

NEW SYNTHESIS OF ALKYLDICHLOROBORANES

Sir:

In view of recent reports¹ pertaining to dichloroborane, HBCl_2 , we wish to record work done in our laboratory on the preparation and some reactions of this compound.

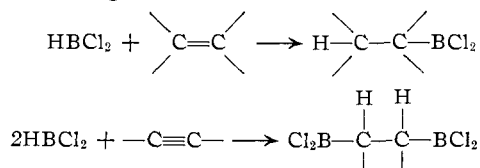
Dichloroborane was prepared by passing a mixture of hydrogen and boron trichloride over granular magnesium maintained at $400\text{--}450^\circ$.^{1a} The spontaneously flammable product was isolated in

The alkyldichloroboranes exhibited two characteristic B-Cl stretching bands similar in frequency to those of dichloroborane ($870\text{--}920\text{ cm.}^{-1}$, $1050\text{--}1110\text{ cm.}^{-1}$) and a C-B absorption at 1310 cm.^{-1} .⁴ Reaction with 1,3-butadiene was extremely exothermic, yielding a liquid, b.p. $127\text{--}130^\circ$ (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 $\text{C}_4\text{H}_8\text{B}_2\text{Cl}_4$: B, 9.96. Found: B, 9.76.

TABLE I
REACTIONS OF DICHLOROBORANE

Olefins	Product	Formula	Boron analyses		Boiling point			
			Theo. (wt. %)	Found	Found		Lit. ³	
					(°C.)	(Mm. Hg)	(°C.)	(Mm. Hg)
Ethylene	Ethyldichloroborane	$\text{C}_2\text{H}_5\text{BCl}_2$	9.8	9.4	50.0	745	50.8	745
Propylene	<i>i</i> -Propyldichloroborane	$\text{C}_3\text{H}_7\text{BCl}_2$	8.7	6.9	71.0	750	72.0	749
Isobutylene	<i>t</i> -Butyldichloroborane	$\text{C}_4\text{H}_9\text{BCl}_2$	7.8	8.0	92.5	760	88.0	744
Cyclohexene	Cyclohexyldichloroborane	$\text{C}_6\text{H}_{11}\text{BCl}_2$	6.6	6.4	165.0	765	167	748

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 ($2\text{--}15\ \mu$) of the pure material showed strong singlet B-H absorption at 2620 cm.^{-1} ^{1c} 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 $10\text{--}30^\circ$, the fragments, H and BCl_2 , adding to the unsaturated carbon atoms:



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 diborane² 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.

(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).

Reaction with acetylene formed a bis-(dichloroborano)-ethane, b.p. $38.5\text{--}39.5^\circ$ (35 mm.), the structure of which has not been determined. *Anal.* Calcd. for $\text{C}_2\text{H}_4\text{B}_2\text{Cl}_4$: B, 11.3. Found: B, 11.0.

(4) J. L. Bellamy, W. Gertard, 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 Fraenkel¹ 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

(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 thermochemical species cited by G. Kortüm, *Angew. Chem.*, **70**, 14 (1958) is possibly due to an uncertainty in the determination of its concentration.

the main features of the spectrum are due to hyperfine interaction with protons on carbon atoms 1, 3, 6, 8 of II (each unpaired electron in II being effectively restricted to one-half of the molecule) while the additional splittings arise from the protons on 2, 4, 5, 7.

Ether solutions of the green form did not reveal any absorption at -77° . However, on warming to -46° a resonance was observed which disappeared as the color disappeared. Possibly some complexing occurs at the lower temperature leading to broadened lines which could not be detected.

A dark green solid may be obtained from I by sublimation onto a glass surface cooled by liquid nitrogen. At -197° this material exhibited a resonance (line width 14 gauss). After one hour at room temperature the material reverted to the yellow species which did not show e.s.r.⁶

The author is deeply grateful to Professors S. I. Weissman and J. Townsend for the availability of their e.s.r. apparatus.

(6) This e.s.r. examination was kindly performed by Dr. J. P. Gordon.

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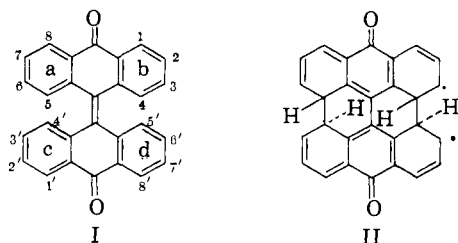
EDEL WASSERMAN

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THE STRUCTURE OF THE THERMOCHROMIC FORM OF BIANTHRONE

Sir:

In solution, yellow $\Delta^{10,10'}$ -bianthrone (I) exhibits a reversible thermochromism involving equilibration with a green form whose concentration increases with temperature.¹ The same green species is obtained by irradiation of the solution at -77° and by the application of pressure to the solid.^{1,2} We propose that the green form is a diradical of which II is one of the resonance structures



In support of II we note that the green form is magnetic.³

We may exclude the possibility that the magnetic species is a diradical in which two planar "anthrone halves" are twisted about a single bond. Harnik and Schmidt's X-ray analysis of I demonstrates that rings a and b are above the plane of the paper, and rings c and d below.⁴ Consequently, a twisted diradical would be stabilized by substituents in the 4 and 4' positions. However, Hirshberg and Fischer's data indicate that the introduction of such

(1) G. Kortüm, *Angew. Chem.*, **70**, 14 (1958), and references cited therein.

(2) E. Wasserman and R. E. Davis, *J. Chem. Phys.*, **30**, 1367 (1959).

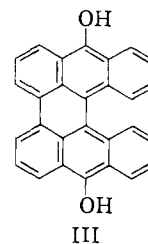
(3) E. Wasserman, *THIS JOURNAL*, **81**, 5006 (1959).

(4) E. Harnik and G. M. J. Schmidt, *J. Chem. Soc.*, 3295 (1954).

groups renders the green form less stable.⁵ The increased lability of II is attributable to steric interactions between the substituents and the d and a rings.

The absence of a betaine structure is demonstrated by the kinetics of the disappearance of the green form at -50° . The rate in ethanol is greater than that in isoöctane by a factor of two.

In neutral solvents, I yields the green form (absorption maximum 6800 Å.) under ultraviolet irradiation at low temperatures. However, pyridine solutions produce a green color with an absorption maximum at 6270 Å. and a shoulder at 5750 Å. which are sensitive to both oxygen and excess I. This is the same band that Brockmann and co-workers have assigned to III, an isomer of II.⁶



Solutions of I react with sodium *t*-butoxide in the absence of light, to yield a red anion. Upon acidification (even methanol is a suitable acid) at -77° , the green form is produced. The formation of the thermodynamically less stable isomer finds precedence in the neutralization of other mesomeric anions.⁷

The piezochromism implies that the green species has a smaller volume than I.

The above data appear to be most compatible with structure II for the green form.

(5) Y. Hirshberg and E. Fischer, *ibid.*, 629 (1953). Data given in Figure 4. The authors do not comment on this effect of substituents.

(6) H. Brockmann, F. Pohl, K. Maier and M. N. Haschad, *Ann.*, **553**, 1 (1942); H. Brockmann and R. Mühlmann, *Chem. Ber.*, **82**, 348 (1949).

(7) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 565.

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RECEIVED JULY 30, 1959

STRUCTURE OF STERCULIC ACID POLYMER. A CYCLOPROPENE REARRANGEMENT

Sir:

Sterculic acid (I)¹ is unstable at room temperature²⁻⁴ and polymerizes with apparent destruction of the cyclopropene group.^{3,4a} We now have established that this polymerization proceeds with ring opening to give the polymeric mixture of compounds IIa-d (where R' and R'' are sterculic acid residues).

(1) For leading references, cf. K. L. Rinehart, Jr., W. A. Nilsson and H. A. Whaley, *THIS JOURNAL*, **80**, 503 (1958).

(2) J. R. Nunn, *J. Chem. Soc.*, 313 (1952).

(3) P. K. Faure and J. C. Smith, *ibid.*, 1818 (1956).

(4) (a) W. A. Nilsson, B.S. Thesis, University of Illinois, 1957; (b) H. A. Whaley, B.S. Thesis, University of Illinois, 1956.