Cyclobutane Compounds. III.[1,2] The Ionic Addition of Hydrogen Chloride, Hydrogen Bromide, and Hydrogen Iodide to Allene and Methylacetylene

Karl Griesbaum, Walter Naegele, and Graham G. Wanless

Contribution from the Central Basic Research Laboratory, Esso Research and Engineering Company, Linden, New Jersey. *Received March 12, 1965*

The ionic addition of hydrogen chloride to allene and of hydrogen bromide to allene and methylacetylene yielded not only the conventional Markovnikov adducts but also variable amounts of the corresponding cis- and trans-1,3-dihalo-1,3-dimethylcyclobutanes. Addition of hydrogen chloride to methylacetylene gave erratic results, while the addition of hydrogen iodide to allene and methylacetylene occurred in a conventional manner and did not lead to detectable amounts of cyclic products. The infrared, n.m.r., and mass spectra of the isomeric cyclobutane compounds are discussed.

Introduction

Until quite recently there appeared to be general agreement in the literature that ionic additions of HX compounds to allene and methylacetylene occur in accordance with Markovnikov's rule to yield 2-substituted propenes and/or 2,2-disubstituted propanes.

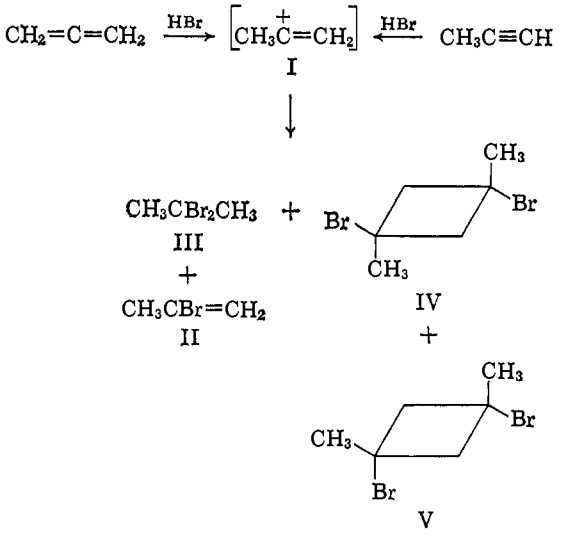
$$CH_2{=}C{=}CH_2 + HX \longrightarrow CH_3C{\equiv}CH + HX$$

$$\downarrow$$

$$CH_3CX{=}CH_2 + CH_3CX_2CH_3$$

Typical examples for this preferred reaction course were the acid-catalyzed hydration of allene[3] and methylacetylene[4] to yield acetone, the addition of hydrogen fluoride to the two substrates to produce 2,2-difluoropropane,[5,6] the hydrochlorination of allene[7] and methylacetylene[7-9] to yield 2,2-dichloropropane and/or 2-chloropropene, and the hydrobromination of methylacetylene[10,11] to yield 2,2-dibromopropane.

In contrast, a recent investigation of the previously unexamined hydrogen bromide addition to allene[12] produced substantial amounts of the cyclodimerization products, *cis*- (V) and *trans*-1,3-dibromo-1,3-dimethylcyclobutane (IV), besides the conventional adducts 2-bromopropene (II) and 2,2-dibromopropane (III). We suspected that the vinyl carbonium ion (I) may be a critical intermediate in this novel cyclization reaction. Since the same intermediate can be anticipated in the hydrogen bromide addition to methylacetylene it seemed worthwhile re-examining it with particular attention to the possible formation of cyclic products. We could indeed show[1] that, contrary to the above cited previous reports,[10,11] this reaction does produce more than 35% of the combined cyclic products IV and V.



After this successful extension of the concept of electrophilically induced cyclodimerization *via* vinyl carbonium ions to another substrate type, we turned our attention to other types of adding agents. In a first attempt to study the effect of various electrophiles, we have now examined the addition of the two closest analogs of hydrogen bromide, *viz.*, hydrogen chloride and hydrogen iodide to allene and methylacetylene. The results of these studies and a detailed description of the briefly communicated hydrogen bromide additions to the two substrates[1,12] are given in the present paper.

Results

Addition of Hydrogen Chloride. It was reported[7] that allene in the absence of a catalyst showed no reaction with hydrogen chloride at −78° after 112 hr. In contrast, we obtained approximately 1% of a liquid adduct mixture after 144 hr. of reaction at −70 to −80°. Capillary g.l.c. analysis showed that the mixture contained the two conventional adducts, 2-chloropropene and 2,2-dichloropropane, as well as two other components with longer retention times. The n.m.r. spectrum of the adduct mixture exhibited two singlet peaks in the relative ratio of 2:3 as the major signals.

(1) Part II: K. Griesbaum, *Angew. Chem.*, 76, 782 (1964); *Angew. Chem. Intern. Ed. Engl.*, 3, 697 (1964).
(2) Presented at the 148th National Meeting of the American Chemical Society, Chicago, Ill., Aug.–Sept. 1964.
(3) G. Gustavson and N. Demjanoff, *J. prakt. Chem.*, [2] 88, 201 (1888).
(4) R. E. Schaad and V. N. Ipatieff, *J. Am. Chem. Soc.*, 62, 178 (1940).
(5) A. V. Grosse and C. B. Linn, *ibid.*, 64, 2289 (1942).
(6) P. R. Austin, U. S. Patent 2,585,529 (1952).
(7) T. L. Jacobs and R. N. Johnson, *J. Am. Chem. Soc.*, 82, 6397 (1960).
(8) E. Réboul, *Compt. rend.*, 74, 669 (1872).
(9) H. Hunziker, *Chimia* (Aarau), 17, 391 (1963).
(10) E. Réboul, *Ann. Chim.* (Paris), [5] 14, 365 (1878).
(11) M. S. Kharasch, J. G. McNab, and M. C. McNab, *J. Am. Chem. Soc.*, 57, 2463 (1935).
(12) First reported as a communication: K. Griesbaum, *ibid.*, 86, 2301 (1964).

Table I. Mass Spectroscopic Data of the Isomeric 1,3-Dihalo-1,3-dimethylcyclobutanes

Compd. Isomer	X	Molecular ions	Relative abundances of corresponding ions P+	(P − X)+	(P − HX)+	(P − CH_2X)+	(P − C_2H_4X)+	(P − C_3H_5X)+
cis	Br	244–242–240	95–190–100[a]	4052–4059	327–17	171–184	288–291	658–640
trans	Br	244–242–240	95–192–100[a]	13712–13853	1191–139	1208–1292	1012–1061	3633–3717
cis	Cl	156–154–152	21–66–100[a]	490–1440	458–1137	1529–4595	271–806	8800–25350
trans	Cl	156–154–152	24–70–100[a]	397–1166	467–1126	1380–4100	188–528	7106–22200

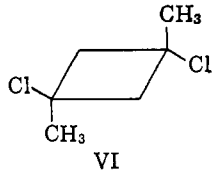
[a] Peaks are scaled relative to 100 units for the lower molecular weight parent isotopic ion.

This pointed to the structure of *trans*-1,3-dichloro-1,3-dimethylcyclobutane (VI) as the major product in this reaction mixture, an indication that could indeed be verified subsequently, although due to the over-all low yield the compound could not be isolated and unequivocally identified at this point.

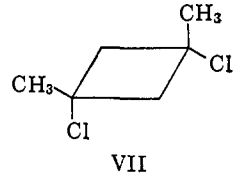
Reaction in a stainless steel cylinder at −70° resulted in an increased yield over that obtained in a glass vessel. The selectivity for the two unidentified higher boiling components dropped, however, considerably. As expected, at room temperature the addition proceeded at an even faster rate, while the selectivity for the two new components decreased to about 1% of the total product mixture.

Combined distillation of several adduct mixtures afforded the two conventional adducts, 2-chloropropene and 2,2-dichloropropane, as distillates and a liquid distillation residue in which the two unidentified components were enriched. Preparative g.l.c. of this residue resulted in the isolation of two crystalline compounds which had retention times, identical with those of the two unidentified components in the crude adduct mixtures.

One of the two isolated compounds analyzed correctly for $(C_3H_5Cl)_n$, and the mass spectra of both compounds afforded a molecular weight of 152, corresponding to the formula $C_6H_{10}Cl_2$ (Table I). The major compound was assigned the structure of *trans*-1,3-dichloro-1,3-dimethylcyclobutane (VI) on the basis of the complete analogy of its infrared and n.m.r. spectra (Table IV) with those of the corresponding dibromo compound IV.[13] Based on a similar set of arguments the minor compound was assigned the structure of *cis*-1,3-dichloro-1,3-dimethylcyclobutane (VII).



VI



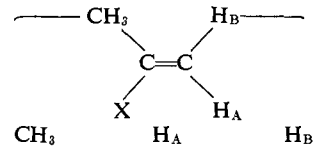
VII

The successful cyclodimerization of allene during the uncatalyzed addition of hydrogen chloride prompted us to re-examine the reported bismuth trichloride catalyzed addition reaction which had been described to yield 2-chloropropene and 2,2-dichloropropane, exclusively.[7] In our hands this reaction produced approximately 30% of the combined cyclic chlorides VI and VII, according to capillary g.l.c. and semiquantitative data from n.m.r. spectra.

(13) While the structure of *trans*-1,3-dibromo-1,3-dimethylcyclobutane (IV) was proven by its reduction to a mixture of the corresponding isomeric 1,3-dimethylcyclobutanes,[12] this compound was isolated only in quantity sufficient for elemental, infrared, n.m.r., and mass spectral analysis.

The uncatalyzed addition of hydrogen chloride to methylacetylene was found to be extremely slow, while in the presence of bismuth trichloride the reaction rate could be increased, in accordance with a previous report.[7] Although there were occasionally indications for the formation of the cyclic dichlorides VI and VII, we could not detect them definitely in these reactions. The conventional adducts 2-chloropropene and 2,2-dichloropropane were the major reaction products, along with some minor by-products. The latter were mainly derived from impurities in the starting methylacetylene (see also footnote *a* in Table III).

Table II. Parameters of N.m.r. Spectra of Some 2-Halopropenes and 2,2-Dihalopropanes[a]



X	CH_3	H_A	H_B	$CH_3CX_2CH_3$ CH_3
Cl	2.07	5.04	5.04	2.14
Br	2.26	5.33	5.52	2.57
I	2.40	5.54	5.93	3.00

[a] The spectra were obtained from neat liquid samples. Chemical shifts of structural units, p.p.m. downfield from TMS internal reference.

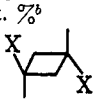
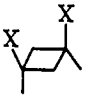
Addition of Hydrogen Bromide.[12] As found in the addition to other olefins,[14,15] the addition of hydrogen bromide to allene occurred at a markedly faster rate than that of hydrogen chloride. The best selectivities (*viz.* 52%) toward the combined cyclic dibromides IV and V were obtained when the reaction was carried out at low temperatures, generally between −70 and −80°. However, for a practical laboratory synthesis, this reaction was too slow. Reaction at room temperature in a pressure vessel, though it proceeded at a faster rate, resulted in a markedly lower selectivity for the cyclic products. In an attempt to compromise between the three factors involved (reaction rate, selectivity, and pressure) we tried the reaction at the intermediate temperature of −34°, *i.e.*, the boiling point of allene. Hydrogen bromide was bubbled into liquefied allene refluxing under atmospheric pressure and under a nitrogen blanket. However, the reaction rate could not be improved significantly enough to overcompensate the decrease in selectivity at this elevated temperature.

A more satisfactory solution was the following procedure. Allene and hydrogen bromide were condensed in a trap either at the temperature of liquid nitrogen

(14) See, *e.g.*, O. Maass and C. Sivertz, *J. Am. Chem. Soc.*, 47, 2883 (1925).

(15) O. Maass and C. H. Wright, *ibid.*, 46, 2664 (1924).

Table III. Some Experimental and Analytical Data of Ionic Additions of HX Compounds to Allene and Methylacetylene

HX	Substrate	HX: C_3H_4	Temp., °C.	Time, days	Conversion,[a] %	Relative amounts of components in adduct mixture, wt. %[b] XCH=CHCH₃	$CH_3CX{=}CH_2$	CH_3CX_2-CH_3		
HCl	$CH_2{=}C{=}CH_2$	1	−70	6	<1	...	5	8	77[c]	10
HCl	$CH_2{=}C{=}CH_2$	1	−70	14	12[d]	...	35	54	8	3
HCl	$CH_2{=}C{=}CH_2$	1	Ambient	7	58	...	30	69	1	<1
HCl	$CH_2{=}C{=}CH_2$	1	−70	14	3[e]	...	17	52	25	6
HCl	$CH_3C{\equiv}CH$	1	−70	7	1	...	56	44	...	...
HBr	$CH_2{=}C{=}CH_2$	0.8	−80	6	40	...	17	36	39	8
HBr	$CH_2{=}C{=}CH_2$	1	−70	28	42	...	13	35	44	8
HBr	$CH_2{=}C{=}CH_2$	1	−70 to Ambient[f]	4	65	...	31	42	21	6
HBr	$CH_2{=}C{=}CH_2$	1	Ambient	3 hr.	8[g]	...	15	72	10	3
HBr	$CH_3C{\equiv}CH$	1	−70	4.5	54	30	17 (24)	24 (34)	23 (33)	6 (9)
HBr	$CH_3C{\equiv}CH$	1	−70	4	6[h]	6	56 (60)	25 (27)	9 (10)	3 (3)
HBr	$CH_3C{\equiv}CH$	1.6	−70	3	31	...	18	60	16	6
HI	$CH_2{=}C{=}CH_2$	1	−70	3	71	...	6	94	...	...
HI	$CH_3C{\equiv}CH$	1	−70	1	86	...	35	65	...	...

[a] Based on product distribution and hydrogen halide. [b] These components comprised 75–98% of the total adduct mixtures, depending on the purity of the starting materials. Typical by-products were $CH_3CHClCH_3$ and $CH_3CHBrCH_3$, formed by addition of HCl or HBr to a propylene impurity, and $CH_3CClBrCH_3$, formed by the addition of HBr to a 2-chloropropene impurity. [c] The high yield of cyclic product in this case may be due to the fact that the lower boiling simple adducts evaporated partly during removal of the unreacted starting materials. [d] Reaction carried out in a stainless steel bomb. [e] 6.5% $BiCl_3$ as catalyst. [f] Reaction mixture was allowed to gradually warm up from −70% to room temperature. [g] Gas phase reation. [h] Hydroquinone used as inhibitor.

or at −80°. Then the mixture was allowed to gradually warm up overnight to room temperature at atmospheric pressure and under a nitrogen blanket. This procedure significantly increased the reaction rate over that of the low-temperature reaction,[16] while the selectivity for the combined cyclic products IV and V could still be maintained in the order of 20–25%.

In the gas phase at ambient temperatures the allene hydrobromination produced approximately 13% of the cyclic dibromides IV and V. This demonstrates that the cyclodimerization reaction is not restricted to the liquid phase and that it is probably more sensitive to the reaction temperature than to the reaction phase.

The low-temperature hydrobromination of methylacetylene seemed at first glance to proceed at a considerably faster rate than the corresponding allene addition. However, the presence of substantial amounts of the isomeric 1-bromopropenes (VIII) (Table III, Figure 1) and small amounts of 1,2-dibromopropane (IX) in the crude adduct mixtures showed that these rate differences were largely due to concurrently occurring free-radical additions.[17] As

$$HBr + CH_3CH{\equiv}CH \longrightarrow \underset{\text{VIII}}{BrCH{=}CHCH_3} \xrightarrow{HBr} \underset{\text{IX}}{BrCH_2\overset{CH_3}{\overset{|}{C}}HBr}$$

expected, this complication was efficiently suppressed either by the presence of an inhibitor in the reaction mixture or by the use of excess hydrogen bromide.[18] The fact that these measures did not prevent the formation of the cyclic products IV and V is additional proof for the ionic character of these cyclodimerizations. If one discounts the amount of the free-radical addition products the methylacetylene additions showed approximately the same selectivities for the four-membered ring compounds IV and V as the allene additions did (numbers in bracket in Table III).

While the crude product mixtures derived from the addition to pure allene consisted of the four components II–V, exclusively (Figure 3), the methylacetylene adduct mixtures generally contained some additional components, usually in small quantities. The lower boiling ones could be essentially traced back either to the above-mentioned, free-radical reactions or to impurities in the starting methylacetylene (see footnote *a* in Table III). Independent from the origin and the purity of the methylacetylene there appeared, however, consistently a small peak (relative area ~0.5%) in the gas chromatogram with a retention time intermediate between those of the two isomeric 1,3-dibromo-1,3-dimethylcyclobutanes IV and V. The same component was found in an enriched amount in the pentane mother liquor from which the two isomeric 1,3-dibromo compounds IV and V had been precipitated. After removal of the pentane from this mother liquor the liquid residue which comprised about 20% of the new component besides residual amounts of IV and V was examined by combined g.l.c.-t.o.f. analysis.[19] This method established that the material eluted at the retention time of the unidentified component had the same triplet parent peak (*m/e* 240–242–244; relative intensities 1:2:1, respectively) and the same fragment peaks [*m/e* 161 and 163 (P − Br) and 81 (P − HBr_2)] as the cyclic products IV and V, pointing to an isomeric structure. Since the n.m.r. spectrum of the above liquid residue did not show any evidence for unsaturation, we believe the new component to be one of the possible isomeric 1,2-dibromo-1,2-dimethylcyclobutanes of the general structure X. Attempts to isolate the pure compound X have been unsuccessful, mainly because of its low occurrence.

(16) F. R. Mayo and J. J. Katz, *J. Am. Chem. Soc.*, **69**, 1339 (1947), reported similar rate increases for the uncatalyzed addition of HX compounds to olefins during warm-up periods.

(17) P. S. Skell and R. G. Allen, *ibid.*, **80**, 5997 (1958).

(18) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p. 294.

(19) R. A. Brown and E. R. Quiram, *Appl. Spectry.*, 17, 33 (1963).

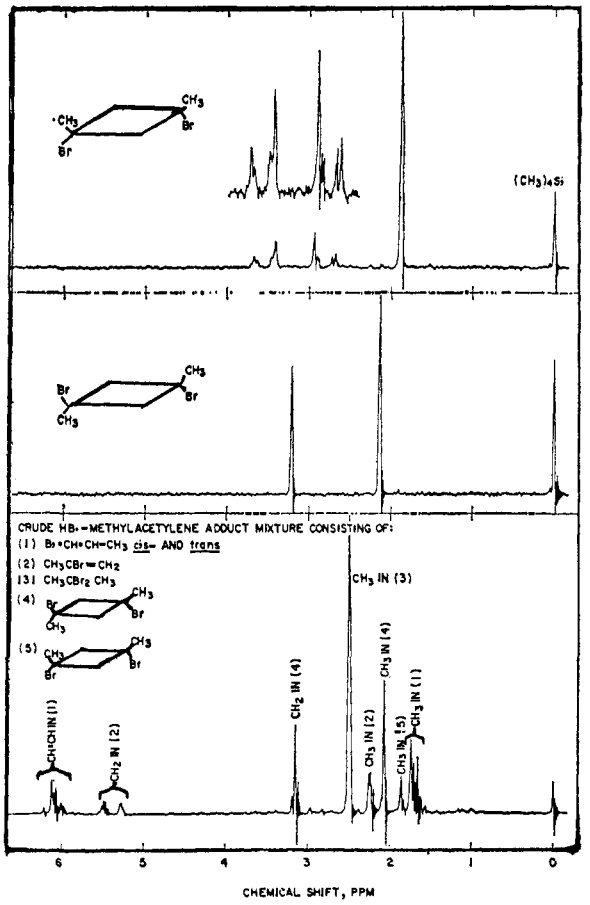
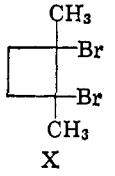


Figure 1. N.m.r. spectra of *cis*- and *trans*-1,3-dibromo-1,3-dimethylcyclobutane and a crude HBr–methylacetylene adduct mixture.

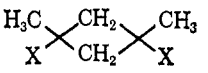


Addition of Hydrogen Iodide. The addition of hydrogen iodide to both allene and methylacetylene at −70 to 80° occurred at a faster rate than the corresponding hydrogen bromide additions. Due to the thermal instability of the diadduct 2,2-diiodopropane, g.l.c. could not be used to analyze the crude adduct mixtures. The data in Table III are therefore based on semiquantitative n.m.r. spectroscopy alone. N.m.r. analysis showed only the signals corresponding to the two Markovnikov adducts 2-iodopropene and 2,2-diiodopropane, and gave no indication for the presence of cyclic products in the crude adduct mixtures.[20] The diadduct 2,2-diiodopropane was in each case the major reaction product.

Infrared Spectra. The infrared spectra of the isomeric 1,3-dihalo-1,3-dimethylcyclobutanes were very simple. In the region between 2 and 9 μ the corresponding chloro and bromo isomers exhibited almost superimposable spectra, independent of the nature of the halogen substituent. Apparent differences existed only in the region above 9 μ.

N.m.r. Spectra. Each of the *trans*-1,3-dihalo-1,3-dimethylcyclobutanes IV and VI gave rise to two sharp singlet signals in the relative ratio of 3:2, corresponding to the methyl and methylene protons, respectively (Figure 1, Table IV). Apparently the puckering of the cyclobutane ring was averaged out by rapid inversion at room temperature, so that all the protons in the respective groups became magnetically equivalent.[21] Due to the stronger deshielding effect of the bromine substituents as compared to that of the chlorine substituents[22] both the methyl and the methylene protons in the spectrum of the dibromo compound IV appeared at lower field positions than those of the dichloro compound VI (Table IV). It may well be that the increase in bond angle, which is effected by the large size of the bromine, as compared to the chlorine substituents, contributed also partly to this downfield shift.

Table IV. Parameters of N.m.r. Spectra of the Isomeric 1,3-Dihalo-1,3-Dimethylcyclobutanes



Compd. X	Isomer	Chemical shift of structural units, p.p.m.[a] CH_3–	–CH_2–
Br	*cis*[b]	1.88 (s)	3.19 (m)[c]
Br	*trans*[d]	2.13 (s)	3.21 (s)
Cl	*cis*[e]	1.69 (s)	2.96 (m)[f]
Cl	*trans*[g]	1.86 (s)	2.88 (s)

[a] Downfield from TMS internal reference. Spectra obtained from solutions in CCl_4: s, singlet; m, multiplet. [b] *Anal.* Calcd. for $C_6H_{10}Br_2$: C, 29.78; H, 4.16; Br, 66.05. Found: C, 29.85; H, 4.16; Br, 66.05. [c] Essentially four-line pattern centered at above value; treated as an AA′ BB′ spin system, J_{AB} = 13 c.p.s., δ_A = 2.84 p.p.m., δ_B = 3.54 p.p.m. Additional splitting due to diagonal spin coupling of *ca.* 2 c.p.s. [d] Analysis reported previously; see ref. 13. [e] Isolated in amounts insufficient for elemental analysis. [f] Same as *c* with J_{AB} = 13 c.p.s., δ_A = 2.72 p.p.m., δ_B = 3.20 p.p.m., and diagonal coupling *ca.* 2 c.p.s. [g] *Anal.* Calcd. for $C_6H_{10}Cl_2$: C, 47.08; H, 6.59; Cl, 46.33. Found: C, 47.44; H, 6.60; Cl, 45.90.

The two *cis*-1,3-dihalo-1,3-dimethylcyclobutanes (V and VII) also showed singlet peaks for the methyl protons, whereas the methylene protons gave rise to a symmetrical, four-line pattern in which the individual lines were further split by transannular coupling. The midpoints of these patterns coincided essentially with the positions of the corresponding methylene singlets in the respective *trans* compounds IV and VI (Table IV). This was taken as proof for the 1,3- (*i.e.*, V and VII, respectively), rather than a 1,2-structure (*e.g.*, of type X), since in the latter structures the methylene groups are vicinal to only one halogen atom each, and

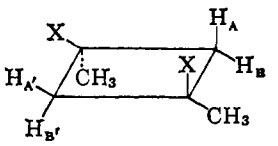
(20) The n.m.r. parameters for *cis*-1,3-dijodo-1,3-dimethylcyclobutane have been described recently: J. F. Coburn, Jr., Dissertation, Yale University, 1963. If one assumes a similar correlation between the chemical shifts of the methylene protons of the *cis*- and the *trans*-diiodide as was observed for the corresponding dichloro- and dibromo compounds, these signals should not coincide with those of the methyl groups in either 2-iodopropene or 2,2-diiodopropane, but they should show up separately in the spectra of the crude adduct mixtures.

(21) See, *e.g.*, J. B. Lambert and J. D. Roberts, *J. Am. Chem. Soc.*, **85**, 3710 (1963); G. S. Rathjens, Jr., N. K. Freeman, W. D. Gwinn, and K. S. Pfitzer, *ibid.*, **75**, 5634 (1953).

(22) L. M. Jackman, "Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press Inc., New York, N. Y., 1959, p. 53.

consequently should appear at higher field positions. Furthermore, in the 1,2-dibromo-1,2-dimethylcyclobutanes one would expect the vicinal *cis* and *trans* couplings to be between 5 and 10 c.p.s.,[23] thus giving rise to an entirely different absorption pattern. Finally, the assignment of *cis*-1,3-structures for V and VII was also supported by the upfield shift of the methyl singlet signals as compared to those in the corresponding *trans* compounds IV and VI. For a 1,2-structure one would expect a shift in the opposite direction due to the combined effect of α- and β-halogen substituents on the methyl protons.

The four-line patterns in the spectra of the *cis* compounds V and VII could be treated as an AA'BB' spin system. Although no definite assignment can be made it seems reasonable to assume that δ_A is attributable to the methylene protons in *cis* position to the



halogen substituent.[24] The geminal coupling constants ($J_{AB} = J_{A'B'}$) were approximately 13 c.p.s. for both the dichloro (V) and the dibromo compound (VII), in good agreement with values reported for similar systems.[20,24,25] The diagonal coupling constants ($J_{AB'}$, $J_{AA'}$, and $J_{BB'}$) were in the order of 2 c.p.s. or smaller.[25]

Table II shows the n.m.r. spectral parameters for the conventional Markovnikov-type mono- and diaddition products, *i.e.*, 2-halopropenes and 2,2-dihalopropanes. In agreement with a previous report[23b] it was observed that the chemical shifts of all the protons increased with decreasing electronegativity of the substituents in contrast to what might be expected from a simple inductive effect. In the spectra of all of the 2-halopropenes the *trans* coupling was found to be smaller than the *cis* coupling.

The integrated n.m.r. spectra could be very effectively used for the qualitative and semiquantitative analysis of the crude adduct mixtures, since all of the adducts formed exhibited at least one typical signal that did not overlap with any signal of the other components present (see Figure 1, lower drawing). Such analyses consistently afforded higher values for the corresponding 2,2-dihalopropanes and lower values for the respective 2-halopropenes than were obtained from the g.l.c. analyses. We suspected that this discrepancy may be due to partial hydrogen halide elimination from the 2,2-dihalopropanes in the heated g.l.c. unit. Examination of spectroscopically pure 2,2-dihalopropanes by g.l.c. showed indeed that 2,2-dichloropropane suffered a 20–26%, and 2,2-dibromopropane an 8–12% cleavage. The values in Table III are corrected correspondingly.

Mass Spectra (see Table I and Figure 2). The dihalo substitution of all the cyclic compounds could be readily recognized in the mass spectra. Thus, the spectra of the dichloro compounds VI and VII exhibited isotopic abundances at the parent ions which are appropriate for compounds containing two chlorine atoms, and isotopic abundances at the P – Cl fragment ions which are appropriate for compounds containing one chlorine atom.[26a] Similarly, the spectra of the dibromo compounds IV and V showed 1:2:1 patterns for the parent peaks and 1:1 patterns for the P – Br fragment ion peaks.[26b] Further proof for the assigned structures of 1,3-dihalo-1,3-dimethylcyclobutanes was obtained from the typical cracking patterns of the respective compounds (Table I, Figure 2).

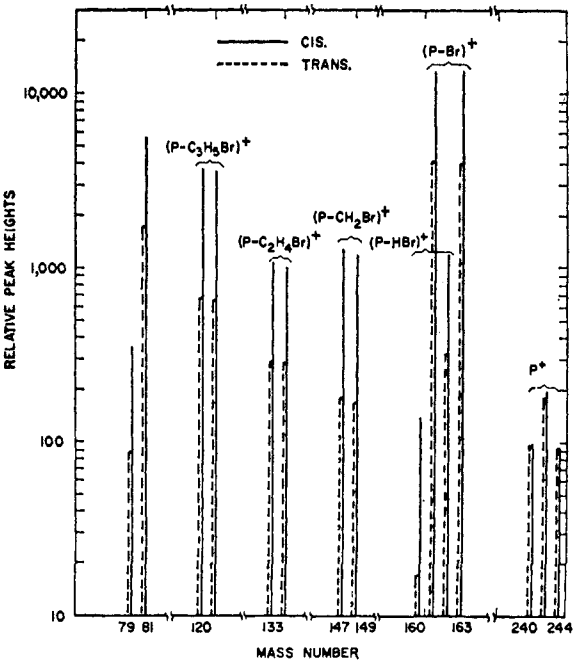


Figure 2. Mass spectra of 1,3-dibromo-1,3-dimethylcyclobutanes.

While both isomers of a given halo compound gave rise to peaks of the same mass numbers, the relative abundances of these peaks were characteristically different for the *cis* and the *trans* isomers, respectively. This adds further evidence to the claim that mass spectroscopy can be used to distinguish between stereoisomers.[27] However, there appears to exist no logical correlation between the stereochemistry and the mass spectrum of a particular isomer pair. In the case of the 1,3-dibromo-1,3-dimethylcyclobutanes, the less crowded *trans* isomer gave rise to a stronger parent ion peak and weaker P – Br and P – HBr fragment ion peaks than the *cis* isomer did. In the case of the 1,3-dichloro-1,3-dimethylcyclobutanes this effect, although it was less pronounced, was just reversed.

Discussion

To our knowledge the reactions described here and in our previous communications of this series[1,12] represent the first examples of proton-initiated cyclo-

(23) Similar cases where the proton in *cis* position to a vicinal halogen substituent absorbed at a higher field position than that in the *trans* position were reported previously. See, *e.g.*, (a) K. B. Wiberg and B. J. Nist, *J. Am. Chem. Soc.*, 85, 2788 (1963), and (b) M. Y. DeWolf and J. D. Baldeschwieler, *J. Mol. Spectry.*, 13, 344 (1964).

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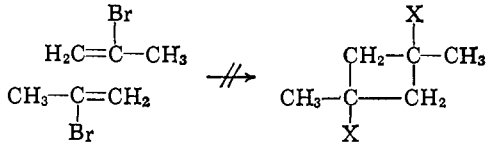
dimerizations of allenic or acetylenic compounds to yield cyclobutane derivatives. Although it was postulated recently that the known acid-catalyzed trimerizations of alkynes which lead to substituted benzenes may also proceed *via* cyclobutene-type intermediates,[28] there appears to be no evidence in the literature for the actual isolation of such an intermediate. Electrophilically induced cyclodimerizations caused by agents other than protons are, however, not completely unknown. An example is the boron trifluoride catalyzed addition of chlorine to 2-butyne which afforded 1,2,3,4-tetramethyl-3,4-dichlorocyclobutene.[29]

We have ascertained that our cyclodimerizations are indeed ionic reactions[30] and that they do not represent a simple head-to-tail dimerization of the concurrently formed 2-halopropene monoadducts.



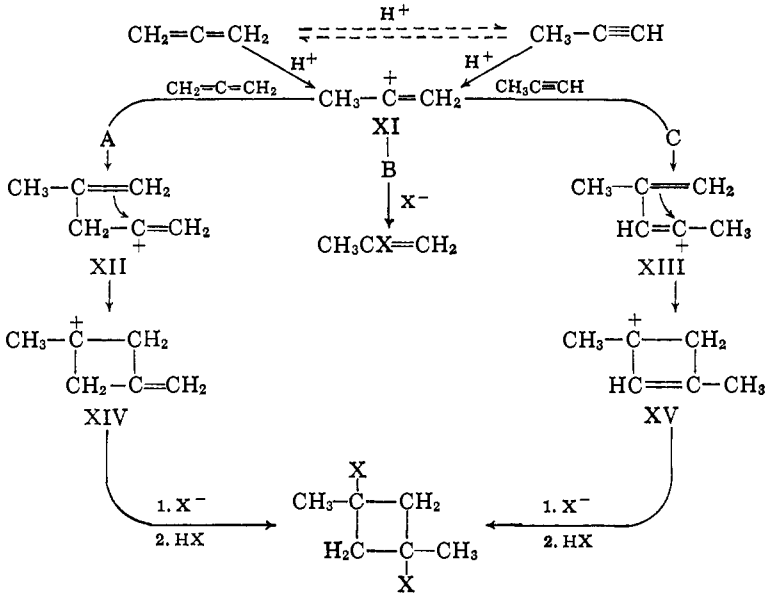
Thus, addition of hydrogen bromide to 2-bromopropene under the conditions of the cyclodimerization reactions produced 2,2-dibromopropane exclusively, while ultraviolet irradiation of 2-bromopropene resulted in a discolored liquid, which essentially consisted of unchanged starting material and showed no traces of the cyclic products IV or V either in the gas chromatogram or the n.m.r. spectrum.

As a working hypothesis for the further exploration of our concept of proton-initiated cyclization reactions, we would like to consider the reaction course outlined in Scheme I. While most parts of this scheme still lack experimental confirmation, it seems certain that vinylic carbonium ions play an important role as intermediates in these cyclizations. Addition of a proton to either allene or methylacetylene leads formally to the common vinylic carbonium ion XI which, like ordinary carbonium ions,[31] apparently has a choice either to further alkylate the starting substrate (routes A or C, respectively) or to combine with halide ion (route B). However, in contrast to substrate alkylations by ordinary carbonium ions, which ultimately lead to acyclic products (*e.g.*, hexyl bromide from the addition of hydrogen bromide to propylene[31]), alkylations by the vinylic carbonium ion XI lead to intermediates (*e.g.*, XII or XIII), with terminal double bonds located such that their further reactions with the respective positive centers favor cyclization (*e.g.*, to form XIV or XV).

While the outlined reaction scheme can explain the failure of cyclization reactions in the presence of the strongly nucleophilic iodide ion, there remain, at the present time, a number of unanswered questions such as: are there indeed two discretely different routes for the allene and the methylacetylene addition?; does the dimeric carbonium ion (*e.g.*, XII and XIII) have to be a vinylic one or can it be an alkyl carbonium ion?; do the *cis-trans* ratios of the products represent the true reaction selectivities or are they due to incidental post isomerizations? Efforts are under way to answer these questions.

The cyclization reactions described here (particularly the hydrogen bromide additions) represent a new one-step synthesis for four-membered ring compounds. Although we have not undertaken any detailed studies for optimizing the rates or the yield of these reactions, preliminary experiments have indicated that catalysis by typical cationic catalysts such as boron trifluoride is possible in both the allene-and the methylacetylene-hydrogen bromide addition. In the case of the methylacetylene hydrobromination, this catalysis did not only increase the rate of the reaction and prevent the

Scheme I. Possible Reaction Courses of Electrophilically Induced Cyclodimerizations of Allene and Methylacetylene by Hydrogen Halides



(28) P. E. Peterson and J. E. Duddey, *J. Am. Chem. Soc.*, 85, 2865 (1963).

(29) R. Criegee and A. Moschel, *Chem. Ber.*, 92, 2181 (1959).

(30) The free-radical addition of hydrogen bromide to allene and methylacetylene did not produce any of the cyclic products IV or V. See K. Griesbaum, A. A. Oswald, and D. N. Hall, *J. Org. Chem.*, 29, 2404 (1964).

(31) See, *e.g.*, F. R. Mayo and M. G. Savoy, *J. Am. Chem. Soc.*, 69, 1348 (1947), and literature cited therein.

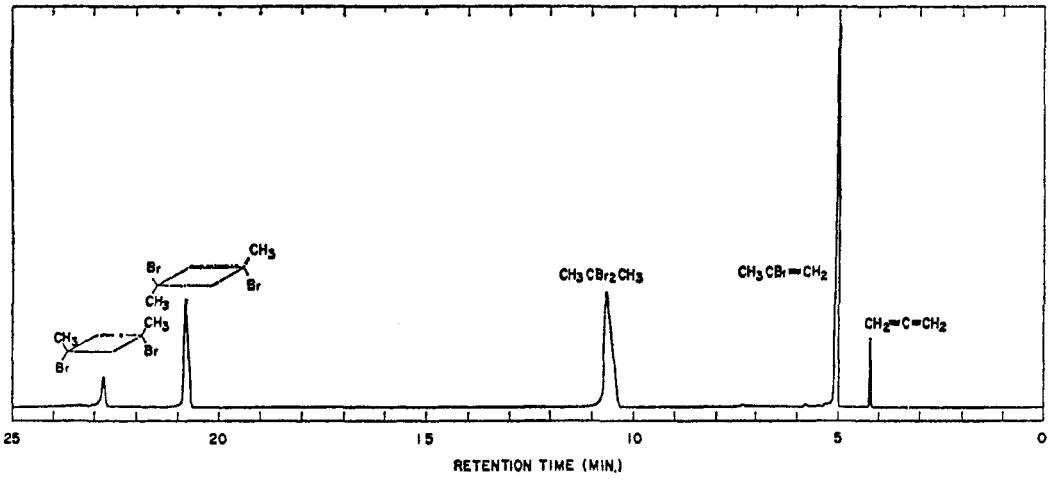


Figure 3. Capillary gas chromatogram of a crude hydrogen bromide–allene adduct mixture.

concurrent free-radical addition, but it resulted also in a higher selectivity toward the cyclic products IV and V than the uncatalyzed reaction did. It is believed that further work in this area may lead to a considerable broadening of the scope of this concept of electrophilically induced cyclodimerizations.

Experimental

Materials. Allene, methylacetylene, hydrogen chloride, hydrogen bromide, and hydrogen iodide were Matheson products. In some cases, allene of 99.5% minimum purity was used.

Method of Analyses. All the adduct mixtures were analyzed by capillary g.l.c. on a Perkin-Elmer Model 226 linear programmed temperature gas chromatograph, which gave very satisfactory separations (Figure 3). A 200 ft. × 0.02 in. i.d. Golay column coated with a mixture of 50% phenylsilicone and 50% silicone nitrile was used. Temperatures of the injection block and detector were 270 and 190°, respectively. The temperature of the column was first held for 10 min. at 50°; afterwards, it was programmed at a rate of 10°/min. up to 160° and then maintained at that temperature isothermally until the end of the analyses. A CRS-1 digital chromatogram integrator (supplied by Infotronics Co., Houston, Texas) was used for recording the peak areas. Data from the integrator were automatically transferred to a printer which in turn printed out peak retention times and peak areas on a printer tape.

The combined g.l.c. t.o.f. analyses were carried out on an F&M Model 500 linear programmed temperature gas chromatograph with a 10-ft. XF 1150 silicone nitrile column. The effluent from the gas chromatograph was metered into a t.o.f. mass spectrometer through a connecting line and a metering valve, heated to 200°. The spectrometer was a Bendix instrument, Type 12-101 which had been modified so as to include a 1.66-m. flight tube, multigate recording, and improved electron beam focusing. A multichannel Minneapolis-Honeywell Visi-corder was used to record the mass spectral data.

The mass spectra of the pure compounds IV–VII were recorded on a General Electric 60° mass spectrometer with a glass mass tube and a thoria-coated iridium filament. The electron beam energy used was 11–12 e.v. Since it was observed that *trans*-1,3-dibromo-1,3-dimethylcyclobutane (IV) underwent gradual thermal decomposition when stored in the mass spectrometer at 150° and 0.05 mm., the spectra were recorded under the most gentle conditions. For this purpose, the samples were sealed in melting point capillaries, and these in turn were sealed into an all-glass sampling device. After evacuating the mass spectrometer system to 0.01 mm., the capillary was opened by an internal breaking device. Thus, the samples vaporized readily at room temperature into the mass spectrometer sample system which was kept at 80°. Equilibrium at a final sample pressure of 0.050 mm. was reached within 3 min. or less. The results reported in Table I represent the mean values of at least four scans taken on the same instrument at different times and with repeat charges of samples. The mean deviation, *e.g.*, for the ratio *m/e* 240:161 in the case of *trans*-1,3-dibromo-1,3-dimethylcyclobutane was 0.00742 ± 5.4%.

N.m.r. spectra were recorded and integrated on a Varian Model A-60 proton resonance spectrometer. The infrared spectra were obtained using a Baird recording spectrophotometer, Model B.

General Procedure for the Addition of Hydrogen Halides to Allene or Methylacetylene. The low-temperature addition reactions were carried out in 100-ml. Pyrex tubes which were closed at the top by a Teflon-tipped needle valve (from Fisher and Porter Co., Clifton, N. J.). Allene (or methylacetylene) and the hydrogen halide were condensed into the previously evacuated tubes at the temperature of liquid nitrogen. Then the closed tubes were transferred into a Freon bath kept at −70 to −80° by means of a low-temperature circulating unit (from Lawler Electrical Mfg. Co., Bayonne, N. J.). After an arbitrary period of reaction time (see Table III), the tubes were transferred to a liquid nitrogen bath and opened. The unreacted gases were allowed to evaporate through a drying tube filled with anhydrous calcium sulfate ("Drierite"). The remaining adduct mixtures in the tubes were colorless to slightly yellow mobile liquids.

The "warm-up" experiments were carried out in a 300-ml. cylindrical Pyrex tube whose outlet was connected to a cold trap and then a drying tube through which nitrogen was purged continuously.

The crude adduct mixtures from these addition reactions were in each case fractionated in order to remove most of the conventional, liquid, Markovnikov-type adducts. In the case of the hydrogen bromide adduct mixtures, the distillation was discontinued after the fraction boiling at 54–56° and 89–90 mm. was collected, and in the case of the hydrogen chloride adduct mixtures, after the fraction boiling at 69–70° was collected. The remaining liquid distillation residue was in each case further separated by preparative g.l.c. if the pure isomers were the desired products. The dibromo compounds could be also obtained as a crystalline mixture consisting of approximately 5–10% of the *cis* and 90–95% of the *trans* isomer by crystallization of the above distillation residue in cold pentane.

Preparative G.l.c. The separation of the isomeric 1,3-dihalo-1,3-dimethylcyclobutanes was carried out on an Aerograph Autoprep Model A-700. A 20 ft. × 3/8 in. i.d. column packed with 20% silicone on Chromosorb was used. Operating conditions for the separation of the isomericl, 3-dichloro-1,3-dimethylcyclobutanes were as follows: detector cell temperature, 150°; detector cell current, 200 ma.; injector part temperature, 148°; collector temperature, 123°; column temperature, 113°; helium flow, 80 cc./min. For the separation of the isomeric 1,3-dibromo-1,3-dimethylcyclobutanes, the conditions were the following: detector cell temperature, 160°; detector cell current, 200 ma.; injector part temperature, 150°; collector temperature, 130°; column temperature, 130°; helium flow, 140 cc./min. The corresponding isomers were in each case collected as colorless, crystalline materials.

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Dehydrohalogenation of Halo- and Dihalocyclopropanes

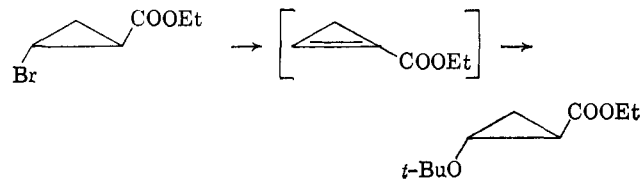
C. L. Osborn, T. C. Shields, B. A. Shoulders, J. F. Krause, H. V. Cortez, and P. D. Gardner

Contribution from the Department of Chemistry, University of Texas, Austin, Texas. *Received March 19, 1965*

The dehydrohalogenation of halocyclopropanes to cyclopropenes has been shown to be a very facile reaction when induced by strong base systems such as potassium t-butoxide in dimethyl sulfoxide. The fate of the cyclopropene is dictated by its gross molecular structure as well as by the base employed in its formation. In the absence of a nucleophile and when the base itself is a poor nucleophile, the product is in general that resulting from double-bond migration to a position of greater stability outside of the three-membered ring. This is followed in some cases by skeletal rearrangement.

The methods most commonly used for the synthesis of cyclopropenes and alkylenecyclopropanes are (a) Hofmann elimination,[1,2] (b) alkylene transfer systems,[3] and (c) condensation reactions involving substituted cyclopropenones.[3] The light-induced decomposition of alkylidenepyrazolines[4] and the Favorskii reaction[5] have also been used with success.

Wiberg, Barnes, and Albin in 1957 described the conversion of ethyl *trans*-2-bromocyclopropanecarboxylate to ethyl *trans*-2-*t*-butoxycyclopropanecarboxylate by reaction with potassium *t*-butoxide (KO-*t*-Bu) in *t*-butyl alcohol and presented good evidence for the intermediacy of a cyclopropene.[6] This appears to be the only example of this rather direct route to cyclopropenes. The ready availability of dihalocyclopropanes[7] and halocyclopropanes[8] makes



the approach appear quite attractive. On the other hand, Parham and co-workers[9] have shown that treatment of *gem*-dichlorocyclopropanes with boiling quinoline or pyridine leads largely to ring opening concurrent

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