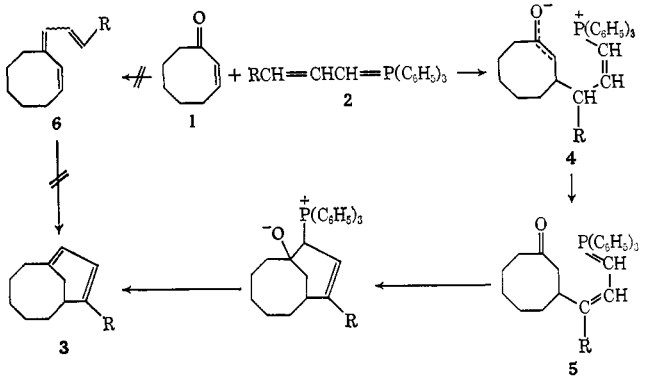
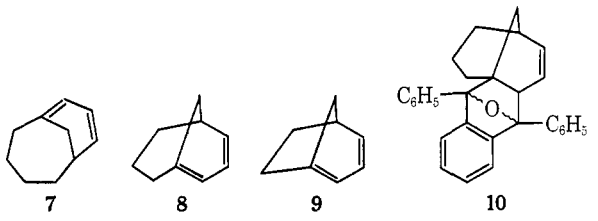
Scheme I



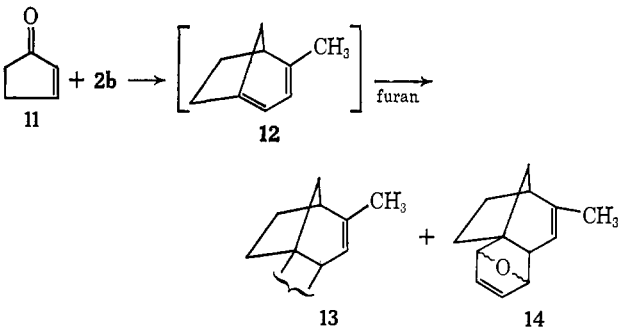
a, R = H
b, R = CH_3
c, R = C_6H_5

proton abstraction must yield ylide **5** followed by an intramolecular Wittig reaction to give the observed products **3a–3c**. The trienes **6a** and **6c** were synthesized independently[10] and were shown not to be intermediates in the formation of the bridgehead alkenes.



Bicyclo[4.3.1]deca-7,9-diene (**7**) was prepared from cyclohept-1-en-3-one and ylide **2a** in tetrahydrofuran at room temperature (yield 52%; bp 80–90° (3 mm); nmr (CCl_4) δ 5.84–5.98 (m, 2 H), 5.35 (br s, 1 H), and 1.2–2.3 (m, 11 H); uv max (cyclohexane) 274 nm (ε 2800)); this material is the most constrained bridgehead diene of this type which is readily isolable. The ultraviolet absorption maxima of **3a–3c** and **7** are in good agreement with data from analogous 1,3-cyclohexadiene derivatives,[11] showing no indication of distortion of the diene chromophore.

The foregoing results suggested that these reactions could be utilized for the synthesis of highly strained bridgehead alkenes such as bicyclo[3.3.1]nona-1,3-diene (**8**) and bicyclo[3.2.1]octa-1,3-diene (**9**). The reaction of cyclohex-1-en-3-one with ylide **2a** at room temperature gave in 63% yield a mixture of three isomeric dimers of **8** in a ratio of 72:24:4 (mass spectrum for $C_{18}H_{24}$, *m/e* 240).[12] The major component was obtained in pure form by chromatography on silica gel. When the reaction was performed in the presence of 1,3-diphenylisobenzofuran, two [4 + 2] cycloaddition adducts of structure **10** were obtained in a ratio of 2:1 (yield 67%; mass spectra *m/e* 390; isomer A, mp 198–199°; isomer B, mp 148–150°). Both isomeric adducts were hydrogenated over Pd–C in ethanol and isomer B upon dihydrogenation yielded a product identical with that derived from the reaction of bicyclo[3.3.1]non-1-ene with the 1,3-diphenylisobenzofuran (mp 181–182°),[3] dihydro isomer A, mp 205–206°.



The reaction of cyclopent-1-en-3-one (**11**) with ylide **2b** in refluxing tetrahydrofuran gave in 86% yield the dimer **13** (mp 78–83°; mass spectrum for $C_{18}H_{24}$, *m/e* 240; nmr (CCl_4) δ 5.15 (br s, 1 H), 1.25–2.7 (m, 11 H)). When the reaction was run in the presence of furan, the diene product **12** was trapped as the [4 + 2] cycloaddition product **14** (yield 37% (and 30% dimer **13**), bp 65–70° (3 mm); mass spectrum for $C_{13}H_{16}O$, *m/e* 188; nmr (CCl_4) δ 5.9–6.5 (m, 2 H), 5.1–5.4 (d, 1 H), 4.4–4.8 (m, 2 H), 0.8–2.4 (m, 11 H)).

At first sight the formation of strained bridgehead alkenes is surprising, but it must be realized that the process proceeds in two steps. The first step is simple ring closure to yield a betaine, the formation of the single bond not greatly affecting the strain energy of the molecule. The second step is introduction of the strained double bond, a reaction which proceeds well owing to the efficiency of $(C_6H_5)_3PO$ as a leaving group.

(13) Stipendiat der Deutsche Forschungsgemeinschaft.

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1,4-, 1,5-, and 1,6-Dibromoalkanes from Ionic Reaction of Bromine with *n*-Butylcyclopropane

Sir:

Ionic brominations of cyclopropanes to produce 1,3-dibromides are possibly the most frequently cited aspect of cyclopropane chemistry; there is an unsatisfactory insight to be gained from these statements, for 1,3-dibromides are often minor products.

Ionic brominations of cyclopropanes are slow reactions if the ring is not heavily substituted with alkyl groups. For example, cyclopropane does not react with bromine without Lewis acid catalysis.[1] After 10-min reaction time at 0° in CCl_4 solvent there is no detectable reaction of ethylcyclopropane with bromine. This is unlike the radical chain bromination which is rapid at −78°.[2]

Further, the dibromides from ethylcyclopropane include significant amounts of 2,3-dibromopentanes (50%), which drives one to consider a variety of exotic explanations. Similarly, 2,3-dibromobutanes were obtained on bromination of methylcyclopropane. These

(10) **6a** and **6c** were synthesized by the reaction of 1-cyclooctenyllithium with acrolein and cinnamaldehyde, respectively, followed by dehydration (**6a**, bp 90–95° (1 mm); **6c**, mp 76–77°).

(11) A. I. Scott, "Interpretation of the Ultraviolet Spectra of Natural Products," Pergamon Press, New York, N. Y., 1964, p 45.

(12) The corresponding bicyclo[3.3.1]non-1-en is stable at room temperature and does not dimerize.[3,6]

(1) N. C. Deno and D. N. Lincoln, *J. Amer. Chem. Soc.*, **88**, 5357 (1966).

(2) K. J. Shea and P. S. Skell, *J. Amer. Chem. Soc.*, in press.

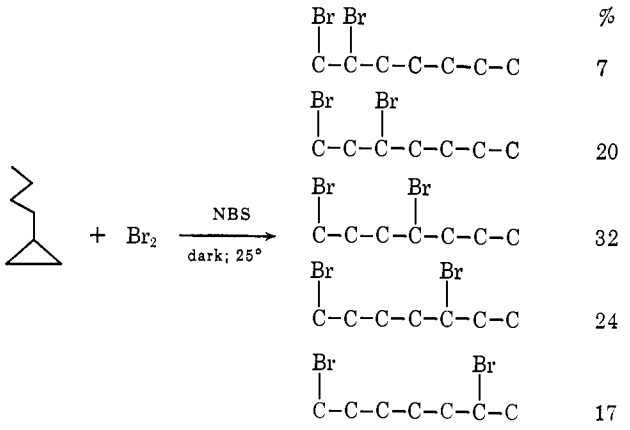
proved to be artifacts attributable to hydrogen bromide formation.

If one uses a 1:1 mixture of HBr and Br_2 in CH_2Cl_2 solvent, addition of the HBr is the exclusive primary reaction of cyclopropane at −78°, a relatively rapid reaction. This behavior contrasts with that of olefins, for which Br_2 is the sole reactant. To the best of our knowledge only Gustavson[3] recognized the extraordinary reactivity of a cyclopropane (1,1-dimethyl-) with hydrogen bromide.

In the presence of NBS, a very fast HBr scavenger,[4] the "strange" products are no longer obtained. For instance, in the presence of NBS and bromine the 2,3-dibromopentanes are not obtained from ethylcyclopropane, and the 2,3-dibromobutanes are not formed from methylcyclopropane.

The products of the reaction of methylcyclopropane with bromine (NBS, dark, 66% conversion in 3 hr at 0°) are 1,2-dibromobutane (13%), 1,3-dibromobutane (37%), and tribromobutanes (48%), identified as a mixture of 1,2,4- and *erythro*- and *threo*-1,2,3-tribromobutanes. These results can be explained by partial rearrangement of the intermediate 1-bromo-3-butyl cation to 1-bromo-2-butyl cation followed by a competition between (a) trapping with bromide ion and (b) elimination of a proton (to make HBr) to produce the crotyl bromides and 4-bromo-1-butene. In the absence of NBS the hydrogen bromide is free to react with methylcyclopropane to form the 2-butyl cation which eliminates to form the butenes; addition of Br_2 to the latter accounts for the formation of the 2,3-dibromobutanes.

The most striking indicator of what is occurring comes from examination of the reactions of ethyl- and *n*-butylcyclopropanes; *1,3-dibromides are minor products*. From ethylcyclopropane the dibromopentane products are 1,2, 1,3, and 1,4 in yields of 4, 9, and 19%, accompanied by 67% of a mixture of tribromides (four). For *n*-butylcyclopropane the dibromide composition is

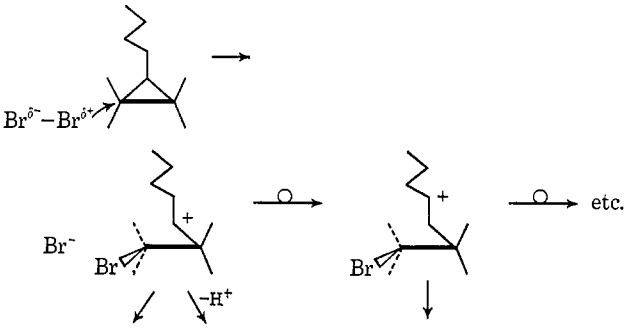


Rearrangements accompany ionic brominations of cyclopropanes, except for cases such as 1,1-dimethylcyclopropane which goes to a tertiary cation in the first step of the reaction.

After completion of this work an example of rearrangement accompanying bromination of the 1,2-dimethylcyclopropanes was published.[5] We too had examined this same reaction and there were substantial differences in our observations (differences italicized). We find the *reaction is slow*, that *2,4-dibromopentanes are not reaction products*, but that 1,2-dibromo-2- and *1,2-dibromo-3*-methylbutanes are the major rearrangement products, accompanied by 30–50% *yields of tribromides*, depending on conditions. These discrepant observations will be considered in detail elsewhere. Important here is that there is little stereoselectivity in these reactions: (1) products from *cis*- and *trans*-1,2-dimethylcyclopropanes show only minor differences in composition and (2) the rearrangement products from active *trans*-1,2-dimethylcyclopropane are largely racemized, retaining 10–15% of the enantiomer purity.

The picture which emerges from these observations can be summarized as follows: (1) initial attack is at the least substituted ring atom, (2) the first intermediate recognized is a free[6] (unencumbered) 1-bromo-3-alkyl cation in extended form, (3) this carbonium ion rearranges with a strong preference to move the positive center away from the bromine substituent, and (4) all cations are trapped by Br^- or eliminate a proton to make a bromoolefin (source of tribromides).

The stereochemistry of the initial attack on the three-membered ring occurs with inversion. This follows from the formation of *a,e*- and *e,e*-2,4-dibromoadamantanes[2] from ionic bromination of dehydroadamantane; *a,a*-dibromide is not a product. These conclusions are exemplified in the following diagram which shows initial attack with inversion to form the separated ion pair which is required to explain the free carbonium ion behavior of this system.[7]



While additions of bromine to alkylcyclopropanes proceed through classical 1-bromo-3-alkyl cations, the unsubstituted member of this family, cyclopropane, may still represent an exceptional case in which protonated cyclopropanes are the intermediates.

Acknowledgment. Financial support from the Air Force Research Office (No. 1983) is acknowledged with gratitude.

(3) G. Gustavson, *J. Prakt. Chem.*, (2) **62**, 270 (1900).
(4) K. J. Shea, D. C. Lewis, and P. S. Skell, in press.
(5) J. B. Lambert and B. A. Iwanetz, *J. Org. Chem.*, **37**, 4082 (1972).
(6) J. T. Keating and P. S. Skell, "Carbonium Ions," G. A. Olah and P. v. R. Schleyer, Ed., Wiley-Interscience, New York, N. Y., 1970, Chapter 15.
(7) A great number of stereochemical ring opening patterns have been reported for other electrophiles reacting with cyclopropanes and in highly substituted and strained cyclopropanes. These are summarized in a review by C. H. DePuy which is in press. See also for lead references S. J. Cristol, *et al.*, *J. Org. Chem.*, **36**, 2773 (1971); C. H. DePuy, *et al.*, *J. Amer. Chem. Soc.*, **92**, 4013 (1970); R. T. LaLonde, *et al.*, *J. Org. Chem.*, **35**, 2657 (1970); J. B. Lambert, *et al.*, *J. Org. Chem.*, **35**, 3214 (1970).

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