Preparation and Reactions of Some [2.2]Paracyclophane Derivatives[1]

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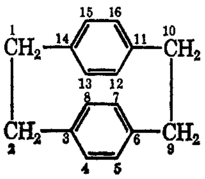
[2.2]Paracyclophane undergoes both normal and abnormal substitution reactions. Direct alkylation of [2.2]paracyclophane at low temperatures results in exclusive monoalkylation instead of the expected polyalkylation. Halogenation of [2.2]paracyclophane gives rise to normal halogenated products with good selectivity. Mono- and dibromo[2.2]paracyclophanes form the corresponding mono- and dilithio[2.2] paracyclophanes upon treatment with butyllithium at elevated temperatures. Treatment of the lithio derivatives with numerous electrophiles results in the formation of substituted paracyclophanes in high yields. Cyanation of 4,16-dibromo[2.2]paracyclophane produces two isomers of dicyano[2.2]paracyclophanes, namely, 4,16- and 8,16-dicyano[2.2]paracyclophanes.

[2.2]Paracyclophane (**1**) is the smallest member of the paracyclophanes known to exist. It exists in a definite geometry with hindered rotation of the benzene rings, and possesses severely deformed and strained bond angles and bond lengths.[2,3] As the result of the strain existing in the molecule, [2.2]paracyclophane can be quantitatively pyrolyzed at 600° and less than 1-mm pressure to form two molecules of *p*-xylylene (**2**). These reactive intermediates polymerize on condensation to form poly(*p*-xylylene) (**3**) as shown.[4]



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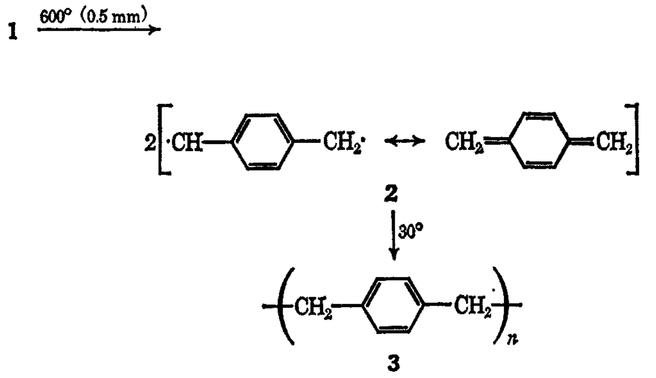
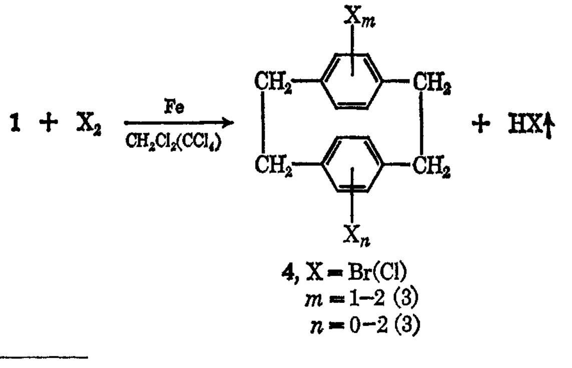


In spite of the numerous monosubstituted derivatives of [2.2]paracyclophane known to date,[3,5-9] di- and polysubstituted [2.2]paracyclophanes, which possess one or more substituents on each benzene ring, were not readily available prior to this work. Cram and coworkers reported the preparation of dinitro[2.2]paracyclophanes,[10] but the yields were poor and the reaction conditions ill-defined.[11] Cram and coworkers have shown that the main difficulty in effecting di- or polysubstitution on both benzene rings is due to the transannular interaction of the two benzene rings functioning as one single nucleophile.[5-8,10,12,13]

As part of our effort to prepare various di- and polysubstituted [2.2]paracyclophanes as novel precursors to different poly(*p*-xylylenes), and also to understand the chemistry of [2.2]paracyclophane in more detail, an investigation of methods for the preparation of di- and polysubstituted [2.2]paracyclophanes was undertaken.

Results and Discussion

Halogenation of [2.2]Paracyclophane.—[2.2]Paracyclophane undergoes bromination and chlorination reactions readily at room temperature in the presence of a catalytic amount of iron powder or other Lewis acids to give brominated and chlorinated [2.2]paracyclophanes **4** in quantitative yield.[14] The products are cleanly ring-brominated and ring-chlorinated [2.2]paracyclophanes containing up to two bromines or three chlorines on each ring. The amount of side-chain halogenation is minimal (<1%). The halogenation reactions are very selective with respect to the number of halogens introduced on each ring. For example, it is possible to obtain dihalogenated [2.2]paracyclophanes ($m = 1$, $n = 1$) with one halogen on each benzene ring in nearly 95% purity as isolated. The impurities consist mainly of lower and/or higher halogenated homologs. Repeated crystallization of the dichlorinated product yields a pure isomer, 4,16-dichloro[2.2]paracyclophane (**5**), mp 212–213°, while the dibrominated



4, X = Br(Cl)
$m = 1\text{–}2\ (3)$
$n = 0\text{–}2\ (3)$

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[1] Presented at the Macromolecular Chemistry (IUPAC) Meeting, Tokyo, Japan, Sept 1966.

[2] C. J. Brown and A. J. Farthing, *Nature*, **164**, 915 (1949); D. J. Cram, *J. Amer. Chem. Soc.*, **73**, 5691 (1951); C. J. Brown, *J. Chem. Soc.*, 3265 (1953).

[3] K. C. Dewhirst and D. J. Cram, *J. Amer. Chem. Soc.*, **80**, 3115 (1958).

[4] W. F. Gorham, *J. Polym. Sci.*, **4**, 3027 (1966); W. F. Gorham (Union Carbide Corp.), U. S. Patent 3,342,754 (1967); U. S. Patent 3,288,728 (1966).

[5] D. J. Cram and N. L. Allinger, *J. Amer. Chem. Soc.*, **77**, 6289 (1955).

[6] D. J. Cram and L. A. Singer, *ibid.*, **85**, 1075 (1963); L. A. Singer and D. J. Cram, *ibid.*, **85**, 1080 (1963).

[7] D. J. Cram, *Rec. Chem. Progr.*, **20** (2), 71 (1959).

[8] D. J. Cram and R. H. Bauer, *J. Amer. Chem. Soc.*, **81**, 5971 (1959).

[9] D. F. Pollart (Union Carbide Corp.), U. S. Patent 3,164,625 (1966).

[10] D. J. Cram, *et al.*, *J. Amer. Chem. Soc.*, **81**, 5977 (1959).

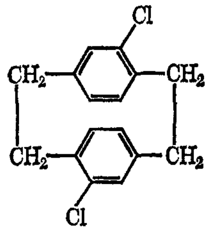
[11] D. J. Cram, private communication.

[12] D. J. Cram and D. J. Wilkinson, *J. Amer. Chem. Soc.*, **82**, 5721 (1960).

[13] D. J. Cram, *et al.*, *ibid.*, **80**, 3126 (1958).

[14] W. F. Gorham (Union Carbide Corp.), U. S. Patent 3,221,068 (1965).

product yields a pure isomer, 4,16-dibromo[2.2]paracyclophane (6), mp 245–246°. Both possess a point of symmetry within the molecule. The structure for 6 was elucidated by Reich and Cram[15] using nmr. Our own studies of 5 and 6 using mass spectroscopy, gas phase chromatography, and polymerization experiments[4] confirm that each benzene ring contains one halogen. The dipole moment data are not conclusive owing to the very limited solubility of 5 and 6 in common solvents.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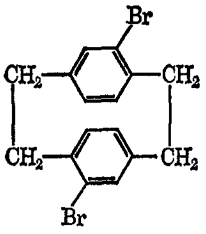
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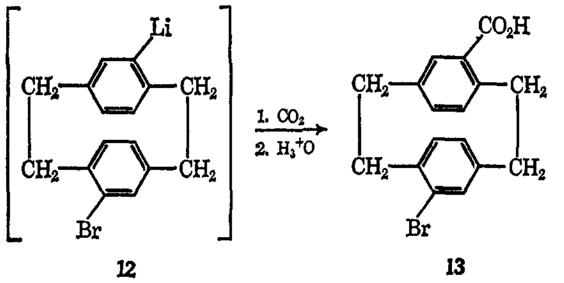
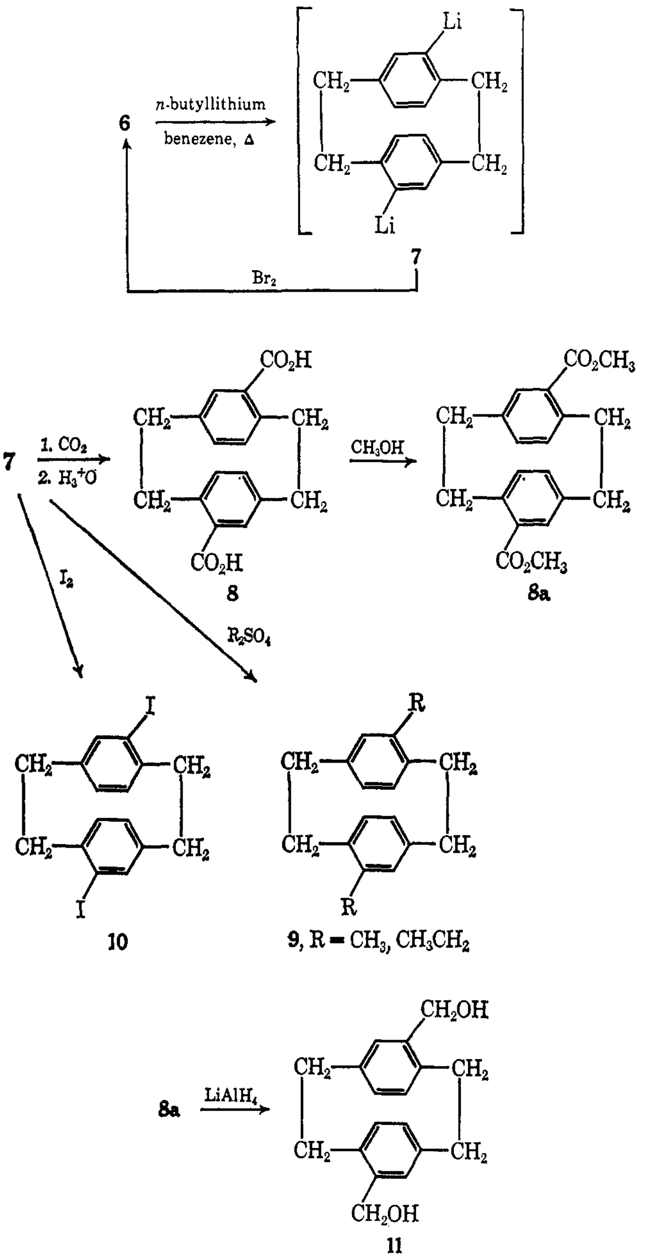
Halogen–Lithium Exchange Reaction.—Halogen-lithium exchange between brominated [2.2]paracyclophane and *n*-butyllithium proceeds in the presence of a catalytic amount of copper powder to form lithio[2.2]-paracyclophanes, a useful reactive intermediate which leads to various substituted [2.2]paracyclophane derivatives.[16–18] For example, treatment of 4,16-dibromo-[2.2]paracyclophane (6) with *n*-butyllithium in refluxing benzene gives, in quantitative yield, 4,16-dilithio[2.2]-paracyclophane (7) which reacts, *in situ*, with various reagents to form substituted [2.2]paracyclophanes 8, 9, 10 (Scheme I). These are just a few examples of the numerous transformations possible from the versatile lithio intermediate. The transformations to the final products from 6 proceed without any isomerization as evidenced by the quantitative recovery of 6 from 7 upon addition of bromine to 7.

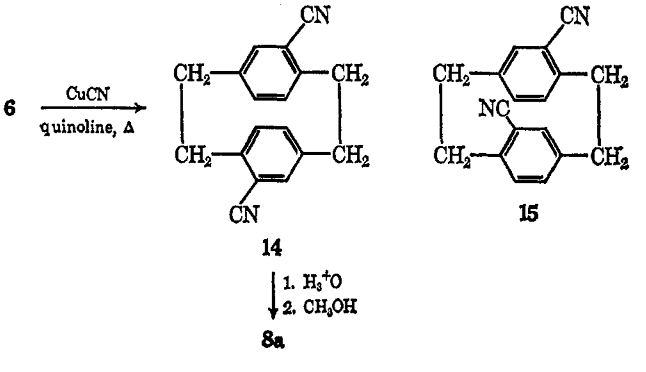
If, however, boiling diethyl ether was used instead of boiling benzene in the exchange reaction of 6 with *n*-butyllithium, only one bromine is replaced by lithium and monolithiomonobromo[2.2]paracyclophane 12 results.



Cyanation Reactions of Brominated[2.2]Paracyclophanes.—Cyanation of 4,16-dibromo[2.2]paracyclophane (6) with cuprous cyanide[19] proceeds smoothly at the temperature range of 230–240° with or without a solvent, although use of a solvent is preferred. A proper reaction temperature is the key to the success of this reaction. This can be shown from the fact that at a temperature lower than 200° or at normal cyanation conditions, *e.g.*, 150° in dimethylformamide, the cyanation reaction of 6 fails to take place. Cyanation of 6 leads to approximately equal amounts (by gas phase chromatography) of two distinct isomers of dicyanated [2.2]paracyclophanes. One of the isomers was shown to be 14, which possesses the same isomeric structure as

SCHEME I





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[15] H. J. Reich and D. J. Cram, *J. Amer. Chem. Soc.*, **91**, 1365 (1968).

[16] Y. L. Yeh (Union Carbide Corp.), U. S. Patent 3,349,142 (1967). For halogen–lithium interchange reactions involving normal aromatic systems, see H. Gilman and J. Morton, *Org. Reactions*, **8**, Chapter 6 (1954).

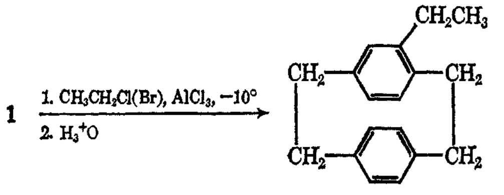
[17] Y. L. Yeh (Union Carbide Corp.), Canadian Patent 705,457 (1965).

[18] Y. L. Yeh (Union Carbide Corp.), Canadian Patent 772,189 (1967).

[19] Y. L. Yeh (Union Carbide Corp.), U. S. Patent 3,155,712 (1964).

6, by its conversion to the same dicarbomethoxy derivative **8a**. Subsequent elegant studies made by Cram and coworkers on this reaction and other related reactions culminated in the finding[20] that the other isomer is **15**, formed by a mechanism of "ring opening" in which either **6** or **14** splits open at one of the cyclophane bridges followed by rotation of one of the benzene rings and subsequent closure of the bridge.

Alkylation Reactions of [2.2]Paracyclophane.—Treatment of [2.2]paracyclophane with alkyl halides in the presence of aluminum chloride at a temperature lower than −10° results in the formation of monoalkyl[2.2]paracyclophane upon hydrolysis.[21] For example, monoethyl[2.2]paracyclophane (**16**) is obtained exclusively when [2.2]paracyclophane is treated with ethyl chloride (or bromide) and aluminum chloride in tetrachloroethane at −10°. Even with a large excess of alkyl halides and aluminum chloride, only monoalkylated products result. Monoalkylated [2.2]paracyclophanes can be alkylated further to give dialkylated [2.2]paracyclophanes. The structures of the dialkylated [2.2]paracyclophanes have not yet been elucidated. However, based on a finding that no detectable amount of the unsubstituted poly(*p*-xylylene) (**3**) was isolated upon polymerization of the diethylated [2.2]paracyclophane, it is probable that the diethylated product consists mainly of **18** and not the expected **17** (see Scheme II); this is possible only through close transannular interaction between the two benzene rings.



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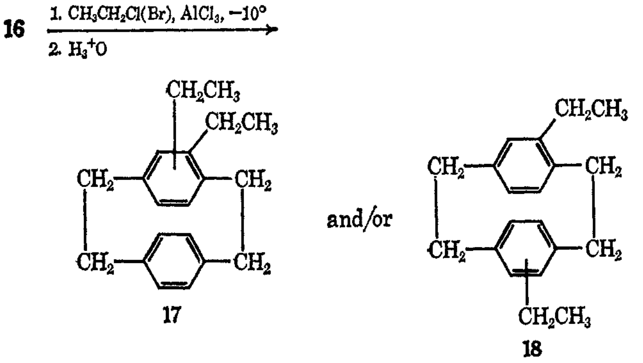
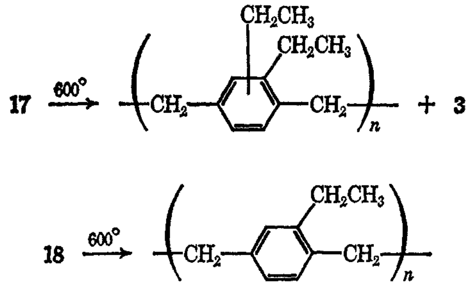
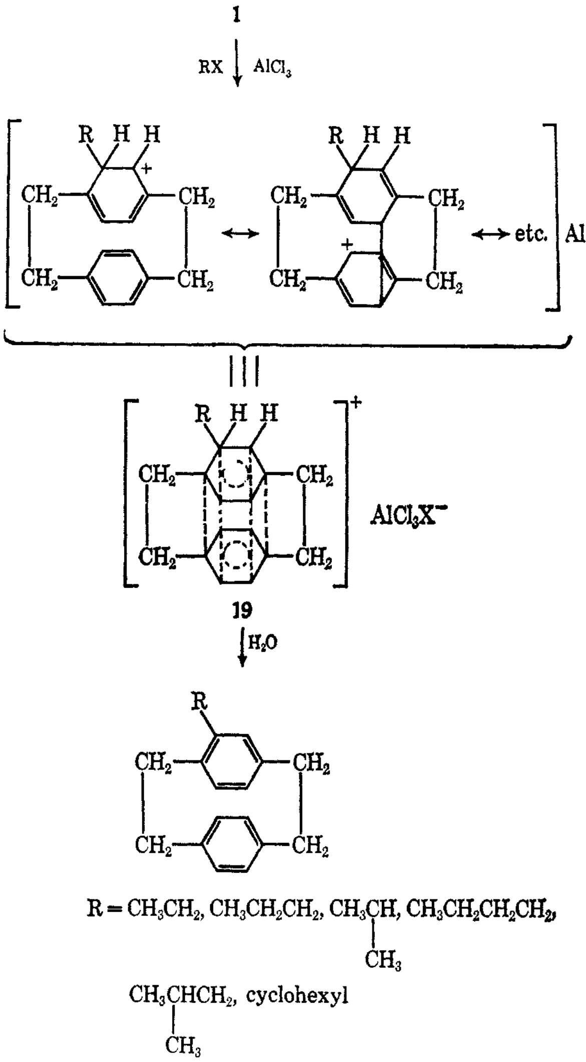


SCHEME II



In order to account for this interesting stepwise alkylation, the formation of a stable carbonium ion complex **19** as an intermediate is postulated (Scheme III).

SCHEME III



The inital carbonium ion formed by the attack of the alkyl cation is stabilized, *via* transannular interaction, by both benzene rings, thus inhibiting further attack by available alkyl cations. Hydrolysis of **19** leads to monoalkyl[2.2]paracyclophane.

Experimental Section

General Procedure for Halogenation of [2.2]Paracyclophane.—Ring chlorination and bromination of [2.2]paracyclophane were carried out in a three-necked flask equipped with a gas inlet tube (for chlorination) or an additional funnel (for bromination), a mechanical stirrer, a reflux condenser, a thermometer, and a drying tube connecting to a gas trap. [2.2]Paracyclophane, a solvent (carbon tetrachloride or methylene chloride), and a small amount of catalyst (iron powder or Lewis acid) were placed in the flask and the mixture was heated to the reaction temperature of 25–50° with vigorous stirring. A stoichiometric amount of chlorine (or bromine) was added slowly to the reaction mixture. The addition should be completed in 1–3 hr depending on the amount of the halogen to be introduced. The mixture was digested for additional 15 min after the completion of the halogen addition. The catalyst was removed either by activated charcoal or by hydrolysis with water. The organic solution was filtered and the filtrate was concentrated to dryness. The crude

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(20) H. J. Reich and D. J. Cram, *J. Amer. Chem. Soc.*, **89**, 3078 (1967).

(21) W. F. Gorham (Union Carbide Corp.), U. S. Patent 3,117,168 (1964).

solid thus obtained was bulk distilled at 200–250° (0.5 mm) to yield a halogenated product in nearly quantitative yield.

4,16-Dichloro[2.2]paracyclophane (**5**).—Dichlorination of [2.2]paracyclophane was carried out according to the general procedure. [2.2]Paracyclophane (200 g), chlorine gas (140 g), iron powder (1 g), and methylene chloride (400 ml) were used in the chlorination. The dichlorinated product (255 g, 96%) was subjected to repeated recrystallization from hot ethanol to yield 56 g (21% of the dichlorinated product) of **5**, mp 212–213°.

Anal. Calcd for $C_{16}H_{14}Cl_2$: C, 69.31; H, 5.05. Found: C, 69.10; H, 5.06.

4,16-Dibromo[2.2]paracyclophane (**6**).—Dibromination of [2.2]paracyclophane was carried out according to the general procedure. [2.2]Paracyclophane (5 g), bromine (10 g), iron powder (0.1 g), and carbon tetrachloride (400 ml) were used in the bromination. The reaction was carried out at 40–50°. The dibrominated product (8 g, 91%) was subjected to repeated recrystallization from hot ethanol to yield 2.2 g (20% of the dibrominated product) of **6**, mp 245–246°.

Anal. Calcd for $C_{16}H_{14}Br_2$: C, 52.44; H, 3.82. Found: C, 52.60; H, 3.85.

4,16-Dilithio[2.2]paracyclophane (**7**).—A mixture of 4,16-dibromo[2.2]paracyclophane (20 g) and dry benzene (1000 ml) was placed in a dry, three-necked flask equipped with a condenser (protected from moisture with a drying tube), a magnetic stirrer, a nitrogen (dry) gas inlet, and a serum cap injection port. The mixture was heated until a complete solution was obtained. A small quantity (0.05 g) of copper powder was added to the solution. *n*-Butyllithium (75 ml, 14–15% in *n*-hexane) was added through the serum cap injection port with a syringe. The resulting mixture was heated to reflux for 1 hr under a dry inert atmosphere and with good stirring. After the period, the milky mixture was allowed to cool to room temperature. The product *in situ* was used immediately for further reactions.

4,16-Dicarboxyl[2.2]paracyclophane (**8**).—The above reaction mixture containing 4,16-dilithio[2.2]paracyclophane (**7**) was poured into a beaker containing powdered Dry Ice (about 500 g). After being allowed to warm to room temperature, the mixture was extracted repeatedly with water until the organic layer became clear. The aqueous extracts were combined, filtered, and acidified with hydrochloric acid. The product which precipitated out as a white solid was collected, washed successively with water and ether, and then dried to yield 15.4 g (95% based on **6**) of the acid, mp >310°. The acid was only sparingly soluble in all the common solvents tested. The crude acid was not purified.

Anal. Calcd for $C_{18}H_{16}O_4$: C, 72.97; H, 5.40; neut equiv, 148. Found: C, 72.70; H, 5.11; neut equiv, 153.

4,16-Dicarbomethoxy[2.2]paracyclophane (**8a**).—The diacid **8** (2 g) was refluxed in dry methanol (100 ml) in the presence of a few drops of concentrated sulfuric acid. After 1 hr, the mixture was concentrated to dryness under reduced pressure. The whole process was reported until all the starting diacid became soluble in boiling methanol. The crude diester obtained after concentration was washed with aqueous sodium bicarbonate and water, and dried. Sublimation followed by recrystallization from boiling methanol provided 2 g (91% based on **8**) of pure product, mp 200–201°.

Anal. Calcd for $C_{20}H_{20}O_4$: C, 74.07; H, 6.17. Found: C, 73.79; H, 6.25.

4,16-Dimethyl[2.2]paracyclophane (**9**).—To the previous reaction mixture containing 4,16-dilithio[2.2]paracyclophane (**7**) was added dry dimethyl sulfate (300 ml) slowly with a syringe through the serum cap. Instant generation of heat was observed and the temperature of the mixture rose to about 75°. The mixture was stirred for an extra 30 min. Water (500 ml) was added to the mixture with stirring. The benzene layer was separated from the aqueous layer, washed with another 250 ml of water, filtered, and concentrated to dryness. Excess dimethyl sulfate was removed from the residual solid by drying the solid under vacuum (0.05 mm) at room temperature. Recrystallization of the residual solid from ethanol gave 11.5 g (90% based on **6**) of pure compound, mp 182–183°.

Anal. Calcd for $C_{18}H_{20}$: C, 91.52; H, 8.48. Found: C, 91.37; H, 8.50.

4,16-Diiodo[2.2]paracyclophane (**10**).—Iodine (55.6 g) was added all at once to the reaction mixture containing 4,16-dilithio[2.2]paracyclophane (**7**) with vigorous stirring. The resulting mixture was digested for 20 min. Excess iodine was removed by extracting the reaction mixture successively with 10% aqueous sodium thiosulfate solution (100 ml) and water. The organic layer was separated, filtered, dried (Na_2SO_4), and concentrated. Recrystallization of the residual solid from hot benzene gave 15 g (60% based on **6**) of pure **10**, mp 272–273°.

Anal. Calcd. for $C_{16}H_{14}I_2$: C, 41.75; H, 3.04. Found: C, 41.89; H, 3.24.

4-Bromo-16-carboxy[2.2]paracyclophane (**13**).—To a mixture of 4,16-dibromo[2.2]paracyclophane (**6** 1 g) in dry ether (100 ml) was added *n*-butyllithium solution (4 ml, 14–15% in *n*-hexane) and a catalytic amount (0.05 g) of copper powder under anhydrous and inert atmosphere. The mixture was stirred at room temperature for 30 min. The mixture was then poured into powdered Dry Ice (10 g) and allowed to warm to room temperature. Water (25 ml) was added, and the organic layer was extracted a few times more with water. The aqueous extracts were combined, filtered, washed with ether, and then acidified with dilute hydrochloric acid. The precipitate was collected and washed with water and ether to yield 0.48 g (50%) of crude **13**, mp 285–287°. Attempts to recrystallize **13** produced only noncrystalline white powders.

Anal. Calcd for $C_{17}H_{15}O_2Br$: C, 61.60; H, 4.52; Br, 24.15; neut equiv, 331. Found: C, 61.21; H, 4.30; Br, 24.09; neut equiv, 355.

13 was converted into the methyl ester, mp 151–153°, by direct esterification with methanol.

4,16- and 8,16-Dicyano[2.2]paracyclophanes (14 and 15).—A mixture of 4,16-dibromo[2.2]paracyclophane (**6**) (7.32 g), dry cuprous cyanide (4.5 g), and freshly distilled dry quinoline (20 ml) was heated to 230–240° under a dry and inert atmosphere with good stirring for 20 hr. After the reaction period, the mixture was cooled to 100° and poured into a mixture of 10% aqueous ammonium hydroxide (100 ml) and benzene (100 ml). The resulting mixture was shaken well in a separatory funnel until all the lumps disintegrated. The benzene layer was separated, washed successively with two 100-ml portions of 10% aqueous ammonium hydroxide and water, filtered, and concentrated. The residual product was sublimed (180°, 0.05–0.10 mm) and recrystallized from ethanol to yield 4.15 g (81%) of a white crystalline product: mp 165–167°; ir (Nujol) 2225 (S, $C{\equiv}N$); vpc (silica gel) indicated the presence of two isomers in equal amount. Repeated recrystallization of the isomer mixture from ethanol–benzene (50/50) yielded a small amount ($\leq 1\%$) of the less soluble isomer **14**, mp 233–235°.

Anal. Calcd for $C_{18}H_{14}N_2$: C, 83.72; H, 5.43; N, 10.85. Found: C, 83.45; H, 5.70; N, 10.54.

4-Ethyl[2.2]paracyclophane (**16**).—A mixture of aluminum chloride (3.4 g), *sym*-tetrachloroethane (50 ml), and ethyl bromide (8.5 ml) was cooled to −15° under anhydrous atmosphere with stirring. To the cooled mixture was added pulverized [2.2]paracyclophane (2.6 g). The deep purple-red mixture was stirred at −10 to −15° for 1 hr. After the period, the mixture was cooled to −30°. Dilute hydrochloric acid (1 *N*, 15 ml) was added dropwise to the mixture with vigorous stirring. The mixture was allowed to warm to room temperature while stirring. The organic layer was separated, washed successively with aqueous sodium bicarbonate and water, and dried (Na_2SO_4). Evaporation of the clear organic solution yielded a crude product which contained a small amount of the unreacted starting material. The crude product was dissolved in *n*-heptane (10 ml) and the insoluble [2.2]paracyclophane was removed by filtration. After removing *n*-heptane, the crude product was purified by sublimination followed by recrystallization from ethanol to give 2.5 g (85%) of **16**, mp 110–111°. A small portion of the product was recrystallized from ethanol to give an analytically pure sample, mp 111–112°.

Anal. Calcd for $C_{18}H_{20}$: C, 91.53; H, 8.47. Found: C, 91.51; H, 8.54.

Diethyl[2.2]paracyclophanes (**17 and/or 18**).—The procedure used in this preparation starting with 4-ethyl[2.2]paracyclophane (**16**, 2.5 g) together with aluminum chloride (3.4 g), ethyl bromide (8.5 ml), and *sym*-tetrachloroethane (50 ml) was identical with the procedure used for the preparation of **16** except for the purification step. After the removal of *sym*-tetrachloroethane, the residual product was distilled under reduced pressure. The distillate, a colorless viscous oil weighing 2.8 g (85%), was analyzed by vpc. It was composed of 68% **17** and/or **18** (broad peak) and 29% starting **16**. A small sample of pure product was isolated from vpc for elemental analysis. Attempts to crystallize the product were not successful.

Anal. Calcd for $C_{20}H_{24}$: C, 90.90; H, 9.09. Found: C, 90.72; H, 9.30.

Diethyl[2.2]paracyclophane was pyrolytically polymerized to give poly(ethyl-*p*-xylylene) by the general procedure described by Gorham.[4]

Registry No.—**5**, 10366-05-9; **6**, 5628-17-1; **7**, 19978-44-0; **8**, 19978-03-1; **8a**, 19978-04-2; **9**, R-CH_3, 10366-08-2; **10**, 19978-46-2; **13**, 19978-47-3; **13** methyl ester, 19978-48-4; **14**, 19978-49-5; **16**, 16070-18-1.

Bromination Reactions on Adsorbent Surfaces[1]

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Bromination of cyclohexene and *cis*- and *trans*-2-butenes on activated carbon is exclusively a *trans* addition. Experimental conditions and results imply that the bromination is a surface reaction. It is suggested that the exclusive *trans* product results from mobility of Br ions on the carbon surface or from the steric constraint imposed by the pores of the adsorbent. Bromination of aromatic hydrocarbons by surface reactions gives ring substitution with a distribution of isomers that depends on the polarity, but not the pore sizes, of the adsorbent. Results are interpreted in the light of steric factors governing accessibility of adsorbed bromine to the aromatic ring.

Brominated activated carbon (BAC) is known to be effective in removing ethylene from air;[2] the action is addition followed by adsorption of the adduct by the carbon.[3] BAC has been used in air purification systems to protect fruit[2] and flowers[4] against the deleterious effects of small concentrations of atmospheric ethylene. These circumstances and the thought that the reaction environment of an adsorbent surface might produce some results different from those occuring in solution led us to the present study of bromination reactions on activated carbon and other adsorbents.

Addition.—The products, kinetics, and stereochemistry of the reaction of bromine with olefins have been extensively studied,[5] and the two-step *trans*-1,2 addition in liquid phase is well known. There are reported examples of *cis* chlorination,[6] but they all involve intermediates capable of existing as stable classical carbonium ions, and probably do not involve broadside approach of the Cl_2 molecule to the double bond. Moreover, since the ability of Cl to bridge two adjacent carbon atoms is markedly less than that of Br, a chloronium ion intermediate and its stereochemical consequences ought to be less important in chlorination than the bromonium ion in bromination. If *cis* bromination were to be successful, a process involving a broadside approach of Br_2 might be promising.

We studied the stereochemical course of addition of bromine to cyclohexene and to *cis*- and *trans*-2-butenes when the reactions occurred at the surfaces of activated carbon or silica gel. For each of these olefins, *cis* and *trans* addition would give different products.

Substitution.—The reaction of bromine with alkylbenzenes uncatalyzed by Lewis acids shows a high intermolecular and intramolecular selectivity (Table I). In all cases shown, the rate of bromination of alkylbenzene is high, and *ortho/para* substitution is observed almost exclusively. Where different relative rates are shown for a particular alkylbenzene they may be attributed to different methods of measurement. Differences in product distributions may be due to different methods of analysis and/or different reaction conditions. In all cases, the attacking reagent is most likely molecular bromine and not an ionic species.

The results of studies of bromination of toluene catalyzed by Lewis acids under nonisomerizing conditions appear in Table II. Zinc chloride in acetic acid gives high intermolecular selectivity as a bromination catalyst, but isomer distribution was not reported.[7] Ferric chloride in nitromethane gives bromination with a low substrate but high positional selectivity.[8] Olah concluded that the substrate-determining step involves a transition state similar to a π complex, but the product-determining step involves σ-complex-type transition states with corresponding high *ortho/para* selectivity. The higher proportions of *ortho* substitution than those found for molecular brominations[7-9] were explained as the result of attack by the incipient bromonium ion, a group with small steric requirements compared with molecular bromine.

The increase in substrate selectivity and decrease in the *ortho/para* ratio with increasing dilution indicate that increasing solvation makes the electrophile weaker and bulkier.[8]

Complexing of either aromatic hydrocarbon[9] halogen[8,10] or attacking with the solvent decreases the *ortho/para* ratio. Adsorption of the halogen on a surface should increase its effective bulk and therefore also decrease the *ortho/para* ratio. Adsorption of the aromatic hydrocarbon, on the other hand, can either increase or decrease this ratio depending on the relative geometry between the hydrocarbon and the surface.

We studied the bromination of toluene, cumene, and *t*-butylbenzene adsorbed on alumina, silica gel, and activated carbon, to determine the resulting isomer distributions and to evaluate them in terms of steric and/or electronic factors.

Indication of Reaction at the Surface.—To support

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