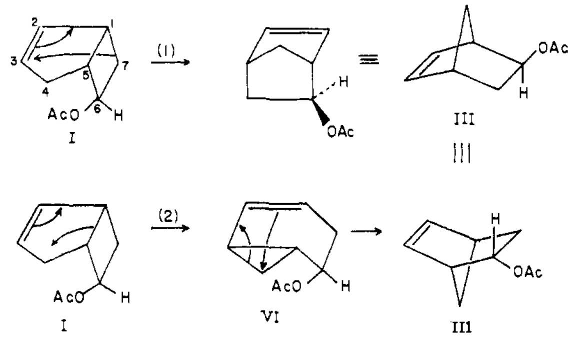
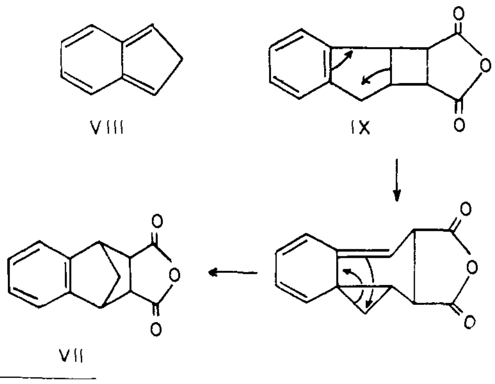
sis (5% conversion), the shortest reaction time that allows an accurate estimate of the *exo*:*endo* ratio, whereas the kinetically determined product ratio from the Diels-Alder addition of cyclopentadiene and vinyl acetate in decalin at 300° is 0.43. These relationships are set out in Fig. 1. There is therefore a path for the I→III reaction that is intramolecular and largely if not completely stereospecific.

The two most likely mechanisms for the I→III conversion are: (1) cleavage at C.1–C.7, establishment of a double bond at C.1–C.2, and re-cyclization by connection of C.7 and C.3; (2) formation of a vinylcyclopropane (VI) from a cyclopentene, followed by conversion of the latter to a different cyclopentene (III). The steps of both mechanisms can also be formulated with diradical intermediates, the concertedness of the electron shifts being presently indeterminate.



Although in simple cases the cyclopentene → vinylcyclopropane reaction is doubtless strongly endothermic and consequently is not expected to occur except at very high temperatures, this restriction is less severe in the I→VI reaction of mechanism (2), much of the price of three-membered ring formation being paid by four-membered ring opening. Several examples analogous to the second step (VI → III) of mechanism (2) are known.[11]

Mechanism (2) may provide an alternative explanation for the reported[12] formation, at elevated temperature, of the adduct VII from indene and maleic anhydride, which is believed[12] to involve the unknown hydrocarbon isoindene VIII as an intermediate. It is conceivable, however, that the reaction takes the course shown here, in which preliminary formation of the cycloaddition product IX, a formal benzo analog of I, is followed by rearrangement according to mechanism (2). We are investigating this possibility.



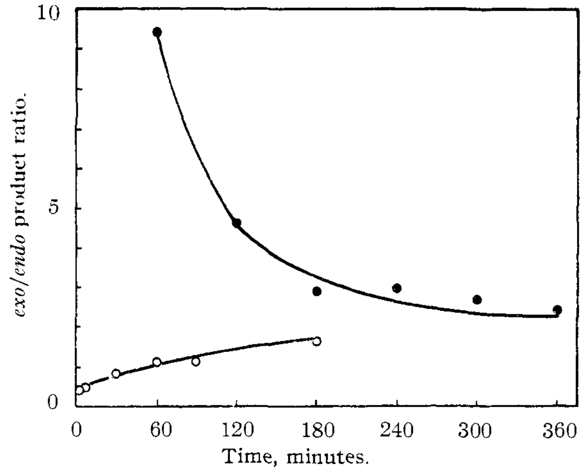


Fig. 1.—Ratio of products III/IV as a function of time and starting material in decalin solution at 300°. Solid circles show products from I; open circles show products from cyclopentadiene and vinyl acetate.

Acknowledgment.—This research was supported in part by a grant from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of this fund. We also are indebted for support to the Office of Scientific Research, Air Research and Development Command, U. S. Air Force, Contract No. AF 49((638)-828). Reproduction in whole or in part is permitted for any purpose of the United States Government.

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[11] (a) E. Vogel, R. Palm and K. H. Ott, unpublished work, cited by E. Vogel, *Angew. Chem.*, **72**, 4 (1960); (b) C. G. Overberger and A. E. Borchert, *J. Am. Chem. Soc.*, **82**, 1007, 4897 (1960); (c) W. von E. Doering and W. R. Roth, unpublished work, cited by W. von E. Doering, M. R. Wilcott, III, and M. Jones, Jr., *ibid.*, **84**, 1224 (1962); (d) M. C. Flowers and H. M. Frey, *J. Chem. Soc.*, 3547 (1961).

[12] K. Alder, F. Pascher and H. Vagt, *Ber.*, **75**, 1501 (1942); K. Alder and M. Fremery, *Tetrahedron*, **14**, 190 (1961).

A NEW AND CONVENIENT ROUTE TO THE AMINE-BORANES

Sir:

The reaction of amine-boranes with olefins to produce trialkylboranes has been reported.[1,2,3] This method of producing trialkylboranes has many advantages over other methods as a route to this important class of compounds. Several other important reactions of amine-boranes also have been reported. Among these are the reaction with sodium hydride to produce sodium borohydride[4] and the reactions with primary and secondary amines to produce borazines and borazenes, respectively. Until now amine-boranes have been prepared either by the reaction of diborane with

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[1] R. Köster, *Angew. Chem.*, **69**, 684 (1957).

[2] M. F. Hawthorne, *J. Org. Chem.*, **23**, 1788 (1958).

[3] E. C. Ashby, *J. Am. Chem. Soc.*, **81**, 4791 (1959).

[4] R. Köster, *Angew. Chem.*, **69**, 94 (1957).

amines[5,6] or by the high pressure hydrogenolysis of trialkylboranes in the presence of amines.[7] Both of these routes utilize difficultly obtainable starting materials. This difficulty has discouraged somewhat the study of the chemistry of the amine-boranes.

Recently we reported the direct synthesis of complex aluminum hydrides, *e.g.*, $NaAlH_4$, from sodium, aluminum and hydrogen.[8,9] Further investigation of the scope of the aluminum–hydrogen system as a route to other metal hydrides, has shown that this system is much more versatile than originally believed.

We wish to report a new and convenient synthesis of amine-boranes which should expand the use of this class of compounds considerably. This synthesis involves the reduction of a readily available borate ester with aluminum and hydrogen in amine solvent under moderate temperature and pressure to produce the amine-borane in high yield.

$$B(OC_6H_5)_3 + Al + 3/2H_2 \xrightarrow{Et_3N} BH_3NEt_3 + Al(OC_6H_5)_3$$

In a typical experiment 30 g. of phenyl borate was dissolved in 100 ml. of triethylamine. To this solution was added 6 g. of activated aluminum powder[10] and 0.25 g. of $AlCl_3$ catalyst. The mixture then was agitated in contact with 2000 psi of hydrogen for 1 hour at 180°. The by-product aluminum phenoxide was insoluble in the resulting mixture and was separated easily by filtration. The amine-borane then was separated from the amine solvent by vacuum distillation. The product distilled at 97° at 12 mm. pressure. The tabulated results were obtained in the amines indicated, with nearly quantitative yields in each case:

Amine	Reaction time, hr.	Conversion, %
Me_3N	1	99
Et_3N	1	92
$C_6H_5NMe_2$	6	60

The use of other solvents, such as ethers and hydrocarbons, is satisfactory in the reduction of phenyl borate, provided the molar ratio of amine to borate ester is at least 2:1. The use of secondary amines to produce borazenes and primary amines to produce borazines is being investigated.

This reaction also has been found to proceed with the boron halides. The yield and rate of reaction decrease in the order $BBr_3 > BCl_3 > BF_3$. The reaction with phenyl borate is preferred, however, due to the greater ease of separation of the product from the aluminum salt by-product. The reduction of several alkyl borates produced amine-boranes only in very low yields. The B–O alkyl bond was reduced extensively only in complex alkyl borates.

$$3\ NaB(OMe)_4 + 4\ Al + 6\ H_2 \xrightarrow{\text{Diglyme}} 3\ NaBH_4 + 4\ Al(OMe)_3$$

The Al–H_2 reduction of other metal halides and metal esters is also being studied. Preliminary results indicate that silicon and phosphorus halides are reduced to silane and phosphine, respectively. Also, organochlorosilanes are easily converted to the corresponding organosilanes in high yields.

$$3/(4 - n)R_nSiCl_{4-n} + Al + 3/2H_2 \xrightarrow{R'_3N} 3/(4 - n)\ R_nSiH_{4-n} + AlCl_3NR'_3 (n = 1, 2, \text{ or } 3)$$

Preliminary results also have shown that the Al–H_2 reduction of phenyl borate, silicon tetrachloride, phosphorus trichloride, etc., in the presence of olefins leads to the formation of the corresponding metal alkyl.

$$B(OC_6H_5)_3 + Al + 3/2H_2 + 3(\text{olefin}) \xrightarrow{R'_3N} BR_3 + Al(OC_6H_5)_3$$

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(5) A. B. Burg and H. I. Schlesinger, *J. Am. Chem. Soc.*, **59**, 780 (1937).

(6) H. C. Brown (to Ethyl Corporation), U. S. Patent 2,860,167 (1958).

(7) R. Köster, *Angew. Chem.*, **69**, 64 (1957).

(8) E. C. Ashby (to Ethyl Corporation), French Patent 1,235,680 (1960).

(9) E. C. Ashby, *Chem. and Ind.*, **5**, 208 (1962).

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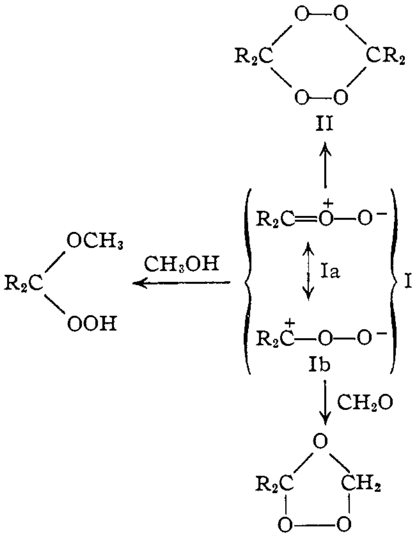
REACTION OF DIPHENYLDIAZOMETHANE WITH OXYGEN. THE CRIEGEE CARBONYL OXIDE

Sir:

Autoxidations invariably lead to products or intermediates in which the two atoms of the oxygen molecule remain bonded to each other. The sequence (1) is thus a reasonable proposal[1] for the photoöxidation of diphenyldiazomethane. Carbonyl oxides such as (I) have been known hitherto only by their participation in the reactions attending ozonization of olefins,[2] where they have been intercepted by aldehydes and by methanol, and isolated in the form of the dimeric ketone peroxides II.[3] It is disturbing that the ketone peroxide II has not previously been isolated as a product of the photoöxidation of a diazo compound, and we

$$Ph_2CN_2 \xrightarrow{h\nu} N_2 + Ph_2C$$
$$Ph_2C + O_2 \longrightarrow Ph_2COO$$
$$Ph_2COO + Ph_2CN_2 \longrightarrow 2Ph_2CO + N_2 \qquad (1)$$



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(1) W. Kirmse, L. Horner and H. Hoffmann, *Ann.*, **614**, 22 (1958).

(2) For summaries of the evidence see R. Criegee, A. Kerckow and H. Zinke, *Chem. Ber.*, **88**, 1878 (1955); R. Criegee, *Record of Chem. Progress*, **18**, 111 (1957).

(3) E. P. Kohler and N. K. Richtmyer, *J. Am. Chem. Soc.*, **52**, 2042 (1930); C. S. Marvel and V. E. Nichols, *ibid.*, **60**, 1455 (1938).