intercept; it was always within 1% of that obtained from the blank or the initial titer. In the solvolysis reaction, the concentration of chloride was 0.008 *M*. Samples of 10 ml. were quenched by draining them into 100 ml. of ice-cold acetone, and the resulting solution was titrated with standard NaOH using a 0.5% alcoholic solution of lacmoid as indicator. Eight samples were taken within 50 min.; the ninth sample was treated with 5 ml. of water and allowed to stand for at least 24 hr. for the determination of the final titer. Runs were conducted to over 90% completion, and the final concentration of chloride was usually 95%. Rate constants were determined graphically, and the probable error in the slope was on the average 1%.

Acknowledgment.—This work was supported by National Science Foundation Grant G-19755, which is gratefully acknowledged. We also acknowledge stimulating discussions with Professor P. B. D. de la Mare.

Macro Rings. XXX. Structure of Anomalous Products of Acylation of [2.2]Paracyclophane*[,1]

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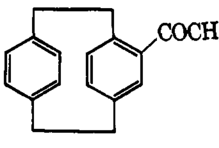
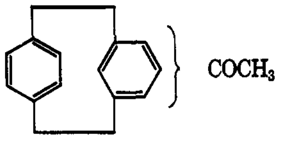
Acetylation of [2.2]paracyclophane with acetyl chloride–aluminum chloride in methylene chloride gave, besides 4-acetyl[2.2]paracyclophane, two isomeric methyl ketones, $C_{36}H_{36}O_2$. Oxidation of the two ketones gave two acids. The same hydrocarbon (VII) was produced from each of the two acids by decarboxylation, and the structure of VII was deduced from comparisons of its ultraviolet, infrared, and n.m.r. spectra with those of model compounds.

Although 4-acetyl[2.2]paracyclophane (I) is the main product of acetylation of [2.2]paracyclophane with acetyl chloride–aluminum chloride in methylene chloride,[2] a number of other products were detected which were not isolated or identified. The structures of these materials appeared interesting because of the possibility that either diacetylated [2.2]paracyclophanes or acetylated [2.2]parametacyclophanes (II) would be produced. The latter notion was strengthened by the observation[3] that small amounts of pyrene were produced when [2.2]paracyclophane was treated with aluminum chloride in dichloromethane.



I



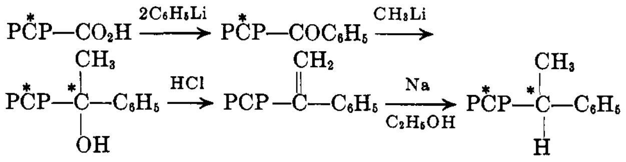
II

Structural Assignments

Careful chromatography on silica gel and fractional crystallization of the acetylated reaction mixture gave besides I (75%), 9% of compound III (m.p. 257°) and 9% of compound IV (m.p. 98–101°). Both III and IV possessed the molecular formula, $C_{36}H_{36}O_2$. Both compounds exhibited bands in their infrared spectra at 5.99 and 7.38 μ typical of acetyl groups attached to benzene rings. The two substances possessed the same ultraviolet absorption spectrum.

Compounds III and IV were oxidized with bromine and potassium hydroxide to their corresponding dicarboxylic acids (V and VI), which had nearly identical ultraviolet spectra, and which exhibited a carbonyl absorption band in their infrared spectra at 5.98 μ. Oxidation of acids V and VI with basic permanganate produced a 50% yield of terephthalic acid, identified as its dimethyl ester in a vapor phase chromatographic (v.p.c.) analysis. No benzoic, phthalic, isophthalic, or aromatic tricarboxylic acids could be detected in the products. As a model for these oxidations, 4-carboxy-[2.2]paracyclophane was similarly oxidized, and the expected terephthalic and trimellitic acids were identified as their methyl esters by v.p.c. analysis. Acids V and VI were decarboxylated with copper and quinoline to give the same hydrocarbon, VII, as shown by mixture melting point determination and identical ultraviolet, infrared, and n.m.r. spectra. Thus, III and IV differed only in the placement of the acetyl groups on their aromatic nuclei.

One of the two diastereomeric hydrocarbons (IXa and IXb) was prepared as spectral model for hydrocarbon VII by the sequence formulated. Optically pure 4-benzoyl[2.2]paracyclophane was prepared from optically pure 4-carboxy[2.2]paracyclophane[2] for use in other studies. Racemic ketone was similarly prepared. Diastereomeric racemic alcohols VIIIa and VIIIb were obtained in almost equal amounts and were separated by fractional crystallization, and their relative configurations were provisionally assigned from their n.m.r. spectra. Isomer VIIIa (m.p. 123–124°) exhibited the following spectrum: protons of benzene ring, τ 2.93 (toluene, τ 2.83); center of gravity of paracyclophane aromatic protons, 3.55 (center of gravity of $PCPCH_2CH_2OCHO$, 3.6)[4]; methylene protons, 6.97; and methyl protons, 8.27. Isomer VIIIb (m.p. 145°) gave a somewhat different spectrum: protons of benzene ring, τ 2.54 (some fine structure); center of gravity of paracyclophane aromatic protons, 3.78; methylene protons, 7.08; and methyl protons, 8.22. Molecular models of the diastereomeric alcohols suggest that the conformations written for the two diastereomeric alcohols should be the most stable. Model VIIIb places the side-chain phenyl group somewhat along side of one of the benzene rings of the paracyclophane



$$\overset{*}{PCP}—CO_2H \xrightarrow{2C_6H_5Li} \overset{*}{PCP}—COC_6H_5 \xrightarrow{CH_3Li} \overset{*}{PCP}—\overset{\overset{CH_3}{|}}{\underset{\underset{OH}{|}}{\overset{*}{C}}}—C_6H_5 \xrightarrow{HCl} PCP—\overset{\overset{CH_2}{\|}}{C}—C_6H_5 \xrightarrow[C_2H_5OH]{Na} \overset{*}{PCP}—\overset{\overset{CH_3}{|}}{\underset{\underset{H}{|}}{\overset{*}{C}}}—C_6H_5$$

VIIIa + VIIIb

IXa + IXb

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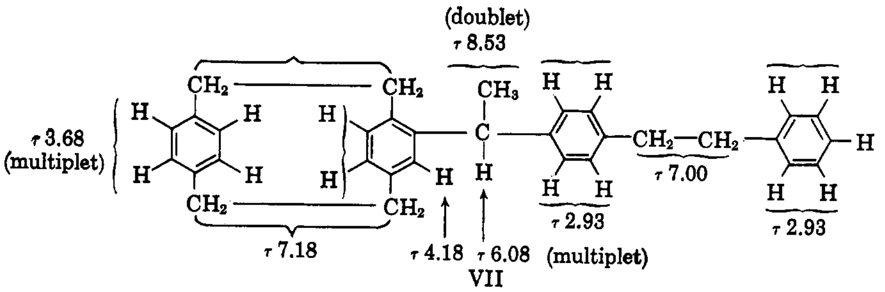
* To Professor Louis F. Fieser.

(1) The authors wish to thank the National Science Foundation for a grant used in support of this research.

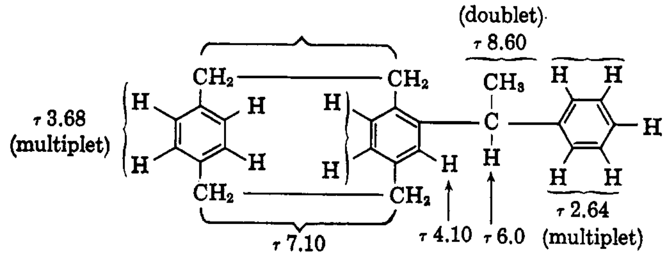
(2) D. J. Cram and N. L. Allinger, *J. Am. Chem. Soc.*, **77**, 6289 (1955).

(3) L. A. Singer, unpublished work.

(4) D. J. Cram and L. A. Singer, *J. Am. Chem. Soc.*, **85**, 1080 (1963).

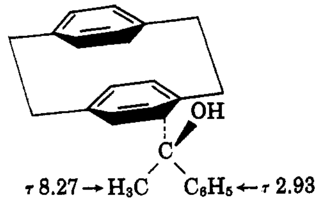


VII

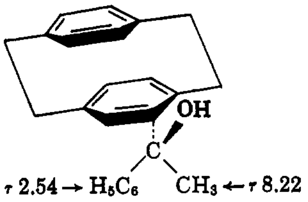


IXb

nucleus, and in that region of the ring current of the paracyclophane nucleus which is deshielding. The protons of the phenyl group in the higher melting isomer are downfield by about τ 0.32 and can therefore be assigned the VIIIb structure (τ 2.86 is normal; see n.m.r. of X below). Conversely, model VIIIa places some of the protons of the side-chain phenyl somewhat over one benzene ring of the paracyclophane nucleus and in that region of the ring current of the paracyclophane nucleus that is shielding. The protons of the phenyl of the lower melting isomer are moved upfield by about τ 0.07, and can therefore be assigned the VIIIa structure.



VIIIa, m.p. 123–124°
more stable structure



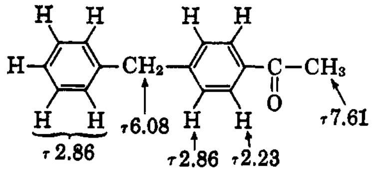
VIIIb, m.p. 145°
less stable structure

Only one of the two diastereomeric racemates of hydrocarbon IX was isolated in a pure state. The n.m.r. spectrum of this substance resembles VIIIb more than VIIIa, particularly the phenyl protons, which absorb at τ 2.64. However, without the other isomer, a structural assignment cannot be made with any assurance.

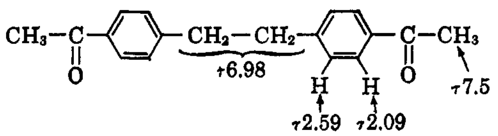
Comparison of the n.m.r. spectra of hydrocarbons VII and IXb suggests that VII has the structure formulated. Support for this assignment was found in ultraviolet spectral comparisons. The spectrum of VII and IXb were nearly identical except for some fine structure and a small peak at 273 mμ in VII that was absent in IXb. This peak is characteristic for *p*-xylenes[5] and *p,p'*-dimethyldibenzyl.[6] The *difference spectrum* of VII and [2.2]paracyclophane exhibited peaks which corresponded in position to those of *p,p'*-dimethyldibenzyl. Thus, aside from the configuration of VII, its structural assignment can be made without ambiguity.

Compounds III and IV differ only in the placement of the two acetyl groups on the skeleton of VII. Ultraviolet spectra of III and IV are nearly identical, and also resemble that of 4-acetyl[2.2]paracyclophane (I) coupled with a second chromophore. The *difference spectra* of III or IV and I are very similar to that of 4-acetyldiphenylmethane (X). Thus it seems likely that one of the acetyl groups of III and IV occupies the *para* position of the terminal benzene ring of the side chain, and the others occupy positions on the paracyclophane rings.

Support for these assignments is found in n.m.r. spectral comparisons. In the spectrum of both III and IV, two proton absorptions are found as doublets at τ 2.30 with a coupling constant of 16 c.p.s. This pattern is typical[7] for *para*-substituted acetophenones such as X and XI. This doublet disappeared in the spectrum of hydrocarbon VII. Absorption due to only two protons are found in the n.m.r. spectra for III and IV in the region τ 2.0–2.3, and therefore III and IV must each possess only one acetyl group in the two benzene rings of their side chains. Thus the second acetyl group must be substituted in the paracyclophane portion of III and IV. This conclusion is also supported by the fact that the n.m.r. spectra of III and IV differ only in the fine structure of the absorption associated with the aromatic protons of the [2.2]-paracyclophane nucleus. The center of gravity of these hydrogens is usually located between τ 3.4 and 3.76 and is dependent on the nature of the substituent.[4]



X



XI

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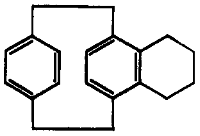
(5) (a) R. Huisgen, F. Jacob, W. Siegel, and A. Cados, *Ann.*, **590**, 1 (1954); (b) F. Wirth and E. Goldstein, *Angew. Chem.*, **46**, 643 (1934).

(6) D. J. Cram and H. Steinberg, *J. Am. Chem. Soc.*, **73**, 5691 (1951).

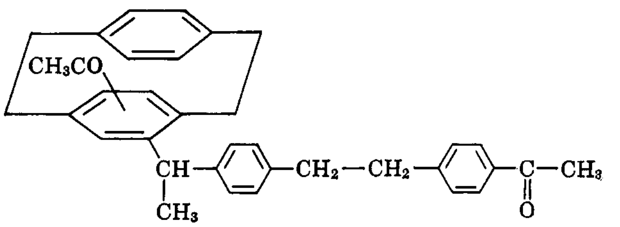
(7) N. S. Bhacca, L. F. Johnson, and J. N. Shoolery, "NMR Spectral Catalogue," Varian Associates, Palo Alto, Calif., 1962.

For example, 4-acetyl[2.2]paracyclophane exhibits absorption due to the proton *ortho* to the acetyl group at τ 3.22 and a center of gravity of the unresolved other aromatic protons at τ 3.60. Compound IV has a center of gravity for its unresolved multiplet of protons (paracyclophane, aromatic) at τ 3.58, whereas in III this peak is broken up into three singlets at τ 3.36, 3.63, and 4.06. This pattern resembles that observed for compound XII,[8] which exhibited three sets of absorption in this region.



XII

The oxidations of acids V and VI each gave about a 50% yield of terephthalic acid and no trimellitic acid, although 4-carboxy[2.2]paracyclophane did give both the dicarboxylic and the tricarboxylic acids under these conditions. These results indicate that III and IV each possess general structure XIII and

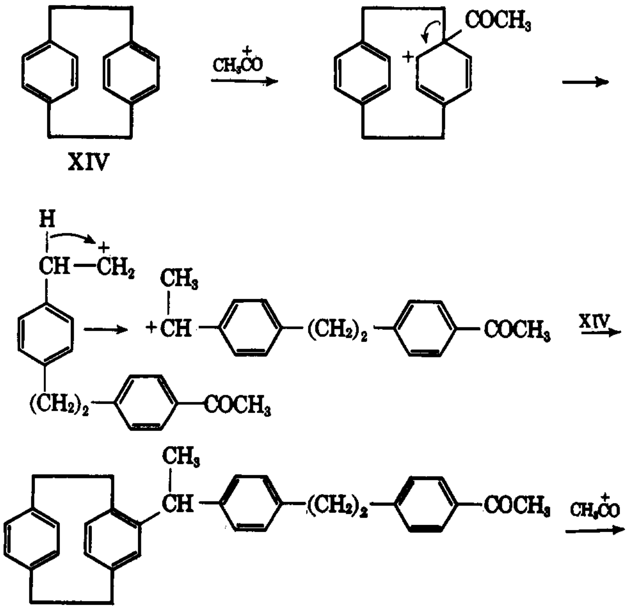


XIII (III and IV)

differ only in the position of substitution of the acetyl group in the paracyclophane nucleus. For steric reasons, the acetyl and alkylaryl side chains are probably not *ortho* to one another.

Mechanism of Formation of Compounds III and IV

Compounds III and IV are formed under Friedel–Craft acylation or alkylation conditions. One acetyl group substituted in the [2.2]paracyclophane nucleus deactivates both rings toward electrophilic attack.[2] Thus it seems reasonable to expect that the nucleus was first alkylated, and then acylated in a second stage. That alkylated [2.2]paracyclophane can be acylated has been demonstrated.[8] The strain in the [2.2]paracyclophane ring system is probably responsible for the ease with which it undergoes ring opening with aluminum chloride. An attractive general mechanistic scheme (1) is formulated. Similar sequences probably account for the low yields obtained in certain other electrophilic substitutions of the ring system.[2,8]



XIII (III and IV) (1)

Experimental

Instrumentation.—The ultraviolet spectra were recorded at 25° in 95% ethanol in a 1-cm. cell with a Cary Model 14 recording spectrophotometer. The n.m.r. spectra were run on a Varian Associates A-60 instrument in 10% solutions of carbon tetrachloride, carbon disulfide, or deuterated dimethyl sulfoxide as solvents and tetramethylsilane as internal standard. All infrared spectra were taken on a Perkin-Elmer recording spectrophotometer, Model 21, in 10% solutions in dichloromethane, or on a Beckman spectrophotometer, Model IR-5. A Perkin-Elmer vapor fractometer, Model 154, was used for v.p.c. analysis of the aromatic esters. A 6-ft. column, 0.25 in. in diameter, of 30% Carbowax on 60–80-mesh firebrick at 176° and a helium pressure of 12 p.s.i. was employed. This column exhibited the following retention times for the following esters: terephthalic acid dimethyl ester (m.p. 139°), 11.6 min.; isophthalic acid dimethyl ester (m.p. 64°), 13.6 min.; phthalic acid dimethyl ester (oil, b.p. 283°), 14.4 min.; trimesic acid trimethyl ester (m.p. 142°), 87 min.; trimellitic acid trimethyl ester (oil), 74 min.; and hemimellitic acid trimethyl ester (m.p. 102°), 100 min. Melting points were taken on a Fisher-Johns melting point block and are not corrected. Thin layer chromatography was carried out on silica gel G (Stahl). The layers were 0.25 mm. thick. A mixture of hexane and acetone (9:1) was used as the mobile phase in most cases. The plates were developed in an iodine tank. The molecular weights were determined in a Mechrolab vapor pressure osmometer, Model 301A. Benzene was used as solvent, and 0.0205 *N* and 0.0394 *N* solutions of benzil were employed to determine the calibration curve.

Acetylation of [2.2]Paracyclophane.—The procedure was different from that previously applied. To a stirred anhydrous mixture of 60 ml. of dichloromethane and 9.5 g. of aluminum chloride at −10° was added 5.5 g. of acetyl chloride in 15 ml. of dichloromethane. To the resulting homogeneous solution was added 8.32 g. of [2.2]paracyclophane (−10°). The resulting homogeneous solution was held at −10° for 15 min., poured onto a slurry of ice and concentrated hydrochloric acid. The major product, 4-acetyl[2.2]paracyclophane (I), was isolated as before (4.5 g., 47%). The thick oil from the filtrates was chromatographed on about 0.5 kg. of 60-mesh silica gel (Merck) with hexane–acetone (9:1) as solvent. From the first 15 100-ml. fractions of the eluate was isolated an additional 2.3 g. (24%) of I (R_f t.l.c. 0.64). The column was then washed with hexane–acetone, 8:3, which eluted a mixture of III and IV in 18 100-ml. fractions (1.73 g., 18%, R_f t.l.c. 0.12). When crystallized twice from acetone, this material gave after reworking of the filtrates a total of 0.82 g. or 8.5% of III, m.p. 156–157°. The final filtrates were concentrated, and hexane was added. After 12 hr. at 0°, IV separated, which after crystallization from hexane gave 0.80 g. (8%) of IV, m.p. 98–101°.

III was characterized by the ultraviolet absorption spectrum, $\lambda_{\max}$ 204 mμ (ϵ 50,000), 253 mμ (ϵ 23,500), and 290 mμ (ϵ 8400); the n.m.r. spectrum (10% solution in carbon tetrachloride), τ 2.12 and 2.26 (doublet, 1.64H), 2.78 (multiplet, 6.0H), 3.36 (singlet, 1.0H), 3.63 (singlet, 2.0H), 4.06 (singlet, 2.2H), 6.10 (multiplet, 1.5H), 6.95 (multiplet, 10.4H), 7.55 (singlet, 3.7H), 7.67 (singlet, 3.3H), and 8.53 and 8.65 (doublet, 3.3H).

Anal. Calcd. for $C_{36}H_{36}O_2$: C, 86.36; H, 7.25; mol. wt., 501. Found: C, 86.29, 86.55; H, 7.30, 7.45; mol. wt., 485.

IV was characterized by its ultraviolet absorption spectrum, $\lambda_{\max}$ 253 mμ (ϵ 23,500) and 290 mμ (ϵ 8000); n.m.r. spectrum (10% solution in carbon tetrachloride), τ 2.19 and 2.31 (doublet, 2.0H), 2.80, 2.95, and 3.20 (multiplet, 6.6H), 3.60 (multiplet, 4.2H), 6.05 (multiplet, 2.2H), 7.16 (multiplet, 9.7H), 7.53 (singlet, 3.0H), 7.67 (singlet, 3.0H), and 8.45 (doublet, 2.9H).

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(8) D. J. Cram, C. K. Dalton, and G. R. Knox, *J. Am. Chem. Soc.*, **85**, 1088 (1963).

Anal. Calcd. for $C_{36}H_{36}O_2$: C, 86.36; H, 7.25; mol. wt., 501. Found: C, 86.64; H, 7.02; mol. wt., 495.

Oxidation of Diketones III and IV to Their Carboxylic Acids V and VI.—To a stirred mixture of 0.730 g. of bromine in 1.0 g. of potassium hydroxide in 3 ml. of water at 0° was added a 0.3 g. of diketone in 5 ml. of dioxane. The mixture was stirred at 0° for 35 min. and allowed to warm to 25°, and 0.4 g. of sodium bisulfite in 10 ml. of water was added. The solution was acidified and extracted with dichloromethane. The combined extracts were dried and evaporated, and the residue was treated with 2 *N* sodium carbonate solution. The resulting sodium salt was filtered and suspended at 50° in 20% hydrochloric acid. The acid was collected and dried, 0.214 g. (71%) of V and 0.234 g. of VI.

Recrystallization of V from acetone–water gave material, m.p. 258–259°, neut. equiv. 227 in 50% methanol–water.

Anal. Calcd. for $C_{34}H_{32}O_4$: C, 80.91; H, 6.39. Found: C, 81.01; H, 6.49.

The ultraviolet spectrum of V gave $\lambda_{\max}$ 227 mμ (ϵ 30,500) and 282 mμ (ϵ 8200). The infrared spectrum (KBr) gave bands at 5.95 and 5.98 μ. The n.m.r. spectrum in deuteriodimethyl sulfoxide gave τ 2.00 and 2.14 (doublet, 2.05H), 2.58 (multiplet, 5.2H), 2.94, 3.52, and 3.96 (multiplet, 5.5H), 6.0 (multiplet, 1–2H), 6.94 (multiplet, 9.1H), and 8.58 and 8.72 (doublet, 2.9H).

Diacid VI recrystallized from acetone–water gave m.p. 269–270°. The ultraviolet spectrum of VI gave $\lambda_{\max}$ 227 mμ (ϵ 30,500) and 280 mμ (ϵ 7700). The infrared spectrum (KBr) gave bands 5.95 and 5.98 μ. The n.m.r. spectrum in deuteriodimethyl sulfoxide gave τ 2.04 and 2.14 (doublet, 2.2H), 3.04 (multiplet, 5.5H), 3.50 (multiplet, 5.6H), 5.84 (multiplet, 1–2H), 7.12 (multiplet, 9.5H), and 8.40 and 8.48 (doublet, 3.8H).

Anal. Calcd. for $C_{34}H_{32}O_4$: C, 80.91; H, 6.39. Found: C, 80.84; H, 6.61.

Decarboxylation of Dicarboxylic Acids V and VI to Hydrocarbon VII.—A 0.10-g. sample of VI (or V), 0.10 g. of copper powder, and 2 ml. of freshly distilled quinoline were mixed and heated under nitrogen to 250°. The mixture was refluxed for 6 hr., cooled, diluted with dichloromethane, and filtered. The filtrate was washed with 2 *N* hydrochloric acid, 2 *N* sodium carbonate, and water. The solution was dried and evaporated. The brown residue was chromatographed on 1 g. of neutral aluminum oxide. Elution of the material with pentane gave 0.042 g. (51%) of hydrocarbon VII. From diacid V was obtained 0.052 g. (63%) of VII.

Recrystallization of VII from pentane or hexane gave m.p. 110–111°. This melting point was undepressed by admixture of the samples from the two sources. Both samples of VII gave the same ultraviolet, infrared, and n.m.r. spectra. The n.m.r. spectrum was taken in a 10% solution in carbon tetrachloride.

Anal. Calcd. for $C_{32}H_{32}$: C, 92.26; H, 7.74; mol. wt., 417. Found: C, 92.49, 92.30; H, 7.75, 7.65; mol. wt., 367.

Oxidations of Diacids V and VI to Terephthalic Acid, and of 4-Carboxy[2.2]paracyclophane to Hemimellitic Acid.—To a mixture of 0.10 g. of V and 0.20 g. of potassium hydroxide in 20 ml. of water at 90° was added in small portions a solution of 1.0 g. of potassium permanganate in 20 ml. of water, until the purple color persisted. The solution was boiled for 1 hr., cooled to 25°, and acidified with 6 *N* sulfuric acid. To reduce the excess oxidant, a 10% solution of sodium bisulfite was added until the mixture was colorless. The mixture was extracted continuously with ether for 6 days, and the ether solutions were dried and evaporated. The white crystalline residue was weighed and dispersed in dry ether. A 1% solution of diazomethane in ether was added to the slurry of the acids in ether in order to esterify the diacids. A 1% solution of diazomethane in ether was added, the solution was allowed to stand for 14 hr. and then evaporated, and the residual oil was submitted to v.p.c. analysis.

Oxidation of 4-carboxy[2.2]paracyclophane gave 0.121 g. (80%) of acids, and the esters exhibited two peaks in the v.p.c., at 11.6 (terephthalic ester) and 74 min. (trimellitic ester). Oxidation of V gave 0.84 g. (53%) of acid, and the ester gave only one peak in the v.p.c., at 11.6 min. (terephthalic ester). Oxidation of VI gave 0.70 g. (45%) of acid, and the ester gave only one peak in the v.p.c., at 11.6 min.

(−)-4-Benzoyl[2.2]paracyclophane.—To a solution of phenyllithium from 0.030 g. of lithium and 0.194 g. of bromobenzene in 5 ml. of dry ether was added a suspension of 0.14 g. of (−)-4-carboxy[2.2]paracyclophane, $[\alpha]^{25}_{546}$ −212° (*c* 0.7, chloroform), in 2 ml. of absolute ether under dry nitrogen at 20°. After 15 min., 20 ml. of dry benzene was added, and the ether was evaporated. The resulting benzene solution was held at reflux for 24 hr. (bath 110°) and cooled to 0°. Water (5 ml.) was added, the layers were separated, and the organic layer was washed with water, dried, and evaporated. The residue was chromatographed on neutral aluminum oxide. Elution with 1:1 pentane–dichloromethane gave 0.163 g. (94%) of (−)-ketone, m.p. 140–145°. Recrystallization of this material from acetone gave 0.105 g. (61%) of pure material, m.p. 145–146°, $[\alpha]^{25}_{589}$ −163° (*c* 1.2, chloroform).

Anal. Calcd. for $C_{23}H_{20}O$: C, 88.36; H, 6.30. Found: C, 88.42; H, 6.45.

From 1.25 g. of racemic 4-carboxy[2.2]paracyclophane was isolated 1.013 g. (66%) of racemic 4-benzoyl[2.2]paracyclophane, m.p. 155–157°.

Anal. Calcd. for $C_{23}H_{20}O$: C, 88.15; H, 6.10. Found: C, 88.42; H, 6.45.

4-[2.2]Paracyclophanylmethylphenylcarbinol (VIIIa and VIIIb).—From 1.00 g. of lithium and 1.4 g. of methyl iodide in dry ether was prepared methyllithium, and to this solution was added 0.400 g. of racemic 4-benzoyl[2.2]paracyclophane in 10 ml. of dry ether. The mixture was stirred for 12 hr. at 30°, 50 ml. of dry benzene was added, and the ether was distilled until the boiling temperature of benzene was reached. The solution was refluxed for 4 hr.; the solution was cooled and mixed with 30 ml. of water. The water layer was washed with benzene and ether, and the combined organic extracts were washed with water, dried, and evaporated. The residue was free of starting ketone (t.l.c., on silica gel with pentane–5% acetone). With t.l.c. on silica gel with pentane–5% ethanol, the mixture separated into diastereomers with R_f values of 3.1 and 4.3. The total residue was submitted to chromatography on silica gel and eluted with pentane–acetone to give 0.378 g. (90%) of the mixture of diastereomers. This oil was dissolved in 3 ml. of methanol and allowed to stand for 12 hr. at −10°, whereupon 0.16 g. (38%) of crude VIIIa separated, m.p. 105–109°. Recrystallization of this material from methanol gave 0.141 g. of pure material, m.p. 123–124°. The initial mother liquors were concentrated and allowed to stand at −10°, whereupon 0.100 g. (24%) of crude VIIIb separated, m.p. 130–140°. Recrystallization of this material from methanol–water gave 0.080 g. of VIIIb, m.p. 146–147°. The filtrates of all crystallizations were concentrated and crystallized from methanol–water to give 0.080 g. of a mixture of the diastereomers which was analyzed.

Anal. Calcd. for $C_{24}H_{24}O$: C, 87.76; H, 7.37. Found: C, 87.92; H, 7.38.

4-α-Phenylethenyl[2.2]paracyclophane.—A diastereomeric mixture of alcohols VIIIa and VIIIb (0.20 g.) was dissolved in 10 ml. of methanol, and 1 ml. of 2 *N* hydrochloric acid was added. The solution was allowed to stand for 1 hr. at 25°, the solvent was evaporated under reduced pressure, and the residue was diluted with 5 ml. of water and extracted with ether. The ether solution was dried and concentrated to an oil. Recrystallization of this material from benzene–pentane gave 0.182 g. (96%) of the substituted styrene, m.p. 131–132°.

Anal. Calcd. for $C_{24}H_{22}$: C, 92.85; H, 7.15. Found: C, 92.80; H, 7.18.

4-α-Phenylethyl[2.2]paracyclophane (IXa and IXb).—To the above styrene compound, 0.190 g. in 5 ml. of boiling ethanol was added 1 g. of sodium in small pieces over a period of 30 min. The solution was cooled and concentrated, and the mixture was shaken with water and hexane. The hexane solution was washed with water, dried, and evaporated. The residue (0.201 g.) was chromatographed on silica gel. Elution with benzene–hexane (1:2) gave 0.031 g. of by-products in the first 3–2 ml. fractions. The following fractions gave 0.16 g. (83%) of a mixture of IXa and b., m.p. 70–80° (hexane). Four recrystallizations of this material from hexane gave what is probably IXb, m.p. 88–90°.

Anal. Calcd. for $C_{24}H_{24}$: C, 92.26; H, 7.74. Found: C, 92.06; H, 7.81.

From the filtrates was obtained 0.030 g. of a mixture of IXa and b, m.p. 70–73°. Thin layer chromatography of the mixture on silica gel with benzene–hexane (1:2) gave two spots with R_f values of 0.37 and 0.44 which did not completely separate.

Ultraviolet Spectral Comparisons.—The ultraviolet spectra of [2.2]paracyclophane,[6] *p,p'*-dimethyldibenzyl,[6] 4-acetyl[2.2]paracyclophane,[9] and 4-carboxy[2.2]paracyclophane[9] have been previously reported. For use as a spectral model, 4-acetyldi-

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[9] D. J. Cram, R. H. Bauer, N. L. Allinger, R. A. Reeves, W. J. Wechter, and E. Heilbronner, *J. Am. Chem. Soc.*, **81**, 5977 (1959).

phenylmethane[10] was prepared, and exhibited λ_{max} at 254 mμ (ε 24,000) and a shoulder at about 316 mμ (ε 150). The difference spectrum between III or IV and I gave λ_{max} 256 mμ (ε 20,000) and a shoulder at about 300 mμ (ε 4500). The ultraviolet spectrum of *p,p'*-diacetyldibenzyl gave λ_{max} 222 mμ (ε 15,000), 266 (1000), and 273 (900). The difference spectrum between hydrocarbon VII and [2.2]paracyclophane gave λ_{max} 222 mμ (ε 14,000), 264 (2000), 273 (10,000), and shoulders at 288 (2400) and at 300 (85). The detailed shapes of the ultraviolet spectra of compounds VII and IXb were very similar, and resembled that of [2.2]paracyclophane except in the 240–280-mμ region. The ultraviolet spectra of 4-carboxy[2.2]paracyclophane and of compounds V and VI very much resembled one another.

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(10) M. H. Duval, *Bull. soc. chim. France*, [4] **7**, 789 (1910).

The Chemistry of 1,2-Bis(*p*-dimethylaminophenyl)-1,2-diphenylethylene. Molecular Complexes with Iodine[*,1]

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Freshly prepared 1,2-bis(*p*-dimethylaminophenyl)-1,2-diphenylethylene diiodide contains no water of crystallization and at room temperature undergoes a slow electron transfer between anion and dication to give a yellow-brown solid (IV) with the same composition as the starting compound. This change is rapid at 75° and the final product (IV) is considered to be an *n* donor complex of iodine and the parent olefin (III). An intermediate in this change shows e.s.r. absorption which is probably due to a Würster-type cation.

In an earlier paper[2] the stability of the monohydrate of tetrakis(*p*-dimethylaminophenyl)ethylene diiodide (I) was reported. It was pointed out that the removal of water[3] at room temperature resulted in significant changes in the e.s.r., infrared spectra, and color of the solid. The suggestion was made that the loss of water permitted a one-electron transfer to occur with the production of a Würster-type cation which was responsible for the e.s.r. absorption. It was also pointed out that the cold benzene extraction of I, which probably removes water, afforded products which indicated a two-electron transfer between anion and dication.

In the present paper we are concerned with some of the properties of 1,2-bis(*p*-dimethylaminophenyl)-1,2-diphenylethylene diiodide (II).

Experimental

Materials. 1,2-Bis(*p*-dimethylaminophenyl)-1,2-diphenylethylene (III).—III was prepared by the method of Buckles and Meinhardt.[4a]

A sample of III was recrystallized for spectral work, from ethanol–chloroform and from ethanol and had m.p. 230–233°.

Certified resublimed reagent grade iodine was used without further treatment. Commercial ethylene chloride was purified according to the careful work of Buckles, *et al.*[4b]

The diperchlorate of III was prepared by the procedure of Wizinger and Fontaine[5] and was recrystallized twice from water.

Anal. Calcd. for $C_{30}H_{30}Cl_2N_2O_8$: Cl, 11.50. Found: Cl, 11.20, 11.20.

Bis(*p*-dimethylaminophenyl)-1,2-diphenylethylene Diiodide (II).—Potassium iodide dissolved in water was added to a cold aqueous solution of diperchlorate III. The purple-black solid II which separated was collected, washed repeatedly with ice-water, and dried for 24 hr. at room temperature. The diiodide II, unlike I, did not contain water of hydration. Compound II was soluble in water while still wet, but no attempt was made to recrystallize it from water.

Anal. Calcd. for $C_{30}H_{30}I_2N_2$: I, 37.79. Found: I, 37.74, 36.97.

There was no change in weight after heating II for 6 hr. at 75°. The color changed from purple-black through gray to yellow-brown; this heated compound, **IV**, was insoluble in water.

Anal. Calcd. for $C_{30}H_{30}I_2N_2$: I, 37.79. Found: I, 37.00, 36.87.

The purple-black compound II was allowed to stand at room temperature for 1 month. During this time it gradually changed to yellow-brown and there was no loss in weight.

Anal. Calcd. for $C_{30}H_{30}I_2N_2$: I, 37.79. Found: I, 36.98.

The yellow diiodide IV in ethylene chloride treated with copper bronze at room temperature yielded the olefin III.

Instrumentation.—Visible and ultraviolet absorption spectra were determined using a Cary Model 14 recording spectrophotometer. Matched silica cells of path length 1.00 ± 0.01 cm. were used to determine the spectra and $2.5 \times 10^{-5}\ M$ concentrations were used for most measurements.

All infrared spectra were obtained using a Perkin-Elmer Model 221 infrared spectrophotometer equipped with double grating.

Electron spin resonance spectra were obtained using a Varian Model 4500 e.s.r. spectrometer fitted with a TE_{102} cavity and a 100-kc. modulation attachment. Ten-milligram samples in 4-mm.-o.d. Pyrex tubes were positioned for maximum signal in the cavity. Estimations of free-radical concentrations were based on comparison with a standard char sample, that had been calibrated in turn against a known amount of diphenylpicrylhydrazyl. Calculations were made by integration of the first derivative of the e.s.r. signals using a planimeter.

Spectroscopic Results

Visible and Ultraviolet Absorption Spectra.—In Figure 1 are shown the spectra in ethylene chloride of $2.5 \times 10^{-5}\ M$ solutions of compound III, compound IV, compound II, and the diperchlorate of III.[6] For comparison, the diperchlorate is also shown in aqueous solution. These spectra show that the association of iodine with the olefin III has brought about a small shift in the absorption bands of III at about 282 and 360 mμ, respectively, accompanied by a small increase in the intensity of absorption. Attempts to calculate the equilibrium constant by means of the Benesi–Hildebrand[7] equation were not successful and no absorption

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[*] To Professor Louis F. Fieser.

(1) Reseach Council of Alberta Contribution 284.

(2) R. M. Elofson, D. H. Anderson, H. S. Gutowsky, R. B. Sandin, and K. F. Schulz, *J. Am. Chem. Soc.*, **85**, 2622 (1963).

(3) This reaction was shown to be reversible. It is interesting to note that the dehydration of the diphenylene iodonium derivative of dimedone. $2H_2O$ is reversible and involves a color change from colorless to yellow: J. W. Greidanus, W. J. Rebel, and R. B. Sandin, *ibid.*, **84**, 1504 (1962).

(4) (a) R. E. Buckles and N. A. Meinhardt, *ibid.*, **74**, 1171 (1952); (b) R. E. Buckles, R. E. Erickson, J. D. Snyder, and W. B. Person, *ibid.*, **82**, 2444 (1960).

(5) R. Wizinger and J. Fontaine, *Ber.*, **60**, 1377 (1927).

(6) There is a marked difference between the spectrum of the diperchlorate of III and the diiodide of III. This is due to the fact that the iodide ion is a good donor of electronic charge. Also in the solid state the diperchlorate of III is relatively stable and is therefore unlike the solid diiodide of III which undergoes a gradual change even at room temperature. All these facts are reminiscent of the marked difference between the dinitrate and the diiodide of tetrakis(*p*-dimethylaminophenyl)ethylene.[1]

(7) H. A. Benesi and J. H. Hildebrand, *J. Am. Chem. Soc.*, **71**, 2703 (1949).