New York, N. Y., 1964, p 248; J. Jortner, *J. Chem. Phys.*, 30, 839 (1959).

[46] H. Normant, *Compt. Rend.*, **239**, 1811 (1954); *Bull. Soc. Chim. France*, 728 (1957).

[47] B. Smith, R. Ohlson, and G. Larson, *Acta Chem. Scand.*, **17**, 436 (1963). See also L. K. Montgomery, K. Schueller, and P. D. Bartlett, *J. Am. Chem. Soc.*, **86**, 622 (1964).

of allyl chloride-1-C^{14} in 10 ml of acetone. The reaction mixture was stirred for 1 hr at 20° and then allowed to stand at room temperature overnight. Water (130 ml) was added, the oily layer was separated, and the aqueous solution was extracted with ether. The combined oily layer and ether extracts were washed with 4% sodium hydroxide and then with water. The solution was dried over Drierite. Distillation, finally through a short Vigreux column, gave 8.3 g (92% yield based on allyl chloride) of product of bp 99-100.5° (7.5 mm). Assay of this product and of the formaldehyde obtained therefrom by ozonization indicated that it consisted of 3.8% of allyl-3-C^{14} and 96.2% of allyl-1-C^{14} *p*-tolyl sulfide.

A similar preparation from 0.20 mole of each reactant in 125 ml of absolute ethanol as solvent at the temperature of an ice-salt, bath, gave 80% yield of sulfide which, however, according to its radioassay and that of formaldehyde obtained therefrom by ozonization consisted of 33.4% of allyl-3-C^{14} and 66.6% of allyl-1-C^{14} *p*-tolyl sulfide. It should be emphasized that the *same* sample of allyl-1-C^{14} chloride was used in both preparations of the *p*-tolyl sulfide and that ozonolysis of this allyl chloride (9 days after the preparation of the sulfide in absolute alcohol) indicated the presence of only 1.1% of allyl-3-C^{14} chloride.

Reactions with Lithium and Sodium in Liquid Ammonia. The apparatus and techniques used were similar to those described previously[2] except that provision was made for stirring the reaction solution with a glass-enclosed magnetic stirring bar. Small liquid samples were added to the reaction solution by means of a hypodermic syringe which was injected through a rubber septum which covered one small opening in the reaction vessel; larger liquid samples were added by means of a dropping funnel. Unless otherwise specified, the volume of liquid ammonia used in each reaction was 50 ± 10 ml, the allyl compound and additional reagents such as NH_4Cl or methanol were dissolved in the ammonia, and alkali metal (cut in ten small pieces) was added last over a period of 3 min to initiate reaction. When excess alkali metal was used, the deep blue color of alkali metal dissolved in liquid ammonia appeared throughout the solution in 3-45 min after addition of alkali metal. In the other mode of addition, the sodium metal was first dissolved in liquid ammonia and then the pulverized quaternary salt was slowly (over a period of 5 min) added to the deep blue solution by suitable rotation and tapping on the retort containing quaternary salt. In one experiment in which crystalline allyltrimethylammonium chloride (1.9 moles) was added in one portion to 6.1 mg-atoms of sodium dissolved in 50 ml of ammonia, the almost violent reaction was complete in 20-30 sec. Reactions at a temperature labeled −33° were run at the boiling point of the liquid ammonia solution; reactions near −70 to −72° were made with cooling by a Dry Ice-ethanol bath. For reactions at −72° in presence of excess ammonium chloride, the cooling bath was removed as soon as all the alkali metal had reacted (generally 5-10 min); while for reactions at −72° with excess alkali metal, the cooling bath was kept in place with stirring for 3 hr before allowing the liquid ammonia to evaporate. All of the allyl compounds and essentially all of the ammonium chloride used in the present reactions were apparently completely soluble in the liquid ammonia solution under the conditions employed.

In the cleavage of allyl *p*-tolyl sulfide the liquid ammonia solution developed a greenish gold color 12 sec after addition of sodium; this color lasted for about 25 sec and was then replaced by the dark blue color of sodium in liquid ammonia. In a similar experiment but with lithium metal in place of sodium, the solution turned a beautiful golden yellow color after 1 min and then after 5 min developed the usual intense deep blue color of lithium dissolved in ammonia. Also in a cleavage of allyl *p*-tolyl sulfide by lithium metal in ethylamine solution, the solution turned light yellow and then light blue. The species responsible for the yellow color in these experiments has not been identified.

The hydrocarbon products were swept from the reaction chamber with gaseous ammonia and collected over saturated brine in the usual manner.[2] The gaseous products then were transferred quantitatively to an Orsat gas apparatus and were bubbled through a saturated brine solution which was 1 *M* in hydrochloric acid until constant volume was attained. The gaseous products were dried by passage back and forth 10 to 12 times through a tube packed with Drierite. For determination of the yields of propylene recorded in Tables V and VI, the product (after suitable dilution by nitrogen) was led into a previously evacuated 10-cm cell with rock salt windows and the sample was slowly scanned from 5.95 to 6.00 μ with a Perkin-Elmer Model 21 recording infrared spectrophotometer. The optical density at the maximum (~5.98 μ) was recorded and the amount of propylene was determined from a calibration curve prepared from a known sample of propylene. Since biallyl has a maximum at about 6.07 μ and no effort was generally made to separate biallyl, except for reactions of allyl chloride where much biallyl is formed, the yields of propylene may sometimes be in error (too high) by as much as 3% of the recorded values in these tables. In other cases the analyses for products were by vapor phase chromatography (see below).

Since for cleavage of allyltrimethylammonium chloride the yield of methane reported in Table III is very low, it was considered possible that an appreciable amount of the methane produced could have been lost by solution in the brine. To check upon this possibility an experiment was performed in which the total volume of brine solutions used in scrubbing the product gases was 700 ml rather than the usual 2300 ml and the volume of liquid ammonia was 50 ml rather than 100 ml. The results obtained here are shown as the third run in Table III. It is noted that, if any change occurred, the amount of methane recovered was less than usual since the ratio of higher molecular weight hydrocarbons to methane (2680) is the highest given in the table. As a further check upon possible loss of methane during collection, a sample of propylene (1.21 mmoles) containing a small amount of methane (7.1×10^{-4} mmole) was introduced into the reaction chamber by means of a gas syringe and then was swept over into the collection system by evaporation of 100 ml of liquid ammonia in the usual manner. The total volume of brine solution used to wash the gas was 2400 ml. The amount of methane recovered (7.6×10^{-4} mmole) was, within experimental error, the same as that introduced.

For reactions in which much biallyl or products derived therefrom were present after completion of reaction, the previously described procedure for separation of products required some modification. To ensure removal of biallyl and derivatives, the reaction vessel, after completion of evaporation of ammonia, was heated in a water bath at 70-74° while it was swept with a stream of ammonia containing a little nitrogen. A measured quantity (about half) of the gaseous product was removed for analysis. The reaction system then was swept with additional ammonia and nitrogen and another measured sample of gaseous product was removed for analysis. This process of sweeping with ammonia and nitrogen was repeated until analysis showed that the concentration of biallyl in the collected gases (after the usual removal of ammonia) decreased in proportion to the dilution. In this manner it could be ascertained that all the biallyl had been brought into the gaseous phase in the collection bulbs for analysis. A somewhat simpler technique was to collect biallyl and derivatives in the liquid state with the apparatus and procedure described below for reaction of allyl-1-C^{14} chloride with sodium. The run with 36.8 mmoles of allyl chloride in Table I and the runs in Table II were performed by this latter technique.

Reactions with Sodium in 2-Propanol. These reactions were conducted in 50 ± 15 ml of the alcohol in the same apparatus and by the same general technique as for reactions in liquid ammonia. The reactions were run under 1 atm of gaseous ammonia and ammonia was used as sweep gas.

Reactions with Zinc in Acetic Acid. These reactions were run in 50 ± 10 ml of glacial acetic acid in the same apparatus and by the same general technique as for reactions in liquid ammonia; however, the reactions were run under 1 atm of carbon dioxide, carbon dioxide was used as sweep gas, and the gaseous products were collected over 10% sodium hydroxide and washed in the Orsat gas apparatus with 10% sodium hydroxide. The zinc dust (Baker reagent grade powdered zinc) was activated by brief treatment with 0.5 *N* hydrochloric acid. Since the reactions were observed to be slow, 5 ml of aqueous sodium iodide was added to attempt to accelerate the reactions; qualitatively the rates remained unaffected.

Analyses of Products by Vapor Chromatography. After drying by passage over Drierite, the gaseous products were analyzed by means of a Perkin-Elmer Model 154 vapor fractometer equipped with a precision gas sampling valve, a 1- or 5-ml gas sample tube, and 2-m columns, 6.25 mm in diameter. For analysis for methane a column packed with silica gel (Perkin-Elmer column J) was used at 33°. For analysis for propane, propylene, cyclopropane, hexenes, biallyl, and isomers of biallyl a column packed with diatomaceous earth coated with 2,4-dimethyltetrahydrothiophene 1,1-dioxide (Perkin-Elmer column E) was operated at 33°. At a flow rate of helium of 25 ml/min, propane, propylene, and cyclopropane came over in 2.2, 2.5, and 4.3 min. For the last run recorded in Table IV, an attempt was made to see if products of higher retention time than cyclopropane were present; however, at a flow rate of 80 ml/min, no additional components were observed even after 87 min. Since a similar check on the reaction products from allyltrimethylammonium chloride revealed products of high retention time, these products generally were analyzed at a flow rate of 43 ml/min, whereby the retention times of propylene, hexenes, and biallyl were 0.8, 7.8-9, and 10.5 min, respectively. While methane, cyclopropane, propylene, and biallyl were determined quantitatively by comparison of peak heights with calibration curves at known partial pressures (samples diluted with helium), hexenes and the remaining hexadienes were determined on the basis of peak areas. For these substances it was assumed that the peak area per mole was the same as that of biallyl run under similar conditions.

The hexenes and hexadienes of Tables I, II, and III were identified qualitatively on the basis of their retention times on Perkin-Elmer column E. At 33° under conditions whereby biallyl had a retention time of 10 min (all retention times will here be measured from the maximum of the air peak), the retention times of the unknown components relative to biallyl were as follows: A, broad peak with two overlapping maxima at about 0.71 and 0.74; B, 0.86; biallyl, 1.00; C, 1.19; D, 1.30; E, 2.01; F, 2.87; G, 3.33; H, 3.61. The reproducibility of these relative retention times was $\pm 1\%$ for samples of shorter retention time than biallyl and $\pm 2\%$ for samples of longer retention time. Under these conditions the relative retention times of some known compounds were found to be: 1-hexene, 0.66; *trans*-2-hexene, 0.76; *cis*-2-hexene, 0.86; *trans*-1,4-hexadiene, 1.20; *cis*-1,4-hexadiene, 1.32; 3-hexyne, 2.99; 1-hexyne, 3.26; 2-hexyne, 3.94. Where comparisons can be made these relative retention times are similar to those reported by Smith, Ohlson, and Larson[47] at 25°. In order to permit a more accurate comparison with retention times of these workers, the product from isomerization of biallyl with sodium amide in one run was chromatographed on the same column but at 25° and a flow rate (25 ml/min) such that *n*-pentane came over in 4.2 min and biallyl in 26.3 min. Under these conditions the retention time relative to biallyl and (given in parenthesis) the assigned structures and reported retention times[47] were as follows: A, 0.699 and 0.732 (*trans*-3-hexene, 0.692; *cis*-3-hexene, 0.737; *trans*-2-hexene, 0.737); B, 0.844 (*cis*-2-hexene, 0.814); biallyl, 1.000; C, 1.21 (*trans*-1,4-hexadiene); D, 1.33 (*cis*-1,4-hexadiene); E, 2.04 (both *cis*- and *trans*-1,3-hexadiene, 2.06); F, 2.95 (*trans,trans*-2,4-hexadiene, 3.00); G, 3.44 (*cis,trans*-2,4-hexadiene, 3.51); H, 3.72 (*cis,cis*-2,4-hexadiene, 3.79).

The combined yields of hydrocarbons reported in the runs of Tables III and IV are seldom more than 80%. While a portion of the remainder of the quaternary salt probably stuck to the upper walls of the reaction tube or otherwise was not transferred to the reaction site, very likely some of the salt underwent side reactions to give amines rather than hydrocarbon. Thus allyltrimethylammonium bromide has been reported[48] to react with sodium amide in liquid ammonia at −33° to yield 3-diethylaminopentene-1 and 1-diethylaminopentene-1 in a type of Stevens rearrangement.

Ozonization Procedure. Ozonizations were conducted in chloroform solution with the ozonization tube cooled in a bath at −60 to −70° according to the general procedure of Sharman, *et al.*[27] For ozonization of propylene two ozonization tubes were joined in series. In the first tube (nearest the ozonizer) was placed 50 ml of chloroform and, in the second, 20 ml. The gases containing propylene were passed slowly into the series of tubes cooled at −60 to −70°. A bubbler containing a solution of potassium iodide and sodium dihydrogen phosphate was attached to the second ozonization tube and oxygen containing about 3% ozone, was bubbled into the system until the potassium iodide solution turned dark brown. The two chloroform solutions containing ozonide were combined and reduced with powdered zinc in an equal volume of water containing acetic acid. The solution after filtration was mixed with 25 ml of an alcoholic solution containing somewhat in excess of 2 moles of 5,5-dimethyl-1,3-cyclohexanedione per mole of expected aldehyde. The solution was allowed to stand overnight. Approximately 50 ml of water was added and the chloroform was boiled off on a steam bath. While dimethone derivatives came out of solution upon cooling, it was found that 2 to 3 days was sometimes required for complete precipitation of the acetaldehyde derivative. The crude mixture of dimethone derivatives after drying under vacuum at room temperature was isolated in yields of 54 to 94% from ozonization of propylene. From ozonization of *p*-tolyl allyl sulfide and allyltrimethylammonium chloride, only formaldimethone, mp 191.5° (cor), was obtained after repeated recrystallization from 95% ethanol.

By the present ozonization procedure both propylene and allyl chloride gave a mixture of formaldehyde and acetaldehyde (doubtlessly acetaldehyde was obtained from allyl chloride by zinc reduction of the expected chloroacetaldehyde; Sharman, *et al.*,[27] do not mention this complication). The dimethone derivatives of these two aldehydes were separated by a modification of the procedure of Vorländer.[30] The mixture of vacuum-dried methone derivatives from 5 to 8 mmoles of allyl compound was mixed with 7-10 ml of glacial acetic acid and heated on a steam bath for 6 hr and then left at room temperature overnight. The next day 10-15 ml of water was added and the mixture was allowed to stand for 1 to 2 hr. The solid which separated was collected by filtration, washed with water, dried, and dissolved in 15-20 ml of chloroform. The chloroform solution was extracted with four 20-ml portions of 4% sodium hydroxide solution. The chloroform layer was washed with water and evaporated to dryness to give a residue of the crude anhydride of acetaldimethone. The latter was recrystallized repeatedly from 95% ethanol until a constant melting point of 178.0-178.5° (cor) was attained. The combined alkaline extracts were neutralized with 2 *N* hydrochloric whereupon formaldimethone precipitated. This derivative was then recrystallized repeatedly from 95% ethanol until a constant melting point (191.5°) was attained. Formaldimethone was ordinarily recrystallized six times and acetaldimethone anhydride four times before making analyses for radioactivity.

Reaction of Allyl-1-C^{14} Chloride with Sodium in Liquid Ammonia. The apparatus was an all-glass system that was designed[1] to permit the separation of liquified biallyl. Ammonia gas, after passage through a tube packed with barium oxide, went into an empty safety trap and then was led almost to the bottom of the reaction tube which could be cooled by a solid carbon dioxide-acetone bath to condense the ammonia. The reaction tube was 5 cm in diameter and 39 cm tall, flattened on the bottom to permit stirring with a glass-enclosed magnet, and joined by ₸ joints to two retorts and a small dropping funnel. One retort held sodium metal and the other ammonium chloride. Upon rotation about the joint the contents of the retort could be dropped into the reaction tube. The dropping funnel was for addition of allyl chloride. A tube led from the top of the reaction vessel to an empty safety trap then through two mercury valves into two scrubbers which were connected in series and separated by a third mercury valve. The scrubbers each contained 1450 ml of a saturated brine solution which was 1 *N* in hydrochloric acid. From the second scrubber gaseous products passed through a drying tube filled with anhydrous calcium sulfate and then into a cold trap for condensing biallyl. From the biallyl trap gaseous products passed through a safety trap into two gas-absorption bubblers, the first of which was filled with 60 ml and the second with 40 ml of chloroform. These bubblers were cooled in a bath at about −60° and were used to absorb propylene.

Run no. 3 in Table VII will be described as a typical run. The reaction system was swept with gaseous ammonia for 15 min with the ammonia being permitted to exit from the system after it had passed through the first mercury valve. The reaction vessel then was cooled in a Dry Ice-acetone bath and about 105 ml of ammonia was allowed to condense. The cooling bath was removed and the liquid ammonia was permitted to boil with stirring by the magnetic stirrer. At this time retorts containing ammonium chloride (2.15 g or 40.2 mmoles) and freshly cut sodium metal (0.889 g or 38.6 mg-atoms in eight pieces) were attached to the system, and the whole system was joined together. The ammonia solution was allowed to boil until 100 ± 5 ml remained and all air had been purged from the reaction vessel. The reaction vessel was then cooled to −72° with a Dry Ice-ethanol bath. Allyl-1-C^{14} chloride (2.70 ml, 33.2 mmoles) was added rapidly from the dropping funnel. The solution was stirred for a few minutes to ensure solution of the allyl chloride (all the allyl chloride dissolved as nearly as could be judged by the naked eye) and then the sodium metal was added piecewise over a period of about 5 min. After 20 min, ammonium chloride was added to the blue solution to destroy sodium amide and the excess sodium metal present in this experiment. A Dry Ice-acetone bath now was placed about the biallyl trap, the bath cooling the reaction vessel was removed, and the liquid ammonia was allowed to evaporate. Magnetic stirring was continued throughout all these reactions until evaporation of ammonia was complete. Water baths kept at 65-70° were placed around the reaction vessel, the two scrubbers, and the drying tube. A slow stream of helium now was led

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(48) H. Hellmann and G. M. Scheytt, *Ann.*, **654**, 39 (1962).

into the bottom of the reaction vessel and allowed to sweep through the entire system. The cooling bath surrounding the biallyl trap now was replaced by a liquid nitrogen bath and sweeping with helium was continued for 7 hr until some 10–15 l. of helium had passed through the system. The biallyl trap was found to contain 0.631 g (7.68 mmoles, 46% yield) of crude biallyl. In the present run the crude biallyl was subjected to ozonization in chloroform solution without prior purification. Half of the ozonide solution was reduced with zinc and aqueous acetic acid and worked up as described above. The dimethone derivative was put through the modified Vorländer procedure for separation of formaldimethone from acetaldimethone but was found to contain only formaldimethone. After three recrystallizations from absolute ethanol, the formaldimethone amounted to 0.371 g of material, mp 190–191.3° (activity 0.0329 ± 0.0003 μcurie/mmole); after another recrystallization from aqueous ethanol the compound had activity of 0.0330 ± 0.0005 μcurie/mmole. The other half of the ozonide solution was worked up according to the procedure of Bailey.[49] Solvent was removed from the ozonide *in vacuo* at room temperature on a rotating evaporator. To the residual thick, syrupy liquid was added 25 ml of 90% formic acid and 12 ml of 30% hydrogen peroxide. The reaction mixture was warmed to initiate reaction; after the initial reaction had ceased the reaction mixture was heated at reflux for 30 min and allowed to stand overnight. The solvent was removed with the aid of a rotating evaporator and the residue of succinic acid was sublimed *in vacuo*. After a second vacuum sublimation, 0.346 g of succinic acid of activity 0.1426 ± 0.0009 μcurie/mmole was obtained. After one recrystallization from water and two more vacuum sublimations the succinic acid had mp 184.2–184.7° and activity of 0.1409 ± 0.0009 μcurie/mmole.

Runs 1 and 2 of Table VII were run similarly except that for these runs the crude biallyl before ozonization was subjected to some purification by vapor phase chromatography on a large preparative column (Perkin-Elmer column E, 3 m long and 25 mm in diameter, operated at 32–34°). In run 4 the sodium amide present was destroyed in the usual manner by addition of ammonium chloride (0.829 g, 15.5 mmoles) 20 min after completion of the addition of sodium. The unreacted allyl chloride was, in the course of the usual sweeping process, collected along with biallyl in the cold trap and then the mixture of biallyl and allyl chloride was separated by vapor phase chromatography at 40° on the preparative column mentioned above (retention time of biallyl, 5.6 min; allyl chloride, 11 min). Ozonization of the recovered allyl chloride was carried out in the usual manner. The sample of allyl-1-C^{14} chloride used in run 4 was subjected to similar vapor phase chromatography before ozonization.

Assays for Radioactivity. Organic samples for radioactivity determinations were converted to carbon dioxide by a wet oxidation method with combustion reagents prepared according to the procedure of Van Slyke, *et al.*[50] The procedure and apparatus were similar to that of Neville[51] but a U tube filled with $SnCl_2 \cdot 2H_2O$ crystals and a tube packed with lead dioxide heated at 180° were placed in the combustion line, in the order given, between the combustion flask and the ionization chamber. Two to three combustions were generally run on each of the present samples.

Radioactivities were measured with a vibrating-reed electrometer (Applied Physics Corp., Model 31) by the "rate of drift method" (the time, in the present work ordinarily 200–500 sec, was measured for a condenser to become charged a predetermined amount by the ionization current arising from the radioactivity). Each sample of radioactive carbon dioxide was counted an average of three times. The numbers given in the tables are the average values of the activity. The ± numbers after each value refer usually to the mean deviation of the average value from the individual values for separate combustions or sometimes to the mean deviation in counting the samples of carbon dioxide, whichever is the larger of these two possibilities. The average of the combined activities of propylene and formaldehyde for eight samples of propylene from a common sample of allyl-1-C^{14}-trimethylammonium chloride in Tables V and VI is 0.3563 ± 0.0066 μcurie/mmole. These values were determined over a period of 5 months and demonstrate reasonable stability of the instrument used for measuring radioactivity. It is believed that the ratios of the activity of formaldimethone to that of acetaldimethone anhydride may be more accurately compared than the magnitude of the individual activities since for each sample of propylene the corresponding ozonolysis products were ordinarily assayed on the same day and therefore small variations in instrument and cell response from day to day should tend to cancel in comparisons of the ratios of activity. Since no primary standard was always available to calibrate our electrometer, the molar activities are reported in self-consistent units which are only approximately those of microcuries per mmole.

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Organic Syntheses by Means of Noble Metal Compounds. XXII.[1] Palladium-Catalyzed Carbonylation of Diphenylacetylene

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Abstract: Diphenylacetylene and carbon monoxide react in ethanol in the presence of palladium chloride and hydrogen chloride to form α,β-diphenyl-γ-crotonolactone. The structure of the lactone was confirmed by several chemical transformations. No carbonylation was observed in the reaction carried out in benzene.

The interaction of palladium chloride with diphenylacetylene to form the tetraphenylcyclobutadiene–palladium chloride complex and related products has been a subject of extensive studies.[2] It is apparent from these studies that palladium chloride and diphenyl-

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