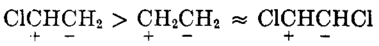
chlorination reaction was found to form *trans*- and *cis*-1,2-dichloroethylene nearly in equilibrium[2] which was independent of the reducing temperature. Very little dechlorination was observed for 1,1,1-trichloroethane and 1,1-dichloroethane (chlorine attached to the same carbon atom), but considerable dechlorination occurred with 1,2-dichloroethane, 1,1,2-trichloroethane, and 1,1,2,2-tetrachloroethane. These facts suggest that this elimination reaction may proceed through an $\alpha\beta$ concerted E2 mechanism similar with the debromination of 1,1,2,2-tetrabromoethane by iodide, which was postulated from an isotopic effect study.[6]

The dechlorination reactivity order after consideration for symmetry number (the combination number of chlorine atoms) was 1,1,2-trichloroethane (7.8 ml/g min^{-1}) > 1,2-dichloroethane (4.9) ≈ 1,1,2,2-tetrachloroethane (4.5) on the catalyst reduced at 450°. This reactivity order is not correlated with the sum of $D_r^R(\mathrm{Cl})$.[5] The hypothetical intermediates are assumed to be stable in the following order by the contribution of the chlorine atom.



$$\mathrm{Cl}\underset{+}{\mathrm{C}}\mathrm{H}\underset{-}{\mathrm{C}}\mathrm{H_2} > \underset{+}{\mathrm{C}}\mathrm{H_2}\underset{-}{\mathrm{C}}\mathrm{H_2} \approx \mathrm{Cl}\underset{+}{\mathrm{C}}\mathrm{H}\underset{-}{\mathrm{C}}\mathrm{HCl}$$

The above stability is considered in the same manner as was the reactivity orders on solid acids in a previous paper.[1]

The chromia reduced at higher temperatures may have more surface chromium ions which have a stronger affinity to chlorine than to hydrogen. The chromia reduced at lower temperatures may have more surface oxygen ions which can attack hydrogen atoms preferably. Thus, the surface change which resulted from reduction of the catalyst may have been responsible for the differences of the 1,1/1,2 and *trans/cis* ratios from 1,1,2-trichloroethane and of dechlorination/dehydrochlorination selectivity as the catalyst was treated at different temperatures.

Acknowledgments.—We are grateful to Dr. Yasukazu Saito and Mr. Jun-ichiro Take for their helpful discussions.

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[6] W. G. Lee and S. I. Miller, *J. Phys. Chem.*, **66**, 655 (1962).

The Addition of Nitrosyl Chloride to 3-Methylbutadiene-1,2

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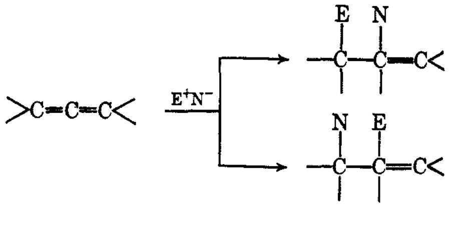
Electrophilic addition to allenes may lead to attachment of the electrophile either to a terminal carbon atom or to the central carbon atom of the allenic system.



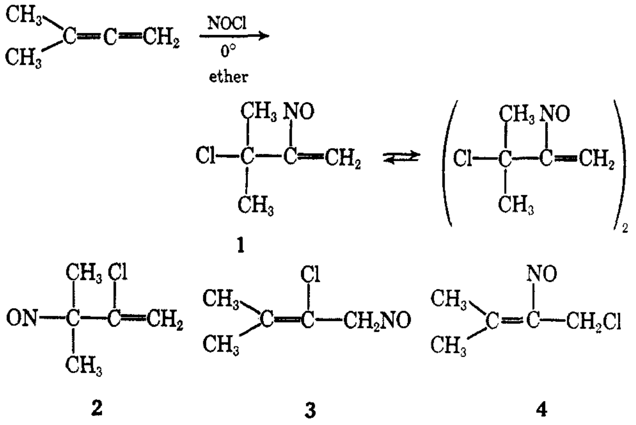
In the report describing the first preparation of allene, Gustavson and Demjanoff[2] noted that hydration in the presence of sulfuric acid afforded acetone. It was subsequently found[3,4] that hydration of monosubstituted allenes gave methyl ketones. Other examples of electrophilic additions to allenes apparently proceeding *via* protonation of an sp^2 hybridized carbon atom are the addition of hydrogen fluoride to allene to give 2,2-difluoropropane,[5] and the addition of methyl alcohol to 1,2-hexadiene in the presence of boron trifluoride and mercuric oxide affording the dimethyl ketal of 2-hexanone.[5]

The formation of a mixture of 2-chloro-2-hexene and 2,2-dichlorohexane upon treatment of 1,2-hexadiene with dry hydrogen chloride established that the terminal double bond can be the first attacked.[5]

In contrast to these cases, Kondakov[6] found that the addition of hydrogen chloride to 3-methylbutadiene-1,2 gave 3-chloro-3-methylbutene by proton attachment at the sp hybridized carbon atom. Jacobs and Johnson[7] observed that while the addition of dry hydrogen chloride to 1,2-butadiene proceeded by proton attachment at a terminal allenic carbon forming 2-chlorobutene, hydrogen chloride addition to 3-methylbutadiene-1,2 resulted in central attachment of electrophile forming a mixture of allylic chlorides.

Griesbaum[8–10] and coworkers observed the formation of cyclobutane derivatives upon heterolytic hydrobromination of allene, showing that this addition is not concerted. Sharma, Shoulders, and Gardner[11] found that attachment of the electrophile during oxymercuration of 1,2-cyclononadiene occurs at the central carbon of the allenic system.

We wish now to report that heterolytic addition of nitrosyl chloride to 3-methylbutadiene-1,2 at 0° in ether results in attachment of the electrophile at the sp hybridized carbon atom giving 2-nitroso-3-chloro-3-methylbutene (**1**).



1 **2** **3** **4**

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[1] General Electric Research & Development Center, P. O. Box 8, Schenectady, N. Y.

[2] G. Gustavson and N. Demjanoff, *J. Prakt. Chem.*, **2**, 38, 201 (1888).

[3] W. H. Carrothers and G. J. Berchet, *J. Amer. Chem. Soc.*, **55**, 1628 (1933).

[4] G. F. Hennison and J. J. Sheehan, *ibid.*, **71**, 1964 (1949).

[5] P. R. Austin, U. S. Patent 2,585,529 (Feb 12, 1952); *Chem. Abstr.*, **46**, 3799 (1952).

[6] I. W. Kondakov, *Chem. Zentr.*, **61**, I, 311 (1890).

[7] T. L. Jacobs and R. N. Johnson, *J. Amer. Chem. Soc.*, **82**, 6397 (1960).

[8] K. Griesbaum, *Angew. Chem.*, **76**, 782 (1964); *Angew. Chem. Intern. Ed. Engl.*, **3**, 697 (1964).

[9] K. Griesbaum, *J. Amer. Chem. Soc.*, **86**, 2301 (1964).

[10] K. Griesbaum, W. Naegele, and G. Wanless, *ibid.*, **87**, 3151 (1965).

[11] R. K. Sharma, B. A. Shoulders, and P. D. Gardner, *J. Org. Chem.*, **32**, 241 (1967).

This unstable blue oil undergoes facile dimerization and polymerization at ambient temperatures. Assignment of structure **1** to the product is based upon mass, infrared, and proton magnetic resonance spectroscopy, and on chemical behavior.

Mass spectrometry (see below) showed that the molecular weight of the product is 133 g/mol indicating a monoadduct. Treatment with ethanolic silver nitrate instantaneously produced a precipitate of silver chloride indicating an active chlorine and ruling out structures **2** and **3** for the adduct. Based on the yield of silver chloride, one calculates that one chlorine atom is present for each 140 atomic weight units. Because the adduct was unstable, satisfactory elemental analysis could not be obtained.

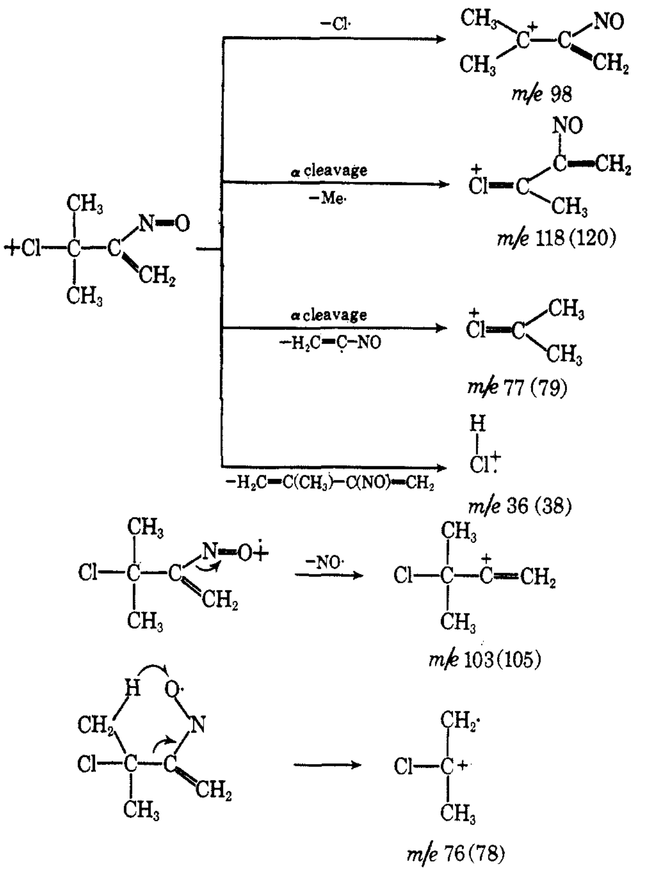
The infrared spectrum of the adduct showed the N=O stretching absorption at 1523 cm^{-1}, the C=C stretching absorption at 1650 cm^{-1}, and bands of low intensity at 1740 and 892 cm^{-1} assigned to the terminal methylene group. Other bands in the 2975–2850-, 1475–1360-, and 1250–1100-cm^{-1} regions were assignable to C–H and C–C bonds.

The proton magnetic resonance spectrum (60 Mc) of the adduct consisted of two sharp singlets at τ 8.14 and 5.75[12] (relative to tetramethylsilane) with areas in the ratio 3:1. Since the spectra of unsymmetrically substituted dimethylethylenes show two types of magnetically unequivalent methyl protons separated by 2–10 cps,[13] the appearance of singlet methyl protons is evidence that addition occurred to the 2,3 double bond of 3-methylbutadiene-1,2, thus ruling out structures **3** and **4** for the adduct. Comparison with the spectrum of 1-nitroso-2-chloro-2-methylpropane prepared from NOCl and isobutylene (methyl protons at τ 8.24) shows that τ 8.14 is a reasonable assignment for the methyl protons of structure **1**.

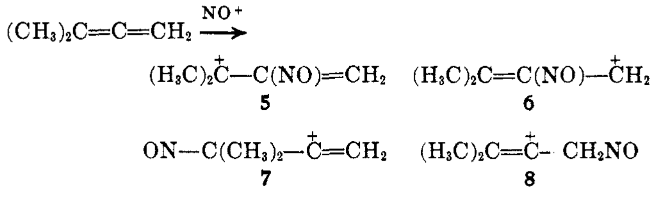
Assignment of structure **1** to the adduct was confirmed by mass spectrometry. The mass spectrum of the adduct showed a parent peak at *m/e* 133 with a P + 2 peak of one-third intensity, indicating a monochlorinated compound of molecular weight 133 g/mol. This assignment was supported by lowering the ionizing voltage which caused the intensity of these peaks to increase relative to that of other peaks in the spectrum.

As would be expected for a compound with active chlorine, the base peak of the spectrum was that of HCl, at *m/e* 36 with an isotope peak one-third as intense at *m/e* 38. Other significant peaks were observed at *m/e* 118, 103, 98, 77, and 76. All but the *m/e* 98 peak were accompanied by an M + 2 peak of one-third intensity showing they contained chlorine. The remainder of the spectrum consisted of peaks assignable as hydrocarbon fragments. Interpretation in terms of the localized charge and radical concept[14] is presented in Scheme I.

Scheme I



The specificity of this addition may be explained on the basis of the electron-donating properties of the methyl groups and/or on a stereochemical basis. One plausible mechanism involves transfer of NO$^+$ to either the central or a terminal carbon atom of the allenic system. Attack at the central atom would initially lead to either a primary (**6**) or tertiary (**5**) carbonium ion since the perpendicular orientation of the π bonds precludes allylic stabilization until rotation about a C–C bond has occurred. To the extent that electrophilic addition to allenes proceed *via* carbonium ions, it would be expected that the products arising from the tertiary cation (**5**) would predominate. That this is an over-simplification is demonstrated by the work of Jacobs and Johnson[7] who found that the primary halide, 1-chloro-3-methylbutene-2, is the major product of hydrochlorination of 3-methyl-butadiene-1,2. Presumably this product arises from either a primary or a bridged carbonium ion.



$$(CH_3)_2C{=}C{=}CH_2 \xrightarrow{NO^+}$$

$$\underset{\mathbf{5}}{(H_3C)_2\overset{+}{C}{-}C(NO){=}CH_2} \qquad \underset{\mathbf{6}}{(H_3C)_2C{=}C(NO){-}\overset{+}{C}H_2}$$

$$\underset{\mathbf{7}}{ON{-}C(CH_3)_2{-}\overset{+}{C}{=}CH_2} \qquad \underset{\mathbf{8}}{(H_3C)_2C{=}\overset{+}{C}{-}\,CH_2NO}$$

A second plausible mechanism involves attack of NO$^+$ to form a cyclic nitrosonium ion. The electron-donating properties of the methyl groups would be expected to make the internal double bond of the allene more nucleophilic resulting in preferential formation of cation **9**. Formation of a tertiary halide may then

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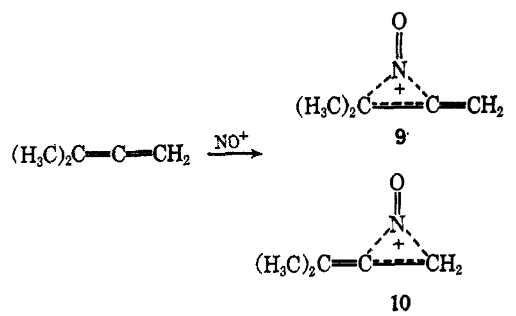
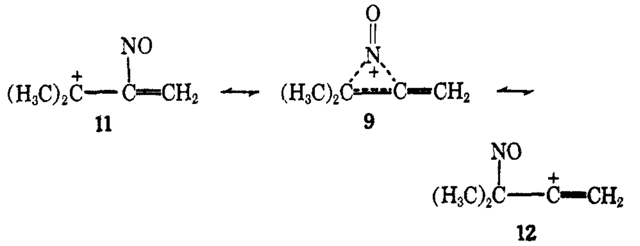
[12] The apperance of singlet protons in the nmr spectrum of an unsymmetrical 1,1-disubstituted ethylene is not without precedent. See, for example, the spectra of 2-propenylacetate and 2-methylene-3,3-dimethylindoline in High Resolution NMR Spectra Catalog, Vol. II, Varian Associates, Palo Alto, Calif., 1963.

[13] See, for example, the spectra of 2,5-dimethyl-2,4-hexadiene and β,β-dimethylacrylic acid in High Resolution NMR Spectra Catalog, Vol. II, Varian Associates, Palo Alto, Calif., 1963.

[14] F. W. McLafferty, "Interpretation of Mass Spectra," W. A. Benjamin, Inc., New York, N. Y., 1966, Chapter 8.

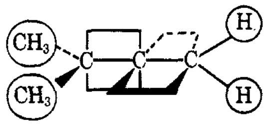


be explained by considering cation **9** to be a resonance hybrid with canonical structures **11** and **12** as major contributors. The ability of the alkyl groups to stabilize adjacent positive charge by hyperconjugation would make structure **11** of greater importance to the hybrid.



Attack of Cl^- would then be directed toward the more electron-deficient tertiary carbon forming 2-nitroso-3-chloro-3-methylbutene (**1**).

Addition to the internal double bond may also be explained on a stereochemical basis. The methyl groups of 3-methylbutadiene-1,2 are in closer proximity to the terminal π orbital than to the internal π orbital.



To form the primary carbonium ion **6** or the cyclic nitrosonium ion **10**, NO^+ must approach in the plane of the terminal π orbital. The methyl groups lie in this plane and pose severe steric restrictions to approach of NO^+ in this manner. Less severe restrictions are imposed by the protons for approach of NO^+ in the plane of the internal π orbital leading to formation of cations **5**, **7**, or **9**. Arguments stated previously can be invoked to explain exclusive formation of the tertiary halide.

Experimental Section

To a 50-ml round-bottom flask fitted with a Dry Ice condenser was added 2.31 g (0.034 mol) of 3-methylbutadiene-1,2, 15 ml of ether, and 2 drops of water. The flask was cooled to 0° and 2.2 g (0.034 mol) of gaseous nitrosyl chloride passed through the reaction solution causing a green color to develop. When the allene was nearly gone as shown by glpc, the mixture was dried over anhydrous $MgSO_4$ and solvent removed at reduced pressure. The resulting yellow-green oil was transferred to a sublimation apparatus and the blue monomer sublimed at 2 μ pressure onto a cold finger containing liquid nitrogen. It was found necessary to store the monomer at −196° prior to characterization to prevent polymerization. Nuclear magnetic resonance spectrometry of the yellow-green oil indicated that 95% of the oil was 2-nitroso-3-chloro-3-methylbutene. Attempts to identify other products were unsuccessful.

Registry No.—**1**, 16162-33-7; nitrosyl chloride, 2696-92-6; 3-methylbutadiene-1,2, 598-25-4.

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The Nucleophilic Displacement of One Dianion by Another

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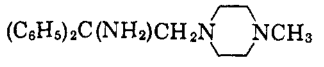
Although it has been known since 1911[1] that benzophenone forms a disodio adduct that can be alkylated, the synthetic utility of this reagent only recently has become the subject of a number of systematic investigations.[2] To add to this number, we have now found that disodiobenzophenone and its analogs can be aminomethylated in fair to excellent yields by sodium aminomethanesulfonates (**1**).

$$\mathrm{R_2NH + \underset{\mathbf{3}}{HOCH_2SO_3Na} \longrightarrow \underset{\mathbf{1}}{R_2NCH_2SO_3Na}}$$

$$\mathrm{Ar_2CO + 2Na \xrightarrow{DME} \left[Ar_2\bar{C}{-}\bar{O}\right] 2Na^+ \xrightarrow[2.\ \ H_2O]{1.\ \ \mathbf{1}} \underset{\mathbf{2}}{Ar_2C(OH)CH_2NR_2}}$$

The solid sulfonate salt **1** is added to a solution of the disodio derivative prepared in 1,2-dimethoxyethane (DME) and stirred at room temperature for 16–19 hr before work-up. Results of a number of such reactions listed in Table I serve to indicate the scope of the reaction. Those amino alcohols derived from the tricyclic diaryl ketones are not readily accessible by other known methods.[3,4]

Extension of this scheme to diphenylketimine gave a low yield (19%) of the triamine **4** in the one reaction tried. Similar reductive alkylations of N-arylimines[5] and oximes[6] with alkylhalides have been reported.



4

$HOCH_2OSO_2Na$

5

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[1] W. Schlenk and T. Weikel, *Ber.*, **44**, 1182 (1911); C. B. Wooster [*J. Amer. Chem. Soc.*, **50**, 1388 (1928)] also showed that disodiobenzophenone could be alkylated with ethyl bromide.

[2] (a) P. J. Hamrick, Jr., and C. R. Hauser, *ibid.*, **81**, 493 (1959); (b) D. V. Ioffe, *Zh. Obshch. Khim.*, **34**, 3900 (1964); *ibid.*, **35**, 1851 (1965); D. V. Ioffe and I. N. Somin, *ibid.*, **34**, 703 (1964); B. Z. Askinazi and D. V. Ioffe, *Zh. Org. Khim.*, **3**, 367 (1967); D. V. Ioffe, *ibid.*, **3**, 535 (1967); (c) M. Miocque and C. Fauran, *Compt. Rend.*, **259** 408 (1964); J. A. Gautier, M. Miocque, C. Fauran, and M. D. d'Engenières, *Bull. Soc. Chim. Fr.*, 3162 (1965); (d) S. Selman and J. F. Eastham, *J. Org. Chem.*, **30**, 3804 (1965); (e) E. L. Anderson and J. E. Casey, Jr., *ibid.*, **30**, 3959 (1965).

[3] A. Schönberg, E. Singer, and W. Knöfel [*Chem. Ber.*, **99**, 3813 (1966)] have reported the preparation of 9-acyloxy-9-aminomethylfluorenes by treating 9-diazofluorene with diaminomethanes in the presence of carboxylic acid anhydrides.

[4] (a) H. E. Zaugg, R. J. Michaels, H. J. Glenn, L. R. Swett, M. Freifelder, G. R. Stone, and A. W. Weston, *J. Amer. Chem. Soc.*, **80**, 2763 (1958); (b) H. E. Zaugg and R. J. Michaels, *ibid.*, **80**, 2770 (1958).

[5] (a) W. Schlenk and E. Bergmann, *Ann. Chem.*, **463**, 281 (1928); (b) B. M. Mikhailov and K. Kurdiumova, *Zh. Obshch. Khim.*, **25**, 1687 (1955), (c) J. G. Smith and C. D. Veach, *Can. J. Chem.*, **44**, 2245 (1966).

[6] J. A. Gautier, M. Miocque, C. Fauran, and A. Y. Cloarec, *Compt. Rend.*, **263**, 1164 (1966).