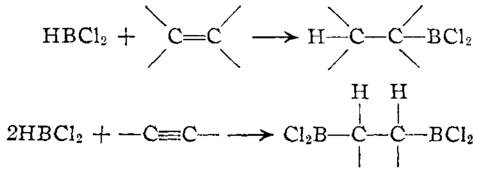
NEW SYNTHESIS OF ALKYLDICHLOROBORANES

Sir:

In view of recent reports[1] pertaining to dichloroborane, $HBCl_2$, we wish to record work done in our laboratory on the preparation and some reactions of this compound.

Dichloroborane was prepared by passing a mixture of hydrogen and boron trichloride over granular magnesium maintained at 400–450°.[1a] The spontaneously flammable product was isolated in 50 to 80% yield (based on BCl_3 which was removed at −125°) by condensation at −135°. A sample placed in an infrared cell was observed spectroscopically to disproportionate at 25°, yielding diborane and boron trichloride.[1b] The spectrum (2–15 μ) of the pure material showed strong singlet B–H absorption at 2620 cm.$^{-1}$ [1e] and two strong doublets at 1098, 1084 cm.$^{-1}$ and 898, 885 cm.$^{-1}$ attributable to B–Cl stretching. The molecular weight (calcd. 82.7; found 81.2) was determined from partial pressures and gas density of a relatively stable equimolar mixture of boron trichloride and dichloroborane. Dichloroborane reacted readily and energetically with olefinic and acetylenic hydrocarbons at 10–30°, the fragments, H and BCl_2, adding to the unsaturated carbon atoms:



$$\mathrm{HBCl_2} + \mathrm{>C{=}C<} \longrightarrow \mathrm{H{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}{-}BCl_2}$$

$$2\mathrm{HBCl_2} + {-}\mathrm{C{\equiv}C}{-} \longrightarrow \mathrm{Cl_2B{-}\overset{H}{\overset{|}{\underset{|}{C}}}{-}\overset{H}{\overset{|}{\underset{|}{C}}}{-}BCl_2}$$

The reaction appears general and occurs in good yield in either gas or liquid phase. This reaction constitutes a new manifestation of the addition of B-H bonds to unsaturated systems, but is apparently more facile than that with diborane[2] in that neither elevated temperatures nor the presence of ethers is required to promote the reaction. In further contrast with the products from diborane, the present reaction apparently leads to Markovnikov addition. No dialkylchloroboranes or trialkylboranes were observed although it has been implied that a similar reaction in the presence of ether leads to the formation of trialkylborane.[1d]

Some reactions of dichloroborane are summarized in the table.

TABLE I

REACTIONS OF DICHLOROBORANE

			Boron analyses (wt. %)		Boiling point Found		Boiling point Lit.[3]	
Olefins	Product	Formula	Theo.	Found	(°C.)	(Mm. Hg)	(°C.)	(Mm. Hg)
Ethylene	Ethyldichloroborane	$C_2H_5BCl_2$	9.8	9.4	50.0	745	50.8	745
Propylene	*i*-Propyldichloroborane	$C_3H_7BCl_2$	8.7	6.9	71.0	750	72.0	749
Isobutylene	*t*-Butyldichloroborane	$C_4H_9BCl_2$	7.8	8.0	92.5	760	88.0	744
Cyclohexene	Cyclohexyldichloroborane	$C_6H_{11}BCl_2$	6.6	6.4	165.0	765	167	748

The alkyldichloroboranes exhibited two characteristic B–Cl stretching bands similar in frequency to those of dichloroborane (870–920 cm.$^{-1}$, 1050–1110 cm.$^{-1}$) and a C-B absorption at 1310 cm.$^{-1}$.[4] Reaction with 1,3-butadiene was extremely exothermic, yielding a liquid, b.p. 127–130° (110 mm.), whose analysis corresponds to a di-addition product, bis-(dichloroborano)-butane, the structure of which has not yet been determined. *Anal.* Calcd. for $C_4H_6B_2Cl_4$: B, 9.96. Found: B, 9.76.

Reaction with acetylene formed a bis-(dichloroborano)-ethane, b.p. 38.5–39.5° (35 mm.), the structure of which has not been determined. *Anal.* Calcd. for $C_2H_4B_2Cl_4$: B, 11.3. Found: B, 11.0.

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(1) (a) D. T. Hurd, THIS JOURNAL, **71**, 20 (1949); (b) T. Wartik, 133rd National Meeting, American Chemical Society, San Francisco, 1958, Abstracts p. 23-L; (c) H. C. Brown and P. A. Tierney, THIS JOURNAL, **80**, 1552 (1958); (d) *J. Inorg. Nucl. Chem.*, **9**, 51 (1959); (e) T. Onak, H. L. Landesman and I. Shapiro, *J. Phys. Chem.*, **62**, 1605 (1958).

(2) H. C. Brown and Subba Rao, *J. Org. Chem.*, **22**, 1136 (1957); H. C. Brown and G. Zweifel, THIS JOURNAL, **81**, 1512 (1959).

(3) P. A. McCusker, E. C. Ashby and H. S. Makowski, *ibid.*, **79**, 5182 (1957).

(4) J. L. Bellamy, W. Gerrard, M. F. Lappert and R. L. Williams, *J. Chem. Soc.*, 2412 (1958).

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THE ELECTRON SPIN RESONANCE OF THE THERMOCHROMIC FORM OF BIANTHRONE

Sir:

Nilsen and Fraenkel[1] observed an electron spin resonance (e.s.r.) absorption with heated $\Delta^{10,10'}$-bianthrone (I).[2] With some derivatives of I hyperfine structure could be resolved, but the complexity of the molecules studied prohibited assignment of the lines.[3] Hirshberg and Weissman did not find e.s.r. with the colored solutions obtained by the low temperature irradiation of substituted I,[4] although the paramagnetism of these samples was established by Kortüm, Littman and Theilacker by bulk susceptibility measurements.[5]

Pyridine solutions of I at 25° displayed a resonance which increased with temperature. The five main components (splitting 3.0 gauss) possessed relative intensities of 1:4:6:4:1 corresponding to the interaction of an unpaired electron with four equivalent protons. Each of the lines exhibited a multiplet structure of three and possibly five lines (splitting 1.0 gauss). A possible assignment is that

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(1) W. G. Nilsen and G. K. Fraenkel, *J. Chem. Phys.*, **21**, 1619 (1953).

(2) Formulas and an introduction are given in the previous communication: R. B. Woodward and E. Wasserman, THIS JOURNAL, **81**, 5007 (1959).

(3) W. G. Nilsen, Ph.D. Dissertation, Columbia University, 1956. This information was kindly made available by Professor Fraenkel prior to publication.

(4) Y. Hirshberg and S. I. Weissman, *J. Chem. Phys.*, **28**, 739 (1958).

(5) G. Kortüm, G. Littman and W. Theilacker, *Z. Naturforsch.*, **12a**, 401 (1957). The apparent diamagnetism of the thermochromic species cited by G. Kortüm, *Angew. Chem.*, **70**, 14 (1958) is possibly due to an uncertainty in the determination of its concentration.