

TABLE I  
MAJOR X-RAY DIFFRACTION LINES OF  $\text{Me}_2\text{NAl}_2\text{H}_5$   
AND  $\text{Me}_2\text{NAlH}_2$

$\text{Me}_2\text{NAl}_2\text{H}_5$		$\text{Me}_2\text{NAlH}_2$	
d(Å.)	I/I <sub>0</sub>	d(Å.)	I/I <sub>0</sub>
4.47	20	7.31	100
		6.41	5
3.85	100	5.94	5
		5.68	100
3.64	20	5.30	60
		3.75	90
3.30	70	3.64	5
		3.50	5
3.23	70	3.40	20
		3.12	10
2.99	30	3.04	10
		2.79	10
2.91	30	2.57	10
		2.48	10
2.66	20	2.29	10
		2.16	10
2.44	20	2.11	10
		2.05	5
2.32	20	1.94	5
		1.74	5
2.23	20		
2.14	20		

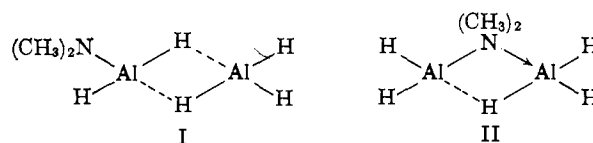
ing at room temperature, indicating that reaction had taken place. Removal of the ether *in vacuo* produced the diethyl ether complex of dimethylaminodialane. *Anal.* Calcd. for  $(\text{CH}_3)_2\text{NAl}_2\text{H}_5 \cdot \text{O}(\text{C}_2\text{H}_5)_2$ : Al, 30.45; active H, 2.84; N, 7.90; H/Al, 2.50. Found: Al, 30.20; active H, 2.70; N, 8.20; H/Al, 2.39. An ebullioscopic molecular weight determination in diethyl ether gave a molecular weight of  $127 \pm 13$  as compared to the calculated value for  $(\text{CH}_3)_2\text{NAl}_2\text{H}_5$  of 103 or a value of 51 calculated for an equimolar mixture of alane and dimethylaminoalane. Attempts to remove the associated ether either at room temperature or at  $66^\circ$  in a vacuum were unsuccessful.

Solvent-free dimethylaminodialane was obtained from a benzene-ether solution containing 20% diethyl ether by volume. Diethyl ether alane was found to form stable solutions in such a mixture for extended periods and the reaction with an equimolar quantity of dimethylaminoalane produced a quantitative yield of the dialane derivative on freeze drying of the solution. The solid was dried *in vacuo* at room temperature for 20 hr. *Anal.* Calcd. for  $(\text{CH}_3)_2\text{NAl}_2\text{H}_5$ : Al, 52.35; active H, 4.89; H/Al, 2.50. Found: Al, 52.88; active H, 5.18; H/Al, 2.62.

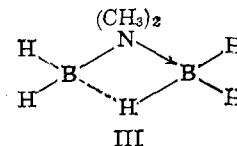
That the product isolated in these reactions is indeed a novel material was shown in several ways. In addition to the failure of diethyl ether alane to precipitate from diethyl ether in the presence of dimethylaminoalane, it was impossible to sublime any dimethylaminoalane from the solid up to  $80^\circ$ , while dimethylaminoalane was sublimed readily from a mixture of the two solids below  $40^\circ$ . The infrared spectrum of the dialane compound shows only one Al-H absorption at  $1725 \text{ cm.}^{-1}$  in THF while a THF solution of dimethylaminoalane absorbs at  $1802 \text{ cm.}^{-1}$ . However, the Al-H absorption of dimethylaminodialane dissolved in benzene appears at  $1802 \text{ cm.}^{-1}$ . Molecular weight determinations in diethyl ether and in benzene showed that dimethylaminodialane was monomeric in both solvents, while dimethylaminoalane is trimeric in

benzene.<sup>6</sup> Finally, the X-ray diffraction pattern of dimethylaminodialane was different from that of dimethylaminoalane (Table I).

Two possible structures can be written for dimethylaminodialane (I and II) depending on whether the nitrogen atom is bridging or not. Both structures show only tetracoordinated aluminum atoms and since the dialane was monomeric in benzene its Al-H absorption in benzene occurred at the frequency characteristic of tetracoordinated aluminum.<sup>5,7</sup> In THF, however,



the Al-H absorption had shifted to the frequency characteristic of pentacoordinated aluminum. Construction of Fisher-Taylor-Hirschfelder models showed that structure I could coordinate with only one THF molecule while II could coordinate with two without steric strain. The Al-H absorption of I, therefore, should split into two bands in THF, one for a tetracoordinated and the other for a pentacoordinated aluminum, while II should show only the pentacoordinated frequency in THF. We favor structure II for dimethylaminodialane since only one Al-H absorption appeared in its infrared spectrum in THF. This structure is also analogous to the structure of dimethylaminodiborane, III.<sup>8</sup>



**Acknowledgment.**—We wish to acknowledge the assistance of Raymond N. Storey in the determination and interpretation of the infrared spectra and the assistance of George Rice in the repetition of one experiment.

(6) J. K. Ruff, *J. Am. Chem. Soc.*, **83**, 2835 (1961).

(7) R. Dautel and W. Zeil, *Z. Elektrochem.*, **64**, 1234 (1960).

(8) H. Hedberg and A. J. Stosick, *J. Am. Chem. Soc.*, **74**, 954 (1952).

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### The Synthesis of the S-Methylthiophenium Ion

Sir:

The sulfur atom of thiophene has an unshared electron pair other than that utilized in the formation of the aromatic sextet, and should therefore be capable of forming S-alkyl derivatives. We report the first synthesis of such a compound. Methylthiophenium hexafluorophosphate (I) was prepared by two procedures. Thiophene was added to a cold suspension of trimethyloxonium fluoroborate<sup>1</sup> in methylene chloride, the mixture was extracted with ice-water, and a saturated solution of sodium hexafluorophosphate was added to the extract to give a white precipitate,

(1) H. Meerwein, G. Hinz, P. Hofmann, E. Kronig, and E. Pfeil, *J. prakt. Chem.*, **147**, 257 (1937).

m.p. 145–163° dec. Alternatively, to a solution of silver perchlorate in thiophene was added methyl iodide, and the reaction mixture was treated as above. *Anal.* Calcd. for  $C_6H_7SPF_6$ : C, 24.7; H, 2.9; S, 13.2;  $PF_6$ , 59.6; mol. wt., 244. Found: C, 24.8, 24.9; H, 2.9, 3.0; S, 14.3, 15.0;  $PF_6$ , 59.3, 59.4; mol. wt. 247. The ultraviolet absorption spectrum showed:  $\lambda_{max}^{H_2O}$  225 (log  $E$  3.49), 269  $m\mu$  (2.75); since hexafluorophosphate anion does not absorb in the 200–400  $m\mu$  region, the spectrum is that of the thiophenium cation. The infrared spectrum included peaks at  $\lambda_{max}^{KBr}$  3.2 (assigned to the onium methyl C–H) and 14.0  $\mu$  (aromatic C–H out-of-plane vibration).<sup>2</sup>

The n.m.r. spectrum ( $DCO_2D$ ) shows a singlet at  $\delta$  3.28<sup>3</sup> which we ascribe to the S–CH<sub>3</sub> hydrogens and a singlet with a slightly broadened base at  $\delta$  7.65 (ring hydrogens) present in the ratio 4:3. A weak band at  $\delta$  3.24 also appears and must be due to the methyl deuterioformate formed by alkylation of the solvent by the thiophenium salt. In repetitive scans of the sample this band showed increasing intensity and the bands at  $\delta$  7.15 and 2.80 decreased (but retained their relative intensities); at the same time, the characteristic multiplet of thiophene centered around  $\delta$  6.9 (barely distinguishable from noise in the first spectrum of the series) became more pronounced.

Hydrogenation of I over palladium yielded a tetrahydro derivative whose infrared spectrum was identical with that of the sulfonium fluorophosphate prepared from thiophane, methyl iodide, and sodium hexafluorophosphate. *Anal.* Calcd. for  $C_6H_{11}SPF_6$ : C, 24.3; H, 4.5. Found: C, 24.1, 23.9; H, 4.5, 4.5.

**Acknowledgment.**—This work was supported in part by an institutional grant to New York University from the American Cancer Society. We wish to thank Mr. John Olsen for technical assistance.

(2) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1958, p. 75.

(3) Since tetramethylsilane reacted with the methylthiophenium ion, chemical shifts were determined with reference to the methyl peak of  $DCO_2CH_3$  and corrected to a TMS internal standard.

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### Selective Reduction of Polyhalogenated Olefins with Sodium Borohydride

Sir:

We wish to report that the reaction of polyhalogenated olefins with sodium borohydride in diglyme at 0° provides a selective reduction of vinylic halogen to yield monohydropolyhalogenated olefins.<sup>1</sup>

In this way 1,2-dichlorohexafluorocyclopentene has been converted in a yield of 88% to 1-hydro-2-chlorohexafluorocyclopentene, b.p. 77.5° (746 mm.),  $n_{20}^{D}$  1.3432, C=C at 1635  $cm^{-1}$ .<sup>3</sup> The proton magnetic

(1) In contrast to the formation of olefins in these reactions, Wartik and Pearson<sup>2</sup> found that the sodium borohydride reduction of vinyl bromide and allyl bromide yielded dialkylboranes.

(2) T. Wartik and R. K. Pearson, *J. Inorg. Nucl. Chem.*, **5**, 250 (1958).

(3) J. A. Sedlak, Ph.D. Thesis, Ohio State University, 1960, reports b.p. 75.2–76.9°, C=C 1637  $cm^{-1}$ .

resonance spectrum<sup>4</sup> exhibited a complex multiplet at  $\tau$  3.50 in agreement with the structure containing a vinylic proton. In a similar manner, 1,2-dichlorotetrafluorocyclobutene was converted in 83% yield to 1-hydro-2-chlorotetrafluorocyclobutene, b.p. 59.5° (744 mm.),  $n_{20}^{D}$  1.3463, C=C 1596  $cm^{-1}$ , vinyl proton multiplet at  $\tau$  3.33,<sup>5</sup> and octafluorocyclopentene was converted in 73% yield to 1-hydroheptafluorocyclopentene, b.p. 45.5° (748 mm.),  $n_{20}^{D}$  1.297, C=C 1695  $cm^{-1}$ , vinyl proton multiplet at  $\tau$  4.07.<sup>6</sup> When 1-chloroheptafluorocyclopentene was subjected to the reduction reaction, 1-hydro-2-chlorohexafluorocyclopentene was obtained in 88% yield by the preferential reduction of vinylic fluorine.

The smooth reduction of these olefins by borohydride contrasts with similar reported reductions with lithium aluminum hydride. Tatlow and co-workers<sup>7</sup> have reported that the reduction of decafluorocyclohexene with lithium aluminum hydride yielded a mixture of eight reduction products formed by vinylic reduction and subsequent rearrangements of the starting olefin and the reduced olefins. Similarly, Sedlak<sup>3</sup> has reported that reduction of 1,2-dichlorohexafluorocyclopentene with lithium aluminum hydride yielded only uncharacterized high boiling material and no simple reduction products. In comparison, the mild reduction observed with sodium borohydride provides a convenient route to polyfluorinated olefins containing vinylic hydrogen. Examination of the scope of this reaction is continuing.

The number of hydrides of the borohydride ion active in the reduction reaction has been found in these examples to be dependent upon the substituents on the olefinic bond. The mole ratio of borohydride to olefin required to effect optimum conversion of the olefin to the monoreduction product was found to be 1:1 for the olefins containing the  $-CCl=CCl-$  grouping, 1:2 for the  $-CF=CF-$  grouping, and 1:3 for the  $-CF=CCl-$  grouping. When the mole ratio of borohydride to olefin exceeded these ratios, the yield of the monoreduction product decreased.

The following procedure is typical. In a four-necked flask was placed 25 ml. of dry diglyme (distilled from  $LiAlH_4$ ) and 22.8 g. (100 mmoles) of 1-chloroheptafluorocyclopentene. This mixture was cooled to 0° and 34.3 ml. of 0.97  $M$  sodium borohydride (33.3 mmoles) in diglyme was added dropwise<sup>8</sup> keeping the temperature below 5°. After the addition of the borohydride was completed, the reaction mixture was stirred at 0° for an additional 0.5 hr. and then cautiously

(4) The proton magnetic resonance spectra were obtained with a Varian A60 spectrometer. The spectra were run on the pure liquids containing tetramethylsilane as an internal standard. In all cases, the proton resonance was observed as a complex multiplet due to coupling with the fluorines. The reported values are the center position of these multiplets.

(5) J. D. Park, L. H. Wilson, and J. R. Lacher, *J. Org. Chem.*, **28**, 1008 (1963), reported b.p. 53.8–54° (625 mm.),  $n_{20}^{D}$  1.3452, C=C 1587  $cm^{-1}$ .

(6) R. J. Heitzman, C. R. Patrick, R. Stephens, and J. C. Tatlow, *J. Chem. Soc.*, 281 (1963), report b.p. 46°, C=C 1696  $cm^{-1}$ .

(7) D. E. M. Evans, W. J. Feast, R. Stephens, and J. C. Tatlow, *ibid.*, 4828 (1963).

(8) During the addition of the borohydride solution 12 mmoles (corrected to S.T.P.) of hydrogen was evolved. The source of this hydrogen is not readily apparent but was observed in all these reactions and was most pronounced in the reaction of the olefins containing the  $-CCl=CCl-$  grouping (33 mmoles of  $H_2$  was evolved when 100 mmoles of 1,2-dichlorohexafluorocyclopentene was treated with 100 mmoles of  $NaBH_4$  solution). The large amounts of hydrogen evolved cannot be due to the scavenging of water by active hydride in the reaction mixture since, in several different reactions, the amount of hydrogen evolved increased in a progressive manner as the reaction was scaled up in size.