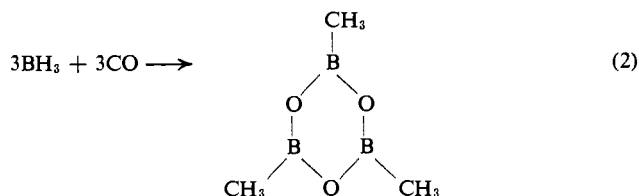


is absorbed by the solution at room temperature and atmospheric pressure, as indicated by curve A, Figure 1. Presumably this absorption is the result of the formation of a small equilibrium concentration of borane carbonyl. However, in the presence of a small catalytic quantity of sodium borohydride, the absorption of carbon monoxide is far more rapid and proceeds to the utilization of 1 mole of carbon monoxide per mole of borane present in the reaction mixture, as is evident from curve B, Figure 1.

Distillation of the reaction mixture provided trimethylboroxine⁴ in a yield of 84%.⁵ Consequently, the reaction is that shown in (2).



One mole of borane in 344 ml of tetrahydrofuran and 0.02 mole of sodium borohydride were placed in the reaction flask of the automatic hydrogenation apparatus.³ Sulfuric acid, 300 ml, maintained at 90°, was placed in the generator flask and anhydrous formic acid, 50 ml, in the buret. Carbon monoxide generated from the reaction of formic acid with the sulfuric acid was used to flush the system, and the reaction was initiated by magnetically stirring the contents of the reaction flask. (The mercury valve automatically meters the formic acid into the generator to maintain the pressure as the carbon monoxide is utilized. Consequently, a reading of the buret indicates the number of moles of carbon monoxide absorbed; 1 ml of formic acid delivers 26.6 mmoles of the gas.) Representative data for reaction in the presence and absence of sodium borohydride are shown in Figure 1. Following completion of the absorption, the tetrahydrofuran solution was carefully fractionated with an efficient column. There was obtained 35.0 g of trimethylboroxine, bp 79–80° at 745 mm (lit.^{4a} bp 79°), n_{D}^{20} 1.3638, trimethylamine adduct mp 67° (lit.^{4a} mp 67°). Further confirmation is provided by the proton nmr spectrum which showed only a single peak at δ 0.39 relative to TMS.

We explored the amount of sodium borohydride necessary to achieve this reaction. As little as 0.3 mole % proved to be effective, although we adopted 2 mole % for the synthetic procedure described above. Since sodium borohydride does not react with carbon monoxide under these conditions, it is probable that it functions by reducing borane carbonyl, and the intermediate thus produced reacts with diborane to regenerate sodium borohydride and a species which then undergoes transformation into the product. We shall elaborate on a proposed mechanism in a later publication.

Sodium borohydride also catalyzes the reaction of trialkylboranes with carbon monoxide,⁶ and we are currently exploring this reaction.

(4) (a) A. B. Burg, *J. Am. Chem. Soc.*, **62**, 2228 (1940); (b) P. A. McCusker, E. C. Ashby, and H. S. Makowski, *ibid.*, **79**, 5179 (1957).

(5) Trimethylboroxine has been obtained previously in an over-all yield of 12% by the dehydration of methylboronic acid, synthesized from methyl borate and methylmagnesium halide.⁴

(6) M. E. D. Hillman, *J. Am. Chem. Soc.*, **84**, 4715 (1962); **85**, 982 (1963).

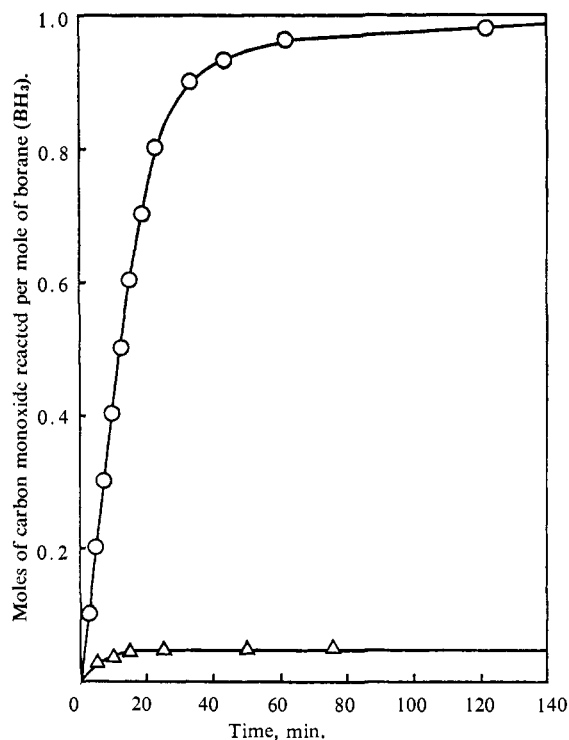


Figure 1. Reaction of carbon monoxide at atmospheric pressure with borane in tetrahydrofuran (0.5 M) at 25°: Δ, curve A, no sodium borohydride; O, curve B, 2 mole % sodium borohydride added.

Finally, we wish to call attention to the fact that tri-*n*-butylboroxine has proven to be a highly useful reagent for the identification and separation of isomeric *cis-trans* diols.⁷ Trimethylboroxine possesses obvious advantages for this application, such as greater volatility of the cyclic esters and greater stability to atmospheric oxygen. Consequently, the ready synthesis of trimethylboroxine *via* the present synthesis should greatly facilitate its availability for this application.

(7) H. C. Brown and G. Zweifel, *J. Org. Chem.*, **27**, 4708 (1962).

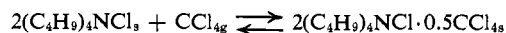
(8) National Science Foundation Fellow, 1964–1966.

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The CCl₃⁻ Species

Sir:

Preliminary studies have revealed evidence of compound formation between carbon tetrachloride and tetrabutylammonium chloride. Figure 1 shows the 0° pressure-composition isotherm for the system CCl₄-(C₄H₉)₄NCl and shows evidence of solid phases having CCl₄/(C₄H₉)₄NCl mole ratios of 0.5, 0.93 (currently interpreted as 1.0), and 4.8. We suggest that (C₄H₉)₄NCl·0.5CCl₄ is a mixed salt containing Cl⁻ and CCl₃⁻ ions. The approximate enthalpy of the reaction



calculated using the van't Hoff equation and decomposition pressures over the temperature range 0° to 70° is -9 ± 2 kcal. (C₄H₉)₄NCl·0.5CCl₄ melts at approximately 80° to give a pale yellow liquid. The re-

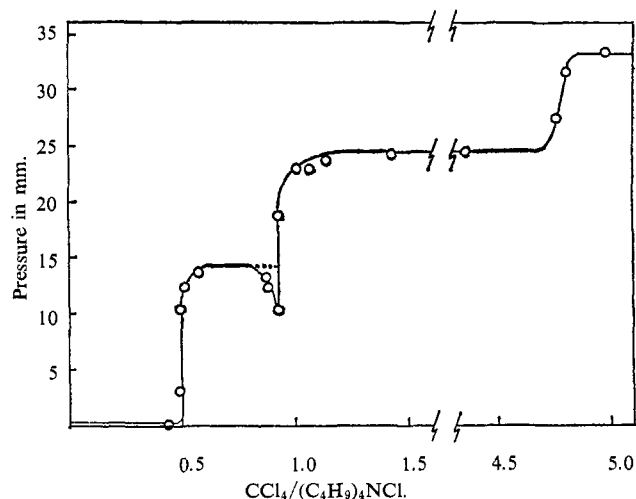


Figure 1. Pressure-composition isotherm at 0° for the system $(\text{C}_4\text{H}_9)_4\text{NCl}-\text{CCl}_4$.

action of CCl_4 with Cl^- does not occur when the tetrabutylammonium ion is replaced by the tetraethylammonium ion and it may thus be concluded that the reaction is lattice inhibited when the cation is as small as $(\text{C}_2\text{H}_5)_4\text{N}^+$.

Tetrabutylammonium chloride was prepared as described elsewhere.¹ Reagent grade carbon tetrachloride was purified by sublimation in the vacuum line prior to use. The materials were handled in a greaseless section of the vacuum line, and came into contact only with mercury and glass.

The bonding in CCl_3^- could be described either by a bicoordinate chlorine, $\text{Cl}_3\text{C}-\text{Cl}-\text{Cl}^-$, or by a penta-coordinate carbon, giving pentachlorocarbonate(IV) ion. The former would be analogous to I_3^- while the latter might resemble CH_5^+ with the occupancy of a nonbonding energy level by the additional electron pair.² The observed color could be explained using either model.

Reports in the literature indicate that carbon tetrahalides interact with many Lewis bases. The earliest work appears to be that of Dehn and Dewey³ who studied the reaction of nitrogen bases with carbon tetrabromide. A survey of complexes of saturated molecules is available;⁴ recent publications treat the interaction of carbon tetrachloride with iodide ions,⁵ aromatic hydrocarbons,⁶ aliphatic amines,^{7,8} and alkyl sulfides.⁹

Acknowledgment. We are grateful to the National Science Foundation for financial support of this work.

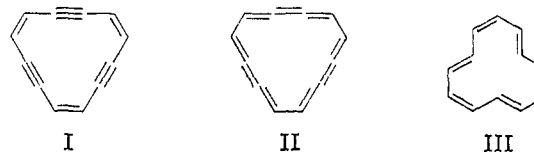
- (1) D. H. McDaniel and R. E. Valleé, *Inorg. Chem.*, **2**, 996 (1963).
- (2) For a qualitative MO treatment of CH_5^+ , based on a trigonal bipyramidal geometry, see W. N. Lipscomb, "Boron Hydrides," W. A. Benjamin, Inc., New York, N. Y., 1963, p 86.
- (3) W. C. Dehn and A. H. Dewey, *J. Am. Chem. Soc.*, **33**, 1588 (1911).
- (4) O. Hassel and Chr. Romming, *Quart. Rev. (London)*, **16**, 1 (1962).
- (5) M. C. R. Symons, *et al.*, *Trans. Faraday Soc.*, **62**, 301 (1966).
- (6) R. F. Weimer and J. M. Prausnitz, *J. Chem. Phys.*, **42**, 3643 (1965).
- (7) G. Heublein, *Z. Chem.*, **5**, 305 (1965).
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- (9) H. L. Morris, *et al.*, *Inorg. Chem.*, **5**, 124 (1966).

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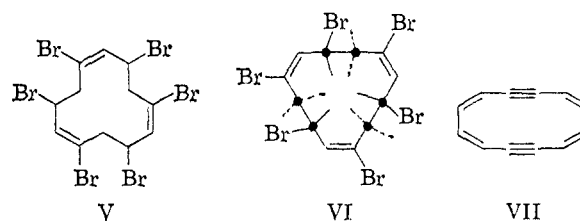
Cyclododecatrienetriyne

Sir:

Cyclododecatrienetriyne¹ (I) should be a planar, strainless, conjugated monocyclic system containing $4n$ π electrons in parallel p orbitals. This molecule was suggested as a potential aromatic system by Sworski.² Although a canonical structure (II) can be written, I is predicted by the Hückel rule not to exhibit aromatic stability. Unlike the hypothetical cyclododecahexaene (III), I does not suffer from interior hydrogen atom repulsions.³ Another unique aspect of I is that it contains six π electrons in p orbitals in the molecular plane which may contribute to a lowering of its ground-state energy by σ overlap.⁴ An MO calculation ($\beta' = [S/(1 + S)]/[S_0/(1 + S_0)]$) predicts such a delocalization energy to be *ca.* 0.8 kcal/mole.



We wish here to report a synthesis and some properties of I. Bromination of 1,5,9-tribromo-*cis,cis,cis*-1,5,9-cyclododecatriene (IV)⁴ with 3 equiv of N-bromosuccinimide (refluxing CCl_4 , 25 min) gave an oily mixture of hexabromocyclododecatrienes. We assign structure V to compounds comprising at least the majority of this product. This assignment is based on the results of analogous reactions with 1-chlorocycloalkenes which gave the 3-bromo derivatives⁵ and on the nearly quantitative yield (calculated for $\text{C}_{12}\text{H}_{12}\text{Br}_6$) obtained of a column chromatographically (SiO_2 ; CHCl_3) uniform product. Structure VI is assigned to one crystalline isomer of V, obtained after chromatography (SiO_2 ; hexane- CCl_4), mp 185°, *ca.* 15%, based on the complete analysis of its nmr spectrum as a four-spin system. The final proof of structure for this and other compounds present in this mixture will be reported later.



The hexabromocyclododecatriene mixture with excess sodium ethoxide in ethanol (35 min, 80°) gave I (65% yield, based on IV, after silicic acid column chromatography). Recrystallization (petroleum ether, bp 30–60°) provided pure I, dark brick-red needles,

- (1) 1,5,9-Cyclododecatriene-3,7,11-triyn or, using the nomenclature introduced by F. Sondheimer, tridelfydro[12]annulene.
- (2) T. J. Sworski, *J. Chem. Phys.*, **16**, 550 (1948).
- (3) For discussions of I, III, and related systems, see (a) W. Baker and J. F. W. McOmie in "Non-benzenoid Aromatic Compounds," D. Ginsburg, Ed., Interscience Publishers, Inc., New York, N. Y., 1959, Chapter IX; (b) K. Mislow, *J. Chem. Phys.*, **20**, 1489 (1952); (c) R. Wolovsky and F. Sondheimer, *J. Am. Chem. Soc.*, **84**, 2844 (1962); (d) F. Sondheimer, *Pure Appl. Chem.*, **7**, 363 (1963); (e) R. Wolovsky and F. Sondheimer, *J. Am. Chem. Soc.*, **87**, 5720 (1965), and references cited therein.
- (4) K. G. Untch and D. J. Martin, *ibid.*, **87**, 3518 (1965).
- (5) B. Eistert and K. Schank, *Tetrahedron Letters*, No. 8, 429 (1964).