α-Methyladipanilide from α-Methyladipic Acid.—While excluding moisture with a nitrogen blanket, 0.102 g. of α-methyladipic acid was refluxed 1 hr. with 1 ml. of thionyl chloride and the excess was removed at 1 mm. at room temperature. The residue was cooled in Dry Ice, 1 ml. of purified aniline was added, and the mixture was shaken and gradually heated, finally for 30 min. at 120°. The reaction product was stirred with boiling dilute hydrochloric acid, cooled, filtered, washed with water, and air dried. Crude α-methyladipanilide[13] was obtained in 74% yield, 0.147 g., m.p. 168–171° (lit.[13] m.p. 172°). Crystallization from 20 ml. of boiling toluene yielded 0.107 g., m.p. 173.5–174.5°.

Anal. Calcd. for $C_{19}H_{22}N_2O_2$: C, 73.5; H, 7.14; N, 9.03. Found: C, 73.52; H, 6.80; N, 9.36.

Preparation of Methyl α-Dichloromethyladipate.—A mixture of 0.5 g. of α-dichloromethyladipic acid, 0.1 g. of *p*-toluenesulfonic acid, 2 ml. of methanol, and 2 ml. of methyl sulfite in a loosely stoppered test tube partly immersed in a bath at 93° was heated for 20 hr. Volatile products were removed at 1 mm. and 120° bath temperature. Then, at 0.01-μ pressure and 65° bath temperature, a colorless oil was distilled. It weighed 0.5 g. (88%).

Anal. Calcd. for $C_9H_{14}Cl_2O_4$: C, 42.04; H, 5.49; Cl, 27.58. Found: C, 43.1; H, 5.74; Cl, 25.08.

N.m.r. Spectra of Dimethyl α-Dichloromethyladipate.—The spectra were made on a 60-Mc. Varian HR-60 instrument in carbon tetrachloride. The chemical shifts with tetramethylsilane as standard were α-dichloromethyl, τ 4.28, a doublet, weight 1; methyl, τ 6.37, singlet, τ 6.48, singlet, weight 6; α-hydrogen, τ, 7.10, sextuplet, weight 1; δ-hydrogen, τ 7.80, triplet, weight 2; and β- and γ-hydrogen, τ 8.30, complex multiplet, weight 4.

Pyrolysis of Dichloronorcarane.—In 2 min., 2 ml. of dichloronorcarane[12] was passed through a 1.6-cm.-diameter tube in a 24-in. furnace at 510°. From g.l.c. analysis, it was seen that the 1 g. of condensate contained 48.7% of toluene but no dichloronorcarane or dichloromethylcyclohexene.

In 45 sec., 2 ml. of dichloronorcarane was passed through a 0.5-cm. diameter tube in a 24-in. furnace at 500°. The 1.6 g. of condensate contained 69.4% of recovered dichloronorcarane, 23.5% of an unknown (likely 1,3,5-cycloheptatriene), 2.8% of toluene, but no dichloromethylcyclohexene.

Decomposition of Chloroform Alone.—Chloroform alone (1.25 moles) was pyrolyzed in the above apparatus for 3 hr. with the voltage at 10. Besides the 0.86 mole of hydrogen chloride formed, g.l.c. analysis of the higher boiling fraction showed 0.16 mole of perchloroethylene, 0.037 mole of pentachloroethane, and 0.102 mole of hexachloroethane.

Acknowledgment.—The n.m.r. spectra were made and interpreted by Mr. T. F. Page, Jr., Battelle Memorial Institute. Dr. Harry Lott of this laboratory made the infrared spectral measurements and interpretation. Helpful discussions with Dr. P. D. Bartlett of Harvard University are also gratefully acknowledged.

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gem-Dimetallic Compounds. Ethane-1,1-diboronic Acid and Ethylidenedimercuric Chloride[1]

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Dibutyl vinylboronate was hydroborated with excess diborane in tetrahydrofuran. Treatment with butanol replaced the hydrido functions on boron with butoxy groups. Tetrabutyl ethane-1,1-diboronate was obtained together with some of the isomeric ethane-1,2-diboronate. Hydrolysis yielded the corresponding boronic acids, which were easily separated by precipitating the relatively insoluble ethane-1,2-diboronic acid from moist tetrahydrofuran with methylene chloride. With a limited amount of diborane, dibutyl vinylboronate yielded a mixture of isomeric tris(dibutoxyborylethyl)boranes. Treatment of tetrabutyl ethane-1,1-diboronate with mercuric chloride and aqueous alkali yielded polyethylidenemercury or ethylidenedimercuric chloride, depending on the proportions of reactants. Polyethylidenemercury reacted with mercuric chloride in refluxing diglyme to yield ethylidenedimercuric chloride, or with iodine to yield ethylidene iodide. Treatment of ethane-1,2-diboronic acid with mercuric chloride and alkali yielded ethylene, boric acid, and mercurous chloride.

Organometallic compounds having two metallic atoms bonded to the same carbon atom have not been generally available, although the first compound of this class, methylenedimercuric iodide, was synthesized by the reaction of mercury with methylene iodide in sunlight in 1881.[2] Unlikely appearing syntheses of ethylenedimercuric chloride, ethanetetramercuric chloride, ethanehexamercuric chloride, and related compounds have been claimed,[3] but recent work indicates that the first material was actually methylmercuric chloride and the last may have been methanetrimercuric chloride.[4] Recently reported *gem*-dimetallic compounds include a number of α-metalloalkylsilicon and *gem*-disilicon compounds,[5] methylenedilithium and methylenemagnesium,[6] some *gem*-bisboranes in solution from the hydroboration of acetylenes,[7,8] and a 1,3,5-triboracyclohexane derivative.[9]

As an extension of our studies of the chemistry of dibutyl vinylboronate,[10] we undertook a study of its hydroboration. At that time no isolation of a *gem*-diboron compound had been reported, but a synthesis of tetrabutyl ethane-1,1-diboronate remarkably similar to ours has recently appeared.[11]

Hydroboration Studies.—The hydroboration of dibutyl vinylboronate was effected by adding the boronic ester to a solution of diborane in tetrahydrofuran. To convert the initially formed boranes to stable, isolable derivatives, we undertook the replacement of the hydrido functions of boron with butoxy groups.

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(1) (a) Supported in part by Grant No. CA-05513 from National Institutes of Health and in part by Grant No. G 19906 from the National Science Foundation. (b) Abstracted in part from the Ph.D. Thesis of J. G. Shdo. (c) Preliminary communication: D. S. Matteson and J. G. Shdo, *J. Am. Chem. Soc.*, **85**, 2684 (1963).

(2) J. Sakurai, *J. Chem. Soc.*, **39**, 485 (1881).

(3) K. A. Hoffman and E. Eichwald, *Ber.*, **33**, 1337 (1900); K. A. Hoffman, *ibid.*, 1328.

(4) S. V. Belshinskii and M. Usubakunov, *Izv. Akad. Nauk Kirg. SSR*, 90 (1963). *Chem. Abstr.*, **60**, 539 (1964).

(5) P. D. George, M. Prober, and J. R. Elliot, *Chem. Rev.*, **56**, 1065 (1956).

(6) K. Ziegler, K. Nagel, and M. Patheiger, *Z. anorg. allgem. Chem.*, **282**, 345 (1955).

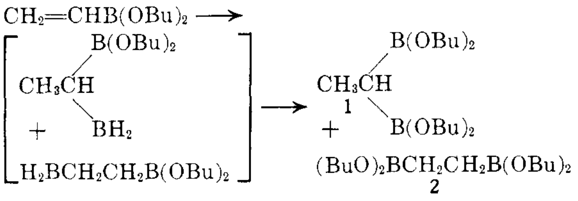
(7) H. C. Brown and G. Zweifel, *J. Am. Chem. Soc.*, **83**, 3834 (1961).

(8) P. Binger and R. Köster, *Angew. Chem.*, **74**, 652 (1962).

(9) R. Köster and G. Benedikt, *ibid.*, **75**, 346 (1963).

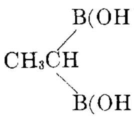
(10) D. S. Matteson, *J. Am. Chem. Soc.*, **82**, 4228 (1960). The name ethyleneboronic acid once used by *Chemical Abstracts* has been changed to etheneboronic acid. We have now decided to call it vinylboronic acid, a name which seems clearer even though it is not strictly systematic.

(11) B. M. Mikhailov and P. M. Aronovich, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1233 (1963).



We first attempted to do this by reaction with butyraldehyde, but the reaction was slow. The infrared spectrum revealed the persistence of B–H bonds and the product decomposed on distillation. In contrast, treatment of the hydroboration product with butanol led to immediate evolution of hydrogen and smooth conversion to a mixture of the isomeric tetrabutyl ethanediboronates **1** and **2** in an over-all yield of 44%.

Hydrolysis of the mixture of esters **1** and **2** yielded the crystalline ethanediboronic acids **3** and **4**. Mikhailov



3

$(HO)_2BCH_2CH_2B(OH)_2$

4

and Aronovich separated the isomers by fractional crystallization of the *o*-phenylenediamine derivatives.[11] However, we found that the widely different solubilities of the boronic acids themselves permitted a one-step separation. The ester mixture was dissolved in tetrahydrofuran containing about three times the theoretical amount of water. Addition of a small amount of methylene chloride precipitated ethane-1,2-diboronic acid (**4**) in 15% yield. Addition of more methylene chloride precipitated ethane-1,1-diboronic acid (**3**) in 67% yield. The infrared spectra indicated that each isomer was free from any detectable amount of the other.

Aliphatic boronic acids often oxidize very readily in air and the esters **1** and **2** were sensitive to oxygen. Although slow air oxidation has been reported,[11] our crystalline samples of boronic acids **3** and **4** appeared stable indefinitely in air.

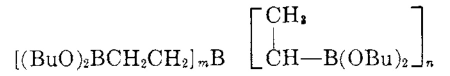
We attempted to circumvent the extra step of going through the butyl esters **1** and **2** and hydrolyze the hydroboration products directly with water, but this led to an intractable mixture of unstable solids.

The structure of ethane-1,1-diboronic acid was proved by deboronation with hydrogen peroxide[10] to acetaldehyde, isolated as the 2,4-dinitrophenylhydrazone in 67% yield, and confirmed by infrared and mixture melting point. The 1,2-isomer (**4**) gave a negative test.

Further structure proof was provided by the 60-Mc. n.m.r. spectra in deuterium oxide. Dioxane was used as the internal standard to relate the chemical shifts to the usual τ-scale based on tetramethylsilane.[12] Ethane-1,1-diboronic acid showed a singlet at τ 5.4, assigned to the hydroxyl protons, and a peak at τ 9.0 partially superimposed on weaker absorptions, assigned to the ethylidene group. A definitive ethylidene pattern was obtained when the ethane-1,1-diboronic acid was converted to the disodium salt with sodium deuteroxide. The hydroxyl protons then appeared at τ 5.3, the methyl doublet was centered at 9.2, and the proton adjacent to the two boron atoms appeared as a quartet at 10.5. The coupling constant was 7.5 c.p.s. The boronic acid decomposed at a moderate rate in basic solution and the spectrum was taken immediately after preparing the solution under nitrogen.

Ethane-1,2-diboronic acid was not sufficiently soluble in deuterium oxide to yield an n.m.r. spectrum except in basic solution. The hydroxyl singlet appeared at τ 5.2, the ethylene singlet at 10.0.

Addition of diborane to an excess of dibutyl vinylboronate in diglyme followed by slow distillation yielded a mixture of tris(dibutoxyborylethyl)boranes (**5**). This mixture yielded acetaldehyde on treatment with hydrogen peroxide.



$$[(BuO)_2BCH_2CH_2]_mB\left[\begin{matrix}CH_3\\ |\\ CH{-}B(OBu)_2\end{matrix}\right]_n$$

5, $m + n = 3$

Distillation of diborane into a tetrahydrofuran solution of dibutyl vinylboronate led to a product which yielded the correct elemental analysis for the bis(dibutoxyborylethyl)boranes (**6**). This material exhibited a B–H band centered at 4.35 μ in the infrared but no bridged B–H dimer band at 6.4 μ.[13] The lack of bridged dimer suggests that ethylidene groups predominate over ethylene groups in the composition.

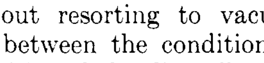
$$[(BuO)_2BCH_2CH_2]_mBH\left[\begin{matrix}CH_3\\ |\\ CH{-}B(OBu)_2\end{matrix}\right]_n$$

6, $m + n = 2$

This borane oxidized rapidly in air but we were able to handle it without resorting to vacuum techniques. The difference between the conditions producing the trialkylboranes (**5**) and the dialkylboranes (**6**) was not clearly defined by our experimental work, and owing to the similarity of composition and the lack of distinctive bands in the infrared spectrum of **5** it seems likely that some of this material was present but undetected in our sample of **6**. Some butyl borate was also apparent in the infrared spectrum of **6**, perhaps from air oxidation.

Mikhailov and Aronovich found dibutyl ethaneboronate among the hydroboration products of dibutyl vinylboronate.[11] We did not look for this product. However, subjecting dibutyl acetyleneboronate to the same hydroboration conditions used with the vinyl compound led to tetrabutyl ethane-1,1-diboronate (**1**) as the major product, identified by its infrared and n.m.r. spectra.[14]

The preferred orientation of hydroboration of dibutyl vinylboronate is that suggested on the basis of molecular orbital calculations.[10] A four-center transition state has been postulated to account for the stereochemistry of hydroborations.[15] Since the α-carbon atom of the vinylboronic ester has the higher electron density,[10] the electrophilic boron atom of the attacking borane would be expected to attack that site. The calculations are valid inasmuch as the π-bond system of the vinylboron compound should be preserved intact



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[12] R. A. Y. Jones, A. R. Katritzky, J. N. Murrel, and N. Sheppard, *J. Chem. Soc.*, 2576 (1962).

[13] G. Zweifel and H. C. Brown, *J. Am. Chem. Soc.*, **85**, 2066 (1963).

[14] K. Peacock, Ph.D. Thesis, Washington State University, 1964, p. 56.

[15] H. C. Brown and G. Zweifel, *J. Am. Chem. Soc.*, **82**, 4708 (1960).

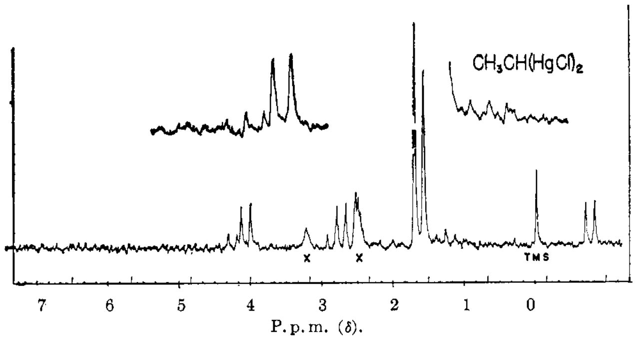
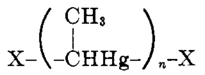


Fig. 1.—The n.m.r. spectrum of ethylidenedimercuric chloride in perdeuteriodimethyl sulfoxide.

though perturbed in the transition state. The molecular orbital calculation is not valid for attacking electrophiles which strongly localize the electron pair in the transition state, leaving essentially none of the π-bonding on which the calculation was based. A possible example of such a reagent is hydrogen bromide, which shows a slight preference for protonating the β-carbon of unsaturated boronic esters, perhaps because of the inductive effect of boron.[16]

The properties of our ethane-1,2-diboronic acid, m.p. 180–190° dec., are in good agreement with those reported by Mikhailov and Aronovich, m.p. 198–200° dec.[11] (Our sample may have contained traces of the 1,1-isomer.) Holliday and Massey have reported the preparation of ethane-1,2-diboronic acid by hydrolysis of the adduct of diboron tetrachloride with ethylene, $Cl_2B–CH_2CH_2–BCl_2$.[17] Their product was incompletely characterized. The reported behavior on heating, loss of water at 130° (perhaps under vacuum?), does not correspond to our observations, but we attribute this to different experimental conditions.

gem-**Dimercury Compounds.**—Honeycutt and Riddle have prepared dialkylmercuries by adding trialkylboranes to aqueous suspensions of mercuric oxide, freshly precipitated by the addition of sodium hydroxide to mercuric chloride.[18] Applying this procedure to ethane-1,1-diboronic acid (**3**), we obtained a gray solid which was mostly polyethylidenemercury (**7**).



$$X\text{–}\left(\text{–}\overset{\displaystyle CH_3}{\overset{|}{C}}HHg\text{–}\right)_n\text{–}X$$

7

Most of the crude solid was slightly soluble in tetrahydrofuran and could be reprecipitated by the addition of water, leading to a partially purified white product. The substance was too insoluble in the usual solvents for a molecular weight determination. Based on the residual chlorine content, 5%, the value of n would appear to be about three, but mercurous chloride is almost certainly a contaminant.

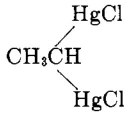
The X-ray powder pattern of polyethylidenemercury indicated that it was crystalline and different from any known compound. However, under irradiation it decomposed to metallic mercury, making a structure determination impossible.[19]

Polyethylidenemercury showed considerable thermal stability. Heating under vacuum for 1 hr. at 150° led to sublimation of only a small portion of the material and no change in the infrared spectrum of the residue.

In contrast to its thermal stability, polyethylidenemercury did not survive grinding with potassium bromide, decomposing extensively to metallic mercury, and the infrared spectrum had to be determined in Nujol. It was moderately soluble in dimethyl sulfoxide but showed signs of some slow decomposition in this solvent. The n.m.r. spectrum was determined on freshly prepared solutions in perdeuteriodimethyl sulfoxide. The methyl group doublet appeared at τ 8.4 with a splitting of 7.5 c.p.s. The Hg^{199} satellites were located 68 c.p.s. upfield but the downfield satellites were no stronger than adjacent impurity absorptions. (Natural mercury is 17% Hg^{199}.) The lone C–H absorptions were evidently located at τ 7.6 and appeared as two overlapping multiplets (as if the polymer chains were short) partially obscured by a peak due to an impurity in the solvent. The solution was too dilute to permit observations of any Hg^{199} satellite of the lone C–H.

A chemical structure proof was provided by the reaction of polyethylidenemercury with iodine in tetrahydrofuran, which yielded ethylidene iodide and mercuric iodide.

Polyethylidenemercury reacted with mercuric chloride in refluxing diglyme to yield ethylidenedimercuric chloride (**8**). Ethylidenedimercuric chloride is crystalline and easily purified. It is more soluble than the polymer (**7**) in the solvents tried. Solutions of **8** in dimethyl sulfoxide appeared to be stable indefinitely and concentrations of 30% could be obtained at 25°.



$$CH_3CH\begin{matrix}\diagup HgCl\\ \diagdown HgCl\end{matrix}$$

8

The n.m.r. spectrum of ethylidenedimercuric chloride (**8**) was determined in perdeuteriodimethyl sulfoxide and is shown in Fig. 1. The methyl group doublet is at τ 8.4 and shows Hg^{199} satellites at 146 c.p.s. downfield and upfield, the latter pair appearing 45 c.p.s. upfield from the tetramethylsilane (TMS) reference peak in Fig. 1. The quartet due to the lone C–H is centered at τ 7.3, one of its peaks being obscured by an impurity in the solvent (X), and the stronger peaks of the Hg^{199} satellites appear clearly at 91 c.p.s. downfield and, with some interference, upfield. The H–H splitting is the usual 7.5 c.p.s. Integration of the CH quartet, the CH_3 doublet, and the upfield side band of the latter yielded the expected ratios.

That the β-H–Hg^{199} coupling, 291 c.p.s., is larger than the α-H–Hg^{199} coupling, 182 c.p.s., is consistent with the observed spectra of dialkylmercuries.[20] For example, diethylmercury exhibits a β-H–Hg^{199} coupling of 120 c.p.s., an α-H–Hg^{199} coupling of 91 c.p.s. As might be expected, polyethylidenemercury shows a β-

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(16) D. S. Matteson and J. D. Liedtke, *Chem. Ind.* (London), 1241 (1963).

(17) A. K. Holliday and A. G. Massey, *J. Chem. Soc.*, 43 (1960).

(18) J. B. Honeycutt, Jr., and J. M. Riddle, *J. Am. Chem. Soc.*, **82**, 3051 (1960).

(19) We thank Dr. R. D. Willett and Mr. J. M. Williams for the X-ray data.

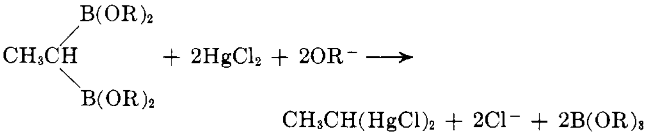
(20) R. E. Dessy, T. J. Flautt, H. H. Jaffé, and G. F. Reynolds, *J. Chem. Phys.*, **30**, 1422 (1959).

H–Hg^{199} coupling of 135 c.p.s., close to the values reported for dialkymercuries.

The reaction of ethane-1,2-diboronic acid with mercuric chloride and sodium hydroxide did not yield polyethylenemercury. Instead, an exothermic reaction occurred with evolution of ethylene (identified by infrared) and precipitation of mercurous chloride, the other product presumably being boric acid. This disappointing result proved useful, inasmuch as it is unnecessary to free ethane-1,1-diboronic acid from the 1,2-isomer before preparing polyethylidenemercury, provided that the mercurous chloride by-product does not interfere with the intended use. For preparation of ethylidenedimercuric chloride, a mixture of the ethanediboronic esters **1** and **2** or the trialkylborane **5** served as satisfactory starting material.

$$(HO)_2BCH_2CH_2B(OH)_2 + 2HgCl_2 + 2OH^- \longrightarrow C_2H_4 + Hg_2Cl_2 + 2B(OH)_3 + 2Cl^-$$

For preparative purposes, the route to ethylidenedimercuric chloride *via* polyethylidenemercury left much to be desired. We therefore treated the crude solution of tetrabutyl ethane-1,1-diboronate and its associated by-products directly with 2 moles of mercuric chloride and added 2 moles of aqueous sodium hydroxide dropwise. The reaction proceeded rapidly and efficiently at 0°. The over-all yield of ethylidenedimercuric chloride once recrystallized from dimethylformamide was 28%, which is satisfactory in view of the limited yield in the hydroboration step and the simplicity of the procedure.



$$CH_3CH(B(OR)_2)_2 + 2HgCl_2 + 2OR^- \longrightarrow CH_3CH(HgCl)_2 + 2Cl^- + 2B(OR)_3$$

Experimental

Tetrabutyl Ethanediboronates (1 and 2).—Our experimental conditions[1c] were so similar to those developed independently by Mikhailov and Aronovich[11] that there is no need to report the details. We also prepared pure tetrabutyl ethane-1,1-diboronate (**1**) by esterification of the boronic acid (**3**), b.p. 80–85° (0.05 mm.), n^{25}_{D} 1.4245 (lit.[11] n^{20}_{D} 1.4265).

Ethane-1,2-diboronic Acid (4).—A 1.6-g. sample (4.7 mmoles) of the mixture of esters **1** and **2** was transferred with a hypodermic syringe and discharged under the surface of a well-stirred solution of 0.5 ml. (28 mmoles) of water in 6 ml. of tetrahydrofuran under nitrogen. Methylene chloride (8 ml.) was added and the solution was stirred 15 min. to complete crystallization of ethane-1,2-diboronic acid (**4**), yield 0.08 g. (15%), m.p. 180–190° dec. The infrared spectrum in Nujol showed strong bands at 3.05, 7.2–7.5, 8.30, 8.67, 8.82, 9.07, 12.1 (broad), and 13.6 (broad) μ.

Anal. Calcd. for $C_2H_8B_2O_4$: C, 20.40; H, 6.85; B, 18.38. Found[21]: C, 20.61; H, 6.84; B, 18.12.

Ethane-1,1-diboronic Acid (3).—To the filtrate from the crystallization of ethane-1,2-diboronic acid there was added an additional 10 ml. of methylene chloride. After stirring 0.5 hr., 0.37 g. (67%) of crystalline ethane-1,1-diboronic acid was collected, m.p. 142–150° dec., lit.[11] m.p. 151–153°. The infrared spectrum in Nujol showed strong bands at 3.1, 7.2–7.5, 7.88, 8.58, 8.90, 9.45, 9.83, and 12.2 (broad, shoulder 12.5–12.9) μ.

Anal. Found: C, 20.57; H, 6.78; B, 18.30.

Bis(dibutoxyborylethyl)boranes (6).—Diborane, generated in the usual manner from 3.6 g. (0.095 mole) of sodium borohydride in 65 ml. of diglyme and 24.2 g. (0.2 mole) of boron trifluoride etherate in 50 ml. of diglyme, was passed into a solution of 47 g. (0.26 mole) of dibutyl vinylboronate in 100 ml. of tetrahydrofuran over a period of 2 hr. (nitrogen atmosphere). The solution was stirred overnight and the solvent was distilled. Fractionation through a 12-cm. column packed with nichrome helices yielded 16.6 g. (17%) of the boranes (**6**), b.p. 77–85° (0.05 mm.). A redistilled sample showed infrared absorption due to B–H at 4.35 μ; the rest of the spectrum was typical of aliphatic boronic esters.

Anal. Calcd. for $C_{20}H_{45}B_3O_4$: C, 62 88; H, 11.87; B, 8.50. Found: C, 63.04; H, 11.83; B, 8.20.

Tris(dibutoxyborylethyl)boranes (5).—The procedure was the same as that used for the preparation of **5** except that the dibutyl vinylboronate was dissolved in diglyme instead of tetrahydrofuran. Fractionation of the product was carried out very slowly over a period of 4 days, keeping the column at about 85° and the distillation flask at about 160°. The infrared spectrum of a redistilled sample showed no butyl borate band at 15 μ and differed only slightly from the spectra of **1** and **5**.

Anal. Calcd. for $C_{30}H_{66}B_4O_6$: C, 63.64; H, 11.75; B, 7.65. Found: C, 63.49; H, 11.71; B, 7.84.

Polyethylidenemercury (7).—(*Caution:* possibility of volatile, highly toxic by-products such as diethylmercury.) A solution of 0.6 g. of ethane-1,1-diboronic acid in 18 ml. of water was added dropwise in 1.5 hr. under nitrogen to a suspension of mercuric oxide in a few milliliters of water, freshly prepared from 0.4 g. of sodium hydroxide and 1.35 g. of mercuric chloride. After stirring 3 hr. longer, the solid was collected and dried. Most of it dissolved slowly in boiling tetrahydrofuran (200 ml., 3 hr.). The solution was filtered and the polyethylidenemercury crystallized on addition of 35 ml. of water, yield 0.6 g. (54%), m.p. 173°. An analytical sample was recrystallized from tetrahydrofuran and water, m.p. 195° dec.

Anal. Calcd. for C_2H_4Hg: C, 10.5; H, 1.8; Hg, 87.7. Found: C, 8.9; H, 2.4; Hg, 79.4; Cl, 5.3.

Polyethylidenemercury was also prepared from 1.70 g. of the tetrabutyl ethanediboronates **1** and **2**. The ester mixture was added in 10 min. to a mercuric oxide suspension prepared from 0.4 g. of sodium hydroxide in 5 ml. of water and 1.35 g. of mercuric chloride suspended in 2 ml. of water. The yield of crude polyethylidene mercury was 0.85 g. (80%). Similarly, 1.68 g. of tris(dibutoxyborylethyl)boranes (**5**) gave an exothermic reaction when added to mercuric oxide from 0.8 g. of sodium hydroxide and 2.7 g. of mercuric chloride and yielded 2.0 g. of polyethylidenemercury.

Polyethylidenemercury to Ethylidene Iodide.—Refluxing 0.2 g. of polyethylidenemercury and 0.36 g. of iodine in 5 ml. of tetrahydrofuran for 2 hr. followed by distillation at reduced pressure yielded 0.13 g. of crude ethylidene iodide and 0.4 g. of mercuric iodide. Redistillation yielded 0.08 g. (33%) of ethylidene iodide, after sodium bisulfite treatment shown by infrared to be identical with an authentic sample.[22]

Ethylidenedimercuric Chloride (8). A. From Polyethylidene mercury.—A solution of 1.47 g. of mercuric chloride in 150 ml. of diglyme was stirred with 1.31 g. of polyethylidenemercury and refluxed under nitrogen for 3 hr. After cooling, addition of 300 ml. of water precipitated 1.51 g. (62%) of ethylidenedimercuric chloride. The product was recrystallized twice by dissolving it in hot tetrahydrofuran and adding water, forming needles, m.p. 217–218° dec., shown by n.m.r. and elemental analysis to be the same as the product from the following part B.

B. From Crude Tetrabutyl Ethane-1,1-diboronate.—All reagents were best commercial grade. In a good hood, a solution of 85 g. of boron trifluoride etherate in 250 ml. of tetrahydrofuran was added under nitrogen in 20 min. to a stirred slurry of 15.8 g. of sodium borohydride in 100 ml. of diglyme and 250 ml. of tetrahydrofuran cooled in an ice bath. After stirring 20 min. at 20°, the mixture was cooled in an ice bath and 92 g. (0.5 mole) of dibutyl vinylboronate (Peninsular ChemResearch, Gainesville, Fla.) was added in 30 min. After 2 hr. at 20–25°, the mixture was cooled in ice and 150 ml. of butanol was added in 1 hr. (vigorous hydrogen evolution). After an additional 30 min. at room temperature, hydrogen evolution ceased. The mixture was cooled in ice and treated with 500 ml. of water followed by 271 g. (1 mole) of mercuric chloride. A solution of 40 g. of sodium hydroxide in 200 ml. of water was added dropwise, slowly enough so that the yellow color of mercuric oxide remained discharged, over a period of 1.5 hr. to the cooled mixture. The mixture was filtered (suction, overnight, large funnel) to remove mercurous

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[21] Microanalyses were by Galbraith Laboratories, Knoxville, Tenn.

[22] R. L. Letsinger and C. W. Hammeyer, *J. Am. Chem. Soc.*, **73**, 4476 (1951).

chloride and the filtrate was diluted with water (1 l.) and concentrated sufficiently at 20 mm. to remove most of the organic solvents. The crude crystals (72 g.) of ethylidenedimercuric chloride were collected and rinsed with acetone. Further dilution of the mother liquor to 3 l. yielded another 35 g. of dubious quality, and extraction of the mercurous chloride precipitate with dimethyl sulfoxide followed by dilution with acetone and water yielded an additional 17 g. of fairly pure crystals. (The mercurous chloride residue was 65 g.) Recrystallization of all the crude fractions from 375 ml. of hot dimethylformamide, with filtration to remove about 15 g. of insoluble material, yielded 55.6 g. of **8** in the first crop and 15.4 g. more after dilution of the mother liquor with 300 ml. of water, both of m.p. 217–221° dec., 28% yield. The analytical sample was recrystallized three times from dimethylformamide, washed freely with acetone, and dried at 55° (0.05 mm.), m.p. 219–221° dec.

Anal. Calcd. for $C_2H_4Hg_2Cl_2$: C, 4.80; H, 0.81; Cl, 14.18; Hg, 80.22. Found: C, 4.79; H, 0.97; Cl, 13.93; Hg, 80.42.

Preparation of Tetracyclines by Photooxidation of Anhydrotetracyclines

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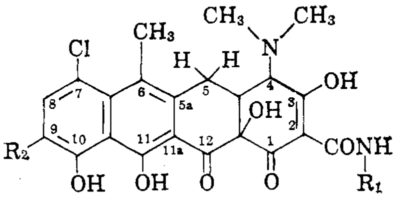
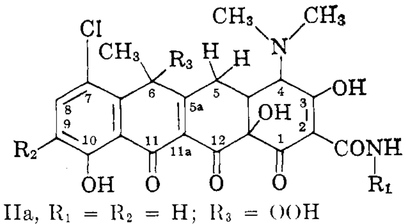
The preparation of N-*t*-butyl-, 9-N-di-*t*-butyl-, and 7-chloro-9-N-di-*t*-butyltetracycline (IIIb–d) by photooxidation of the corresponding 7-chloroanhydrotetracycline derivatives Ib and c and subsequent reduction is described. The oxidation is catalyzed by 3,4-benzpyrene and leads to the crystalline 5a,11a-dehydro derivatives IIb and c.

Possibilities for chemical modifications of the tetracycline molecule (IIIa) always have been limited severely by the presence of the acid-labile, C-6 benzylic hydroxyl function. For this reason many reactions in the past were carried out employing the C-6 deoxy derivatives of this important class of antibiotics.[1] A new important route to tetracycline derivatives containing the C-6 hydroxyl function became available when Scott and Bedford discovered the conversion by photooxidation of 7-chloroanhydrotetracycline (Ia) to 7-chloro-6-deoxy-6-peroxydehydrotetracycline[2] (IIa). Reduction of the latter compound yields tetracycline (IIIa). We wish to report on the application of this procedure to the preparation of N-*t*-butyl- and 9-N-di-*t*-butyltetracyclines (IIIb–d) and on some observations made during these studies.

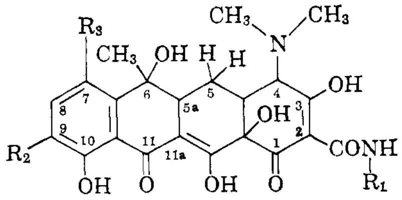


Ia, $R_1 = R_2 = H$
b, $R_1 = t$-butyl; $R_2 = H$
c, $R_1 = R_2 = t$-butyl

$\Big\downarrow h\nu\text{-}O_2$



IIa, $R_1 = R_2 = H$; $R_3 = OOH$
b, $R_1 = t$-butyl; $R_2 = H$; $R_3 = OOH$
c, $R_1 = R_2 = t$-butyl; $R_3 = OOH$
d, $R_1 = R_2 = H$; $R_3 = OH$
e, $R_1 = R_2 = t$-butyl; $R_3 = OH$



IIIa, $R_1 = R_2 = R_3 = H$
b, $R_1 = t$-butyl; $R_2 = R_3 = H$
c, $R_1 = R_2 = t$-butyl; $R_3 = H$
d, $R_1 = R_2 = t$-butyl; $R_3 = Cl$

For our experiments we employed mercury vapor lamps with a Pyrex glass filter. Irradiation and oxygenation of a benzene solution of 7-chloroanhydrotetracycline (Ia) yielded the product IIa which crystallized spontaneously from the reaction mixture, as has been described already.[2] However the addition of small quantities of 3,4-benzpyrene greatly accelerated this process. The effect of the catalyst was especially pronounced with weak radiation sources (Table I). In general, a yield of 80% could be obtained in relatively short time without recycling.

TABLE I

YIELDS OF PHOTOOXIDATION PRODUCTS UNDER VARIOUS CONDITIONS

Lamp, w.	Irradiation, hr.	Yield, %
450	4	42
450	4[a]	78
100	5	0
100	5[a]	28

[a] With catalyst.

Crystallization of the product during the reaction was highly desirable to avoid decomposition of the newly formed compound by further irradiation. Since the alkylated dehydrotetracycline derivatives are highly soluble in benzene, different solvent systems were employed for these compounds to ensure adequate yields. Thus, cyclohexane appeared to be the solvent of choice for the oxidation of 9-N-di-*t*-butyl-7-chloroanhydrotetracycline (Ic). For N-*t*-butyl-7-chloroanhydrotetracycline (Ib) a mixture of benzene and cyclohexane was employed. Under these conditions the desired prod-

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(1) Many independent studies have appeared. For leading references, *cf.* (a) C. R. Stephens, J. J. Berreboom, H. H. Rennhard, P. N. Gordon, K. Murai, R. K. Blackwood, and M. Schach von Wittenau, *J. Am. Chem. Soc.*, **85**, 2643 (1963); (b) J. J. Spencer, J. J. Hlavka, J. Petisi, H. M. Krazinski, and J. H. Boothe, *J. Med. Chem.*, **6**, 405 (1963).

(2) A. I. Scott and C. T. Bedford, *J. Am. Chem. Soc.*, **84**, 2271 (1962).