acetylene and $(Br_2)_T$ is the total bromine concentration. The third term in the expression is only included in the presence of added bromide ion. At low bromine concentrations the term second order in bromine becomes negligible, so that by studying the kinetics at initial bromine concentrations of less than $3 \times 10^{-4}\ M$ (using 10-cm cuvettes in a Cary 16 spectrophotometer) k_2 can be evaluated. This value of k_2 was then used to obtain k_3 from kinetic runs at higher bromine concentrations. Values of the rate constants and their mean deviations for acetic acid at 24.8° are $k_2 = (2.46 \pm 0.06) \times 10^{-3}\ M^{-1}\ sec^{-1}$ and $k_3 = 2.7 \pm 0.3\ M^{-2}\ sec^{-1}$.

In the presence of added bromide ion the formation of tribromide ion lowers the free bromine concentration so that the rate expression becomes

$$-\frac{d(Br_2)_T}{dt} = k_2(MPA)(Br_2) + k_{Br^-}(MPA)(Br_2)(Br^-) \qquad (2)$$

but

$$-\frac{d(Br_2)_T}{dt} = k_{obsd}(MPA)(Br_2)_T \qquad (3)$$

and

$$Br^- + Br_2 \rightleftharpoons Br_3^-$$

$$K = \frac{(Br_3^-)}{(Br_2)(Br^-)} \qquad (4)$$

so that

$$(Br_2)_T = (Br_2) + (Br_3^-) \qquad (5)$$

where k_{obsd} is the observed second-order rate constant and K is the tribromide equilibrium constant.[3] Solution of eq 2–5 gives eq 6, which makes it possible to

$$[1 + K(Br^-)]k_{obsd} = k_2 + k_{Br^-}(Br^-) \qquad (6)$$

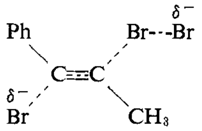
obtain the separated rate constants by studying k_{obsd} as a function of bromide ion concentration. Rates were followed by a potentiometric method[3] with LiBr concentrations from 0.02 to 0.10 M and ionic strength kept constant at 0.10 with added $LiClO_4$. A plot of $[1 + K(Br^-)]k_{obsd}$ *vs.* (Br^-) gives values of $k_2 = (8.1 \pm 7.6) \times 10^{-3}\ M^{-1}\ sec^{-1}$ and $k_{Br^-} = 2.88 \pm 0.03\ M^{-2}\ sec^{-1}$ from the intercept and slope of the least-squares line.

Equation 1 is kinetically indistinguishable from eq 7

$$-\frac{d(Br_2)_T}{dt} = k_2(MPA)(Br_2) + k_3(MPA)(Br_2)^2 + k_{Br_3^-}(MPA)(Br_3^-) \qquad (7)$$

since the tribromide and bromide ion concentrations are related by the equilibrium shown in eq 4.[4] Therefore $k_{Br^-} = Kk_{Br_3^-}$. Equation 1 represents a bromide ion catalyzed attack of molecular bromine whereas eq 7 corresponds to a direct electrophilic attack by tribromide ion.[4] In the case of aromatic brominations, where no bromide ion catalysis is possible, tribromide ion terms have only been observed for the most reactive substrates.[5,6] For bromine additions to olefins, however, the results are not clear. Bell[7,8] has provided evidence that in aqueous solution, for a series of olefins covering a range of reactivity of 10^{10}, the tribromide ion process is occurring rather than the bromide ion catalyzed one, except for diethyl fumarate (the least reactive olefin studied). Kanyaev[9] has published results that disagree with Bell's and indicate that the process is a bromide ion catalyzed reaction for all cases. Our results for bromination of methylphenylacetylene in acetic acid strongly indicate that a bromide ion catalyzed process is most probable, at least for acetylenes. We believe this to be one of the few cases where a clear-cut decision can be made between these kinetically indistinguishable processes.

The ratio $k_{Br^-}(Br^-)/k_2$ is approximately 35 at 0.1 M lithium bromide, so that very little bromination by free bromine is occurring. The complete *trans* stereospecificity of dibromide formation and the dramatic decrease in bromoacetate formation under these conditions are consistent with a termolecular process (Ad_E3)[10] passing through a transition state like VI but would be very difficult to explain on the basis of attack by electrophilic tribromide ions. Such a direct electrophilic attack would be expected to give a similar intermediate cation and hence similar stereochemistry to that observed for the reaction with molecular bromine in the absence of added bromide ion.



VI

Further work on substituted phenylacetylenes is in progress to study the relationship of the observed products to the various cationic intermediates that are possible for electrophilic additions in acetic acid.[11–13]

Acknowledgment. The continued financial support of the National Research Council of Canada and the award of a Studentship to J. A. P. are gratefully acknowledged.

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[3] J. H. Rolston, Ph.D. Thesis, University of Toronto, 1967.

[4] Since lithium bromide is probably very little dissociated in acetic acid, both the Br^- and Br_3^- referred to in all these equations are present mainly as ion pairs.

[5] R. P. Bell and D. J. Rawlinson, *J. Chem. Soc.*, 63 (1961).

[6] J.-E. Dubois, P. Alcais, G. Barnier, and R. Uzan, *Bull. Soc. Chim. France*, 605, 611, 617 (1968).

[7] J. R. Atkinson and R. P. Bell, *J. Chem. Soc.*, 3260 (1963).

[8] R. P. Bell and M. Pring, *J. Chem. Soc., B*, 1119 (1966).

[9] N. P. Kanyaev, *J. Gen. Chem. USSR*, **29**, 825 (1959).

[10] R. C. Fahey and D.-J. Lee, *J. Am. Chem. Soc.*, **90**, 2127 (1968).

[11] M. L. Poutsma and J. L. Kartch, *ibid.*, **89**, 6595 (1967).

[12] R. C. Fahey and D.-J. Lee, *ibid.*, **88**, 5555 (1966).

[13] R. C. Fahey and D.-J. Lee, *ibid.*, **89**, 2780 (1967).

James A. Pincock, Keith Yates
Department of Chemistry, University of Toronto
Toronto 5, Canada

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The Addition of Halomethylene to 1,2-Dimethylcyclobutene, a Methylene–Olefin Reaction Involving a Novel Rearrangement[1]

Sir:

Recently we reported that photolyses of polyiodomethanes in neat cyclohexene led to the formation of norcaranes.[2] We suggested that the photolysis of a

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[1] This work was supported by the U. S. Atomic Energy Commission Contract No. AT-(11-1)-1043. A preliminary account of this work was presented at the 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968, Abstracts, No. P73.

[2] T. Marolewski and N. C. Yang, *Chem. Commun.*, 1225 (1967). For related work, see D. C. Blomstrom, K. Herbig, and H. E. Simmons, *J. Org. Chem.*, 30, 959 (1965); R. C. Neuman, Jr., and R. G. Wolcott, *Tetrahedron Letters*, 6267 (1966).

Table I[a]

Polyhalo-methane, g	Olefin, g	Solvent, ml	Yield of adduct, % (*syn*:*anti*) Isolated	Vpc
CHI_3, 8	Cyclohexene, 16.4	Benzene, 100	69 (1:2)	
CHI_3, 8	Cyclohexene, 4.1	CH_2Cl_2, 100	70 (1:1)	
CHI_3, 2	Cyclohexene, 0.82	CH_2Cl_2, 50		86 (1:1)
$CHBrI_2$, 1	Cyclohexene, 16.4	CH_2Cl_2, 100		85 (1:1)
$CHClI_2$, 1	Cyclohexene, 16.4	CH_2Cl_2, 100		74 (1:1)
CHI_3, 1	*cis*-2-Butene, 17	CH_2Cl_2, 100		61 (2:1)[b]
CHI_3, 1	*trans*-2-Butene, 17	CH_2Cl_2, 100		54
CHI_3, 8	*trans*-2-Butene, 4	CH_2Cl_2, 100	41	
CHI_3, 8	1-Hexene, 8.4	CH_2Cl_2, 100	25 (1:1)	
CHI_3, 8	2,3-Dimethyl-2-butene, 4.2	CH_2Cl_2, 100	31	
CHI_3, 1	1,3-Butadiene, 11	CH_2Cl_2, 200		61 (2:1)
CHI_3, 8	1,3-Butadiene, 17	CH_2Cl_2, 300	33 (2:1)	

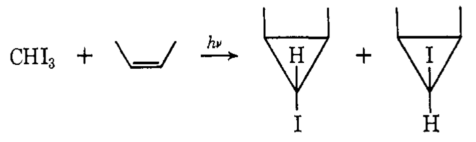
[a] All reactions were carried out in the presence of an aqueous solution of sulfurous acid to remove the iodine formed, and the yields were calculated on the basis of polyhalomethane used. [b] No isomerization of *cis*-2-butene was detected by vpc.

polyiodomethane proceeds *via* two primary processes, (i) dissociation to form an iodine atom and a radical (reaction 1) and (ii) dissociation to form an iodine molecule and a methylene intermediate (reaction 2). In order to explore the possible synthetic application of this reaction, the reaction conditions were modified in order to improve the yield of norcaranes. Since the major competing side reaction, the Kharasch addition of polyhalomethane to olefins, is a radical-chain reaction, it was minimized by carrying out the photolysis in a solution of the olefin in an inert solvent such as benzene or dichloromethane. Since the molecular iodine formed in the photolysis will trap the reactive intermediates generated, it was removed by stirring the reaction mixture with aqueous sulfurous acid. With these two modifications, halonorcaranes and other cyclopropanes may be prepared conveniently in good yield (Table I).

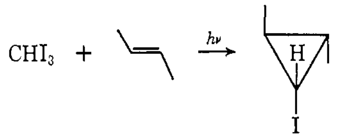
$$CHXI_2 \xrightarrow{h\nu} CHXI\cdot + I\cdot \qquad (1)$$

$$CHXI_2 \xrightarrow{h\nu} CHX\colon + I_2 \qquad (2)$$

With this improved technique, the photolysis of iodoform was carried out in the presence of *cis*- or *trans*-2-butene. We found that the formation of 2,3-dimethyl-1-iodocyclopropane from either olefin was stereospecific (reactions 3 and 4), and there was no detectable isomerization of the *cis*-2-butene recovered from its reaction mixture (Table I). If the formation of cyclopropane from 2-butenes proceeded *via* radical intermediates, we would expect nonstereospecific formation of cyclopropanes as well as rapid isomerization of *cis*-2-butene. Therefore, we conclude that halomethylenes are the intermediates in the formation of halocyclopropanes from the photolyses of diiodohalomethanes in olefins (reaction 5). In contrast to methylene, fluoromethylene and chloromethylene possess a singlet ground state;[3] therefore iodomethylene is also expected to possess a singlet ground state. The stereospecific addition of iodomethylene generated by the photolysis of iodoform to 2-butenes is in agreement with this assignment.[4]



(3)



(4)

When the photolysis of iodoform was carried out in a solution of 1,2-dimethylcyclobutene (I) in dichloromethane, two and only two adducts (IIa and IIIa) corresponding to the addition of iodomethylene to the olefin were isolated by preparative vpc in 12% yield each.[5] The nmr of compound IIa exhibits cyclopropyl protons at δ 0.60 (s (broad), 4), methyl protons at 1.18 (s, 3), allylic methyl protons at 1.85 (d, 3, J = 1.5 Hz), and an olefinic proton at 5.88 (q, 1, J = 1.5 Hz), while that of IIIa exhibits cyclopropyl protons at δ 0.45 and 0.65 (t, 2 and 2, J = 1.5 Hz), methyl protons at 1.19 (s, 3), allylic methyl protons at 1.83 (d, J = 1.1 Hz), and an olefinic proton at 6.00 (q, 1, J = 1.1 Hz). Both compounds may be readily reduced to the known 2-(1-methylcyclopropyl)propene (IV) by tri-*n*-butyltin hydride.[6] Compounds IIa and IIIa are thus identified to be isomeric 2-(1-methylcyclopropyl)-1-iodopropene. Structure IIa with iodine *trans* to the methyl group was assigned to the isomer with more positive solvent shift of the allylic methyl proton signals in the nmr induced by benzene.[7] When the addition of chloromethylene generated from the photolysis of diiodochloromethane to I was carried out under similar conditions, two adducts (IIb and IIIb) were isolated in 18% yield each.[5] The structures of adducts were assigned on the basis of their nmr. Compound IIb exhibits nmr signals at δ 0.51 (t, 2, J = 1.5 Hz), 0.62 (t, 2, J = 1.5 Hz), 1.17 (s, 3), 1.75 (d, 3, J = 1.5 Hz), and 5.75 (q, 1, J = 1.5 Hz); IIIb exhibits nmr signals at δ 0.44 (t, 2, J = 2 Hz), 0.60 (t, 2, J = 1.5 Hz), 1.12 (s, 3), 1.76 (d, 3, J = 1.5 Hz), and 5.88 (q, 1, J = 1.5 Hz).

Since the thermolysis of bicyclopentanes leads to the formation of cyclopentenes,[8] compounds II and III are not likely to be formed by way of vibrationally excited bicyclopentanes as the intermediates. Our observations are consistent with the interpretation that halomethylenes generated from the photolysis of diiodohalomethanes may add in their singlet state to a strained olefin in a stepwise mechanism. The addition

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(3) A. J. Merer and D. N. Travis, *Can. J. Phys.*, **44**, 525, 1541 (1966).

(4) For a review on the stereochemistry of methylene additions to olefins, see G. L. Closs in "Topics in Stereochemistry," Vol. 3, N. L. Allinger and E. L. Eliel, Ed., John Wiley & Sons, Inc., New York, N. Y., 1968, pp 193–234.

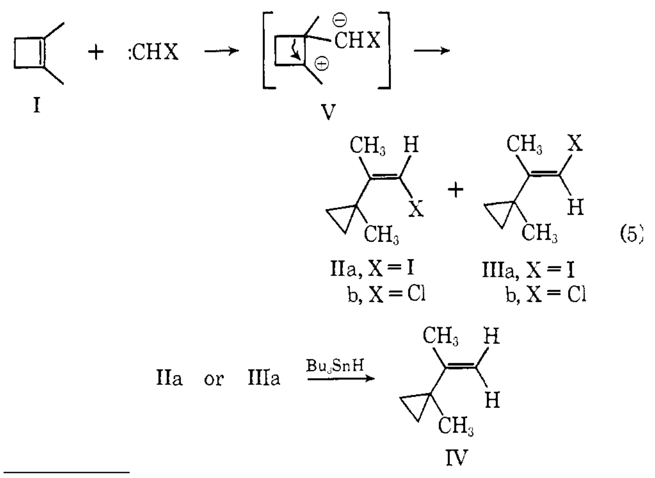
(5) Satisfactory elemental analyses had been obtained for all new compounds. The balance of material was accounted for by high-boiling products.

(6) L. Skattebøl, *Acta Chem. Scand.*, **17**, 1962 (1963).

(7) J. Ronayne and D. H. Williams, *J. Chem. Soc.*, *B*, 540 (1967).

(8) R. Criegee and A. Rimmelin, *Ber.*, **90**, 414 (1957); C. Steel, R. Zard, P. Hurwitz, and S. G. Cohen, *J. Am. Chem. Soc.*, **86**, 679 (1964); M. J. Jorgenson and T. J. Clark, *ibid.*, **90**, 2188 (1968).

may proceed *via* a dipolar intermediate (V) which subsequently rearranges to give vinylcyclopropanes II and III as the final products (reaction 5).



I

V

IIa, X = I
b, X = Cl

IIIa, X = I
b, X = Cl

IIa or IIIa

IV

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(9) National Institutes of Health Predoctoral Fellow, 1967–1968.

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N. C. Yang, Theodore A. Marolewski[9,10]
Department of Chemistry, University of Chicago
Chicago, Illinois 60637

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Photolysis of Benzene Vapor at 1849 Å. Formation of *cis*-1,3-Hexadien-5-yne[1]

Sir:

In two recent studies[2,3] of the photolysis of benzene vapor at 1849 Å, benzene was found to disappear with high quantum yield forming two major products: polymer and an isomer with a highly structured absorption spectrum centered near 2350 Å. This isomer was subsequently identified[4,5] as fulvene. We now wish to report that an open-chain isomer, *cis*-1,3-hexadien-5-yne, is also formed from benzene vapor at 1849 Å. Studies of the photochemistry of the products in the vapor phase reveal that they undergo isomerization both at 1849 and 2537 Å.

Most of the irradiations in the present study were performed in an atmosphere of N_2 in a silica cell 2 cm in diameter and 10 cm long. A 1-cm cell of the same diameter was used for benzene at pressures above 1 torr. The cells were filled by flushing either with N_2 saturated with benzene at an appropriate temperature or with a chromatographic effluent containing fulvene or hexadienyne. They were irradiated with a flat helical Suprasil Hg-resonance lamp, using either a γ-irradiated LiF filter[6] to exclude 2537-Å radiation or a Corning 7910 filter to exclude 1849-Å radiation. The input to the cell was 4×10^{15} quanta/sec of 1849-Å radiation or 2×10^{16} quanta/sec of 2537-Å radiation. Ultraviolet absorption spectra were monitored with a Cary Model 14 spectrophotometer. Aliquots from irradiated cells were analyzed by gas chromatography with flame-ionization detection; absorbance of deposits on the cell windows was measured after sweeping with N_2.

Benzene at pressures of 0.05–20 torr in 1 atm of N_2 was irradiated at 1849 Å for varying times. At each pressure, the absorbance at 2350 Å attributable to volatile products reached or approached a maximum value which appeared to be proportional to the amount of benzene in the cell. Samples irradiated to the maximum absorbance contained 4–5% fulvene and about 2% each of *cis*- and *trans*-1,3-hexadien-5-yne. The photoproducts were identified as *cis*- and *trans*-1,3-hexadien-5-yne by the correspondence of their gas-chromatographic retentions, uv spectra, and photochemical behavior with those of authentic samples.[7] Their retentions on a variety of columns are shown, together with those of fulvene, in Table I. In pentane solution, each exhibited a uv maximum at 2520 Å, log ϵ 4.4, and was converted ($\Phi \sim 0.1$) to its stereoisomer without formation of other monomeric products upon irradiation at 2537 Å. The vapor-phase uv spectra of the hexadienynes show maxima at 2400 Å, close to that previously deduced[5] for a then unidentified photoproduct.

Table I. Gas Chromatographic Retentions of Photoisomers Relative to Benzene

Column[a]	Temp, °C	Fulvene	1,3-Hexadien-5-yne *cis*	1,3-Hexadien-5-yne *trans*
Apiezon L	50	0.80	0.65	0.87
Didecyl phthalate	23	0.83	1.06	1.20
Tri-*o*-tolyl phosphate	23	0.86	1.21	1.34
Carbowax-KOH[b]	50	0.95	1.79	2.03

[a] Chromosorb G support. [b] 5% Carbowax-750, 2% KOH.

To investigate their origin, the distribution of products in the photolysis of 20 torr of benzene in 1 atm of N_2 was studied as a function of time. Expressed as per cent of benzene, yields of fulvene and *cis*- and *trans*-hexadienyne, respectively, were: 0.10, 0.022, <0.002 after 15 sec; 0.40, 0.075, 0.014 after 1 min; 1.4, 0.29, 0.15 after 5 min; 4.2, 1.2, 1.0 after 20 min. It may be noted that the ratio of *trans*- to *cis*-hexadienyne increases from less than 0.1 to almost unity as photolysis proceeds, and that the ratio of hexadienynes to fulvene increases only from 0.22 to 0.31 while the fulvene concentration increases 14-fold. It can be concluded from these results, and from similar results at lower benzene pressures, that *cis*-1,3-hexadien-5-yne is formed from benzene at about one-fourth the rate of fulvene formation, and that the *trans* isomer is produced by secondary photolysis.

To aid in understanding later stages of the photolysis, fulvene and *cis*-hexadienyne at pressures *ca.* 0.01 torr in 1 atm of N_2 were irradiated at 1849 Å. *cis*-Hexadienyne isomerized to the *trans* compound and "polymerized" at comparable rates, yielding no other volatile product. Fulvene disappeared at a similar rate ($t_{1/2} \sim 30$ sec) yielding "polymer," benzene, and hexadienyne in a ratio of 2:1:1. The photolysis rates are consistent with the observed limiting concentrations of fulvene

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(1) Based on work performed under the auspices of the U. S. Atomic Energy Commission.

(2) J. K. Foote, M. H. Mallon, and J. N. Pitts, Jr., *J. Am. Chem. Soc.*, **88**, 3698 (1966).

(3) K. Shindo and S. Lipsky, *J. Chem. Phys.*, **45**, 2292 (1966).

(4) H. R. Ward, J. S. Wishnok, and P. D. Sherman, Jr., *J. Am. Chem. Soc.*, **89**, 162 (1967).

(5) L. Kaplan and K. E. Wilzbach, **89**, 1030 (1967).

(6) J. L. Weeks, S. Gordon, and G. M. A. C. Meaburn, *Nature*, **191**, 1186 (1961).

(7) F. Sondheimer, D. A. Ben-Efraim, and Y. Gaoni, *J. Am. Chem. Soc.*, **83**, 1682 (1961).