carboxyl group is 3.8 A away. The exterior is almost completely hydrocarbon-like, which could account for the low solubility of monensic acid salts in water.

A. Agtarap, J. W. Chamberlin
The Lilly Research Laboratories
Eli Lilly and Company, Indianapolis, Indiana 46206

M. Pinkerton, L. Steinrauf
Department of Biochemistry
Indiana University School of Medicine
Indianapolis, Indiana 46207

Received July 31, 1967

Structure, Isomerization, and Cleavage of 1,2-Bis(dichloroboryl)ethylene

Sir:

Recent interest[1-3] in the stereochemistry of the addition of tetrachlorodiborane(4) to unsaturated organic compounds prompts us to report results obtained in this laboratory on the structure, isomerization, and cleavage reactions of the 1:1 addition product of B_2Cl_4 with acetylene. This compound was of interest in connection with a study[4] of the relative reactivities of a series of unsaturated organometallic derivatives with B_2Cl_4, for which materials of known stereochemistry were required.

The previously known[5] 1:1 addition product (I) was obtained in 88% yield from the reaction of B_2Cl_4 with excess C_2H_2 at room temperature and an initial pressure of about 2 atm. The proton magnetic resonance spectrum of the pure liquid at 60 MHz consisted of a broad single line at -6.57 ppm (external tetramethylsilane reference) which narrowed significantly when the sample was simultaneously irradiated at 19.25 MHz to decouple the ^{11}B nuclei. In addition, when the spectrum was sharpened by $^1H-\{^{11}B\}$ double resonance, two satellite doublets ($J = 17.5$ Hz), centered at 73.5 Hz on either side of the principal peak, could be observed.

The presence of a single line in the principal spectrum and the simplicity of the satellite spectrum suggested strongly that the addition product I is a single isomer. The doublet structure of the satellites is attributable to H–H coupling, observable in the spectrum of a 1,2-disubstituted ethylene containing one ^{13}C atom because of the magnetic nonequivalence of the protons.[6] Thus, the possibility that I is the asymmetric isomer, 1,1-bis(dichloroboryl)ethylene, must be eliminated, since the satellite lines in the spectrum of that compound would be singlets.

Irradiation of I for 17 hr at room temperature with a medium-pressure mercury lamp (85%, 2537 A) gave, in addition to other products, a 50% yield of a new compound, II. Examination of the proton magnetic resonance spectrum of II indicated that the photochemically produced product contained less than 5% of unconverted I. Analysis for chloride liberated on hydrolysis with water (72.1% found; 75.2% calcd)[7] and molecular weight (vapor density: 180 found; 188 calcd) were consistent with the formulation of II as an isomer of I. The $^1H-\{^{11}B\}$ spectrum of II was similar to that of I, with a strong singlet in the olefinic proton region at -7.07 ppm. Satellite doublets ($J = 19.6$ Hz) at 76.0 Hz above and below the principal peak confirmed that this compound is also a 1,2-disubstituted olefin.

The infrared spectrum of I is essentially identical with that reported by Rudolph[2] and assigned by him to *cis*-1,2-bis(dichloroboryl)ethylene on the basis of coincidences between the infrared and Raman spectra. The infrared spectrum of II is considerably simpler than that of I. Frequencies (cm^{-1}) and relative intensities of principal bands in the gas-phase spectrum are as follows: 3010 w, 1580 w, 1275 s, 1135 s, 1092 vs, 1015 m, 985 s, 835 vw, 810 vw, 560 m. The weak band at 1580 cm^{-1} is believed to be due to the presence of the small amount of I mentioned above. We have assigned *cis* and *trans* structures to I and II, respectively, on the basis of the considerably simpler spectrum of the latter and the presence of a band of medium intensity in the C=C stretching region in the spectrum of I.

Cleavage of the deuterated analog of I (obtained by the reaction of B_2Cl_4 with C_2D_2) with silver oxide in ammonium hydroxide gave exclusively *cis*-C_2H_2D, identified from the infrared spectrum.[8] The infrared spectrum of the irradiation product of the deuterated compound showed that isomerization of *cis*-$Cl_2BCD{=}CDBCl_2$ (under the conditions used for the undeuterated material) was incomplete, and the resulting *trans* compound was not separable from the *cis* isomer by vacuum-line fractionation. Silver cleavage of the impure product consequently gave both *cis*- and *trans*-$C_2D_2H_2$. Treatment of I with glacial CH_3COOD at 80° for 24 hr gave a mixture of *cis*- and *trans*-$C_2H_2D_2$. The total amount of ethylene recovered was approximately 50% of that expected for complete cleavage. At lower temperatures, smaller amounts of ethylene, containing both isomers, were obtained.

The results obtained in this work are in accord with the recent findings of Rudolph[2] and of Wartik and his co-workers[3] which indicate that the reaction of B_2Cl_4 with acetylenic compounds is predominantly a *cis* addition. A sample of I isolated from a reaction of B_2Cl_4 with C_2H_2 in 2:1 molar ratio (which gave principally the 2:1 addition product) contained a small amount of material with a proton chemical shift identical with that of the *trans* isomer, II. This may indicate that the reaction is not completely stereospecific or that isomerization of the product may occur under the conditions of our experiments.

Protonolysis of alkenylboranes derived from the hydroboration of internal acetylenes has been shown to yield *cis*-olefins,[9] and the acetic acid cleavage reaction has been used to infer the stereochemistry of unsaturated organoboron compounds from that of the resulting

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[1] H. K. Saha, L. J. Glicenstein, and G. Urry, *J. Organometal. Chem.* (Amsterdam), **8**, 37 (1967).

[2] R. W. Rudolph, *J. Am. Chem. Soc.*, **89**, 4216 (1967).

[3] M. Zeldin, A. R. Gatti, and T. Wartik, *ibid.*, **89**, 4217 (1967).

[4] T. D. Coyle and J. J. Ritter, to be published.

[5] C. Chambers and A. K. Holliday, *J. Chem. Soc.*, 3459 (1965).

[6] The complete satellite spectrum of a 1,2-disubstituted ethylene consists of *four* pairs of doublets. In the compounds studied here, the two inner pairs, being obscured by the strong line from the $^{12}C_2$ species, were not observed. The intensity of each line in the satellite spectrum is approximately 0.28% of that of the principal line.

[7] Analyses were performed by Mr. Rolf Paulson of the Microchemical Analysis Section of the National Bureau of Standards.

[8] B. L. Crawford, J. E. Lancaster, and R. G. Inskeep, *J. Chem. Phys.*, 21, 678 (1953).

[9] H. C. Brown and G. Zweifel, *J. Am. Chem. Soc.*, **81**, 1512 (1959).

olefins.[10] The production of both *cis*- and *trans*-$C_2H_2D_2$ in our experiments indicates that isomerically pure olefins are not obtained with the isomerically pure vicinal diboron compound. The reductive cleavage, or alkaline hydrolysis,[3] thus appears to be better suited to elucidation of stereochemistry in this type of organoboron derivative.

It is of interest to note the rather surprising similarity in the proton–proton spin-coupling constants for the *cis* and *trans* isomers of 1,2-bis(dichloroboryl)ethylene (17.5 and 19.6 Hz, respectively). The magnitudes of vicinal H-H couplings have been widely used to assess the stereochemistry of olefinic derivatives, on the premise that *cis* and *trans* proton–proton couplings have distinct and characteristic values (6 to 14 Hz and 11 to 18 Hz, respectively).[11] Exceptions to this generalization are known, particularly in vinyl derivatives of relatively electropositive elements.[12] The present results emphasize the need for caution in basing structural assignments on this criterion.

Acknowledgments. We thank Dr. R. B. Johannesen for obtaining the double resonance spectra and Dr. F. E. Brinckman for helpful discussions during the course of this work.

[10] M. F. Lappert and B. Prokai, *J. Organometal. Chem.* (Amsterdam), 1, 384 (1964)

[11] L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," International Series of Monographs on Organic Chemistry, Vol. 5, Pergamon Press, New York, N. Y., 1959, p 85.

[12] T. Schaefer, *Can. J. Chem.*, 40, 1 (1962).

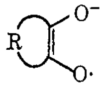
T. D. Coyle, J. J. Ritter
Inorganic Chemistry Section, National Bureau of Standards
Washington, D. C. 20234

Received August 18, 1967

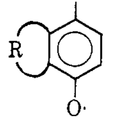
The Maleic Anhydride Radical Anion Grouping. A Useful Spin Label

Sir:

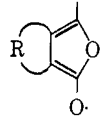
Studies of the effect of stereochemistry upon long-range splittings in esr spectra have been carried out using the semidione[1] (A) and semiquinone[2] (B) groups to introduce spin to the hydrocarbon group.[3] We wish to report studies using a third spin label group, maleic anhydride anion (C, which we shall call the "semifuraquinone" group). This group is particularly convenient to introduce into the rigid bicyclic systems which yield the most information. Reduction of vicintual dihalogenated compounds is well known to lead to elimination to form olefins. We have used this fact to generate semifuraquinones for esr studies[4] by *intra muros* reduction of Diels–Alder adducts of dichloromaleic anhydride[5] (eq 1). An alternate path is to carry out a one-electron reduction of the substituted maleic anhydride, prepared by using dimethyl acetyldicarboxylate as the dienophile, hydrolyzing the ester groups, and dehydrating with acetic anhydride.[6] The nonconjugated double bond of either adduct is catalytically reduced without dehalogenating or saturating the conjugated double bond.[7]



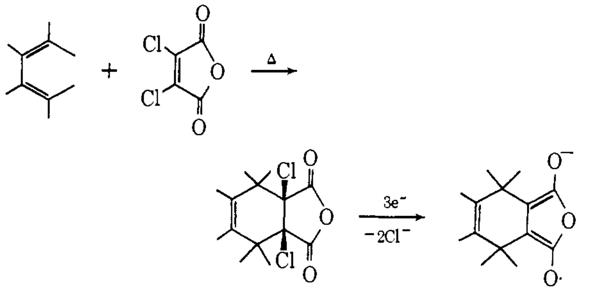
A



B



C



(1)

Splittings for semifuraquinones from adducts of butadiene[8] (**1C**), cyclohexadiene[9] (**2C**), the saturated cyclohexadiene adduct[10] (**3C**), cyclopentadiene[11] (**4C**), and the saturated cyclopentadiene adduct[12] (**5C**) are compared with values for the other spin labels in Table I. From the 7.0-gauss methyl splitting of *cis*-dimethylsemidione,[13] ρ_α (the π spin density at the carbons to which the alkyl groups are attached) is about 0.30 (using a reasonable $|Q_{CH_3}{}^H|$ of 23 gauss). For 2,3-dimethylbenzosemiquinone, the methyl splitting of 1.714 gauss[14] yields a ρ_α of 0.075. The β splittings of **1C** give ρ_α of about 0.19 (taking the average dihedral angle as 30°, then $|Q_\beta{}^H| \approx 1.5|Q_{CH_3}{}^H|$[15]). Assuming the H_a splitting in **2** and **3** to be directly proportional to ρ_α, and using the ρ_α values derived above for the semidiones and semiquinones, ρ_α values for **2C** and **3C** are interpolated to be 0.187 and 0.203 from the H_a splittings. This shows that the H_a splittings in **2** and **3** are essentially proportional to ρ_α.

The 0.2-gauss H_v splitting of **1C** shows that detectable spin density reaches a γ-vinyl group even without β

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[1] (a) G. A. Russell and K-Y. Chang, *J. Am. Chem. Soc.*, 87, 4381 (1965); (b) G. A. Russell, G. Holland, and K-Y. Chang, *Tetrahedron Letters*, 1955 (1967); (c) G. A. Russell, G. Holland, and K-Y. Chang, *J. Am. Chem. Soc.*, in press.

[2] (a) D. Kosman and L. M. Stock, *ibid.*, 88, 843 (1966); (b) D. Kosman and L. M. Stock, *Tetrahedron Letters*, 1511 (1967).

[3] The high degree of σ character of the spin-carrying nitrogen orbital of iminoxy radicals makes spin delocalization in these radicals a considerably different problem. See R. O. C. Norman and B. C. Gilbert, *J. Phys. Chem.*, 71, 14 (1967), for long-range splittings in these systems.

[4] Reductions were carried out at room temperature in the Varian flat quartz cell; splittings were determined using a Varian V-4502 spectrometer and benzoquinone anion as calibration standard (a_H = 2.42 in DMSO: J. Gendell, J. H. Freed, and G. K. Fraenkel, *J. Chem. Phys.*, 37, 2832 (1962)).

[5] Dichloromaleic anhydride adducts of cyclopentadiene and some methylated butadienes are reported by A. M. Clifford and C. E. Glaim, U. S. Patent 2,391,276 (1945) (*Chem. Abstr.*, 40, 3136 (1946)).

[6] O. Diels and K. Alder, *Ann.*, 479, 236 (1931).

[7] For dibromomaleic anhydride adduct reductions see O. Diels and K. Alder, *ibid.*, 478, 137 (1930).

[8] Generated by reduction of 3,6-dihydrophthalic anhydride prepared by the method of N. P. Sopov and V. S. Miklashevskaya, *J. Gen. Chem. USSR*, 26, 2133 (1956).

[9] Generated by reduction of the dichloromaleic anhydride adduct (mp 241–243°) prepared by refluxing the components in toluene.

[10] Generated by reduction of the saturated dichloromaleic anhydride derivative (mp 210–220° dec).

[11] Generated both from the dichloromaleic anhydride adduct of cyclopentadiene (mp 193–194°, lit.[5] 188–189°) and from the maleic anhydride derivative, prepared by treatment of the acid[6] with acetic anhydride (mp 145–147°). The esr spectra were identical.

[12] From the maleic anhydride derivative, prepared by treatment of the acid[6] with acetic anhydride (mp 95–97°; lit.[6] 98–99°).

[13] G. A. Russell, E. T. Strom, E. R. Talaty, and S. A. Weiner, *J. Am. Chem. Soc.*, 88, 1998 (1966).

[14] S. B. Venkatranen, B. G. Segal, and G. K. Fraenkel, *J. Chem. Phys.*, 30, 1006 (1959).

[15] For a recent discussion see T. M. McKinney and D. H. Geske, *J. Am. Chem. Soc.*, 89, 2806 (1967).