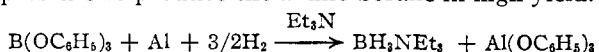


amines^{5,6} or by the high pressure hydrogenolysis of trialkylboranes in the presence of amines.⁷ Both of these routes utilize difficultly obtainable starting materials. This difficulty has discouraged somewhat the study of the chemistry of the amine-boranes.

Recently we reported the direct synthesis of complex aluminum hydrides, *e.g.*, NaAlH₄, 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.

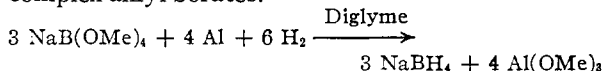


In a typical experiment 30 g. of phenyl borate was dissolved in 100 ml. of triethylamine. To this solution was added 6 g. of activated aluminum powder¹⁰ and 0.25 g. of AlCl₃ catalyst. The mixture then was agitated in contact with 2000 psi of hydrogen for 1 hour at 180°. The by-product aluminum phenoxide 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 ₃ N	1	99
Et ₃ N	1	92
C ₆ H ₅ NMe 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 BBr₃ > BCl₃ > BF₃. 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.



(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).

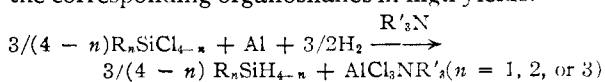
(7) R. Köster, *Angew. Chem.*, **69**, 64 (1957).

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

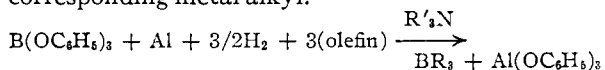
(9) E. C. Ashby, *Chem. and Ind.*, **5**, 208 (1962).

(10) H. E. Redman (to Ethyl Corporation), U. S. Patent 2,895,314, (1959).

The Al-H₂ 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.



Preliminary results also have shown that the Al-H₂ reduction of phenyl borate, silicon tetrachloride, phosphorus trichloride, etc., in the presence of olefins leads to the formation of the corresponding metal alkyl.

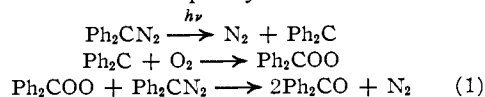


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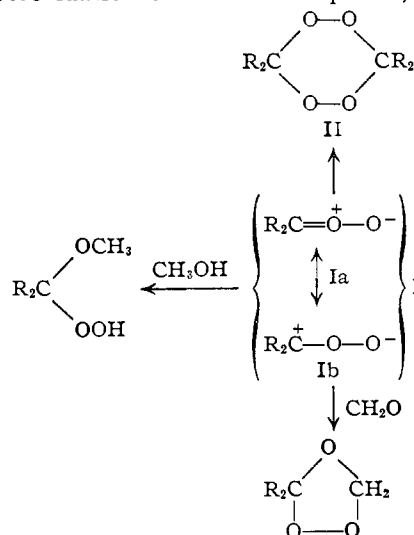
REACTION OF DIPHENYLDIAZOMETHANE WITH OXYGEN. THE CRIEGEE CARBONYL OXIDE

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 proposal¹ for the photooxidation of diphenyldiazomethane. Car-



bonyl 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 photooxidation of a diazo compound, and we

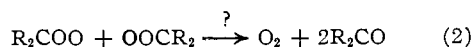


(1) W. Kirmse, L. Horner and H. Hoffmann, *Ann.*, **614**, 22 (1958).

(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).

have considered the possibility that the carbonyl oxide (I) might also disappear by Reaction 2.



If (I) is regarded as having diradical character, 2 appears analogous to the mode of interaction recently established for the cumylperoxy radical.⁴

An experiment with the isotopic oxygen technique has eliminated Reaction 2 as a step of any importance in the photooxidation of diphenyldiazomethane. A solution of 0.1827 g. (0.95 mmole) of diphenyldiazomethane in 8 ml. of chlorobenzene was cooled in Dry Ice, evacuated to about 0.005 mm. for thirty minutes, and sealed into a 50 ml. round bottomed flask with about half an atmosphere of mixed ³²O₂ and ³⁶O₂ with a little argon as an internal standard. The flask carried a side tube permitting the removal of a sample of the final gas. A control tube containing only an identical gas phase was placed beside the reactor, seven inches from a Hanovia 0802N lamp. The reactor was shaken for forty minutes and the solution decolorized. The following table shows the results of mass spectrometric analysis of the gas in the two tubes. The statistical isotopic composition of the

RELATIVE PEAK HEIGHTS IN GAS FROM PHOTOOXIDATION OF DIPHENYLDIAZOMETHANE

	28	32	34	36	40	% ¹⁸ O	% ¹⁶ O ₂	% ¹⁸ O ₂
Control tube	391	5940	50.7	73.0	951	1.57	0.836	1.152
Starting gas	469	8130	34.4	118.8	1329	1.60	.416	1.395
Remaining gas	5200	4300	21.5	63.5	1203	1.60	.491	1.358

oxygen would have been 3.15% ³⁴O₂ and 0.026% ³⁶O₂. The failure to approach this composition shows that little if any of the oxygen went through Reaction 2. There was less isotopic redistribution caused by the photooxidation than by the ultraviolet irradiation in the control tube.

On the other hand, a careful separation of the products from a similar photooxidation of 2.24 g. of diphenyldiazomethane with ordinary oxygen yielded 0.175 g. of an ethanol-insoluble residue melting at 160–170°. Recrystallization from acetone raised the melting point to 213.5–214°. *Anal.* Calcd. for II, C₂₆H₂₀O₄: C, 78.80; H, 5.09. Found: C, 78.66; H, 4.93. The infrared spectrum in a mineral oil mull showed principal peaks at 6.91, 7.81, 8.40, 8.53, 9.81, 9.95, 10.12, 13.26, 13.39, and 14.35 μ, in agreement with spectra kindly furnished to us by Professors R. Criegee² and D. H. Hey.⁵ This solid, having no band at 6 μ in the infrared, was heated fifteen minutes at 210–230° to produce a gas containing 80% oxygen and 10% each of masses 44 and 28, and an oil having an infrared spectrum almost identical with that of benzophenone. The latter was the only other product isolated from the photooxidation but a thermal oxidation at 100° yielded in addition small amounts of tetraphenylethylene and benzophenone azine, m.p. 152–153°, both identified by their infrared spectra. A small amount of the latter was seen to

(4) T. G. Traylor and P. D. Bartlett, *Tetrahedron Letters*, No. 24, 30 (1960).

(5) J. I. G. Cadogan, D. H. Hey and W. A. Sanderson, *J. Chem. Soc.*, 4897 (1960).

be present in the spectrum of the crude peroxide (m.p. 160–170°) from the photooxidation.

The isolation of dimeric benzophenone peroxide provides confirmation of the involvement of benzophenone oxide in the oxidation of diphenyldiazomethane as proposed by Kirmse, Horner and Hoffmann.¹ The ability of diphenylmethylene to react rapidly with oxygen has been viewed⁶ as an evidence of its triplet character. The product of this interaction, however, is not sufficiently like a peroxy radical to react with itself head-to-head with return of oxygen as cumylperoxy radicals do; nor is it a strong donor of a single oxygen atom to such acceptors as cyclohexene or diphenyl sulfide.¹ Its behavior is that of a strongly dipolar molecule with the negative charge always on the outer oxygen atom.

Acknowledgment.—This work was supported by a grant from the National Institutes of Health. Our thanks also are due to Mr. Arthur W. Mosen of the General Atomic Division of General Dynamics Corp., San Diego, California, for the mass spectral data.

(6) R. M. Etter, H. S. Skovronek and P. S. Skell, *J. Am. Chem. Soc.*, 81, 1008 (1959).

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RECEIVED JUNE 29, 1962

THE SYNTHESIS AND DEFLUORINATION OF PERFLUOROAZACYCLOPENTANE (PERFLUOROPYRROLIDINE)

Sir:

During a recent study of the action of elementary fluorine upon tetrafluorosuccinonitrile, a novel cyclization has been shown to take place, leading to the formation of perfluoroazacyclopentane (I). When the dinitrile was fluorinated in a single jet two-stage reactor at the molar reaction ratio (F₂: sample:N₂) of 4.2:1:14 at 145°, I was obtained in approximately 20% yield. After purification by distillation and preparative chromatography, it was a colorless stable liquid, b.p. 19.3 ± 0.1° (extrapolated), mol. wt., 231 ± 4 (calcd. 233), Δ*H*(vap.) 6.50 kcal./mole, and Trouton's constant 22.2 cal./deg. mole. The infrared spectrum exhibited its most intense absorption at 10.26 μ and was similar to that of perfluorocyclopentane.¹ The μ F¹⁹ n.m.r. spectrum showed three peaks at +34.4, +43.9, and +53.8 p.p.m., referred to CF₃COOH, the relative areas of which were in the ratio of 4:1:4. A lower yield of I was obtained by shaking tetrafluorosuccinonitrile with excess silver difluoride at 100°. It is also of interest that the infrared spectrum of I was identical with that of a small sample prepared by Chen² from the fluorination of pyrrole in a packed reactor.

The pyrolytic defluorination of I produced heptafluoro-1-azacyclopent-1-ene (heptafluoro-1-pyrroline) (II) in approximately 50% yield by volume.

(1) D. C. Smith, *et al.*, Naval Research Lab. Report 3567, 129 (1949).

(2) T. C. Chen, *Duke University* (1952), unpublished results.