[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MICHIGAN, ANN ARBOR, MICH.]

A Nonaromatic Route to a Paracyclophane: A Study of the 1,2,4,5-Tetramethylenecyclohexane to Tetramethyl[2.2]paracyclophane Conversion[1a]

BY DANIEL T. LONGONE AND FRITZ-PETER BOETTCHER[1b]

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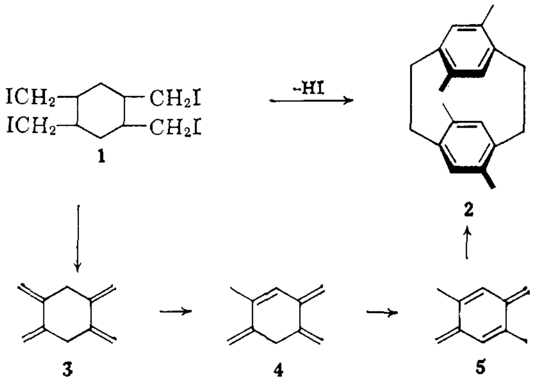
Dehydroiodination of 1,2,4,5-tetrakis-(iodomethyl)-cyclohexane affords 1,2,4,5-tetramethylenecyclohexane in good yield. In the basic medium this tetraene isomerizes to 1-methyl-3,4,6-trimethylenecyclohexene. The ultimate nonpolymeric products isolated from the isomerization medium are the spiro-dimer 6,7-dimethyltetralin-2-spiro-(3′-methyl-4′,6′-dimethylene-2′-cyclohexene) and a tetramethyl[2.2]paracyclophane (5,11,13,15-tetramethyltricyclo[8.2.2.$2^{4,7}$]hexadeca-4,6,10,12,13,15-hexaene). The latter dimer is derived from 1-methyl-3,4,6-trimethylenecyclohexene, presumably *via* the isomeric 2,5-dimethyl-*p*-xylylene. The relative reactivities of the isomeric tetraene monomers are examined in nonbasic media. The significantly greater stability of 1,2,4,5-tetramethylenecyclohexane allows for a convenient preparation of its solutions from the tetraiodide precursor. Spectral and chemical characterization of both monomers and their derivatives are summarized.

Introduction

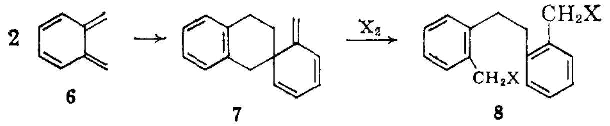
In a preliminary report[2] we described the formation, in remarkably high yield (25%), of the tetramethyl-[2.2]paracyclophane **2** from base dehydroiodination of 1,2,4,5-tetrakis-(iodomethyl)-cyclohexane (**1**). Assignment of the paracyclophane structure to the dehydroiodination product was based on its chemical and spectral properties. We have since confirmed the structure of **2** by two quite different unequivocal syntheses. Both the intramolecular Wurtz coupling of 2,2′,5,5′-tetramethyl-4,4′-bromomethylbibenzyl and the Hofmann elimination of duryltrimethylammonium hydroxide yield the same paracyclophane **2**.[3] The Hofmann method undoubtedly[4,5] gives **2** *via* formation and subsequent dimerization of 2,5-dimethyl-*p*-xylylene (**5**).

We viewed[2] 1,2,4,5-tetramethylenecyclohexane (**3**) as the primary product in the dehydroiodination of **1** and the formation of **2** as arising from dimerization of the *p*-xylylene **5**, the latter generated from **3** *via* 1-methyl-3,4,6-trimethylenecyclohexene (**4**). Although alternative, more complex, routes to **2** were considered, the simple combination of base-catalyzed prototropic shifts[6] and a *p*-xylylene dimerization appeared attractive. This paper summarizes our efforts directed toward the elucidation of the detailed genesis of **2**.

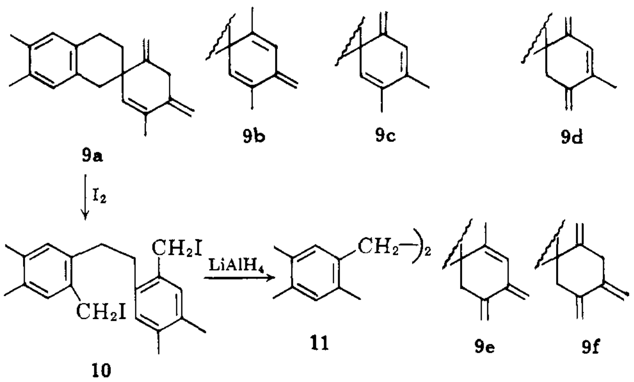


Results and Discussion

Dehydroiodination Products of 1.—In a dehydroiodination experiment similar to the one which had originally[2] produced dimer **2**, tetraiodide **1** was treated with a large excess of potassium hydroxide in refluxing ethanol. Careful work-up of the resulting reaction mixture afforded, in addition to oxygen-containing polymer, 13% paracyclophane **2** and 3% of a second hydrocarbon, m.p. 77–78°. Elemental and molecular weight analyses revealed that the latter compound, like **2**, is dimeric. Initial characterization of the new dimer indicated chemical behavior reminiscent of that of "spiro-di-*o*-xylylene" (**7**), a dimer of *o*-xylylene (**6**).[5] Thus the new dimer, although quite stable in the solid state, when in solution is slowly converted to a hydrocarbon-insoluble polymer. The dimer decolorizes a solution of iodine in carbon tetrachloride and rapidly absorbs one equivalent of bromine in the same solvent. Further reaction with bromine takes place only very slowly and is accompanied by the evolution of hydrogen bromide.



Six enantiomorphic pairs of spiro-dimers (**9a–f**) can result from Diels–Alder adductions[7] of monomers (**3**, **4**, and **5**), utilizing all possible exocyclic double bonds as dienophiles and assuming subsequent aromatization of the monomer moiety functioning as diene. Structures **9e** and **f**, each containing a conjugated exocyclic diene system, can be immediately removed from consideration by the observation that the dimer does not react with maleic anhydride. Of the remaining four, spectral



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(1) (a) Research supported by the U. S. Army Research Office (Durham); (b) Postdoctoral Fellow, The University of Michigan Institute of Science and Technology, 1962–1964.

(2) D. T. Longone and C. L. Warren, *J. Am. Chem. Soc.*, **84**, 1507 (1962).

(3) D. T. Longone, J. Chow, and L. Simanyi, unpublished results.

(4) H. E. Winberg, F. S. Fawcett, W. E. Mochel, and C. W. Theobald, *J. Am. Chem. Soc.*, **82**, 1428 (1960).

(5) L. A. Errede, *ibid.*, **83**, 949 (1961).

(6) Recent work on base-catalyzed rearrangements of *exo* to *endo* double bonds in alkylidenecycloalkanes has been reported by A. Schriesheim, R. J. Muller, and C. A. Rowe, Jr., *ibid.*, **84**, 3164 (1962).

(7) Errede (ref. 5) considers the conversion **6** → **7** as occurring *via* a di-*o*-xylylene–diradical intermediate. We prefer to view this transformation as a Diels–Alder adduction. The conjugated exocyclic diene 1,2-dimethylenecyclopentane is reported (ref. 8) to dimerize rapidly to a spiro-adduct on heating. There is no compelling evidence to suggest such dimerizations occur by other than Diels–Alder cyclization.

(8) A. T. Blomquist, J. Wolinsky, Y. C. Meinwald, and D. T. Longone, *J. Am. Chem. Soc.*, **78**, 6057 (1956).

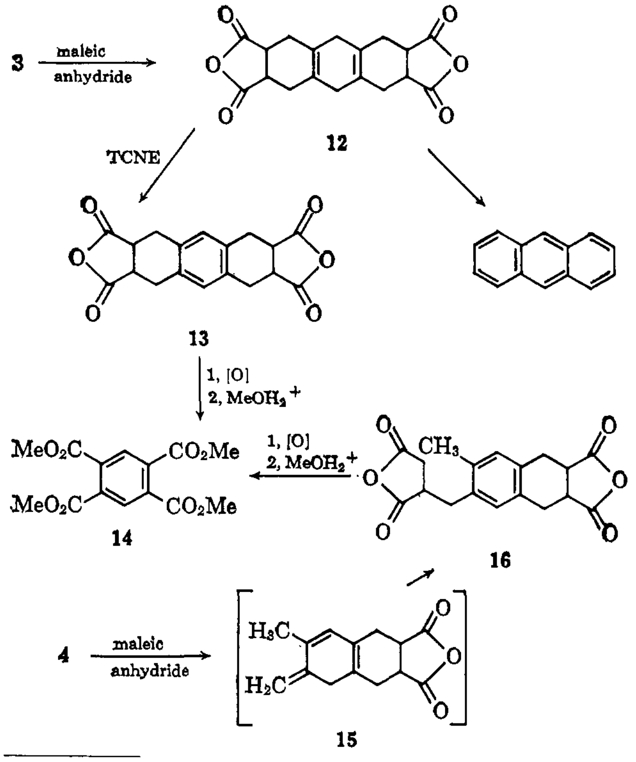
data allow assignment of structure **9a** to the dimer. In addition to methyl, olefinic, and aromatic absorptions in other regions, the infrared spectrum of the hydrocarbon exhibits three strong bands at 915, 906, and 875 cm.$^{-1}$ (vinylidene hydrogen out-of-plane deformations). The position and character of these bands are essentially identical with those displayed by the model triene 3,5-dimethylenecyclohexene[9a] (917, 902, and 877 cm.$^{-1}$).[10] The ultraviolet spectrum is particularly revealing with strong absorption with fine structure centered at λ_{max} 232 mμ (log ϵ 4.31). This agrees well with the spectrum reported[9a] for 3,5-dimethylenecyclohexene: λ_{max} 233 mμ (log ϵ 4.20). Structures **9b**, **c**, and **d** are eliminated by the absence of the 1-methylene-2,5-cyclohexadiene (λ_{max} 257 mμ),[11] 1-methylene-2,4-cyclohexadiene (λ_{max} 303 to 313 mμ),[5,12] and 3,6-dimethylenecyclohexene (λ_{max} 263 mμ)[9] chromophores, respectively. In addition to a six-proton singlet at 7.74 τ ($ArCH_3$) the n.m.r. spectrum[13] displays a four-proton complex pattern at 4.9–5.2 τ ($=CH_2$) and a three-proton doublet at 8.14 τ ($C=C-CH_3$), the latter coupled (*J* 1.2 c.p.s.) with a lone vinyl proton (incompletely resolved quadruplet) at 4.32 τ. The above data and the remainder of the spectrum fully support structure **9a** for the dimer.[14]

Repetitive dehydroiodination experiments allowed the accumulation of larger amounts of **9a** and encouraged verification of the proposed skeletal structure by chemical means. The fact that spiro-di-*o*-xylylene (**7**) reacts readily with halogen to give good yields of the corresponding 2,2′-bis-(halomethyl)-bibenzyls (**8**) prompted us to attempt the analogous rearrangement with **9a**. In carbon tetrachloride solution dimer **9a** does indeed absorb iodine to give a product which analyzes correctly for the diiodide **10**.[15] The skeletal structure of **10** was conveniently established by lithium aluminum hydride reduction to biduryl (**11**).[2]

Diels–Alder Adducts of Monomers 3 and 4.—The formation of paracyclophane **2** is not easily envisaged without invoking the intermediacy of monomer **3** and its proximate isomers. The isolation of spirodimer **9a** strengthens the postulate that these intermediates are precursors of **2**. It seemed unlikely that monomers **3** and **4** would be so reactive toward isomerization, dimerization, and polymerization that chemical trapping or actual isolation would be precluded. The use of a two-phased dehydroiodination system (methanolic base–*n*-heptane) both minimized contact of monomers with the basic medium and facilitated the examination of products during the course of the elimination. The heptane extracts from such a system were treated with maleic anhydride to affect Diels–Alder adduction of monomers. A mixture of two products (69% yield based on **1**) resulted. Subsequent quantitative infrared analysis indicated the mixture contained 35% of a low-melting and 65% of a high-melting adduct. The purified adducts, on the basis of elemental analyses and neutralization equivalents, were shown to be isomeric and derived from one equivalent of monomer and two equivalents of maleic anhydride.

The higher-melting adduct[16] proved to be the symmetric one[18] **12** derived from monomer **3**. In addition to the ultraviolet spectrum of **12**, which exhibits only end absorption, the infrared and n.m.r. spectral data are consistent but not definitive for the assigned structure. Confirmation of structure was accomplished by chemical degradation. The gross skeletal structure of the dianhydride was established by simultaneous decarboxylation and aromatization to anthracene. Evidence for the presence of the 1,4-dihydrobenzenoid structure in **12** was obtained by selective aromatization of this moiety with tetracyanoethylene (TCNE). Tetracyanoethylene has been shown[19] to be a particularly mild and efficient agent for the aromatization of 1,4-dihydrobenzenoids. The derived product **13**, obtained in essentially quantitative yield, is characterized by an ultraviolet absorption spectrum[20] virtually identical with that of 1,2,3,4,5,6,7,8-octahydroanthracene. Permanganate oxidation of **13** gives pyromellitic acid (52%, as the tetramethyl ester **14**).

The lower-melting Diels–Alder adduct is assigned structure **16** and arises from monomer **4** *via* the monoadduct **15**.[21] Structural characterization of this diadduct was facilitated by spectral revelation of its aromatic moiety. The n.m.r. spectrum[13] of **16** displays a three-proton singlet at 7.72 τ ($ArCH_3$) and a two-proton singlet at 2.99 τ (ArH). In addition, the ultraviolet



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[9] (a) R. E. Benson and R. V. Lindsey, Jr., *J. Am. Chem. Soc.*, **81**, 4250 (1959); (b) W. J. Bailey and R. Barclay, Jr., *ibid.*, **81**, 5393 (1959).

[10] We are indebted to Dr. R. E. Benson for a copy of the infrared spectrum of 3,5-dimethylenecyclohexene.

[11] W. von E. Doering, M. Saunders, H. G. Boyton, H. W. Earhart, E. F. Wadley, W. R. Edwards, and G. Laber, *Tetrahedron*, **4**, 178 (1958).

[12] W. J. Bailey and R. A. Baylouny, *J. Org. Chem.*, **27**, 3476 (1962); J. F. Eastham and V. F. Raaen, *Proc. Chem. Soc.*, 149 (1958); C. R. Hauser and D. N. Van Eenam, *J. Am. Chem. Soc.*, **79**, 5512 (1957).

[13] Spectrum obtained at 60 Mc. We are indebted to Dr. George Slomp and his associates at The Upjohn Co. for the determination and discussion of this spectrum.

[14] The spectrum exhibits a two-proton complex multiplet centered at *ca.* 6.7 τ ($-CH_2-$). The low field position of this band is highly indicative of a *diallylic* methylene; if this interpretation is correct, the n.m.r. spectrum *alone* allows assignment of structure **9a** to the dimer.

[15] Structure **10**, rather than the isomeric 2,4′-bis-(iodomethyl)-bibenzyl, is assigned to the diiodide arbitrarily.

[16] This adduct is apparently the same one as derived (ref. 17) from 1,2,4,5-tetramethylenecyclohexane prepared *via* acetate pyrolysis.

[17] W. J. Bailey, E. J. Fetter, and J. Economy, *J. Org. Chem.*, **27**, 3479 (1962).

[18] Inspection of molecular models indicates that both possible geometric isomers (anhydride groups mutually *cis* and *trans*) would be formed from **3**. The irregular melting point behavior of **12** and its derived products undoubtedly reflects such a mixture. Separation of the geometric isomers of **12** was not attempted; purification for chemical degradations was limited to complete removal of adduct **16**.

[19] D. T. Longone and G. L. Smith, *Tetrahedron Letters*, 205 (1962).

[20] See Experimental section.

[21] That intermediate **15** is not derived, *via* a prototropic shift, from a monoadduct of **3** is evidenced by the fact that pure **3** on treatment with maleic anhydride gives only diadduct **12** (*vide infra*).

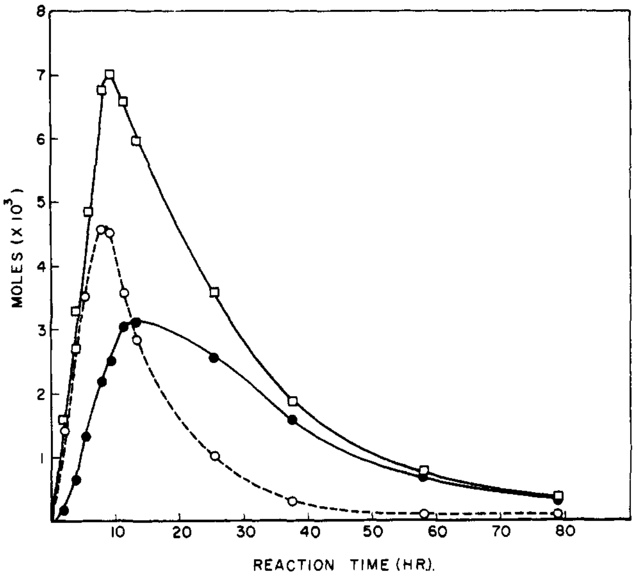

Fig. 1.—Total moles (in both heptane and methanol layers) of monomers during dehydroiodination of 0.010 mole of **1**: 1,2,4,5-tetramethylenecyclohexane (**3**), ○; 1-methyl-3,4,6-trimethylenecyclohexene (**4**), ●; and sum of **3** and **4**, □.

absorption spectrum is virtually identical with that of the structurally related compound **13**. Permanganate oxidation of **16** gives pyromellitic acid (64%, as the tetramethyl ester **14**).

The formation of **16** from maleic anhydride and the intermediate monoadduct **15** represents an unusual example of "additive substitution" of a dienophile and presumably occurs *via* a concerted addition–abstraction mechanism.[22] Products derived from normal Diels–Alder addition of maleic anhydride to **15** were not at all observed. Additive substitution rather than 1,4-addition, under particularly mild reaction conditions, is undoubtedly the result of an extreme case where aromatization provides the driving force for the former and steric factors hinder the latter mode of addition.[23]

Isolation of 1,2,4,5-Tetramethylenecyclohexane (3).—The entrapment of the isomeric tetraenes **3** and **4** (as **12** and **16**, respectively) in high yield and after prolonged dehydroiodination reaction times[20] attested their stabilities and prompted actual isolation. Utilizing vapor phase chromatography it was possible to obtain pure **3** from heptane solutions containing both **3** and **4** as well as minor amounts of nonhydrocarbon materials. Under a variety of chromatographic conditions monomer **4** failed to survive the separation.

Pure 1,2,4,5-tetramethylenecyclohexane displays the anticipated infrared absorption spectrum with pertinent bands (CCl_4): 3082(m), 1802(m), and 891(vs) cm.$^{-1}$, CH stretching and deformation vibrations in $=CH_2$; and 1643(s) and 1610 cm.$^{-1}$(m), C=C stretching vibrations in conjugated dienes.[24] The ultraviolet spectrum of **3** has $\lambda_{\max}^{\text{isooctane}}$ 229 mμ (log ϵ 3.98),[25] indicative of the 1,2-dimethylenecyclohexane chromophore.[26]

Under comparable reaction conditions that yield diadducts **12** and **16** from solutions containing both **3** and **4**, pure **3** reacts with maleic anhydride to generate only **12**. This fact precludes the possibility that intermediate **15** (and subsequently product **16**) is derived from **3**.

Isomerization of 3 and 4.—While monomer **4** appeared to be the likely precursor of diadduct **16** we sought additional evidence for its existence in the dehydroiodination mixture. Utilizing the methanol–heptane two-phased medium, the progress of the elimination reaction was conveniently monitored spectrophotometrically. Aliquots of the heptane layer were periodically removed and examined in the ultraviolet region. During the early stages of the reaction the spectra revealed the accumulation of monomer **3**; however, the presence of a second chromophore soon became evident and eventually dominated the spectra at later stages. We attribute the appearance of the latter chromophore to the formation of monomer **4**. Along with samples withdrawn for spectral characterization, aliquots were removed for monomer adductions with maleic anhydride. During the entire course of the elimination reaction, mixtures of diadducts **12** and **16** were obtained. In accord with our conclusions based on the qualitative ultraviolet data, early aliquots gave mixtures with **12** as the main component and late aliquots afforded principally **16**.

Although the infrared spectra of **12** and **16** do not differ greatly, it was possible to analyze quantitatively mixtures of these compounds.[20] Assuming that the formation of **12** and **16** from monomers was essentially quantitative, the concentrations of both **3** and **4** could be determined at all stages of the elimination reaction. Figure 1 summarizes the results of one such determination in the system: 0.010 mole of tetraiodide **1**, 0.50 mole of potassium hydroxide in 350 ml. of methanol, and 100 ml. of heptane; medium at reflux (63°). The accumulation and subsequent decay of both monomers are evident. Also, the elimination reaction is notably efficient; after the optimum reaction time (*ca.* 10 hr.), a monomer mixture is present which represents 70% of the initial amount of tetraiodide. By suitable adjustment of reaction times, as dictated by the data in Fig. 1, solutions of known composition and enriched in either of the two monomers could be prepared. From the spectra of such solutions and the knowledge of the absorption spectrum of pure **3**, the quantitative ultraviolet spectrum of monomer **4** was derived.[27] The spectrum confirmed the identity of **4**, revealing: $\lambda_{\max}^{\text{heptane}}$ 259, 269, and 280 mμ (log ϵ 4.35, 4.44, and 4.36, respectively); compare 3,6-dimethylenecyclohexene: $\lambda_{\max}^{\text{cyclohexane}}$ 256, 264, and 274 mμ (log ϵ 4.40, 4.48, and 4.33, respectively).[9] A bathochromic shift of about 5 mμ in the spectrum of **4** is anticipated owing to the added methyl substituent on the conjugated triene chromophore.

The availability of pure **3** from vapor phase chromatography of monomer solutions allowed confirmation of the origin of **4**. Pure 1,2,4,5-tetramethylenecyclohexane (**3**) in *n*-heptane was added to a refluxing methanolic potassium hydroxide solution—conditions comparable to those present in the standardized dehydroiodinations. Aliquots of the heptane layer were periodically removed and examined in the ultraviolet region. After 2 hr. contact time, the characteristic absorption bands of 1-methyl-3,4,6-trimethylenecyclohexene (**4**) were quite prominent. Subsequent moni-

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[22] R. Huisgen and H. Pohl, *Ber.*, **93**, 527 (1960).

[23] The reaction of ethyl azodicarboxylate with conjugated diene and triene systems affords both additive substitution and 1,4-addition products. The predominant mode of addition is determined largely by steric factors and is quite sensitive to minor changes in structure. *Cf.* B. T. Gillis and P. E. Beck, *J. Org. Chem.*, **27**, 1947 (1962), and B. Franzus and J. H. Surridge, *ibid.*, **27**, 1951 (1962). Maleic anhydride gives additive substitution products with nonconjugated olefins only at elevated temperatures. *Cf.* M. Günzl and W. Günzl, *Angew. Chem.*, **72**, 219 (1960).

[24] L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1958, Chapter 3.

[25] The spectral data reported here for **3** agree well with those reported for the same compound prepared *via* ester pyrolysis of 1,2,4,5-tetra-(acetoxymethyl)-cyclohexane (ref. 17).

[26] *Cf.* A. T. Blomquist and D. T. Longone, *J. Am. Chem. Soc.*, **79**, 3916 (1957).

[27] The derived spectrum was reasonably reproducible utilizing solutions containing monomers **3** and **4** in the range of ratios 46:54 to 63:37, respectively.

toring of the heptane layer revealed the continuous loss of **3** and accumulation of **4**. These results paralleled those of the monitored dehydroiodination reaction described above. The maximum concentration of **4** occurred after a total contact time of *ca.* 10 hr. Beyond this time its concentration steadily decreased and the spectra became more complex owing to the formation of transformation products; however, the spectrum of **4** was discernible even after 70 hr. While we cannot rigorously exclude the possibility that small amounts of **4** are formed, in the dehydroiodinations, from an iodine-containing precursor, it is clear that this monomer is primarily the product of **3**.

In a related fashion the paracyclophane dimer **2** was obtained in good yield (30%) on treatment of **3** with ethanolic base (homogeneous solution). The separation of dimer **2** from other reaction products (small amounts of polymer and spiro-dimer **9a**) was facilitated by its formation of a stable 1:1 complex with silver nitrate.[28] The complex derived from monomer rearrangement reactions is identical with that prepared directly from dimer **2** and silver nitrate.

In the light of our cumulative results we considered it highly unlikely that significant amounts of **2** were derived from **3** *via* routes not at all involving **4** as an intermediary; however, we explored this possibility. Unsuccessful in our attempts to isolate pure **4**, we examined the rearrangement of mixtures of **3** and **4** utilizing "natural" heptane solutions[29] with varying monomer ratios. All such homogeneous medium rearrangements afforded significantly higher yields (to 56%) of **2** than did solutions containing **3** alone. These results coupled with the observation that **3** rapidly isomerizes to **4** in the basic medium reveal clearly the dominant role of **4** in the formation of **2**.

It should be emphasized that all of the monomer mixtures utilized for the *homogeneous* medium rearrangements described above were aliquots of the heptane layers from methanol–heptane *heterogeneous* dehydroiodinations. In each case the monomer solution represented from 60 to 70% of the starting tetraiodide **1** and contained no appreciable amounts of dimer **2** (as evidenced by infrared spectra). However, in order to ensure the validity of the conclusions drawn above, it was necessary to determine the maximum amount of dimer **2** that could be formed during the heterogeneous dehydroiodinations.

A heptane solution containing **3** and **4** in a ratio of *ca.* 2:1, respectively, and representing *ca.* 70% of the amount of starting tetraiodide, was heated over methanolic base. After a total reflux time of 70 hr. only *ca.* 5% of the amount of monomers originally present had survived. Work-up of the entire system afforded, unexpectedly, spiro-dimer **9a** as the major dimeric product (33% yield based on total amount of both monomers initially present). The yield of dimer **2** amounted to only 3%. These results were qualitatively reproducible. Both **3** and **4** are appreciably soluble in the hot methanol layer; the distribution coefficients (heptane–methanolic base at *ca.* 63°) are 3.6 for **3** and 4.0 for **4**. At the present time we cannot readily account for the virtually exclusive formation of dimer **9a** in the heterogeneous medium.

Relative Stabilities of 3 and 4.—The relative stabilities of monomers **3** and **4** in several nonbasic media were examined. Monomer **3** proved to be more stable, both to acid and heat. In all cases heptane solutions containing a ratio of **3** to **4** of *ca.* 2 to 1 were utilized.

Monomer solutions stored under nitrogen and at 5° for prolonged periods of time suffer no measurable loss of **3**. However, gradual loss of **4** and concomitant formation of a colorless flocculent precipitate does occur. As an example, a solution which had been stored for 4 months retained 100% of the original amount of **3** but only 29% of **4**. A monomer solution after refluxing (98°) for 14 hr. under a nitrogen atmosphere contained only 47% of the original amount of **3** and **4**. The ratio of monomers was markedly altered by this treatment, 33% of **3** and 94% of **4** having been consumed.

In an attempt to prepare dimer **2** *via* acid-catalyzed isomerizations of **3** and **4**, a concentrated monomer solution was added to a chloroform solution of *p*-toluenesulfonic acid monohydrate.[30] Examination of the clear and colorless solution after 5.5 hr. of refluxing revealed the loss of 50% of **3** and 95% of **4**; however, no trace of dimer **2** was found.[31] The nearly total destruction of **4** in the acidic medium suggested a simpler technique for its complete removal. Extraction of a monomer solution with concentrated hydrochloric acid afforded a residual heptane solution containing 70% of the original amount of **3** but with no detectable quantity of **4**. Such selective extraction[32] allowed the convenient and rapid preparation of heptane solutions of **3**, free from **4**, and in high yield based on tetraiodide **1** (*ca.* 30%).

The reactivity of **3** toward a variety of reagents is being examined and will be summarized in detail in a subsequent publication.

Experimental[33]

Dehydroiodination of 1,2,4,5-Tetrakis-(iodomethyl)-cyclohexane (1). Ethanolic Base.—To a solution of 69.0 g. (1.23 moles) of potassium hydroxide in 1230 ml. of anhydrous ethanol was added 48.2 g. (0.0749 mole) of tetraiodide 1.[34] The vigorously stirred suspension was refluxed under a nitrogen atmosphere for 6 hr. During this time, the tetraiodide gradually disappeared and subsequently a white, crystalline solid separated out. Addition of 800 ml. of water to the cooled reaction mixture gave a clear solution which was extracted with two 250-ml. portions and three 100-ml. portions of benzene. The combined extracts were washed with two 30-ml. portions of water and dried over anhydrous magnesium sulfate. The resulting benzene solution did not form a precipitate with maleic anhydride, indicating the absence of monomers 3 and 4; however, bromine was rapidly absorbed.

Solvent was removed from the remaining benzene solution (90% of the original volume) under diminished pressure. Distillation of the oily residue (9.5 g.) gave 1.15 g. of a colorless liquid, b.p. 57–100° (0.4 mm.), and 3.95 g. of a slightly yellow oil, b.p. 133–135° (0.2 mm.); the latter fraction solidified after cooling below room temperature. A yellow, transparent glass remained in the distillation flask.

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[28] Stable silver nitrate complexes of alicyclic polyenes are not uncommon (*cf.* A. C. Cope and F. A. Hochstein, *J. Am. Chem. Soc.*, **72**, 2515 (1950); M. Avram, E. Sliam, and C. D. Nenitzescu, *Ann.*, **636**, 184 (1960); and J. G. Traynham, *J. Org. Chem.*, **26**, 4694 (1961)); however, the argentation constants for aromatic hydrocarbons are generally quite low (*cf.* N. Ogimachi, L. J. Andrews, and R. M. Keefer, *J. Am. Chem. Soc.*, **78**, 2210 (1956), and M. A. Muhs and F. T. Weiss, *ibid.*, **84**, 4697 (1962)). The enhanced π-basicities of paracyclophanes, relative to open-chain models, have been examined utilizing tetracyanoethylene as the π-acid: D. J. Cram and R. H. Bauer, *ibid.*, **81**, 5971 (1959); L. A. Singer and D. J. Cram, *ibid.*, **85**, 1080 (1963).

[29] A portion of the heptane layer in a methanol–heptane dehydroiodination system.

[30] This reagent readily converts 3,5-dimethylenecyclohexene (ref. 9a) and 1,2,4- and 1,3,5-trimethylenecyclohexane (R. E. Benson and R. V. Lindsey, Jr., *J. Am. Chem. Soc.*, **81**, 4247 (1959)) to the corresponding aromatized isomers.

[31] In the generation of **3** *via* acetate pyrolysis (ref. 17), the pyrolysate products were carefully examined. Apparently no $C_{20}H_{24}$ hydrocarbon was detected; the acidic medium undoubtedly precluded the formation of dimer **2**.

[32] Addition of mineral acid to certain methylenecyclohexenes structurally related to **4** generates the conjugate acids as relatively stable carbonium ions: N. C. Deno, H. G. Richey, Jr., J. D. Hodge, and M. J. Wisotsky, *J. Am. Chem. Soc.*, **84**, 1498 (1962), and ref. 11.

[33] All melting points are uncorrected. The infrared spectra were obtained with a Perkin–Elmer Infracord or a Perkin–Elmer spectrophotometer, Model 21; the ultraviolet spectra with a Cary spectrophotometer, Model 11. Analyses by Spang Microanalytical Laboratory, Ann Arbor, Mich., and Schwarzkopf Microanalytical Laboratory, New York, N. Y.

[34] D. T. Longone, *J. Org. Chem.*, **28**, 1770 (1963).

Boiling *n*-pentane extracted a viscous oil (1.9 g.) from the distillation residue. Treatment of the pentane-insoluble material (1.75 g.) with 500 ml. of benzene gave a viscous solution which, after filtration, was poured into 300 ml. of *n*-pentane. The resulting flocculent precipitate was separated by centrifugation, washed three times with *n*-pentane, and dried *in vacuo* to give a white powder (0.73 g.) which exhibited a strong aliphatic ether absorption band (1102 cm.$^{-1}$) in the infrared region. Intense bands at 1498 and 889 cm.$^{-1}$ suggested the presence of 1,2,4,5-tetrasubstituted benzene rings. Elemental analysis (C, 85.07; H, 8.30; O, 6.63) gave the empirical formula $C_{17}H_{29}O$; the average molecular weight (osmometric) was 5633.

The first distillation fraction exhibited strong absorption at 259, 267, and 276 mμ (isooctane) in a pattern very similar to that of 3,6-dimethylenecyclohexene[9]; the infrared spectrum included an intense band at 1118 cm.$^{-1}$ (aliphatic ether). Its elemental analysis (C, 79.96; H, 10.18; O, 10.14) corresponded to the empirical formula $C_{21}H_{32}O_2$; the average molecular weight (osmometric) was 440.

The second distillation fraction and the solid from the pentane extract of the distillation residue had identical infrared spectra and were combined. A part of this material (3.2 g.) was recrystallized three times from methanol, affording 0.7 g. of paracyclophane **2**, m.p. 103–105°. Two subsequent crops (0.15 g., m.p. 104–106°, after recrystallization from methanol) were obtained by concentrating the combined mother liquors, taking advantage of the fact that the paracyclophane separated out on the surface of the solution in the form of slowly solidifying oil droplets; this facilitated its separation from the fast-settling crystals of the spiro-dimer **9a**. The latter compound was redissolved in the mother liquor; upon cooling, 0.2 g. of a mixture melting between 65 and 90° was obtained. Further concentration of the filtrate gave 0.12 g. of spiro-dimer **9a**, m.p. 72–75°, which on recrystallization from methanol yielded a first crop (0.05 g.) with m.p. 77–78° and a second crop (0.04 g.), m.p. 74.5–77.5°.

Another portion (0.7 g.) of the combined second distillation fraction and distillation residue extract was recrystallized twice from methanol to yield 0.1 g. of paracyclophane **2**, m.p. 103–105°. *Concentration of the filtrate from the last recrystallization gave a* second crop (0.1 g.), m.p. 104–107°. The combined mother liquors were subjected to column chromatography on alumina (Merck) using pentane as the eluting solvent. The first three eluant fractions (20 ml. each) contained no solute. From the following four fractions there was obtained 0.13 g. of spiro-dimer **9a**, m.p. 75–76°, after recrystallization from methanol. Subsequent elution of the column with 190 ml. of pentane afforded 0.20 g. of paracyclophane **2**, which after recrystallization (methanol) had m.p. 104–105°.

Attempts to separate paracyclophane **2** and spiro-dimer **9a** on a larger scale by column chromatography utilizing several types of alumina were unsuccessful. The first fractions were usually somewhat enriched in spiro-dimer **9a**, but pure products could not be obtained.

The various separation processes described above afforded a total of 1.18 g. of paracyclophane **2** and 0.25 g. of spiro-dimer **9a**; utilizing 90% of the reaction crude (see above), the yields were 13.2 and 2.8%, respectively (based on tetraiodide **1**). In addition, however, considerable amounts of a mixture of the two dimers were recovered from various mother liquors.

The paracyclophane **2** was identified by its ultraviolet and infrared spectra and by mixture m.p. determination with a sample previously described.[2]

Spectral data were most instrumental in the assignment of structure **9a** to the dimer of m.p. 77–78°. In the ultraviolet region, the compound has the following absorption maxima (cyclohexane): 226, 232, 240, 248sh, 267, 272, 274, and 282 mμ (log ϵ 4.29, 4.31, 4.32, 4.15, 2.96, 3.11, 3.06, and 3.13). The infrared spectrum (KBr) includes bands at (cm.$^{-1}$): 1642m (C=C); 1606m, 1506m, 860m (aromatic); 915sh, 906s, 875m (=CH_2). Other bands occur at 3075w, 2913s, 2855s, 1453m, 1432m, and 1381w (cm.$^{-1}$).

In addition to the n.m.r. absorptions described in the Discussion section, the compound exhibits (in carbon tetrachloride): a two-proton singlet at 2.94 τ (ArH); a four-proton overlap of multiplets in the region 7.1–7.3 τ (Ar–CH_2); and a two-proton triplet (*J* 7 c.p.s.) at 8.14 τ (Ar–C–CH_2–).

Anal. Calcd. for $C_{20}H_{24}$: C, 90.85; H, 9.15; mol. wt., 264. Found: C, 90.63; H, 9.14; osmometric mol. wt., 262.

A sample of the compound was titrated with bromine in carbon tetrachloride. One molar equivalent of bromine was absorbed rapidly; further reaction took place only very slowly and was accompanied by the evolution of hydrogen bromide. No reaction was observed when the spiro-dimer and a twofold excess of maleic anhydride were dissolved in a 2:1 mixture of *n*-heptane and benzene.

Silver Nitrate Complex of Paracyclophane 2.—Work subsequent to that described above revealed that complexation of paracyclophane **2** with silver nitrate allows the convenient removal of this dimer from mixtures also containing spiro-dimer **9a** and oxygen-containing dehydroiodination by-products. Addition of a concentrated silver nitrate solution (90% ethanol) to such a crude mixture, dissolved in a small amount of absolute ethanol, led to the immediate formation of the crystalline complex. Recrystallization of the product from 85% ethanol, with prior filtration of the hot solution through Celite to remove traces of silver, gave the pure complex in the form of white needles, m.p. (sealed capillary) 228° dec. The infrared spectrum has a strong band at 468 cm.$^{-1}$ (Ag–C stretching frequency)[35]; other strong bands occur at 1496, 1460, 1425, 1400, 1282, 1028, 923, and 708 cm.$^{-1}$; weak bands at 3070–2870, 1591, and 812 cm.$^{-1}$. An identical product was obtained in the same way directly from pure paracyclophane **2** and silver nitrate.

Anal. Calcd. for $C_{20}H_{24}\cdot AgNO_3$: C, 55.31; H, 5.57; N, 3.23. Found: C, 55.23; H, 5.71; N, 3.44.

Recovery of paracyclophane **2** was accomplished by adding a hot solution of 40.9 mg. (0.700 mmole) of sodium chloride in 15 ml. of 85% ethanol to a hot solution of 152 mg. (0.350 mmole) of silver nitrate complex in 20 ml. of the same solvent. After heating on the steam bath for *ca.* 10 min. to coagulate the precipitate of silver chloride, the mixture was filtered hot through Celite, and the filtercake carefully washed with warm 85% ethanol. The combined filtrate and washings were evaporated to dryness and the residue treated with 15 ml. of water on the steam bath. The undissolved material was filtered off, washed with water, and dried over phosphorus pentoxide at 56° and 0.2 mm. for 4 hr. to give 81.9 mg. (88.3%) of paracyclophane **2**, m.p. 106–108°. A mixture m.p. determination with an authentic sample of **2** (obtained by fractional recrystallization of the crude product from a dehydroiodination reaction) confirmed the identity of the product.

Diiodide 10 from Spiro-dimer 9a.—A carbon tetrachloride solution of a dehydroiodination crude product mixture, known to contain significant amounts of spiro-dimer **9a** (infrared), was added slowly to a solution of iodine in carbon tetrachloride. After the iodine color faded, additional iodine solution was added until decolorization ceased. Concentration of the solution at room temperature and under a stream of nitrogen led to the precipitation of light brown crystals of the diiodide **10**, which were filtered off and washed with small amounts of carbon tetrachloride. An analytical sample, m.p. 188–190°, was obtained by recrystallization from carbon tetrachloride. Product **10** has a strong absorption band (KBr) at 885 cm.$^{-1}$ (out-of-plane deformation of isolated proton on a 1,2,4,5-tetrasubstituted benzene) and a very strong band at 1148 cm.$^{-1}$; the latter is not present in the derived hydrocarbon **11** and may be characteristic of the iodomethyl groups.[36]

Anal. Calcd. for $C_{20}H_{24}I_2$: C, 46.35; H, 4.67; I, 48.98. Found: C, 46.41; H, 4.90; I, 48.66.

Reduction of 73 mg. (0.14 mmole) of diiodide **10** with 256 mg. (6.8 mmoles) of lithium aluminum hydride in 20 ml. of dry tetrahydrofuran utilizing the Soxhlet extraction technique for the addition of **10**, gave, after the usual work-up, 29 mg. (79%) of biduryl (**11**), m.p. 134–136° (after recrystallization from absolute ethanol). Product **11** was identified by mixture m.p. determination with an authentic sample of biduryl[2] and by its infrared spectrum.

Dehydroiodination of 1. Methanol–Heptane Heterogeneous Medium.—In the standard procedure, 12.8 g. (19.9 mmoles) of tetraiodide **1** and 0.08 g. of phenothiazine[37] were added to a two-phased system consisting of 300 ml. of dry *n*-heptane and a solution of 56.0 g. (1.00 mole) of potassium hydroxide in 700 ml. of anhydrous methanol. The vigorously stirred mixture was heated to 63° under a nitrogen atmosphere until the suspended tetraiodide had completely dissolved (approximately 9–11 hr.). After cooling to room temperature and separation of the two layers, the methanolic solution was extracted with three 100-ml. portions of *n*-heptane. The combined original heptane layer and heptane extracts were treated with anhydrous calcium chloride to remove small amounts of methanol. To determine the yield of monomers **3** and **4**, an aliquot (10 ml.) of the filtered heptane solution was added to a solution of 0.2 g. (2 mmoles) of maleic anhydride in 5 ml. of dry benzene. After 2 hr. the resulting white precipitate was filtered off, washed three times with benzene, and dried *in vacuo*. The combined yield of monomers **3** and **4** calculated from the amount of Diels–Alder adducts obtained varied from 62 to 63%, based on tetraiodide **1**. The composition of the Diels–Alder adduct mixture varied slightly, depending on the dehydroiodination reaction time. Quantitative infrared analysis (*vide infra*) indicated the mixture consisted on the average of 35% dianhydride **16** and 65% dianhydride **12**.

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(35) H. P. Fritz, J. F. W. McOmie, and N. Sheppard, *Tetrahedron Letters*, **26**, 35 (1960). See, however, M. Avram, *et al.*, *Tetrahedron*, **19**, 187 (1963).

(36) The strongest absorption band in the spectrum of tetraiodide **1** occurs similarly at 1196 cm.$^{-1}$.

(37) Added as polymerization inhibitor.

Additional amounts of monomers **3** and **4** representing 5 to 7% of the starting tetraiodide **1** were obtained by diluting the methanolic phase with 250 ml. of water and extracting the resulting solution with three 100-ml. portions of *n*-heptane. The total yield in six runs averaged close to 69%.

Analogous results were obtained when sodium methoxide was substituted for potassium hydroxide in the dehydroiodination reaction. The use of aqueous rather than methanolic potassium hydroxide led to the complete recovery of tetraiodide **1**, probably due to the insolubility of **1** in water. Attempts to dehydroiodinate **1** with pyridine as base (5 mmoles of tetraiodide **1**, 20 mg. of phenothiazine, and 250 ml. of dry pyridine heated to 61°) were not successful; rapid formation of a precipitate, m.p. 228–230° dec., apparently the tetrapyridinium salt of **1**, resulted (89% yield).

Dianhydrides 12 and 16. Separation of the Diels–Alder Adducts of Monomers 3 and 4.—A portion of the heptane layer (200 ml.) from a dehydroiodination reaction was added to a solution of 4.0 g. of maleic anhydride in 100 ml. of dry benzene. After 10 hr. the resulting white precipitate was filtered off and washed three times with benzene. The dried material (1.25 g.) was triturated with 100 ml. of tetrahydrofuran for 1 hr. at the reflux temperature; the mixture was filtered hot and the filter-cake washed with hot solvent to leave 0.70 g. of $\Delta^{4a(9a),10a(8a)}$-decahydroanthracene-2,3,6,7-tetracarboxylic dianhydride (**12**), which exhibits the following melting behavior[38]: shrinking between 315 and 320°; melting with slow evolution of a gas over a 10–15° range between 330 and 355° (reported[17] m.p. 389–391° dec.). Subsequent recrystallizations of the compound from acetonitrile (or alternatively 2-butanone[17]) did not noticeably improve the melting point or change the infrared spectrum. A second crop of the dianhydride **12** (0.03 g.) was obtained by reducing the tetrahydrofuran filtrate to a volume of 50 ml.

Anal. Calcd. for $C_{18}H_{16}O_6$: C, 65.85; H, 4.91; O, 29.24; neut. equiv., 82.1. Found: C, 65.51; H, 5.04; O, 29.46; neut. equiv., 83.5.

Ultraviolet spectra of **12** taken in 0.1 *N* sodium hydroxide solution or in a potassium bromide disk[39] (1.0 mg. of sample/200 mg. of KBr) show only end absorption. Strong bands in the infrared region (KBr disk) appear at 1838, 1774, and 1242 cm.$^{-1}$ (5-membered cyclic anhydride); other bands occur at 2952m, 2907m, 2845m, 2815m, 1666w, 1434m, 1347m, 1337m, 1312m, 1264sh, 1187m, 1160s, 1143s, 1052s, 974s, 946s, 889m, 785m, 733m, 705m, and 699m (cm.$^{-1}$).

The n.m.r. spectrum[13] of **12**, obtained in sodium deuteroxide–deuterium oxide, was poorly resolved and exhibited overlapping bands centered at 7.2 τ (multiplet, $-\mathrm{CH}\overset{|}{\mathrm{C}}{=}\mathrm{O}$), 7.5 τ (singlet, diallylic methylene), and 7.7 τ (multiplet, allylic methylene).

Acidification of a solution of dianhydride **12** in 0.1 *N* sodium hydroxide afforded the corresponding tetraacid, m.p. 355° dec.,[38] in quantitative yield.

Anal. Calcd. for $C_{18}H_{20}O_8$: C, 59.34; H, 5.53; O, 35.13. Found: C, 59.14; H, 5.54; O, 34.84.

The mother liquor from the second crop of **12** afforded dianhydride **16**. Addition at *ca.* 45° of *n*-pentane (75 ml.) to the tetrahydrofuran solution (50 ml.) and cooling to room temperature gave a flocculent precipitate of 7-methyltetralin-2,3-dicarboxy-6-(2,3-dicarboxypropyl) dianhydride (**16**), which was filtered off and washed three times with a 2:3 mixture of tetrahydrofuran and *n*-pentane. The vacuum-dried precipitate (0.32 g.) melted at 243–247° (sealed capillary) with slow decomposition. A second crop (0.18 g., m.p. 232–238° dec.) was obtained from the filtrate after concentration and addition of *n*-pentane. Repeated recrystallizations of the dianhydride **16** from tetrahydrofuran–*n*-pentane mixtures improved the melting point only slightly. An analytical sample free from traces of the dianhydride **12** was obtained by: dissolution of prepurified **16** (0.21 g.) in a boiling mixture of 50 ml. of tetrahydrofuran and 200 ml. of benzene; filtration to remove small amounts of insoluble material; and addition of 200 ml. of hot cyclohexane to the boiling filtrate. On slow cooling, thin needles of **16** were deposited. The crystals were separated, washed four times with a tetrahydrofuran–benzene–cyclohexane mixture (1:4:4), and dried *in vacuo*. In a sealed capillary, the purified sample has m.p. 252–256° (slow dec.); as in the case of dianhydride **12**, the melting behavior is somewhat dependent on the rate of heating.

Anal. Calcd. for $C_{18}H_{16}O_6$: C, 65.85; H, 4.91; neut. equiv., 82. Found: C, 66.05; H, 4.86; neut. equiv., 80.

The ultraviolet spectrum (0.1 *N* sodium hydroxide) has $\lambda_{\max}$ 272 and 280.5 mμ (log ε 3.12 and 3.16, respectively); a spectrum taken in a potassium bromide disk (0.4 mg. of sample/200 mg. of KBr) has strong absorption at *ca.* 230 mμ and weaker absorptions at 261, 264, 268, 273, and 278 mμ. In the infrared region, strong bands occur at 1842 (with 1858 sh), 1780, and 1229 cm.$^{-1}$ (5-membered cyclic anhydride); a medium-strong band at 1503 cm.$^{-1}$ is assigned to the aromatic ring. Other bands appear at 3037–2790w, 1623w, 1438m, 1408w, 1348w, 1321m, 1301m, 1204s, 1147m, 1067s, 1053s, 1018m, 956s, 929s, 920s, and 720m (cm.$^{-1}$).

In addition to the n.m.r. absorptions cited in the Discussion section, **16** exhibits (in sodium deuteroxide–deuterium oxide, poorly resolved spectrum): a six-proton singlet (?) at 7.00 τ ($ArCH_2-$), a three-proton multiplet at 7.23 τ, and a two-proton multiplet centered at *ca.* 7.5 τ (five α-carbonyl protons).

Attempts to prepare the free acid from dianhydride **16** by acidification of its solution in 0.1 *N* sodium hydroxide were unsuccessful; concentration of the ether extract of the resulting clear solution gave a glassy material, which analyzed incorrectly and did not melt sharply.

The availability of pure samples of the dianhydrides **12** and **16** allowed quantitative infrared analyses of mixtures of the two compounds. Owing to the insolubility of both **12** and **16** in suitable organic solvents, potassium bromide disks were utilized. An absorption band at 1503 cm.$^{-1}$, found only in the spectrum of **16** and uninfluenced by the presence of **12**, was selected for the construction of a calibration curve relating peak height with concentration of **16** in the disk. Nine samples of pure **16**, ranging in weight from 0.25 mg. to 2.36 mg. and each mixed with 300 mg. of potassium bromide, were used to construct the curve. In the analysis of mixtures of **12** and **16**, the percentage of **16** in the sample was obtained from the curve; the difference between this figure and 100% gave the percentage of **12**. Results were reproducible to *ca.* ±0.6%. Compositions obtained by this method were compared, in several cases, to those derived from quantitative ultraviolet analyses of the same mixtures, using the absorption maxima of **16** (272 and 280.5 mμ); agreement was excellent.

Degradation of Dianhydride 12 to Anthracene and Pyromellitic Acid. (A) Anthracene.—An intimate mixture of 80.0 mg. (0.244 mmole) of dianhydride **12**, 100 mg. of 5% palladium-on-charcoal, and 50 mg. of copper chromite was heated slowly to 340° and maintained at this temperature for 3 hr. Crude anthracene, m.p. 205–209°, was deposited on a cold finger as a white sublimate and identified by mixture m.p. and comparison of its infrared spectrum with an authentic sample; the yield was 18.6 mg. (43%).

(B) 1,2,3,4,5,6,7,8-Octahydroanthracene-2,3,6,7-tetracarboxylic Dianhydride (13).—A solution of 328 mg. (1.00 mmole) of dianhydride **12** and 154 mg. (1.20 mmoles) of freshly sublimed tetracyanoethylene in 270 ml. of acetonitrile was refluxed under nitrogen for 12 hr.; colorless needles of the new dianhydride **13** deposited after *ca.* 6 hr. The mixture was cooled, filtered with suction, the solid washed with acetonitrile, and subsequently dried *in vacuo* to give 270 mg. of dianhydride **13** exhibiting the following melting behavior[38]: shrinking between 320 and 330°, melting with slow evolution of a gas over a 10–20° range between 355 and 370°. Concentration of the filtrate afforded a second crop (40 mg.) and increased the total yield to 95%. Product **13** exhibits an ultraviolet spectrum (0.1 *N* sodium hydroxide) virtually identical with that of 1,2,3,4,5,6,7,8-octahydroanthracene[40] with $\lambda_{\max}$ 221(sh), 228(sh), 266, 269, 273, 277, and 283 mμ (log ε 3.65, 3.49, 2.57, 2.68, 2.86, 2.83, and 2.93). The infrared spectrum shows strong absorption at 1836, 1775, and 1242 cm.$^{-1}$ (5-membered cyclic anhydride) and a weak band at 1494 cm.$^{-1}$ (aromatic); other absorptions occur at 2961w, 2913w, 2855w, 2818w, 1445m, 1435m, 1425w, 1349m, 1338w, 1310m, 1264sh, 1196m, 1190m, 1163m, 1145m, 1073m, 1055s, 975s, 945s, 916m, 891m, 787m, 769m, 732m, and 704m (cm.$^{-1}$).

Anal. Calcd. for $C_{18}H_{14}O_6$: C, 66.25; H, 4.33. Found: C, 65.98; H, 4.41.

Acidification of a solution of dianhydride **13** in 0.1 *N* sodium hydroxide gave 1,2,3,4,5,6,7,8-octahydroanthracene-2,3,6,7-tetracarboxylic acid in 90% yield, m.p.[38] 388–392° dec.

Anal. Calcd. for $C_{18}H_{18}O_8$: C, 59.67; H, 5.01. Found: C, 59.49; H, 5.24.

(C) Pyromellitic Acid.—To a refluxing solution of 128.6 mg. (0.394 mmole) of dianhydride **13** in 15 ml. of 0.2 *N* sodium hydroxide was added, over a period of 2 hr., 1.2 g. (7.6 mmoles) of potassium permanganate. After refluxing for another 6 hr., the excess permanganate was destroyed with a few drops of methanol. The mixture was then cooled to room temperature, acidified to *ca.* pH 3 with 2 *N* sulfuric acid and reheated to reflux. A 10% potassium permanganate solution was added dropwise until the characteristic color persisted for several minutes. Solid sodium hydrogensulfite was then added to the cooled re-

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[38] The decomposition temperature (sealed capillary) of this compound varies markedly with heating time. Reproducible readings were obtained using rapid heating and introduction of the sample into a heating block at 250°.

[39] W. H. Waggoner and M. E. Chambers, *J. Org. Chem.*, **26**, 2981 (1961).

[40] "Catalog of Ultraviolet Spectral Data," American Petroleum Institute Research Project 44, National Bureau of Standards, Washington D. C., spectrum No. 261.

action mixture until the precipitate of manganese dioxide had dissolved; the pH was maintained at *ca.* 3 by addition of 2 *N* sulfuric acid. The final colorless solution was evaporated to dryness on a steam bath, the residue dried *in vacuo*, and then continuously extracted (Soxhlet) with acetone for 6 hr. Removal of solvent from the acetone solution gave crude pyromellitic acid, which on esterification[41] (12 hr.) using 1 ml. of absolute methanol, 3 ml. of 1,2-dichloroethane, and 0.15 ml. of concentrated sulfuric acid afforded 63.7 mg. (52.1% based on dianhydride **13**) of tetramethyl pyromellitate (**14**), m.p. 142–143° (after recrystallization from methanol; lit.[42] m.p. 146°). A mixture m.p. with an authentic sample was undepressed.

Degradation of Dianhydride 16 to Pyromellitic Acid.—Oxidation of 132.4 mg. (0.403 mmole) of dianhydride **16** with potassium permanganate in the same manner as described above for dianhydride **13** afforded crude pyromellitic acid which was esterified[41] (12 hr.) to give 80.1 mg. (64.0% based on dianhydride **16**) of tetramethyl pyromellitate, m.p. 142–143° (after recrystallization from methanol). A mixture m.p. with an authentic sample was undepressed.

Isolation of 1,2,4,5-Tetramethylenecyclohexane (3).—Heptane layers (from the standardized dehydroiodinations) containing monomers **3** and **4** were concentrated under reduced pressure at room temperature to *ca.* one-tenth of their original volume. The ratio of **3** to **4** in the resulting 2 to 3% solutions was *ca.* 2:1, as determined by quantitative infrared analysis of the corresponding maleic anhydride adducts (*vide supra*). These solutions were subjected, in portions of 0.5 ml., to vapor phase chromatography on a 215 × 0.9 cm. U-shaped column filled with 30% silicone oil on firebrick at a temperature of 150° (injection port at 200°, detector cell at 250°, argon flow *ca.* 150 ml./min.), using a Barber–Colman Model 10 gas chromatograph. 1,2,4,5-Tetramethylenecyclohexane (**3**), the major fraction (retention time *ca.* 10 min.), and several minor and incompletely resolved fractions with retention times of *ca.* 22 to 35 min. were collected in traps cooled with Dry Ice–acetone. The traps were removed from the instrument, quickly sealed with rubber serum caps, and weighed; a suitable solvent was then injected into the traps with a hypodermic syringe and the resulting solutions examined immediately.

Re-injection of a small portion of monomer **3** in heptane solution into the same column gave a chromatogram free from spurious fractions. When monomer **3** directly from the column or in heptane solution was treated with a benzene solution of maleic anhydride, pure dianhydride **12**, identified by comparison of its melting point and infrared spectrum with those of an authentic sample, was obtained. The following bands are present in the infrared spectrum (CCl$_4$) of **3**: 3082m, 2980sh, 2955m, 2870w, 2814w, 1802m, 1643s, 1610m, 1426vs, 1389w, 1282m, 1204w, 1175w, 1157w, 1020w, 948w, and 891vs (cm.$^{-1}$). The ultraviolet spectrum has $\lambda_{\max}^{\text{isooctane}}$ 229 mμ (log ϵ 3.98).

The chromatography fractions of higher retention times did not react with maleic anhydride. On the basis of infrared spectra (CCl$_4$), they consisted of aromatized oxygen-containing materials (bands at 1503 and 1118 cm.$^{-1}$). Monomer **4** was not at all detected in the chromatographic effluent.

Formation and Decay of Monomers 3 and 4 in the Standardized Dehydroiodination Reaction.—A dehydroiodination system consisting of 28.0 g. (0.500 mole) of potassium hydroxide dissolved in 350 ml. of absolute methanol, 6.4 g. (10 mmole) of tetraiodide **1**, 0.04 g. of phenothiazine, and 100 ml. of dry *n*-heptane was stirred vigorously at room temperature for 24 hr. Examination in the ultraviolet region of a 10-ml. aliquot of the heptane layer indicated that no reaction had occurred during this time. The mixture was then heated to 63°. Periodically, the system was cooled rapidly to room temperature, small samples were withdrawn from the heptane layer, and an equal amount of fresh heptane was added before reheating to 63°. After 9.3 hr., the suspension of tetraiodide **1** had disappeared and both phases were clear. Additional heptane samples were collected until heating was discontinued after a total of 79 hr.

The heptane samples were treated with calcium chloride to remove traces of methanol. Aliquots were then examined in the ultraviolet region, while the remainder was added to a benzene solution of maleic anhydride; quantitative infrared analysis of the resulting Diels–Alder adduct mixture provided the ratio of dianhydride **12** and **16**, thus the ratio of monomers **3** and **4**.

To calculate the total yield of **3** and **4** it was necessary to determine the distribution of both monomers between the two phases. Samples taken after 9.3 hr. from both layers of the dehydroiodination system at 63° were assayed for monomers **3** and **4** *via* Diels–Alder adducts; from these data distribution coefficients (heptane/methanolic base at 63°) of 3.6 for **3** and 4.0 for **4** were obtained, assuming that the solubility of the two monomers in methanolic base was not limited. The distribution coefficients at room temperature were the same within accuracy of the assay method.

The combined data allowed the calculation of total moles of monomers **3** and **4** in both phases of the dehydroiodination system at various times. The results of this calculation are summarized in Fig. 1. After a reaction time of 9.5 hr. a total of 7.0 mmoles of monomers **3** and **4** was present in the system, representing 70% of the amount of starting tetraiodide **1**.

Ultraviolet Spectrum of Monomer 4.—Spectra of known mixtures of monomers **3** and **4** obtained in the preceding experiment and the knowledge of the absorption spectrum of pure **3** permitted the construction of the quantitative absorption spectrum of monomer **4**. Data obtained from three different solutions with ratios of **3** to **4** varying between 46:54 and 63:37 agreed well; average values for the three absorption maxima of monomer **4** in *n*-heptane are 259, 269, and 280 mμ (log ϵ 4.35, 4.44, and 4.36, respectively).

Isomerization of Monomer 3 to 4.—Pure monomer **3** (16.9 mg., 0.128 mmole), obtained from vapor phase chromatography, was dissolved in 9.9 ml. of *n*-heptane and added to a solution of 1.8 g. (32 mmoles) of potassium hydroxide in absolute methanol. The heterogeneous system was heated with vigorous stirring to 63° under a nitrogen atmosphere. Samples of the heptane layer were withdrawn at 2-hr. intervals—after rapidly cooling the system to room temperature—and treated with calcium chloride to remove traces of methanol. Examination of the samples in the ultraviolet region revealed, after a 2-hr. reaction time, the characteristic absorption bands of monomer **4**. The concentration of **4** went through a maximum at *ca.* 10 hr. and decreased slowly thereafter. However, even after 70 hr. the spectrum of **4** could be detected underlying the spectra of transformation products.

Isomerization of Monomer 3 to Paracyclophane 2.—A solution of 15.3 mg. (0.116 mmole) of monomer **3**, obtained from vapor phase chromatography, in 1.75 ml. of dry *n*-heptane was added over 1.5 hr. to a refluxing solution of 820 mg. (14.6 mmoles) of potassium hydroxide in 5 ml. of absolute ethanol; the reaction was carried out under nitrogen. After the addition was completed, the homogeneous mixture was refluxed for another hour and then kept overnight at room temperature. Addition of 5 ml. of water to the system gave a clear solution which was extracted with four 5-ml. portions of *n*-heptane. After drying the extracts over calcium chloride, the solvent was removed under reduced pressure at room temperature. The partially crystalline residue (19.0 mg.) was dissolved in 0.8 ml. of absolute ethanol; some insoluble material was filtered off and the clear filtrate added to a solution of 25 mg. (0.15 mmole) of silver nitrate in 1.5 ml. of 90% ethanol. Precipitation of the silver nitrate complex of paracyclophane **2** occurred immediately. The mixture was filtered, the solid washed with absolute ethanol and dried *in vacuo* to give 7.6 mg. (30% yield based on monomer **3**) of the complex, which did not depress the melting point of an authentic sample obtained directly from paracyclophane **2** (*vide supra*). In a second run under similar conditions, the yield of **2** (determined *via* complexation with silver nitrate) was 27%.

Isomerization of Mixtures of 3 and 4 to Paracyclophane 2.—Aliquots of the heptane layers from standardized dehydroiodinations and containing monomers **3** and **4** in a ratio of *ca.* 2:1 (determined *via* Diels–Alder adducts), were concentrated to a small volume at room temperature and under reduced pressure. The resulting *ca.* 0.4 *M* solutions of **3** and **4**, which on the basis of infrared spectra contained no appreciable amounts of paracyclophane **2**, were added slowly to refluxing 2.95 *M* solutions of potassium hydroxide in ethanol. The reaction mixtures were worked up as described in the preceding section. Yields of paracyclophane **2**, determined *via* the silver nitrate complex, ranged from 48 to 51%, based on the total amount of both monomers initially present. The infrared spectrum of a crude reaction product prior to complexation indicated the presence of small amounts of spiro-dimer **9a** and oxygen-containing materials.

Utilizing the data in Fig. 1 it was possible to prepare heptane solutions enriched in monomer **4** from the standardized dehydroiodinations. One such solution, containing **3** and **4** in a 43:57 ratio, was heated with ethanolic potassium hydroxide in the same manner as described above. The yield of paracyclophane **2**, as the complex, was 56%.

Isomerization of Mixtures of 3 and 4 to Spiro-dimer 9a.—The heptane layer from a standardized dehydroiodination reaction and containing 3.63 mmoles of monomers **3** and **4** (representing 70.2% of starting tetraiodide **1**) in a ratio of 64:36 was reduced to a volume of 55 ml. under diminished pressure at room temperature. The concentrated solution was heated to 63° with a solution of 1.29 g. (23 mmoles) of potassium hydroxide in 175 ml. of absolute methanol and with vigorous stirring; the resulting system closely resembled that present at the end (9–10-hr. reaction time) of a standardized dehydroiodination experiment. Quantitative determination of the monomer content *via* Diels–Alder adducts showed that after 70 hr. of heating only 4.4% of the amount of monomers originally present had survived. The reaction mixture was then cooled to room temperature; after addition of 100 ml. of water, the heptane layer was separated and the methanolic layer extracted with three 50-ml. portions of heptane. The combined original heptane layer and heptane

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[41] The method of R. O. Clinton and S. C. Laskowski, *J. Am. Chem. Soc.*, **70**, 3135 (1948).

[42] H. I. X. Mager and W. Berends, *Rec. trav. chim.*, **76**, 28 (1957).

extracts were dried over calcium chloride and the solvent removed to leave an oily residue which, dissolved in 4 ml. of carbon tetrachloride, was added to a solution of 70 mg. of iodine in 10 ml. of carbon tetrachloride. After several minutes the iodine color had faded almost completely and another portion (50 mg.) of iodine in carbon tetrachloride (7 ml.) was added. The resulting slightly red-brown solution was concentrated at room temperature under a stream of nitrogen and the residue recrystallized from a small amount of carbon tetrachloride to give, in two crops, 294 mg. of diiodide **10**, m.p. 186–189°, identified by mixture m.p. with an authentic sample described above. Based on the amount of **3** and **4** consumed during the base treatment, the yield of spiro-dimer **9a**, isolated as diiodide **10**, was 33%.

The mother liquor from the recrystallization of diiodide **10** was washed with sodium thiosulfate solution and water and then evaporated to dryness. Trituration of the residue with ethanol, addition of the extracts to a solution of silver nitrate in 90% ethanol, filtration of the resulting hot mixture to remove silver iodide, and concentration of the filtrate gave 16.8 mg. of silver nitrate complex of paracyclophane **2** (3.3% yield based on the amount of monomers consumed).

Thermal Stabilities of Monomers 3 and 4.—A 0.02 *M* heptane solution of monomers **3** and **4** in a ratio of 64:36 was stored at 5° under nitrogen; the solution became cloudy after *ca.* 7 days as the formation of a colorless flocculent precipitate began. Quantitative determination of the monomer contents *via* Diels–Alder adducts showed that after 4 months 100% of the original amount of **3** but only 29% of **4** remained.

Refluxing a 0.024 *M* heptane solution of monomers **3** and **4** (ratio *ca.* 2:1) led to the recovery of 47% of the original amount; no precipitate was formed. Analysis of the solution after heating revealed that 33% of **3** and 94% of **4** had been consumed.

Attempted Acid-Catalyzed Isomerization of 3 and 4.—A heptane solution of 1.0 mmole of monomers **3** and **4** (ratio 71:29) was concentrated under reduced pressure at room temperature to one-twentieth of its original volume. The concentrate (2 ml.) was added to a solution of 5 mg. of *p*-toluenesulfonic acid monohydrate in 10 ml. of chloroform. After refluxing under a nitrogen atmosphere for 5.5 hr., the clear and colorless solution was washed with 5% sodium bicarbonate solution and water, dried over anhydrous magnesium sulfate, and concentrated. The oily residue was dissolved in 50 ml. of *n*-heptane and added to a solution of 1.0 g. of maleic anhydride in 25 ml. of benzene to give 125 mg. of Diels-Alder adducts, equivalent to a recovery of 37% of the original amount of monomers. Quantitative infrared analysis of the adducts revealed the loss of 50% of **3** and 95% of **4**.

The mother liquor from the preparation of the Diels-Alder adducts was evaporated to dryness, the methanol extract of the residue diluted with water and extracted with heptane. The solvent was removed from the heptane solution, the residue dissolved in ethanol, and the resulting solution added to silver nitrate in 90% ethanol; the mixture remained clear, indicating the absence of paracyclophane **2**.

An aliquot (20 ml.) of the heptane layer from a dehydroiodination experiment and containing 0.37 mmole of monomers **3** and **4** (representing 70% of starting tetraiodide **1**) in a ratio of 71:29 was extracted with three 20-ml. portions of concentrated hydrochloric acid. The heptane layer was washed with water and dried over anhydrous magnesium sulfate. Examination of the Diels–Alder adduct from this solution revealed the complete destruction of monomer **4** in the acidic medium; however, 70% of the original amount of **3** was present. In the two-step procedure—dehydroiodination and acid treatment—a solution of monomer **3** free from **4** was obtained in 35% yield based on starting tetraiodide **1**.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, FLORIDA STATE UNIVERSITY, TALLAHASSEE, FLA.]

The Synthesis and Decomposition of *o*-Iodosophenylacetic Acid[1]

BY J. E. LEFFLER, L. K. DYALL, AND P. W. INWARD

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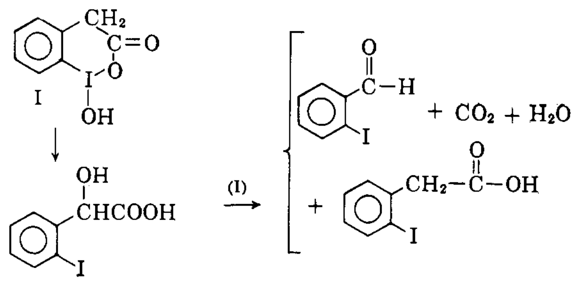
o-Iodosophenylacetic acid, a cyclic derivative of trivalent iodine, is stable at room temperature but decomposes in solution at 80–100°. *o*-Iodomandelic acid is an intermediate in the decomposition; in acid or neutral solution it is rapidly oxidized by the starting material to *o*-iodobenzaldehyde. The initial attack on the active methylene group is catalyzed by protons and by a phosphate buffer component. In sulfate–bisulfate buffers there is a kinetic term corresponding to proton catalysis and a term apparently corresponding to a complex pre-equilibrium involving bisulfate. The latter term is of the form $[H^+][SO_4^{-2}]^{1/2}$.

Introduction

The decomposition of *o*-iodobenzoyl[2,3] and *β*-iodopropionyl[4] peroxides is accelerated by a concerted attack of the iodo group on an oxygen atom of the cleaving peroxide bond. No similar effect is observed in the decomposition of *o*-iodophenylacetyl peroxide.[5] In order to rule out the possibility that the *six-membered* iodine heterocycle required in the latter reaction might be of prohibitively high energy, we undertook the synthesis of compound I. Compound I proved to decompose only at much higher temperatures than *o*-iodophenylacetyl peroxide and to give quite different products.

The kinetics and mechanism of the decomposition of I are unusual in some respects. Although the reaction at first appears to be a straightforward acid- and base-catalyzed hydroxylation of the active methylene group, the expression for the pseudo-first-order rate constant in sulfate–bisulfate buffers contains a term of the form $[H^+][SO_4^{-2}]^{1/2}$, or its equivalent $[H_2SO_4]^{1/2}$.[6]



Reaction Products.—The decomposition of *o*-iodosophenylacetic acid[7] (I) in water at 100° gives *o*-iodobenzaldehyde and *o*-iodophenylacetic acid. In 0.1 *M* sodium carbonate solution the major product is *o*-iodomandelic acid. In acidic or neutral aqueous solutions *o*-iodomandelic acid reacts rapidly with *o*-iodosophenylacetic acid to give *o*-iodobenzaldehyde and

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(1) This research was part of an investigation into the decomposition mechanisms of trivalent iodine compounds. It was supported by a grant from the National Science Foundation.

(2) J. E. Leffler, R. D. Faulkner, and C. C. Petropoulos, *J. Am. Chem. Soc.*, **80**, 5435 (1958).

(3) W. Honsberg and J. E. Leffler, *J. Org. Chem.*, **26**, 733 (1961).

(4) J. E. Leffler and J. S. West, *ibid.*, **27**, 4191 (1962).

(5) J. E. Leffler and A. F. Wilson, *ibid.*, **25**, 424 (1960).

(6) A kinetic term proportional to $[H_2SeO_3]^{1/2}$ has been noted in the selenious acid oxidation of 1,2-dibenzoylethane in acetic acid: J. P. Schaefer, *J. Am. Chem. Soc.*, **84**, 713 (1962).

(7) This substance, like *o*-iodosobenzoic acid, exists in the cyclic form. It has a K_A of 5.1×10^{-7} in water at 95°, ionic strength 0.096. In contrast, K_A for *o*-iodophenylacetic acid under the same conditions is 1.23×10^{-4}.