Carbenoid Decomposition of the Grignard Reagent from 4-Bromo-1-chloro-1-butene[1]

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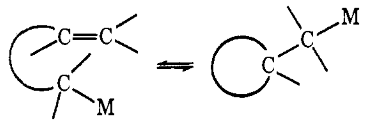
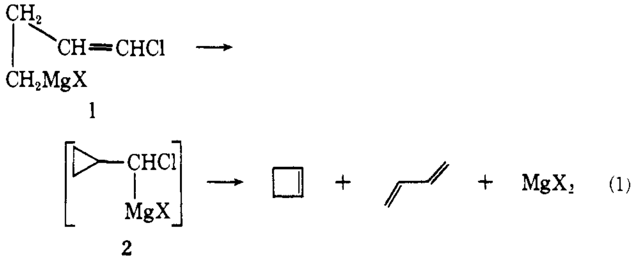
Abstract: The Grignard reagent from 4-bromo-1-chloro-1-butene undergoes decomposition on heating in a variety of ether solvents to yield principally cyclobutene. A mechanism involving cyclization to the cyclopropyl carbenoid **2** is in best accord with the data, including deuterium labeling experiments which demonstrate equivalence of the two methylene groups. From comparison with related systems, it is concluded that neither phenyl nor chlorine substituted on the double bond enhances the rate of cyclization of the unsaturated Grignard reagents. A previously proposed concerted mechanism is consistent with this result.

The interconversion between cyclopropylmethyl and 3-buten-1-yl Grignard reagents was originally established by Roberts and coworkers,[2] and is now recognized to be an example of a general organometallic "ring–chain interconversion" rearrangement.[3] In this paper, we report a study in which this ring closure is utilized to generate an α-haloorganomagnesium carbenoid, which undergoes rearrangement to cyclobutene and 1,3-butadiene, typical of cyclopropylcarbene and related carbenoid species in solution.[4]



Results and Discussion

The preparation of 4-bromo-1-chloro-1-butene[4] was carried out in straightforward fashion as shown in eq 2. The starting material **3** was a mixture of cis and trans isomers, as was the product **4**. The mixture of isomers was used in most of the experiments that follow, although in some cases samples partially separated by distillation or resolved by gas chromatography were used.



Bromide **4** reacted readily with magnesium in ether or tetrahydrofuran to yield a Grignard reagent. An nmr spectrum of the Grignard solution showed a high-field triplet (J = 8.6 Hz) at about −0.6 ppm in THF and −0.5 ppm in ether. The integral of the CH_2Mg resonances in the Grignard reagent was sufficient to account for 60–80% of the bromide originally present. Hydrolysis of the solution yielded a mixture of *cis*- and *trans*-1-chloro-1-butene. In addition, small amounts of C_4 hydrocarbons—cyclobutene, 1,3-butadiene, and 1-butene—were found by gas chromatography, though they were not present in sufficient quantity to detect in the nmr spectrum of the Grignard reagent solution. Most of the C_4 hydrocarbon product could be removed with the solvent before hydrolysis by pumping under vacuum. When a solution of the Grignard reagent was heated, either under reflux or in sealed tubes, and in a variety of solvents (diethyl ether, tetrahydrofuran, 1,2-dimethoxyethane, or di-*n*-butyl ether), decomposition of the Grignard reagent occurred. The principal organic product of this decomposition was cyclobutene, accompanied by smaller amounts of 1,3-butadiene. From integration of the nmr spectrum of a heated sample of Grignard reagent, cyclobutene formation appeared to occur in at least 80% yield from the Grignard reagent. In tetrahydrofuran, the decomposition had approximate half-lives of 500 hr at 61.5° and 2 hr at 107°.

$$\underset{\mathbf{3}}{ClCH{=}CHCH_2Cl} \xrightarrow{NaCN} ClCH{=}CHCH_2CN \xrightarrow[H_2O]{HCl} ClCH{=}CHCH_2COOH \xrightarrow{LiAlH_4} ClCH{=}CHCH_2CH_2OH \xrightarrow[pyridine]{PBr_2} \underset{\mathbf{4}}{ClCH{=}CHCH_2CH_2Br} \quad (2)$$

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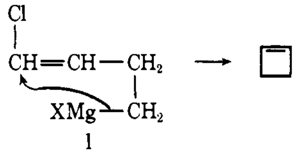
[2] (a) M. S. Silver, P. R. Shafer, J. E. Nordlander, C. Rüchardt, and J. D. Roberts, *J. Amer. Chem. Soc.*, **82**, 2646 (1960); (b) D. J. Patel, C. L. Hamilton, and J. D. Roberts, *ibid.*, **87**, 5144 (1965).

[3] (a) E. A. Hill, H. G. Richey, Jr., and T. C. Rees, *J. Org. Chem.*, **28**, 2161 (1963); (b) E. A. Hill and J. A. Davidson, *J. Amer. Chem. Soc.*, **86**, 4663 (1964); (c) E. A. Hill, R. J. Theissen, and K. Taucher, *J. Org. Chem.*, **34**, 3061 (1969); (d) E. A. Hill and H.-R. Ni, *ibid.*, 36, 4133 (1971); (e) H. G. Richey, Jr., and T. C. Rees, *Tetrahedron Lett.*, 4297 (1966); (f) H. G. Richey, Jr., and A. M. Rothman, *ibid.*, 1457 (1968); (g) H. G. Richey, Jr., and W. Kossa, Jr., *ibid.*, 2313 (1969); (h) W. C. Kossa, Jr., T. C. Rees, and H. G. Richey, Jr., *ibid.*, 3455 (1971); (i) D. O. Cowan, N. G. Krieghoff, J. E. Nordlander, and J. D. Roberts, *J. Org. Chem.*, 32, 2639 (1967); (j) P. T. Lansbury and F. O. Caridi, *Chem. Commun.*, 714 (1970); (k) S. A. Kandil and R. E. Dessy, *J. Amer. Chem. Soc.*, **88**, 3027 (1966); (l) A. Maercker and K. Weber, *Angew. Chem., Int. Ed. Engl.*, **8**, 912 (1969); (m) A. Maercker and R. Guess, *ibid.*, **9** 909 (1970).

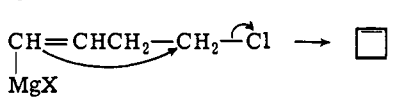
[4] (a) L. Friedman and H. Shechter, *J. Amer. Chem. Soc.*, **82**, 1002 (1960); (b) J. A. Smith, H. Shechter, J. Bayless, and L. Friedman, *ibid.*, **87**, 659 (1965); (c) H. G. Richey, Jr., and E. A. Hill, *J. Org. Chem.*, **29**, 421 (1964); however, for different results from gas-phase reactions and reactions of carbenes generated by atomic carbon reactions, see: (d) C. MacKay and R. Wolfgang, *J. Amer. Chem. Soc.*, **83**, 2399 (1961); (e) M. J. Welch and A. P. Wolf, *ibid.*, **91**, 6584 (1969); (f) P. B. Shevlin and A. P. Wolf, *ibid.*, **88**, 4735 (1966); (g) P. S. Skell and R. R. Engel, *ibid.*, **88**, 4883 (1966).

Several mechanisms might be envisioned for formation of cyclobutene from the Grignard reagent **1**. In addition to the mechanism proposed in eq 1, reasonable possibilities might include the intramolecular nucleophilic displacements in eq 3 and 4 and an addition–β-elimination sequence (eq 5).



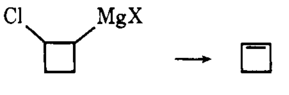
(3)

$\mathrm{ClCH{=}CHCH_2CH_2MgX \longrightarrow}$



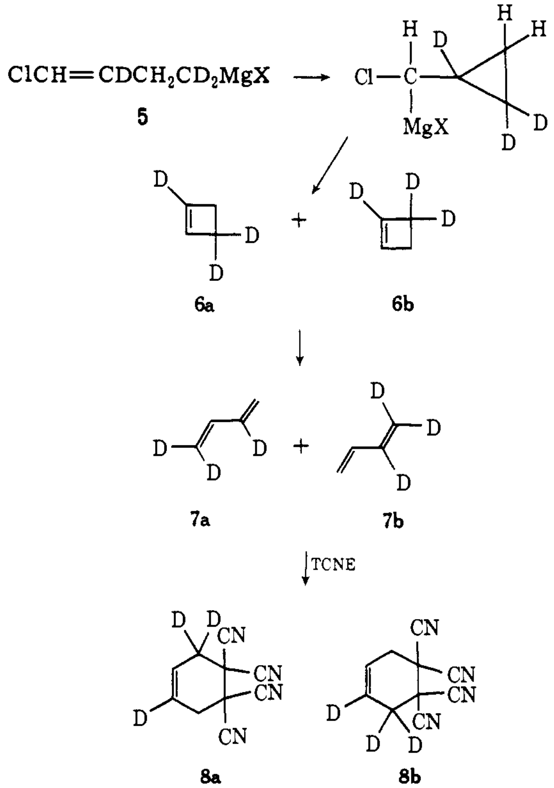
(4)

$\mathrm{ClCH{=}CHCH_2CH_2MgX \longrightarrow}$



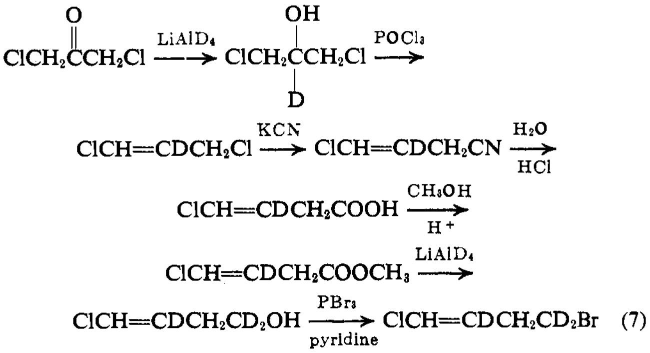
(5)

It is possible by means of deuterium labeling to eliminate all mechanisms which do not include an intermediate with the symmetry of the cyclopropyl carbenoid **2**. In the mechanism of eq 1, the two methylene groups of the Grignard reagent become equivalent with respect to the remainder of the molecule. In the trideuterated reagent **5**, this should produce an equimolar mixture of the two isomerically labeled cyclobutene molecules **6a** and **6b** (eq 6).



(6)

The appropriate 4-bromo-1-chloro-1-butene-*2,4,4-d*$_3$ was synthesized by the route shown in eq 7. Additional experiments were carried out using the *4,4-d*$_2$ analog, prepared in similar fashion. The deuterium distribution of the cyclobutene-d_3 (**6**) formed by heating the Grignard reagent in di-*n*-butyl ether was ascertained by several methods. Since this result is critical to the conclusion of the paper, these determinations will be detailed briefly.



$$\mathrm{ClCH_2\overset{O}{\overset{\|}{C}}CH_2Cl \xrightarrow{LiAlD_4} ClCH_2\overset{OH}{\underset{D}{C}}CH_2Cl \xrightarrow{POCl_3}}$$

$$\mathrm{ClCH{=}CDCH_2Cl \xrightarrow{KCN} ClCH{=}CDCH_2CN \xrightarrow[HCl]{H_2O}}$$

$$\mathrm{ClCH{=}CDCH_2COOH \xrightarrow[H^+]{CH_3OH}}$$

$$\mathrm{ClCH{=}CDCH_2COOCH_3 \xrightarrow{LiAlD_4}}$$

$$\mathrm{ClCH{=}CDCH_2CD_2OH \xrightarrow[pyridine]{PBr_3} ClCH{=}CDCH_2CD_2Br} \quad (7)$$

The nmr spectrum of the **6** mixture was determined with deuterium decoupling, to give narrower lines. The spectra, which have been published elsewhere,[5] were consistent with an approximately 1:1 mixture of isomers **6a** and **6b**, but with vinyl allylic coupling constants substantially different from those previously deduced[6] from analysis of the ^{13}C side bands of cyclobutene. A reinterpretation of the ^{13}C side-band spectra, necessitated by the discrepancy, yielded results consistent with the spectra of cyclobutene-d_3 and -d_2 prepared in this research. The ir spectrum of **6** also suggested an isomer mixture: in the gas phase, sharp Q branches appeared in *pairs* at 685 and 695, 836 and 851, and 999 and 1006 cm^{-1}.

Cyclobutene was largely converted to 1,3-butadiene by passage through a gc detector maintained at 310°. The deuterium-decoupled nmr spectrum of the butadiene-d_3 (**7**) so obtained, after rechromatography, could be interpreted completely as a mixture of **7a** and **7b**, with coupling constants similar to those in the literature for the undeuterated compound.[7] The ir spectrum of **7** also indicated a mixture of the expected isomers. Out-of-plane bending modes of the vinyl group are readily recognized in gas-phase spectra by their sharp, intense Q branches. Examination of the literature and additional spectra resulting from other studies suggests the following correlations for deuterated vinyl groups:[8,9] undeuterated, 990, 910, *ca.* 600;

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(5) E. A. Hill and J. D. Roberts, *J. Amer. Chem. Soc.*, **89**, 2047 (1967).

(6) S. Borčić and J. D. Roberts, *ibid.*, **87**, 1056 (1965).

(7) R. T. Hobgood, Jr., and J. H. Goldstein, *J. Mol. Spectrosc.*, **12**, 76 (1964).

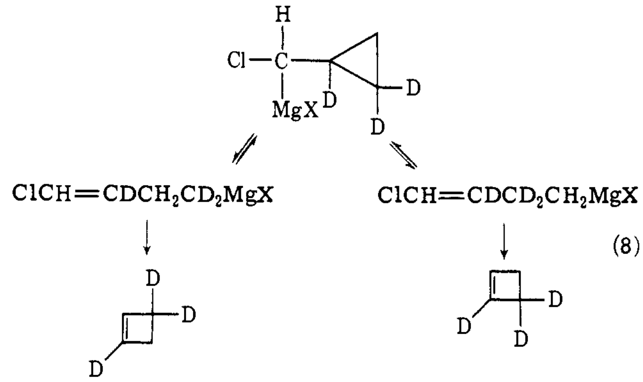
(8) L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," Wiley, New York, N. Y., 1958, pp 34–56.

(9) (a) Coupling of the 990-cm^{-1} modes of 1,3-butadiene results in ir and Raman bands at 1013 and 967 cm^{-1}, respectively, in the undeuterated compound;[9l] (b) correlations for deuterated vinyl groups are based upon the following data: propene-*cis-1-d*, 800,[9c] 798;[9d] 1-hexene-*cis-1-d*, 800;[9e] styrene-*cis-1-d*, 808;[9e] propene-*trans-1-d*, 977 and 812,[9c] 975;[9d] 1-hexene-*trans-1-d*, 985, 830, and 554;[9e,f] styrene-*1-d*, 978 and 845;[9e] propene-*1,1-d*$_2$, 910 and 728;[9c] 1-pentene-*1,1-d*$_2$, 932 and 730;[9g] 1,3-butadiene-*1,1-d*$_2$, 931, 729, and 442;[9h] propene-*2-d*, 912 and 850;[9c] 1-hexene-*2-d*, 910, 844, and 629;[9f] 1,3-butadiene-*2-d*, 925, 880, and 630 or 500;[9i] propene-d_6, 734, 712, and 434;[9j] propene-d_3, 705;[9k] 1,3-butadiene-d_6, ~750, 710, 475;[9l]; 1,3-butadiene-*1,1,2-d*$_3$, 992, 911, 792 (w), 711, 438;[9m] (c) M. Farina and M. Peraldo, *Gazz. Chim. Ital.*, **90**, 973 (1970); (d) W. P. Norris, *J. Org. Chem.*, **24**, 1579 (1959); (e) H. Kuivila and R. Sommer, *J. Amer. Chem. Soc.*, **89**, 5616 (1967); (f) H. W. Schrotter and E. G. Hoffmann, *Justus Liebigs Ann. Chem.*, 672, 44 (1964); (g) E. A. Hill, unpublished results; (h) this work; (i) I. S. Borshagovskaya, Yu. N. Panchenko, and Yu. A. Pentin, *Opt. Spektrosk.* **22**, 355 (1967); (j) R. C. Lord and P. Venkateswarlu, *J. Opt. Soc. Amer.*, **43**, 1079 (1953); (k) S. Murahashi, S. Nozakura, and K. Yasufuku, *Bull. Chem. Soc. Jap.*, 37, 854 (1964); (l) Yu. N. Panchenko, Yu. A. Pentin, V. I. Tyulin, and V. M. Tatevskii, *Opt. Spektrosk.*, 16, 992 (1964); (m) Yu. N. Panchenko, T. X. Hoang, and Yu. A. Pentin, *Vestn. Mosk. Univ., Khim.*, 22, 32 (1967).

cis-1-d, 800; *trans-1-d*, 980, 830 ± 15; *1,1-d*$_2$, 930, 730; *2-d*, 910, 845; *1,1,2-d*$_3$, 792 (w), 710. An additional band present for the vinyl-d_3 group at about 730 cm^{-1} is seen with difficulty due to low intensity and overlapping, and may be uncertain in position. From the form of the vinyl group normal modes at 990 and 910 cm^{-1},[10] it would appear that analogous frequencies in deuterated vinyl groups should be relatively independent of mechanical coupling effects with the remainder of the molecule, though the lower frequency vibration (*ca.* 600 cm^{-1}) should be much more subject to variation. **7** had bands at 989, 944, 907, 826, 790 (vw), 732, 708, and 673 cm^{-1}, sufficient to account for characteristic bands of all four expected deuterium distributions, assuming coincidence of 910-cm^{-1} bands of undeuterated and *2-d* vinyl groups. The extra band at 673 cm^{-1} was relatively weak, and could be an additional band for one of these groups. The butadiene isolated directly from the reaction had a similar spectrum, as did butadiene from pyrolysis of the cyclobutene generated *during* Grignard formation. However, the butadiene generated during Grignard formation was weaker or lacking in the 990- and 710-cm^{-1} bands, suggesting that it may contain mainly **7a**, formed without rearrangement. The spectrum of butadiene-*1,1-d*$_2$, derived from dideuterated chlorobromide in similar fashion, had only the expected peaks, and matched the spectrum of an authentic sample prepared by reduction of 1,1-dichloro-1,3-butadiene with zinc dust in deuterium oxide.

The adduct **8** with tetracyanoethylene was formed from **7**. The methylene protons in the deuterium-decoupled nmr spectrum appeared as a clean four-line pattern, interpreted as a doublet for each of **8a** and **8b**, while the vinyl protons appeared as a pair of overlapping triplets. The coupling constants (3.8 and 2.2 Hz) derivable from these spectra appear to be compatible with the literature[11] for three- and four-bond vinyl–allyl coupling constants in cyclohexenes. The ratio of isomers was 1.0 ± 0.10.

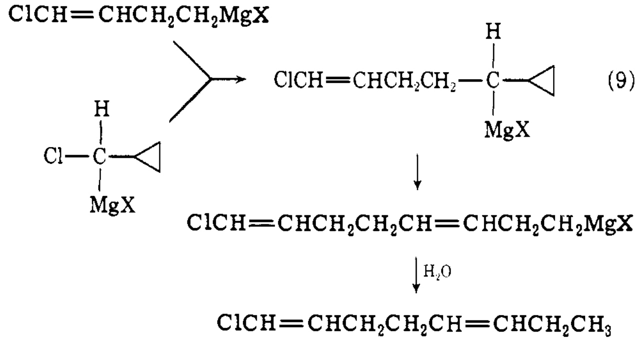
Results with the trideuterated Grignard reagent demonstrate the equivalence of the two methylene groups, as predicted by the mechanism of eq 1. An alternative route to this equivalence is shown in eq 8.



(8)

If equilibration of isomers occurs more rapidly than decomposition to cyclobutene, then the product should show the same equivalence of methylene groups. Another consequence of this rapid equilibration of eq 8 is cis–trans isomerization about the double bond. In several experiments with different heating times and temperatures, and with different isomer distribution in the bromide used to prepare the Grignard, the 1-chloro-1-butene isolated by hydrolysis of the remaining Grignard reagent had a similar isomer distribution to that of the original bromide. In addition to demonstrating a lack of cis–trans isomerization, these experiments also show that cis and trans isomers react at comparable rates. The nmr spectra of 1-chloro-1-butene isolated from reactions of deuterated Grignard reagents also showed the absence of extensive isomerization of the deuterium label, though these experiments were of lower reliability.

In an attempt to trap the cyclopropyl carbenoid intermediate, a decomposition of the Grignard was performed in the presence of cyclohexene. There was no new component detected of the volatility expected for a C_{10} hydrocarbon. However, it is likely that another bimolecular trapping of the carbenoid did occur, as shown by the presence of a minor higher boiling component isolated by hydrolysis of the Grignard *after* heating. The product appeared to be a cis–trans mixture of 1-chloro-1,5-octadiene (**9**). The nmr spectrum showed a methyl triplet, six allylic hydrogens, and two olefinic hydrogens each in the regions typical of an isolated internal double bond and a –CH=CHCl group. The infrared spectrum had a band at 972 cm^{-1}, appropriate to a trans dialkyl-substituted ethylene, and 1-chloro-1-alkene bands at 940 cm^{-1} (trans) and 742 and 710 cm^{-1} (cis). The mass spectrum indicated the presence of one chlorine in the molecular ion; particularly prominent fragment ions *m*/*e* 69 and 75 correspond to cleavage of the doubly allylic C–C bond, and a variety of other major fragment ions are logically derivable from the molecular ion after hydrogen scrambling. A likely source of this product is shown in eq 9.



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The results in this paper strongly suggest that the decomposition of the Grignard reagent from 4-bromo-1-chloro-1-butene has as its rate-determining step the intramolecular addition of the organomagnesium function to the olefinic double bond. Such intramolecular additions, and the cleavage reactions that are their reversal, are the subject of a number of studies in the literature.[3] Kinetics studies of the ring cleavage of the cyclobutylmethyl Grignard[3b] have led to the proposal of a concerted four-center mechanism, and the rejection of carbanion and radical mechanisms as less likely. More recently, an electron-transfer mechanism has been discussed for some intermolecular[12] and intra-

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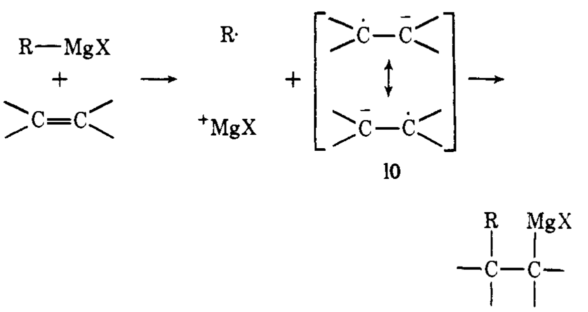
(10) J. R. Scherer and W. J. Potts, *J. Chem. Phys.*, 30, 1527 (1959); W. J. Potts and R. A. Nyquist, *Spectrochim. Acta*, 15, 679 (1959).

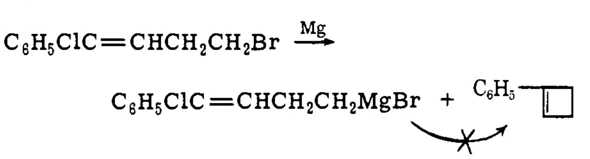
(11) See S. Sternhell, *Quart. Rev., Chem. Soc.*, 23, 236 (1969), and references therein.

molecular[3g] additions of Grignard reagents to carbon–carbon multiple bonds (eq 10 and variations thereof).


(10

In the context of this mechanistic question, the present result may be usefully contrasted with two other studies.

First, in a reaction which superfically appears to be very similar to the present one, 4-bromo-1-chloro-1-phenyl-1-butene reacts with magnesium to yield 1-phenylcyclobutene, along with other products (eq 11).[13] Deuterium labeling experiments similar to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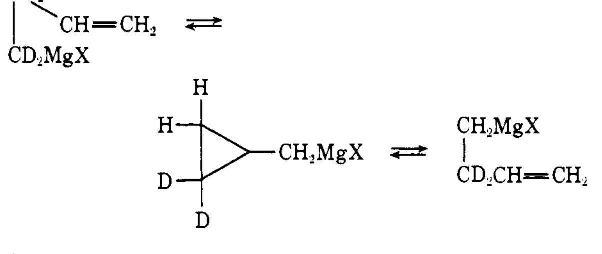
those reported in this paper indicated an intermediate of similar symmetry. However, the phenylcyclobutene is not derived from the Grignard reagent. Although yields of phenylcyclobutene over 25% were found immediately following the reaction with magnesium, Grignard reagent which was generated concurrently did not rearrange readily to form more phenylcyclobutene.[13c] The Grignard was stable after 4 hr at 60°; on heating for 4 hr at 115°, decomposition of Grignard reagent did occur, and nmr absorption probably corresponding to phenylcyclobutene appeared as the most prominent feature of a rather complex olefinic region of the nmr spectrum. In the present instance, a half-life of about 40 min was found at 107° in ether. Thus, the presence of the phenyl group does not appear to accelerate the ring closure to a cyclopropyl carbenoid, and, indeed, may hinder that reaction.

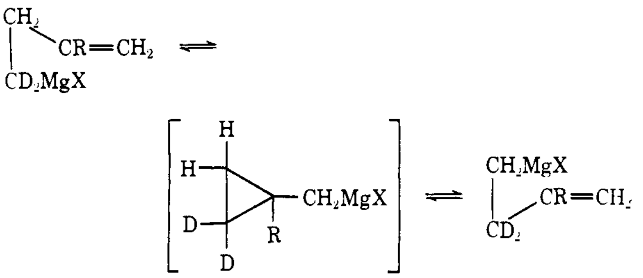
The other comparison is with the rearrangement of labeled 3-buten-1-yl (allylcarbinyl) Grignard reagent, studied by Roberts and coworkers (eq 12).[2] A half-


(12)

life of 40 min was found for this rearrangement at 55.5° in diethyl ether, and an activation energy of 26 kcal/mol. In the present study, rather crude half-lives of 2 hr at 107° and 500 hr at 59.5° were found in tetrahydrofuran, corresponding to an activation energy of about 30 kcal/mol. The reaction was probably about 2.5 times as fast in ether (at 107°). This solvent effect is comparable with that observed in the ring cleavage reaction of cyclobutylmethyl organomagnesium compounds,[3b] and so it is likely that introduction of a chlorine on the double bond is responsible for the observed decrease in rate, a factor of over 10^3.

The interesting conclusions may then be drawn that neither a phenyl nor a chlorine, as substituted in the present cases, accelerates the intramolecular addition of a Grignard reagent to a carbon–carbon double bond, and both probably depress the rate substantially. Since both chlorine and phenyl have the well-documented ability to stabilize either radicals or carbanions,[14] this result tends to confirm the unacceptability of carbanion or radical mechanisms, and makes the radical anion **10** of the electron-transfer mechanism similarly appear less attractive. The rate-depressing effects of phenyl and chlorine may be attributed to steric hindrance in a concerted mechanism.

In two other cases, the effect of phenyl substitution in the cyclopropylmethyl-3-butenyl system has been reported. Maercker and Weber[31] found that both phenyl and methyl, substituted on the other end of the double bond, depress the rate. In this position, a



phenyl substituent should stabilize the radical anion **10**, so again the electron-transfer mechanism does not fit the results. Roberts and coworkers[17] found that the diphenyl analog was completely rearranged by the time of its first observation, and concluded that the phenyl substituents markedly accelerate the rate of equilibration. However, it is interesting to note that no data in their paper require that any rearrangement occurs *after* formation of the reagent, and that all of their results would be consistent with complete equilibration *during* formation of the reagent (perhaps *via* an intermediate free radical).[17a]

(12) H. G. Richey, Jr., and F. W. von Rein, *J. Organometal. Chem.*, 20, P32 (1969); J. J. Eisch and J. H. Merkley, *ibid.*, **20**, P27 (1969); J. J. Eisch and R. L. Harrell, *ibid.*, 21, 21 (1970).

(13) E. A. Hill and M. R. Engel, *J. Org. Chem.*, 36, 1356 (1971); A. J. Frey and R. H. Moore, *ibid.*, 33, 425 (1968); M. S. Newman and G. Kaugars, *ibid.*, **30**, 3295 (1965).

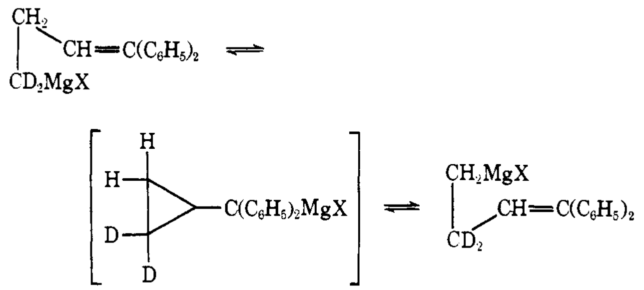
(14) The effect of chlorine or phenyl substitution on free-radical stabilities or on the rate of addition of radicals to a double bond may be ascertained from C–H bond strengths, and from methyl affinities of alkenes or copolymerization data.[15] The effect of chlorine or phenyl groups on carbanion stability may be inferred from p*K* and hydrogen exchange data for weak organic acids, and from the ability to undergo anionic polymerization.[16]

(15) E. S. Huyser, "Free Radical Chain Reactions," Wiley-Interscience, New York, N. Y., 1970, pp 67–88, 353–370; P. I. Abell, *Trans. Faraday Soc.*, 60, 2214 (1964); A. M. Hogg and P. Kebarle, *J. Amer. Chem. Soc.*, 86 4558 (1964).

(16) E. M. Kosower, "An Introduction to Physical Organic Chemistry," Wiley, New York, N. Y., 1968, pp 21–44; J. Hine, N. W. Burske, M. Hine, and P. B. Langford, *J. Amer. Chem. Soc.*, **79**, 1406 (1957); L. Reich and A. Schindler, "Polymerization by Organometallic Compounds," Interscience, New York, N. Y., 1966, pp 176–242, 548–668.

(17) M. E. Howden, A. Maercker, J. Burdon, and J. D. Roberts, *J. Amer. Chem. Soc.*, **88**, 1732 (1966).

(17a) Note Added in Proof. We are informed by Professor H. G. Richey, Jr., that he has evidence in another case that a similarly positioned phenyl group leads to a significant reduction in the rate of the 3-buten-1-yl–cyclopropylmethyl Grignard interconversion.



Formation of 1,3-butadiene by rearrangement from cyclopropylcarbene or -carbenoids[4a-c] represents a rather drastic molecular reorganization. It is probable that part or perhaps all of the butadiene may be explained as electrocyclic rearrangement of the primary reaction product, cyclobutene.[18] However, in some cases, it appears that the rearrangement of cyclobutene may be too slow at the reaction temperature to account for all that was formed; also, in some runs in the present study, there was no indication of an increase in the proportion of butadiene with heating time. Routes involving the intermediacy of bicyclo[1.1.0]butane appear to be unlikely.[4b] A possible route to butadiene that bypasses *ground-state* cyclobutene might be visualized. Although it is generally agreed that deactivation of vibrationally excited molecules in solution is rapid enough to preclude any importance of "hot" reactions,[19] the present case may be an especially favorable one. The reaction coordinate from cyclopropylcarbene to butadiene resembles the ring torsion mode of cyclobutene. This mode is of the same symmetry species as the allowed conrotatory conversion of cyclobutene to butadiene. It is possible that this relationship in symmetry may permit efficient use of excess vibrational energy before it is dispersed by molecular collision.[19a]

Ethylene and acetylene, products found in other studies,[4] were not formed in the present case in amounts sufficient to characterize. It may be noted that the magnesium carbenoid, which is probably the least energetic of the species studied, gives the most selective production of cyclobutene.

Experimental Section[20]

4-Chloro-3-butenoic Acid. 4-Chloro-3-butenonitrile was prepared from 1,3-dichloropropene and sodium cyanide by the method of Vessiére.[21] The crude product was hydrolized to the acid with HCl. The yield for the two steps was 64%: bp 111-115° (14 mm) [lit.[21] bp 103-104 and 111-112° (13 mm)]. The methyl ester was prepared by refluxing the acid in 3% methanolic sulfuric acid: bp 71-78° (14 mm).

4-Chloro-3-buten-1-ol. To 13.3 g (0.35 mol) of lithium aluminum hydride in 750 ml of anhydrous ether was added 50 g (0.42 mol) of 4-chloro-3-butenoic acid in 100 ml of ether over a period of 2 hr. After an additional hour of stirring at reflux, the reaction mixure was hydrolyzed by dropwise addition of saturated sodium chloride, followed by dilute hydrochloric acid. The product was isolated in 73% yield by extraction with ether, drying (K_2CO_3), and distillation: bp 98-99.5° (56 mm). The product was found by gc on column A to contain nearly equal amounts of the cis and trans isomers, with the cis isomer eluted first. Reduction of the methyl ester gave similar results. Small samples of the isomers were isolated by preparative gc on columns A or B. Both isomers had ir bands at 3320, 3080, 2900, 2800, 1640, and 1055 cm^{-1}; the trans isomer had a strong band at 942 cm^{-1} and the cis isomer a series of bands at 750, 738, and 714 cm^{-1}, which appear to be characteristic of the ClCH=CHR group.[22] The nmr spectra differed somewhat in chemical shift, in the appearance of the olefinic multiplet and the "higher order" perturbation of the allylic resonance: cis (CCl_4) δ 2.51 (q, 2, J = 6.8 Hz, allylic), 3.73 (t, 2, J = 6.7 Hz, CH_2OH), 3.91 (s, 1, OH), 5.78-6.35 ppm (m, 2, olefinic); trans (CCl_4) δ 2.32 (q, 2, J = 6.6 Hz), 3.68 (t, 2, J = 6.5 Hz), 3.95 (s, 1), 5.75-6.35 ppm (m, 2).

Anal. Calcd for C_4H_7ClO (mixture of isomers): C, 45.15; H, 6.63. Found: C, 44.88; H, 6.42.

4-Bromo-1-chloro-1-butene. To a mixture of 25.5 g (0.24 mol) of 4-chloro-3-buten-1-ol and 6.4 g (0.081 mol) of pyridine at −10° was added 32.5 g (0.12 mol) of phosphorus tribromide over 30 min. After an additional 30 min, the mixture was warmed to room temperature over 45 min and then distilled at about 10 min from a less volatile residue. The distillate was washed with saturated aqueous sodium bicarbonate and sodium chloride solutions, dried over Drierite, and redistilled to yield 40.6 g (59%) of the dihalide: bp 49-52° (12 mm). The isomers were partially separated by distillation through a 6-in. helix-packed column, and small samples of the pure isomers were obtained by preparative gc on column A. In the ir, both isomers absorbed at 3080, 2960-2850, 1630, 1420, and 1350-1200 cm^{-1}; the cis isomer absorbed at 730, 710, and 680 (sh) cm^{-1}, and the trans at 930 and 805 cm^{-1}; nmr (CCl_4), trans, δ 2.61 (approx q, 2, $J \cong 7.1$ Hz, allylic), 3.33 (approx t, 2, $J \cong 6.9$ Hz, CH_2Br), 5.7-6.2 ppm (m, 2, olefinic); cis, δ 2.80 (approx q, 2, $J \cong 7.1$ Hz,) 3.38 (approx t, 2, $J \cong 7.0$ Hz), 5.7-6.2 ppm (m, 2); at 100 MHz, the latter absorption was a quartet (J = 6.8 Hz) at 5.83 and a doublet of triplets (J = 7.1, 1.4 Hz) at 6.15 ppm.

Anal. Calcd for C_4H_6BrCl (mixture of isomers): C, 28.35; H, 3.57. Found: C, 28.48; H, 3.67.

1,3-Dichloropropene-*2-d*. A suspension of 5.4 g (0.13 mol) of lithium aluminum deuteride in 150 ml of ether was added over 75 min to a solution of 60 g (0.47 mol) of 1,3-dichloropropanone in 160 ml of ether, maintained below 0°. After 30 min more at 0°, the mixture was hydrolyzed with 45 ml of concentrated hydrochloric acid, washed, and dried (Na_2SO_4). Distillation yielded 54.5 g (89%) of 1,3-dichloro-2-propanol-*2-d*, bp 89.5-93° (25 mm) [lit.[23] bp 70-73° (14 mm) for isotopically normal product]. The alcohol was dehydrated with phosphorus oxychloride by the method of Hatch, *et al.*,[24] in 36% yield, bp 102-112° [lit.[24] bp 104 and 112° for isotopically normal isomers]. Integration of the nmr spectrum gave 1.0 ± 0.1 olefinic hydrogen. Analysis of the splitting pattern of the trans isomer gave $J_{\text{H-H}} = J_{\text{allylic H-D}}$ = 1.20 Hz; $J_{\text{vinyl H-D}}$ = 2.05 Hz.

4-Bromo-1-chloro-1-butene-*4,4-d*$_2$ and 4-bromo-1-chloro-1-butene-*2,4,4-d*$_3$ were prepared by the methods described above for undeuterated material: reduction of methyl 4-chloro-3-butenoate was run with lithium aluminum deuteride, and for the trideuterated analog, the synthesis was started with 1,3-dichloropropene-*2-d*. In all cases, the nmr integrals were correct within experimental error, and less than 5% of one hydrogen was present in the CD_2 group.

Infrared spectra were obtained for cis and trans isomers of undeuterated and deuterated analogs of a number of compounds involved in these preparations (1,3-dichloropropene, 4-chloro-3-

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(18) R. W. Carr, Jr., and W. D. Walters, *J. Phys. Chem.*, 69, 1073 (1965).

(19) See, for instance, H. M. Frey in "Carbene Chemistry," W. Kirmse, Ed., Academic Press, New York, N. Y., 1964, p 219.

(19a) Note Added in Proof. It has recently been proposed that dimethylcyclopropylcarbene, generated in carbon atom reactions, fragments and rearranges before loss of excess vibrational energy, even though it is generated on a liquid N_2 cooled surface (J. Villaume and P. S. Shell, *J. Amer. Chem. Soc.*, 94, 3455 (1972)).

(20) Spectra were run on Varian Associates A-60 and HA-100 nmr spectrometers, and Beckman IR-5 and IR-8 and Perkin-Elmer 521 infrared spectrometers. Gas chromatography was carried out on Aerograph A-90-P chromatographs with columns as follows: A, 0.25 in. × 10 ft, 25% Ucon polar on firebrick; B, 0.25 in. × 10 ft, 20% Carbowax 20M on Chromosorb P; C, 0.25 in. × 10 ft, 20% Dow Hi-Vac silicone stopcock grease on Chromosorb W; D, 0.25 in. × 10 ft, 20% silicone QF-1 on Chromosorb P; E, 0.5 in. × 10 ft, 20% Dow Hi-Vac silicone stopcock grease on Chromosorb W; F, 0.5 in. × 10 ft, 17% Apiezon J on Chromosorb P; G, 0.25 in. × 10 ft, tricresyl phosphate on firebrick. Elemental analyses were run by Schwartzkopf Microanalytical Laboratories. Melting and boiling points are uncorrected.

(21) R. Vessiére, *Bull. Soc. Chim. Fr.*, 1268 (1959).

(22) W. C. Wolff, H. M. Doukas, and J. S. Ard, *J. Amer. Chem. Soc.*, 78, 627 (1954).

(23) J. B. Conant and O. R. Quayle, "Organic Syntheses," Collect. Vol. I, Wiley, New York, N. Y., 1941, p 292.

(24) L. F. Hatch, A. N. Brown, and H. P. Bailey, *J. Amer. Chem. Soc.*, 72, 3198 (1950).

buten-1-ol, 4-bromo-1-chloro-1-butene, and 1-chloro-1-butene obtained on hydrolysis of the Grignard reagent from the latter). Except in the fairly obvious case of CD stretching bands at about 2220 and 2120 cm^{-1}, most of the spectral changes brought about by deuteration could *not* be *simply* interpreted as the shift of a group frequency by $\sqrt{M_{\mathrm{H}}}/\sqrt{M_{\mathrm{D}}}$, even though some relatively consistent bands did result. In the trans analogs with no deuterium substitution on the double bond, the characteristic band remained at about 940–935 cm^{-1}. When an olefinic deuterium was present, a strong band appeared instead at about 800–790 cm^{-1}. All the cis isomers had at least one, and generally two or three, strong bands in the vicinity of 700–750 cm^{-1}, regardless of deuterium substitution; in addition, deuterium substitution on the double bond resulted in a strong band at 1020 cm^{-1}. All compounds, cis or trans, with an olefinic deuterium, had a strong band at 850 cm^{-1}. Alcohols with the CD_2OH group lacked a 1055-cm^{-1} band present in the undeuterated compounds, but had a strong band at 975–965 cm^{-1}. Numerous weaker bands were present in this region. There were also sizable changes in the region 1450–1100 cm^{-1}.

Grignard Reagent from 4-Bromo-1-chloro-1-butene. In a typical preparation, the Grignard reagent was prepared in a well-dried flask with a sealed condenser and a side arm located above the condenser.[3b] To the flask were added 0.437 g (0.0180 g-atom) of turnings from sublimed magnesium, 2.77 g (0.0163 mol) of 4-bromo-1-chloro-1-butene, and 10 ml of tetrahydrofuran which had been purified by distillation from lithium aluminum hydride under a slow stream of nitrogen. The reaction mixture was heated at reflux 45 min after the spontaneous reaction subsided, and the volatiles were then pumped at room temperature under a vacuum of about 5 μ to a cold trap. A white to pale yellow oily residue remained. Nitrogen was admitted, and the residue was dissolved in 8 ml of dry THF. The resulting solution was transferred by syringe to sample tubes and an nmr tube, which were sealed under less than 1 atm of nitrogen. Sample tubes were heated for various periods of time and opened under a nitrogen atmosphere in a dry bag. The tubes, which were equipped with a ground joint, were attached by an adapter to a vacuum system, and volatiles were pumped to a cold trap. The residual Grignard reagent was hydrolyzed (in various cases with water, methanol, and butanol) and volatile materials were again pumped to a trap. The concentration of the Grignard reagent was determined in some cases by acid titration after hydrolysis.

A number of variations from the basic procedure for preparing and treating the Grignard reagent were studied. In some cases, the Grignard reagent was heated in the flask in which it was prepared, while a slow flow of nitrogen swept volatile components from the top of the condenser to a cold trap. This was particularly successful when the tetrahydrofuran, in which the Grignard reagent had been prepared, was replaced by di-*n*-butyl ether or 1,2-dimethoxyethane. Grignard reagents were also prepared and heated in diethyl ether. In some cases, the magnesium was allowed to react with the bromide in a sealed nmr tube, and in other cases, the solvent and bromide were distilled into the reaction flask or nmr tube on a vacuum line.

Volatile products were analyzed in various instances by gas chromatography on columns A–G, and preparatively separated on columns E–G. *cis*- and *trans*-1-chloro-1-butene were compared gas chromatographically and by ir and nmr spectra with authentic samples separated from a commercial mixture. Cyclobutene and 1,3-butadiene were identified by comparison of ir[25] and nmr[6,7] spectra with published spectra, and gc retention times of 1,3-butadiene and 1-butene were compared with commercial samples. Characteristically, the solvent pumped from the preparation contained a small amount of C_4 hydrocarbons (*ca.* 1% yield), consisting of 1,3-butadiene and cyclobutene in a ratio varying from 3:1 to 1:3 in various preparations. A somewhat larger yield of the 1-chloro-1-butene was found. In the solvent pumped from the heated Grignard reagents, cyclobutene was the major C_4 hydrocarbon product. This was accompanied by about 3–5% as much 1,3-butadiene, and small amounts of the 1-chloro-1-butene. Hydrolysis of the Grignard reagent gave small amounts (*ca.* 1%) of C_4 hydrocarbons, consisting of cyclobutene, 1,3-butadiene, and 1-butene, along with larger amounts of the 1-chloro-1-butenes, depending upon the extent of decomposition.

A Grignard reagent was prepared from a sample of the trans isomer, separated by gc, which was at least 98% pure trans. The solvents pumped from the Grignard reagent preparation, and from the Grignard reagent heated until about 90% decomposed, contained the 1-chloro-1-butene isomers in cis:trans ratios of 0.14:1.00 and 0.05:1.00, respectively. Hydrolysis of the Grignard reagent led to a cis:trans ratio of less than 0.01:1.00. A similar experiment indicating a lack of cis:trans isomerization of the Grignard reagent was carried out with a reagent with a ratio of 2.2:1.0.

The nmr spectrum of the Grignard reagent exhibited a prominent triplet absorption at high field due to the CH_2Mg protons at -0.58 ppm in tetrahydrofuran and -0.47 ppm in ether, with $J = 8.6$ Hz. There was no indication of a difference in chemical shift between isomers. Olefinic absorption was a complex multiplet at about 5.5–6.2 ppm. In the Grignard reagent from pure cis isomer, observed at 100 MHz, the multiplet approximated a quartet and a doublet, each with $J \approx 7$ Hz, similar to the spectra of the corresponding *cis*-4-bromo-1-chloro-1-butene, but less well separated. The integral of the olefinic resonance was determined to be the same in the Grignard reagent as in the chlorobromide from which it was made, by comparison with an internal benzene reference. The integral of the CH_2Mg protons ranged from about 60 to 80% of the olefinic resonance in various preparations. A methyl triplet at 0.99 ppm was insufficient in size to account for all of the bromide not converted to Grignard reagent. On heating for periods of time varying from 60 min to several hours at 107°, the nmr spectrum underwent several significant changes. The CH_2Mg triplet grew weaker; the integral of the olefinic proton resonance remained approximately constant, but much of the intensity of the multiplet absorption of the Grignard reagent was replaced by a singlet at 5.59 ppm; a singlet developed at 2.51 ppm. The latter absorptions were absent in the original reagent, and are in agreement with the published spectrum of cyclobutene.[6] There was little change in the 0.99-ppm triplet of 1-chloro-1-butene.

1-Chloro-1,5-octadiene. Gas chromatographic examination on column C of the mixture obtained by hydrolysis of the Grignard solution showed the presence of a high boiling component which increased to several per cent of the total product after heating for over a half-life. This appeared to be a mixture of isomers in cases where the starting bromide was a mixture. The product from such a reaction, isolated by preparative gc, had the following spectral properties: ir (neat) 1640, 972, 940, 942, and 710 cm^{-1}; nmr (CCl_4) δ 0.98 (t, 3, $J = 7.2$ Hz), 1.7–2.5 (m, 6), 5.2–5.55 (m, 2), 5.6–6.0 ppm (m, 2); mass spectrum (70 eV) *m/e* (rel intensity) 146 (0.17), 144 (0.50), 110 (4), 109 (50), 95 (4), 88 (8), 79 (10), 77 (11), 75 (16), 70 (12), 69 (100), 68 (12), 67 (34), 55 (12), 53 (22), 51 (12), 41 (100), 39 (59).

Decomposition of Grignard Reagent 1 in the Presence of Cyclohexene. In one set of reactions, cyclohexene was added to two tubes to make up 20 and 50% of the solution by volume, respectively. The tubes were heated at 61° for a time equivalent to about 1.5 half-lives, and worked up as before. There was less than 0.1% yield of product in the fraction pumped from the Grignard reagent before hydrolysis in the retention time range expected of a C_{10} hydrocarbon.

Kinetics of Decomposition of the Grignard Reagent 1. Approximate kinetics were obtained from gc results at 61.5° and by nmr at 107°. In the former cases samples of Grignard reagent in tetrahydrofuran, 0.86 *M* in **1** and about 0.3 *M* *n*-pentylmagnesium bromide, were sealed in tubes. The cis:trans ratio of the bromide was about 1:16. The tubes were heated at 61.5° for periods of time up to 568 hr, and worked up by removal after volatiles under vacuum, followed by hydrolysis with methanol or *n*-butyl alcohol. The concentration of C_4 hydrocarbons in the volatiles before hydrolysis increased with time; *n*-pentane and 1-chloro-1-butene increased at a slower rate. In the products from hydrolysis, the C_4 hydrocarbons remained about constant, and the *n*-pentane and 1-chloro-1-butene decreased, at different rates. It was assumed that the loss of *n*-pentyl Grignard reagent can be taken as a model for loss of the chlorobutenyl Grignard by all pathways other than conversion to cyclobutene. Then, a plot of log (1-chloro-1-butene/*n*-pentane) *vs.* time was approximately linear, with a half-life of 500 ± 100 hr. The initial rate of cyclobutene formation had a half-life of 620 hr. The ratio of cis: trans 1-chloro-1-butene varied randomly from 1:12 to 1:18, probably within the limits of error.

A solution of the chlorobutenyl Grignard in tetrahydrofuran was determined to be 1.4 *M* by comparison of the integral of the CH_2Mg resonance with an external standard. Redetermination of the spectrum after periods of heating at 107° led to a fairly good first-order plot, with a half-life of 123 ± 15 min. Integration of the cyclobutene CH_2 resonance was insufficiently accurate to permit an independent rate determination, but it did indicate about an 80%

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[25] (a) R. C. Lord and D. G. Rea, *J. Amer. Chem. Soc.*, **79**, 2401 (1957); (b) Infrared Spectral Data, American Petroleum Institute, Research Project 44, Spectra No. 916-919.

conversion to cyclobutene. A more dilute sample appeared to react more slowly. A similar sample in ether reacted more rapidly, with a very approximate half-life of 40 min. A crude value of $\Delta H^{\ddagger}$ for the reaction in tetrahydrofuran is 30 kcal/mol.

Decomposition of the Grignard Reagent from 4-Bromo-1-chloro-1-butene-*2,4,4*-d_3. A Grignard reagent was prepared from the trideuterated bromide (3.15 g, 0.00182 mol) in tetrahydrofuran (15 ml), as previously described. Volatiles were removed under vacuum, and replaced by di-*n*-butyl ether (distilled from lithium aluminum hydride). A slow flow of nitrogen was introduced at the top of the flask, and allowed to pass over the top of the condenser, out the side arm, and through a trap maintained at liquid nitrogen temperature. The flask was heated gradually to a bath temperature of 150°, and maintained there for 7 hr. Gas chromatography of the condensate on column F showed cyclobutene and 1,3-butadiene in a ratio of 25:1. Preparative chromatography was carried out, with the detector temperature maintained at 310° (which had been shown previously to largely isomerize cyclobutene to 1,3-butadiene). The "cyclobutene" peak was rechromatographed, using a detector temperature of 135°, which produced no isomerization. Gas-phase infrared spectra were obtained for (1) 1,3-butadiene obtained in the first chromatographic separation; (2) 1,3-butadiene from isomerization of cyclobutene; and (3) cyclobutene. In another experiment, ir spectra were obtained for components pumped from the Grignard reagent before it was heated. Nmr spectra were obtained for (2) and (3). Prominent features of the ir spectra are enumerated in the body of the paper. The nmr spectrum of (3) has been reported previously.[5] The nmr spectrum of (2) was obtained with deuterium decoupling. It may be interpreted as a mixture of 1,3-butadiene-*1,1,2*-d_3 (**7b**) and-*1,1,3*-d_2 (**7a**). First-order analysis of the spectra led to coupling constants $J_{\text{cis}} = 9.9$ Hz, $J_{\text{trans}} = 17.0$ Hz, $J_{\text{gem}} = 1.85$ Hz, and $J_{\text{H-D, vic}} = 1.5$ Hz from **7b**, and $J_{4\text{-cis}} = J_{4\text{-trans}} = 0.85$ Hz and $J_{\text{gem}} = 1.8$ Hz from **7a**.

A portion of the 1,3-butadiene-d_3 in carbon tetrachloride was distilled on a vacuum line into a flask containing a deficiency of tetracyanoethylene, and allowed to stir at room temperature for 0.5 hr. The volatiles were removed, and the residue recrystallized from methanol. The nmr spectrum was determined in acetone solution. The allylic methylene absorption had four equal, unevenly spaced peaks, which could be interpreted as doublets from two isomers separated by 0.17 Hz, $J = 3.8$ and 2.25 Hz, or separated by 0.77 Hz, $J = 3.2$ and 2.85 Hz, or separated by 3 Hz, $J = 0.93$ and 0.60 Hz. Only the former was consistent with the overlapping triplets of the vinyl proton spectrum, which was obtained with lower resolution.

Grignard Reagent from 4-Bromo-1-chloro-1-butene-*4,4*-d_2. A sample of Grignard reagent was prepared in the customary manner, transferred to sample tubes, and heated for 500 hr at 61.5°. After removal of volatile materials by pumping, the sample was hydrolyzed with deuterium oxide. The nmr spectrum showed less than 0.5 methyl proton in the 1-chloro-1-butene isolated. The spectra of the hydrocarbons pumped off before hydrolysis were similar to those in the following.

Another sample was prepared and decomposed in di-*n*-butyl ether, as previously described for the trideuterated Grignard reagent. The ir and nmr spectra of the 1,3-butadiene-*1,1*-d_2 were identical with those of an authentic sample (*vide infra*). The ir spectra (gas) of the cyclobutene-*3,3*-d_2 contained prominent bands at 1300, 1010, 925, 842, and 722 cm^{-1}. The nmr spectrum of this component has been reported previously.[5]

1,3-Butadiene-*1,1*-d_2 was prepared by a method reported for the perdeuterio compound.[26] A mixture of 20 g of zinc dust, 0.3 g of potassium iodide, 1.0 g of cuprous chloride, and 25 ml of deuterium oxide was heated to reflux, and 9.3 g of 1,1-dichloro-1,3-butadiene[27] was added dropwise over 25 min. Reflux was continued for 30 min more. The volatiles evolved were condensed in a Dry Ice trap. In addition to 1,3-butadiene, the major product, spectra of two other sizable components isolated preparatively from an undeuterated reaction, permitted identification as 1,2-butadiene [ir (gas) 1965, 1710, 860 cm^{-1}; nmr (CCl_4) δ 1.66 (m, 3, $J = 3.6, 7.2$ Hz, CH_3), 4.6 (m, 2), 5.1 ppm (m, 1)] and 1-chloro-1,3-butadiene [nmr (CCl_4) δ 5.0–5.6 (m, 2), 5.9–7.2 ppm (m, 3)]. 1,3-Butadiene-*1,1*-d_2 was isolated by preparative gc: ir (gas) 3070, 3010, 2325, 2230, 1810, 1640, 1570, 1000, 940, 910, 734 cm^{-1}; (CS_2) 1808, 1021 (w), 991, 931, 902, 807 (w), 729, 442 cm^{-1}.

(26) D. Craig and R. B. Fowler, *J. Org. Chem.*, 26, 713 (1961).

(27) We are indebted to Dr. Harold Pitt of the Stauffer Chemical Co. for a gift of 1,1-dichloro-1,3-butadiene.