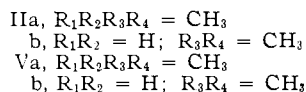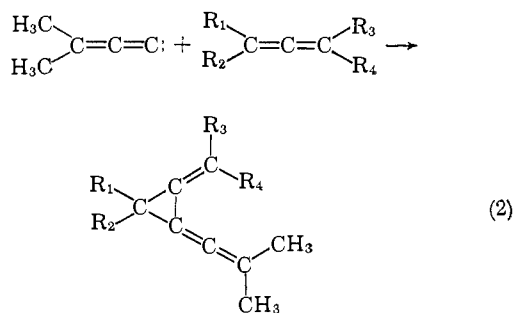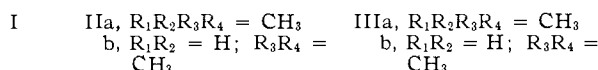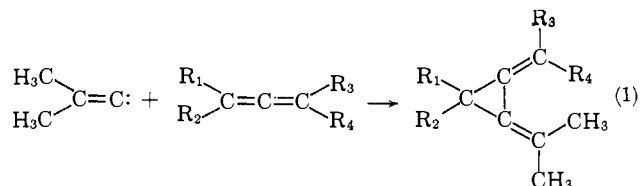## Substituted Dimethylenecyclopropanes. Capture Reactions of Alkylidene and Vinylidene Carbenes by Allenes

Sir:

Remarkable progress has been made in synthesizing and determining the chemistry of highly unsaturated three-membered ring compounds such as cyclopropenes,[1a] cyclopropenium derivatives,[1b] alkylidenecyclopropenes,[1c] and benzocyclopropenes.[1d] Dimethylenecyclopropane, the parent member of an unreported system of conjugated cyclopropane derivatives, has been calculated[1e] to be a fairly stabilized molecule, but its free-radical index at the methylene positions ($\sim$1.0) allows prediction of marked susceptibility to reaction. We now wish to report the synthesis of 1,2-dialkylidenecyclopropanes (III, eq. 1) and substituted 1-alkylidene-2-vinylidenecyclopropanes (V, eq. 2) by addition of isopropylidene carbene[2-4] (I) and dimethylvinylidene carbene[5] (IV), respectively, to various allenes (II). Hydrocarbons of types III and V are derivatives of dimethylenecyclopropane as well as highly strained open-chain analogs of benzocyclopropenes.[6] The methods described in the present report

are also of interest in that they may allow entry to synthesis of trimethylenecyclopropanes[6] (VI).

VI

Adduct IIIa, 2,3-bis(isopropylidene)-1,1-dimethylcyclopropane, was obtained in >12% yield by addition of a solution of methyllithium to an equivalent amount of 1,1-dibromo-2-methyl-1-propene and excess (fivefold) tetramethylallene under nitrogen at $-40°$ and isolation by preparative gas chromatography on silicone gum rubber (GE-SE 30). Product IIIa is a white crystalline solid, m.p. 27–28°, of proper analysis which exhibits infrared absorption at 5.52 μ (for strained double bonds exocyclic to the cyclopropane ring) and 6.0 μ (C=C stretching), and ultraviolet absorption at $\lambda_{max}^{95\% EtOH}$ 256 (ϵ 26,200) and 266 mμ (ϵ 23,200), as anticipated for a strained tetrasubstituted conjugated diene. The nuclear magnetic resonance spectrum is decisive for the structure IIIa in that the hydrogens of the methyl groups attached to the cyclopropane ring absorb as a singlet at τ 8.82 and those of the isopropylidene groups as singlets at τ 8.13 and 8.20 in a ratio of 1:1:1.

Adduct IIIb has been prepared by reaction of 1,1-dimethylallene, 1,1-dibromo-2-methyl-1-propene, and methyllithium; capture of the isopropylidene carbene thus occurs at the terminal unsaturated center of 1,1-dimethylallene.[7] The structure of IIIb was confirmed by its absorption at 5.55 and 6.0 μ (*exo* unsaturation and C=C stretch), $\lambda_{max}^{95\% EtOH}$ 255 (ϵ 21,000) and 265 mμ (ϵ 19,300), and its nuclear magnetic resonance for cyclopropyl hydrogens (τ 8.75, complex multiplet) and methyl hydrogens (τ 8.15, triplet; 8.08, triplet) in a ratio of 1:3:3. Both IIIa and IIIb are sensitive to heat and acids; they absorb oxygen[8] rapidly and must be stored in an inert environment at reduced temperatures.

Synthesis of Va, 2-isopropylidene-1,1-dimethyl-3-(2-methylpropenylidene)cyclopropane (a white crystalline solid, m.p. 26.7–27.0°; b.p. 38° (1 mm.); n^{25}D 1.5124), was effected in 35% yield upon adding potassium *t*-butoxide to 1 equiv. of 3-chloro-3-methylbutyne and a fivefold excess of tetramethylallene, IIa, at $-40°$ under nitrogen. Its structure was indicated from its analysis, mass spectrum (m/e = 162; theory 162), strong infrared absorption (5.04 and 5.68 μ for an allenic group and *exo* unsaturation), and ultraviolet spectral properties ($\lambda_{max}^{95\% EtOH}$ 217 (ϵ 22,300), 233 (ϵ 23,400), and 251 mμ (ϵ 21,600)). The nuclear magnetic resonance spectrum of I showed absorption due to ring methyls (singlet) at τ 8.70, olefinic methyls (singlet) at 8.22, and allenic methyls (singlet) at 8.15 in a ratio of 1:1:1. Ozonolysis of Va in absolute ethanol at 0° gave acetone in >59% yield as isolated as its 2,4-dinitrophenylhydrazone.

$$\begin{array}{c} H_3C \\ H_3C \end{array}\!\!C\!\!=\!\!C\!: \;+\; \begin{array}{c} R_1 \\ R_2 \end{array}\!\!C\!\!=\!\!C\!\!=\!\!C\!\!\begin{array}{c} R_3 \\ R_4 \end{array} \longrightarrow \qquad (1)$$

I   IIa, $R_1R_2R_3R_4 = CH_3$ IIIa, $R_1R_2R_3R_4 = CH_3$
        b, $R_1R_2 = H$; $R_3R_4 = CH_3$ b, $R_1R_2 = H$; $R_3R_4 = CH_3$

$$\begin{array}{c} H_3C \\ H_3C \end{array}\!\!C\!\!=\!\!C\!\!=\!\!C\!: \;+\; \begin{array}{c} R_1 \\ R_2 \end{array}\!\!C\!\!=\!\!C\!\!=\!\!C\!\!\begin{array}{c} R_3 \\ R_4 \end{array} \longrightarrow \qquad (2)$$

IIa, $R_1R_2R_3R_4 = CH_3$
b, $R_1R_2 = H$; $R_3R_4 = CH_3$
Va, $R_1R_2R_3R_4 = CH_3$
b, $R_1R_2 = H$; $R_3R_4 = CH_3$

(1) (a) G. L. Closs, L. E. Closs, and W. A. Böll, *J. Am. Chem. Soc.*, **85**, 3796 (1963); (b) R. Breslow, *ibid.*, **79**, 5318 (1957), and subsequent papers on this subject; (c) A. S. Kende, *ibid.*, **85**, 1882 (1963); M. A. Battiste, *ibid.*, **86**, 943 (1964); W. M. Jones and J. M. Denham, *ibid.*, **86**, 944 (1964); (d) R. Anet and F. A. L. Anet, *ibid.*, **86**, 525 (1964); G. L. Closs, private communication, University of Chicago, 1964; (e) C. F. Sheley, private communication, The Ohio State University.

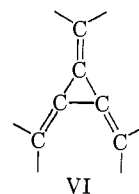(2) H. D. Hartzler, *ibid.*, **86**, 526 (1964).

(3) Synthesis of 1,2-dialkylidenecyclopropanes (III) in the present laboratory by addition of carbenic reagents to the central double bonds of butatrienes has as yet been unsuccessful.

(4) (a) Additions of dibromocarbene,[4b,c] dichlorocarbene,[4e] and diazo compounds[4d,e] to allenes have been reported previously to give alkylidenecyclopropanes; (b) W. J. Ball and S. R. Landor, *Proc. Chem. Soc.*, 246 (1961); (c) A. Bezaquet and M. Delépine, *Compt. rend.*, **254**, 3371 (1962); (d) I. A. D'Yakonov, *J. Gen. Chem. USSR*, **15**, 473 (1945); (e) H. M. Frey, *Trans. Faraday Soc.*, **57**, 951 (1961).

(5) H. D. Hartzler, *J. Am. Chem. Soc.*, **83**, 4990 (1961).

(6) Prior studies of possible syntheses of dimethylenecyclopropane and trimethylenecyclopropane are described by D. T. Longone, Ph.D. Thesis, Cornell University, 1958; A. T. Blomquist and D. T. Longone, *J. Am. Chem. Soc.*, **81**, 2012 (1959); M. F. Wilcox. Ph.D. Thesis, Cornell University, 1961; and D. J. Connolly. Ph.D. Thesis, Cornell University, 1962.

(7) 2-Isopropylidene-1,1-dimethyl-3-methylenecyclopropane as derived by addition of the isopropylidene carbene to the internal double bond of 1,1-dimethylallene is also apparently formed. Its yield and stability are such as to prevent extensive study of its chemistry as yet.

(8) Adduct IIIa absorbs at least 1 mole of oxygen on exposure to air. The structures of the oxidation products are unknown.

Reaction of excess 1,1-dimethylallene (IIb), 3-chloro-3-methylbutyne, and potassium t-butoxide at $-40°$ resulted in formation of 1-isopropylidene-2-(2-methyl-propenylidene)cyclopropane (Vb), b.p. $39–41°$ (2 mm.), of fair purity in 19% yield. Considerable polymerization occurs during addition, and 1,1-di-methyl-2-methylene-3-(2-methylpropenylidene)-cyclopropane (Vc), the product anticipated by capture of dimethylvinylidene carbene (IV) by the internal double bond of IIb, has as yet not been isolated. The structure of Vb was assigned on the basis of its analysis, its infrared absorption at 5.03 and 5.72 μ for allenic and *exo* unsaturation, and its n.m.r. peaks for cyclo-propyl hydrogens (multiplet) at τ 8.63, olefinic methyls (multiplet) at 8.26, and allenic methyls (multiplet) at 8.15.[9] Adducts Va and Vb are affected rapidly by heat, acids, and oxygen; studies of their trans-formation products are in process.[10,11]

(9) The distillation product does not exhibit n.m.r. absorption for vinyl protons as anticipated if Vc were present.

(10) Product Va rearranges almost quantitatively to an isomeric hydro-carbon when heated under nitrogen at 90–150° or when gas chromatographed at 150° on Carbowax 20M or SE-30. Vb rearranges into other products under such conditions.

(11) This research has been supported by the Petroleum Research Fund, Grant 454-A.

DEPARTMENT OF CHEMISTRY   ROLAND F. BLEIHOLDER
OHIO STATE UNIVERSITY   HAROLD SHECHTER
COLUMBUS, OHIO

RECEIVED AUGUST 4, 1964

Differences in the Behavior of Bromine Isotopes Activated by Neutron Capture in Bromoethane

Sir:

Several recent papers[1–3] have reported differences in the isotopic yields of organic radiobromine formed by neutron capture in organic bromides. Some of these effects, for example, in bromoform,[1] were shown to be due to thermal exchange reactions. Longer lived isotopes may then show a greater degree of exchange, and yields are dependent upon the time of irradiation.[4] The other isotope effects reported for liquid systems[2,3] are found in chloro- or fluorobromomethanes, and are discussed extensively by Filatov.[5]

The effects reported in the bromopropanes[6,7] have been in dispute for some years, and Willard has re-ported[8] several unsuccessful attempts to reproduce the results of Capron and his co-workers, who claimed to have found a greater total organic yield for ^{82}Br than for ^{80m}Br.

We wish to report isotopic effects in mixtures of bro-moethane and bromine irradiated in the thermal column of British Experimental Pile O., at A.E.R.E., Harwell (slow neutron flux 4×10^9 cm.$^{-2}$ sec.$^{-1}$; γ-ray flux less than 10^4 r./hr.). Inorganic bromine, as Br_2 or HBr, was first removed with an aqueous wash, and after addition

(1) A. N. Nesmeyanov, A. E. Borisov, and I. Zvara, *Radiokhimiya*, **1**, 325 (1959).

(2) A. N. Nesmeyanov, A. E. Borisov, E. S. Filatov, V. I. Kondratenko, C.-H. Chang, K. Panek, and B. M. Shukla, *ibid*, **1**, 712 (1959).

(3) A. N. Nesmeyanov and E. S. Filatov, *ibid.*, **3**, 501 (1961).

(4) M. Milman and P. F. D. Shaw, *J. Chem. Soc.*, 2101 (1956).

(5) E. S. Filatov, *Usp. Khim.*, **3**, 752 (1962).

(6) P. C. Capron and E. Crevecoeur, *J. Chem. Phys.*, **21**, 1843 (1953).

(7) D. J. Apers, P. C. Capron, and L. Gilly, *J. chim. phys.*, **54**, 314 (1957).

(8) J. E. Willard, "Chemical Effects of Nuclear Transformations," International Atomic Energy Agency, Vienna, 1961, p. 215.

of carriers, separations were made by gas chromatogra-phy using a 3-m. silicone grease column with tempera-ture programming. Fractions were trapped at the end of the column, and after dissolving in ethanol, they were counted in a liquid-sheath Geiger counter. Two measurements were made: the first, 4 hr. after collection, to establish transient equilibrium between ^{80m}Br and its daughter, and the second after 20 hr., so that ^{80m}Br (4.5 hr.) and ^{82}Br (36 hr.) were both deter-mined in the same experiment.

The total activity obtained from the column was normalized to the over-all organic yield determined independently from a small portion of the irradiated material taken before analysis. Table I shows values for the isotope ratios, established on the basis of several experiments, of the seven major products from neutron-irradiated bromoethane. Variation of the time of irradiation from 1 to 24 hr. did not alter the observed ratios, so that the effects cannot be ascribed to thermal exchange or slow reactions of the inorganic bromine with small amounts of impurities in the irradiated mixtures.

TABLE I

RATIOS OF ISOTOPIC YIELDS OF PRODUCTS FROM NEUTRON-IRRADIATED BROMOETHANE

| Product | Yield for ^{80m}Br/yield for ^{82}Br | | | | |
| | Molar fraction of Br_2 present during irradiation | | | | |
	10^{-3}	0.1	0.2	0.5	0.75
C_2H_5Br	0.96	1.03	1.47	1.47	1.58
CH_3Br	2.40	2.15	2.40	2.50	3.05
CH_2Br_2	1.82	1.76	2.02	2.15	2.28
$CHBr_3$	1.06	1.08	1.30	1.47	1.53
$CH_2Br \cdot CH_2Br$	0.74	0.72	0.74	0.70	0.61
$CH_3 \cdot CHBr_2$	0.77	0.80	0.86	0.93	0.89
$CH_2BrCHBr_2$	0.45	0.46	0.52	0.53	0.61
Total organic	0.96	0.98	1.08	1.13	1.09

The root-mean-square deviation of yields from re-peated runs was $\pm 5\%$, except in the case of the methyl bromide fractions, where larger errors ($\pm 20\%$) were obtained; apart from this fraction, the errors only slightly exceeded those expected from the statistics of counting ($\pm 3\%$).

Wexler and Davies have shown[9] that the percentage of charged atoms formed by neutron capture is different for each bromine isotope, and Nesmeyanov and others (see ref. 5) have attempted to explain isotopic differences on the basis of ion–molecule reactions. The recent discovery[10] that most ^{82}Br is produced through an isomer ^{82m}Br (6.2-min. half-life) suggests that the prod-ucts from this isotope may arise predominantly from processes associated with internal conversion, for example, the formation of highly charged atoms[11] by emission of Auger electrons. Reactions could then proceed by charge transfer from neighboring molecules, or through interaction with localized radiolysis products formed by the Auger electrons.[12] Differences in the isotopic yields would then be expected if the activation of ^{80m}Br was predominantly through recoil.

(9) S. Wexler and T. H. Davies, *J. Chem. Phys.*, **20**, 1688 (1952).

(10) (a) J. F. Emery, 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept., 1964, Abstract R26; (b) O. U. Anders, *ibid.*, Abstract R25.

(11) (a) S. Wexler and T. H. Davies, *J. Chem. Phys.*, **18**, 376 (1950); (b) S. Wexler, *Phys. Rev.*, **93**, 182 (1954).

(12) P. R. Geissler and J. E. Willard, *J. Phys. Chem.*, **67**, 1675 (1963).