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### GRIGNARD SYNTHESIS OF ALKYL DECABORANES Sir:

Inorganic Grignard reagents derived from decaborane, and the condensation reaction to prepare benzyldecaborane recently have been reported.<sup>1</sup> We subsequently found that these reagents could not be used readily to prepare a series of alkyl decaboranes by the normal Grignard condensation reaction, using *n*-alkyl chlorides, bromides and iodides. Seeking a general method for preparing alkyl decaboranes, other types of condensing agents were tried with  $B_{10}H_{12}MgX$ . Success with a tri-alkyl oxonium salt,  $R_3OBF_4$ ,<sup>2</sup> led us to believe that alkyl fluorides might be used as condensing agents. Although alkyl fluorides have not been used in Grignard condensation reactions<sup>3</sup> (presumably because of the strong carbon-fluorine bond in *n*-alkyl fluorides), we found that  $B_{10}H_{12}MgX$  could be condensed successfully with a series of *n*-alkyl fluorides, and an alicyclic fluoride. The substituted decaboranes prepared by this principle are shown in Table I.

TABLE I

Substituted decaborane	Yield, %	Elemental analyses, %					
		Theoretical			Found		
		C	H	B	C	H	B
Butyl <sup>a</sup>	25	26.9	12.4	60.1	25.6	12.5	59.7
Amyl <sup>a</sup>	40	31.3	12.5	56.3	31.2	12.7	58.1
Hexyl <sup>a</sup>	24	35.0	12.6	52.4	35.1	12.8	53.2
Cyclohexyl <sup>b</sup>	6	35.3	11.8	52.9	33.8	11.8	51.9
Heptyl <sup>a</sup>	23	38.2	12.7	49.0	37.5	12.7	51.1
Octyl <sup>a</sup>	16	41.0	12.8	46.1	40.9	12.6	44.9

<sup>a</sup> Colorless liquid. <sup>b</sup> White solid, m.p. 90–91°.

Since this reaction appeared to be of general interest to organic chemistry, we tested it with a simple organic Grignard reagent that could not be alkylated with the usual *n*-alkyl halides. Accordingly, after ethylmagnesium bromide failed to react with *n*-butyl bromide, the former was treated with *n*-butyl fluoride. This resulted in a substantial yield of *n*-hexane (11%) and 3-methylpentane (7%); the latter were identified by their mass spectra.

**Experimental.**— $B_{10}H_{12}MgBr$  was prepared by the reaction of equivalent quantities of decaborane and  $CH_3MgBr$ , using 5 to 6 g. of decaborane. The ether solvent was then distilled and a two-fold excess of alkyl fluoride was added. The resulting solution was stirred for 48–64 hours under nitrogen, at ambient temperature; in some cases an ice-bath was necessary initially. After the prolonged standing the highly volatile components were distilled and the residues were extracted with dried

(1) B. Siegel, J. Mack, J. Lowe and J. Gallagher, *THIS JOURNAL*, **80**, 4523 (1958).

(2) H. Meerwein, *et al.*, *J. prakt. Chem.*, **154**, 83 (1939).

(3) The only report on this subject was a recent Russian article in which, in the specialized instance of several tertiary fluorides, greater yields of condensation were obtained than was the case with tertiary chlorides: A. D. Petrov, *et al.*, *Chem. Abstracts*, **50**, 16657 (1956).

petroleum ether. These extracts were fractionally vacuum distilled. The substituted decaboranes were characterized by elemental composition and cryoscopic molecular weight.

The *n*-alkyl fluorides were prepared by<sup>4</sup> adding mercuric fluoride slowly to an alkyl bromide or iodide, at 40–50°. The product was then vacuum distilled and redistilled at atmospheric pressure.

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(4) A. L. Henne and T. Midgley, *THIS JOURNAL*, **56**, 884 (1936).

U. S. NAVAL PROPELLANT PLANT  
INDIAN HEAD, MD.

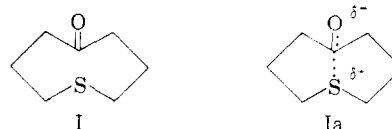
JOHN GALLAGHAN  
BERNARD SIEGEL

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### TRANSANNULAR SULFUR-CARBONYL INTERACTION

Sir:

We have now obtained evidence of transannular sulfur-carbonyl interaction across an eight-membered ring in the model compound 1-thiacyclooctan-5-one (I). Prediction of the occurrence of



such interaction was made earlier,<sup>1</sup> as methods were being developed for the detection of nitrogen-carbonyl interaction in cyclic aminoketones and aminoacyloins of medium ring size.<sup>2</sup>

Compound I was obtained (45% crude yield) by the Dieckmann cyclization of diethyl  $\gamma,\gamma'$ -thiabis-butyrates<sup>3</sup> using potassium *t*-butoxide in xylene under high dilution conditions, with high speed stirring under nitrogen,<sup>4</sup> then hydrolysis and decarboxylation, and was purified by recrystallization from ether-pentane and sublimation, colorless needles, m.p. 53.2–54.2° (*Anal.* Calcd. for  $C_7H_{12}OS$ : C, 58.29; H, 8.39. Found: C, 58.21; H, 8.36).<sup>5</sup> A by-product, when the addition rate of the sulfide diester was relatively rapid (25 hours),<sup>6</sup> was the sixteen-membered ring compound, 1,9-dithiacyclohexadecane-5,13-dione, colorless needles, m.p. 65–66°,  $\nu_{max}^{CO}$  1715  $cm^{-1}$  (*Anal.* Found: C, 58.64; H, 8.25; mol. wt., 252 (calcd. 288)).

Indication of the contribution of S-C=O "interacted" forms (Ia) of 1-thiacyclooctan-5-one was found in the infrared carbonyl maximum (shoulder) at 1684

(1) N. J. Leonard, R. C. Fox and M. Ōki, *THIS JOURNAL*, **76**, 5708 (1954).

(2) For the most recent articles in the series on transannular nitrogen-carbonyl interaction, see: (a) N. J. Leonard, J. A. Adamcik, C. Djerassi and O. Halpern, *ibid.*, **80**, 4858 (1958); (b) N. J. Leonard, D. F. Morrow and M. T. Rogers, *ibid.*, **79**, 5476 (1957).

(3) Made in this laboratory in 1954 by T. Hashizume, private communication.

(4) N. J. Leonard and R. C. Sentz, *ibid.*, **74**, 1704 (1952).

(5) This product was identical with a sample of the same material kindly forwarded to us by Dr. Charles G. Overberger of the Polytechnic Institute of Brooklyn and described in the accompanying Communication by C. G. Overberger and A. Lusi; see also: A. Lusi, Master's Thesis, Polytechnic Institute of Brooklyn, 1959.

(6) N. J. Leonard, M. Ōki and S. Chiavarelli, *ibid.*, **77**, 6234 (1955).