6 *N* sodium hydroxide, followed by the addition of 30% hydrogen peroxide. Glpc examination of the ether extract, however, revealed that the yield of 1,2-heptadiene amounted to less than 1%. After removal of the solvents, distillation gave 68% of 2,3-dimethyl-*trans*-5-decen-4-ol. Apparently, one siamyl group migrates in the presence of base to the adjacent carbon with concurrent shift of the double bond and loss of chloride. Oxidation of the allyl boron intermediate gives the allylic alcohol. It should be noted here that saturated γ-chloroorganoboranes undergo cyclization to give cyclopropane derivatives on treatment with bases.[9]

It is evident that monohydroboration of substituted propargyl chlorides should be of wide utility in synthesizing allenes, *cis*-allyl chlorides, and allyl alcohols. We continue to explore the potentialities of organoboranes derived from propargyl chlorides, including 1,3-disubstituted propargyl chlorides, in organic syntheses.

(9) M. F. Hawthorne, *J. Amer. Chem. Soc.*, **82**, 1886 (1960); P. Binger and R. Köster, *Tetrahedron Lett.*, 156 (1961); P. Binger and R. Köster, *Angew. Chem.*, **74**, 652 (1962); H. C. Brown and S. P. Rhodes, *J. Amer. Chem. Soc.*, **91**, 2149 (1969).

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Alkyldiazenes

Sir:

The first alkyldiazene to be directly observed (*t*-butyldiazene) was found to disappear rather quickly.[1] A later report suggested that methyldiazene was "surprisingly stable."[2] We now report a complete series of alkyldiazenes, for which we have made the following observations: (a) all alkyldiazenes, like alkenyldiazenes[3] and aryldiazenes,[4a,d,5] undergo a bimolecular reaction with themselves; (b) the rate of the bimolecular reaction is fairly sensitive to the nature of the alkyl group; (c) methyldiazene has a bimolecular decomposition rate about like that of phenyldiazene;[4a–d,6] (d) all alkyldiazenes react rapidly with oxygen, as do all other monosubstituted diazenes;[1,3–6] and (e) the hydrocarbon (RH) derived from the bimolecular reaction of alkyldiazenes (RN=NH) is formed in less than quantitative yield.

Alkyldiazenes were generated either by elimination[7–10] or decarboxylation[1,4–6] (eq 1-3). The methyl alkyldiazenecarboxylates were derived from the corresponding hydrazo compounds by oxidation for all alkyl

$$\mathrm{TsNHNH_2 \xrightarrow[LiH]{RX} RN(Ts)NH_2 \xrightarrow[EtOH]{0.1\ \mathit{M}\ OEt^-} RN{=}NH} \qquad (1)$$

$$\mathrm{Ts} = p\text{-}\mathrm{CH_3C_6H_4SO_2};\ \mathrm{R} = \mathrm{CH_3, CH_3CH_2, (CH_3)_2CH}$$

$$\mathrm{RNHTs \xrightarrow[OEt^--EtOH]{NH_2OSO_3^-Na^+} [RN(Ts)NH_2] \longrightarrow RN{=}NH} \qquad (2)$$

$$\mathrm{R} = \mathrm{CH_3, CH_3CH_2, (CH_3)_2CH, (CH_3)_3C,}\ c\text{-}\mathrm{C_3H_5},\ c\text{-}\mathrm{C_6H_{11}}$$

$$\mathrm{RN{=}NCOOCH_3 \xrightarrow{KOH}}$$
$$\mathrm{RN{=}NCOO^-K^+ \xrightarrow[EtOH]{ImH^+Cl^-} \xrightarrow{-CO_2} RN{=}NH} \qquad (3)$$

$$\mathrm{Im = imidazole;\ R = CH_3,^{11}\ CH_3CH_2, (CH_3)_2CH, (CH_3)_3C,}\ c\text{-}\mathrm{C_3H_5},\ c\text{-}\mathrm{C_6H_{11}}$$

groups.[12]

Quantitative conversion of the methyl ester to the carboxylate ion with sodium hydroxide was utilized for the measurement of absorption coefficients of the anions with R = c-C_3H_5, c-C_6H_{11}, $(CH_3)_3C$, and $(CH_3)_2CH$. Under the same conditions, the esters with R = CH_3 and CH_3CH_2 partially isomerized to the hydrazone, so that it was necessary to assume that the absorption coefficient for the anions, $CH_3N{=}NCOO^-$ and $CH_3CH_2N{=}NCOO^-$, were the same as that of $(CH_3)_2CHN{=}NCOO^-$.

Absorption coefficients for the n → π^* transition of the alkyldiazenes were obtained through quantitative decarboxylation of the anion by treatment with imidazolium hydrochloride in ethanol.[4a,b] With the aid of these reasonably accurate absorption coefficients, it was possible to obtain rate constants for the bimolecular decompositon of the alkyldiazenes. Spectroscopic and kinetic data are listed in Table I.

Table I. Properties of Alkyldiazenes

RN=NH, R =	λ_{max}, Å (ϵ_{max})[a]	10^2k_2,[a,b] M^{-1} sec^{-1}	Bimolecular reaction product[c]
c-C_3H_5	3490 (28)	1.5	Cyclopropane (>50%)
CH_3	3610 (18)[d]	3.0	
CH_3CH_2	3670 (18)	42	
$(CH_3)_2CH$	3680 (20)	60	Propane (75%)
c-C_6H_{11}	3680 (20)	58	Cyclohexane (82%)[e]
$(CH_3)_3C$	3750 (17)	280	Isobutane (75%)

[a] In ethanol solution. [b] Rate constants are approximately ±25%, including constants for diazenes generated by more than one method. [c] Identification by complete infrared spectra; yield by measurement of a number of infrared band intensities and pressure. [d] Taken as equal to that of ethyldiazene. [e] Identification by glpc retention time; yield by peak area comparison with that of an authentic sample of similar concentration.

Previous studies on the products of the bimolcular reaction of aryldiazenes[4d,5] and alkenyldiazenes[3] indicated that the major product in all cases but one[15]

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(1) P. C. Huang and E. M. Kosower, *J. Amer. Chem. Soc.*, **89**, 3911 (1967).

(2) M. N. Ackermann, J. L. Ellenson, and D. H. Robinson, *ibid.*, **90**, 7173 (1968). We have confirmed their preparation of methyldiazene from CH_3NHOH and $NH_2OSO_3^-Na^+$ and have found that the bimolecular disappearance rate constant in ethanol or acetonitrile is similar to that found for methyldiazene generated in other ways.

(3) T. Tsuji and E. M. Kosower, *ibid.*, **91**, 3375 (1969).

(4) (a) P. C. Huang and E. M. Kosower, *ibid.*, **89**, 3910 (1967); (b) *ibid.*, **90**, 2354 (1968); (c) *ibid.*, **90**, 2362 (1968); (d) *ibid.*, **90**, 2367 (1968).

(5) E. M. Kosower, P. C. Huang, and T. Tsuji, *ibid.*, **91**, 2325 (1969).

(6) E. M. Kosower and P. C. Huang, *ibid.*, **87**, 4645 (1965).

(7) J. S. McFayden and T. S. Stevens, *J. Chem. Soc.*, 584 (1936).

(8) A. Nickon and A. Sinz, *J. Amer. Chem. Soc.*, **82**, 753 (1960).

(9) A. Nickon and A. S. Hill, *ibid.*, **86**, 1152 (1964).

(10) D. J. Cram and J. S. Bradshaw, *ibid.*, **85**, 1108 (1963).

(11) Slight change in procedure for this alkyl derivative.

(12) Methyl alkyldiazenecarboxylates vary greatly in stability. All compounds exhibited either nmr or mass spectrum consistent with structure. The compounds $RNHNHCOOCH_3$ (R = CH_3, CH_3CH_2, $(CH_3)_2CH$, c-C_6H_{11}) were prepared by hydrogenation of the appropriate carbomethoxyhydrazones over Raney nickel. Methyl cyclopropyldiazanecarboxylate (*cf.* ref 4c for nomenclature) was prepared from cyclopropylamine by the method of Lwowski[13] and methyl *t*-butyldiazanecarboxylate was made by the method of Chaco and Rabjohn.[14] Details will be given in the full publication.

(13) W. Lwowski and T. J. Maricich, *J. Amer. Chem. Soc.*, **87**, 3630 (1965).

(14) M. C. Chaco and N. Rabjohn, *J. Org. Chem.*, **27**, 2765 (1962).

(15) The bimolecular reaction of 4-nitrophenyldiazene yielded 35% nitrobenzene, the major product being 1,2-bis(4-nitrophenyl)diazane.[5]

was the corresponding hydrocarbon. In no case was the hydrocarbon formed quantitatively, a result which holds for the alkyldiazenes (eq 4). Data on product formation are included in Table I.

$$2RN{=}NH \longrightarrow RH + \text{other products} \qquad (4)$$

The alkyldiazenes so often postulated as intermediates can now be regarded as well-established, highly reactive compounds which have a significant and interesting chemistry. Further reports on monosubstituted diazenes will be made in due course.

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[16] On leave from the Department of Chemistry, Faculty of Engineering Science, Osaka University, Osaka, Japan.

[17] The authors are grateful for support from the National Institutes of Health, the Army Research Office (Durham), and the donors of the Petroleum Research Fund (PRF-3695-A1), administered by the American Chemical Society.

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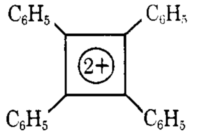
Stable Carbonium Ions. CI.[1] The Tetraphenylcyclobutadiene Dication[2]

Sir:

We have recently reported the preparation and ^{1}H and ^{13}C nmr spectroscopic studies of the tetramethylcyclobutadiene dication,[3] the first well-defined four-membered ring (2 π electron) aromatic system.

Freedman reported previously the preparation of the tetraphenylcyclobutadiene dication **1** from 3,4-dibromotetraphenylcyclobutene and stannic bromide[4] but subsequently it was shown that only the monocation monodonor–acceptor complex **2** was obtained.[5-7]



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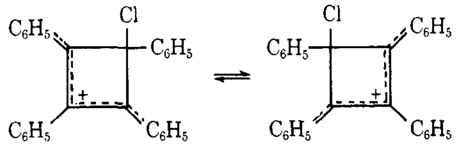
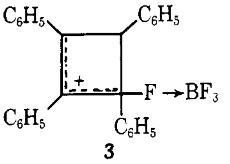


2

In continued work, Freedman and Young studied the metathetic reaction of 3,4-dibromotetraphenylcyclobutene with silver tetrafluoroborate[8] which indeed may have yielded the dication **1**. Unfortunately, with the exception of finding the expected 2 mol equiv of silver bromide eliminated in the reaction and observing the ^{19}F nmr of the tetrafluoroborate anion (from which, however, it may be difficult to differentiate the dication from a rapidly exchanging monofluoro cation–BF_3 system, **3**) no further characterization was given. Thus,



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until now, **1** was not satisfactorily characterized and we felt it of interest to extend our investigations to this ion.

We wish to report now the generation and characterization of the tetraphenylcyclobutadiene dication **1** by using the very strong SbF_5 and $FSO_3H–SbF_5$ acid systems as appropriate ionizing agents. When a saturated solution of antimony pentafluoride in sulfur dioxide was added with vigorous stirring at about −60° to a suspension of 3,4-dibromotetraphenylcyclobutene in sulfur dioxide, a dark red solution of **1** was obtained (it is uncertain whether the color is entirely due to the dication or to some possible impurities formed from the starting dibromide). The pmr spectrum of this solution (Figure 1a) shows a typical pattern of equivalent phenyl groups attached to a strong electron-withdrawing center: a doublet at δ 8.64 (*ortho*-), a triplet at δ 8.26 (*para*-), and a triplet at δ 7.87 (*meta*-hydrogen nuclei).[9] Further splitting of the main signals is due to long-range couplings. The best fitting nmr parameters were obtained from a computer-simulated spectrum[10] (Figure 1b): δ_o 8.644; δ_p 8.263; δ_m 7.868; $J_{om} = J_{o'm'} = 8.05$; $J_{op} = J_{o'p} = 1.15$; $J_{om'} = J_{o'm} = 0.30$; $J_{oo'} = 2.0$; $J_{mp} = J_{m'p} = 7.40$; $J_{mm'} = 0.80$ Hz. The proton deshielding in the *precursor* (δ 6.7–7.9),[11a] *monocation* (δ 7.5–8.3),[11b] *dication* (δ 7.9–8.7),[11c] sequence provides good evidence for the dication structure.

Methanolysis of solutions of **1** in the presence of sodium methoxide at −78° gave a mixture of dimethoxytetraphenylcyclobutenes (identified by nmr but not further studied relative to isomer distribution).

Carbon-13 magnetic resonance measurements strongly support the structure **1**. Using the indor technique we have found a ^{13}C chemical shift of +17.6 ppm (upfield from $^{13}CS_2$) for the four-membered ring carbon atoms; the aromatic ^{13}C atoms gave two broad absorptions at 50 and 74 ppm, tentatively assigned to the *ortho* and *para*, and α and *meta* positions, respectively.

Comparing the δ ^{13}C +17.6 ppm value obtained for the tetraphenylcyclobutadiene dication to that (−14.4 ppm) reported for the tetramethylcyclobutadiene dication[3] suggests a significant participation of the phenyl rings in charge delocalization.

Using the simple HMO method (the size of the molecule did not allow use of extended Hückel or SCF

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[1] Part C: G. A. Olah, A. M. White, J. R. DeMember, A. Commeyras, and C. Lui, *J. Amer. Chem. Soc.*, in press.

[2] Reported in part at the 21st National Organic Chemistry Symposium of the American Chemical Society, Salt Lake City, Utah, June 1969.

[3] G. A. Olah, J. M. Bollinger, and A. M. White, *J. Amer. Chem. Soc.*, **91**, 3667 (1969).

[4] H. H. Freedman and A. M. Frantz, *ibid.*, **84**, 4165 (1962).

[5] D. G. Farnum and B. Webster, *ibid.*, **85**, 3502 (1963).

[6] R. F. Bryan, *ibid.*, **86**, 733 (1964).

[7] H. H. Freedman and A. E. Young, *ibid.*, **86**, 734 (1964).

[8] A method found effective to produce carbonium ions under acid-free conditions [G. A. Olah, A. E. Pavlath, and J. A. Olah, *ibid.*, **80**, 6540 (1958)].

[9] The same pattern is obtained with a $FSO_3H–SbF_5–SO_2$ solution, however, with some loss of resolution and a downfield shift (*ca.* 0.4 ppm) of the lines. Resolution is further impaired in the $SbF_5–SO_2ClF$ solution.

[10] Program, LAOCOON III (A. A. Bothner-By and S. Castellano); computer, Univac 1108; recorder, CALCOMP 663 (California Computer Prod., Inc.).

[11] Actually the deshielding is probably larger in the monocation–dication step, since we have made no solvent-shift correction (in SO_2 signals would appear at a higher field); (a) in SO_2 solution at −60°; (b) methylene chloride solution, reported by Freedman;[4] (c) $SbF_5–SO_2$ solution, present work.