Anal. Calcd. for $C_{13}H_{18}O$: C, 82.05; H, 9.54. Found: C, 82.27; H, 9.50.

The shoulder was collected and identified as 2,2-dimethyl-6-phenylpyran (mixed with the furan) on the basis of analysis (C, 82.31; H, 9.58) and infrared spectrum.

β-Phenylethylmethylcarbinyl Hypochlorite.—Products of a decomposition in CCl_4 were separated as above. Acetone and β-phenylethyl chloride were collected and identified. The only other product was a small amount of the parent carbinol.

Methylpropylbutylcarbinyl Hypochlorite.—Products were separated on a DEGS column at 60–230°. Propyl chloride, butyl chloride, 2-pentanone and 2-hexanone were collected and identified by comparison with authentic samples. The chloroalcohols were cyclized and the furans collected separately. The 2,5-dimethyl-2-propyltetrahydrofuran, b.p. 146–147°, $n^{25}D$ 1.4197, was identified by spectra and analysis; infrared: strong ether band at 9.4 μ; n.m.r.: multiplet at 8.58 τ and at 6.11 τ, ratio of areas 17:1.

Anal. Calcd. for $C_9H_{18}O$: C, 76.00; H, 12.65. Found: C, 76.12; H, 12.61.

The 2-methyl-2-butyltetrahydrofuran, b.p. 148–149°, was identified similarly, the n.m.r. results providing the basis for distinguishing between the two; infrared: strong ether band at 9.3 μ; n.m.r.: multiplet at 8.57 τ, triplet at 6.46 τ, ratio of areas 8:1.

Anal. Found: C, 75.65; H, 12.56.

Methylbutylisopentylcarbinyl Hypochlorite.—Products were separated as above. Butyl chloride, isopentyl chloride, 2-hexanone and 5-methyl-2-hexanone were collected and identified. Base treatment of the reaction mixture gave three new products which were separated and collected: 2,5-dimethyl-2-isopentyltetrahydrofuran from the 2,5-dimethyl-8-chloro-5-nonanol present, and two olefins, 2,5-dimethyl-2-nonene-5-ol and 2,5-dimethyl-1-nonene-5-ol (in a ratio of 4.5:1), from the 2,5-dimethyl-2-chloro-5-nonanol present. All were identified by spectra and analysis.

2,5-Dimethyl-2-isopentyltetrahydrofuran: infrared strong ether band at 9.2 μ; n.m.r.: multiplets at 8.88, 8.15 and a multiplet at 5.98 τ ratio of areas 12:9:1. *Anal.* Calcd. for $C_{11}H_{22}O$: C, 77.58; H, 13.02. Found: C, 77.23; H, 12.97.

2,5-Dimethyl-2-nonene-5-ol: decolorized Br_2 in CCl_4 instantly; infrared: hydroxyl at 2.9 μ, olefin at 10.4 μ; n.m.r.: singlet at 6.97 τ, triplet at 4.87 τ, ratio of areas *ca.* 1:1. *Anal.* Calcd. for $C_{11}H_{22}O$: C, 77.58; H, 13.02. Found: C, 77.14; H, 12.93.

2,5-Dimethyl-1-nonene-5-ol: decolorized Br_2 in CCl_4 instantly; infrared: hydroxyl at 2.9 μ, 1-olefin at 10.1 and 10.75 μ; n.m.r.: singlets at 6.94 and 5.42 τ, ratio 1:2.

1-Butylcyclopentyl Hypochlorite.—Products were separated on a Carbowax column at 60–210°. The 1-chloro-5-nonanone was collected and identified by infrared spectrum (carbonyl at 5.85 μ) and analysis.

Anal. Calcd. for $C_9H_{17}ClO$: C, 61.18; H, 9.70; Cl, 20.07. Found: C, 61.54; H, 9.63; Cl, 19.98.

The 1-(3-chlorobutyl)-cyclopentanol was cyclized to 2-methyl-1-oxaspiro-[4.4]-nonane, b.p. 179–180°, $n^{25}D$ 1.4524; infrared: strong ether band at 9.2 μ; n.m.r.: doublet and multiplet at 8.87 and 8.42 τ, multiplet at 6.13 τ, ratio *ca.* 15:1.

Anal. Calcd. for $C_9H_{16}O$: C, 77.16; H, 11.42. Found: C, 77.23; H, 11.36.

1-Butylcyclohexyl Hypochlorite.—Products were separated as above. 10-Chloro-5-dacanone was collected and identified by infrared spectrum (carbonyl at 5.87 μ) and analysis.

Anal. Calcd. for $C_{10}H_{19}ClO$: C, 62.98; H, 10.0; Cl, 18.59. Found: C, 62.42; H, 9.97; Cl, 18.06.

The 1-(3-chlorobutyl)-cyclohexanol was cyclized to 2-methyl-1-oxaspiro-4.5-decane, b.p. 186–187°, $n^{25}D$ 1.4555; infrared: strong ether band at 9.2 μ; n.m.r.: doublet and multiplet at 8.88 and 8.44 τ, multiplet at 6.07 τ, ratio of areas 17:1.

***n*-Butyl Hypochlorite.**—Products were separated on a DEGS column at 62–210°. Butyraldehyde, 1-butanol, butyl butyrate, butyryl chloride and 4-chloro-1-butanol were collected and compared with authentic materials.

***n*-Pentyl Hypochlorite.**—Products were separated as above. Valeraldehyde, *n*-pentyl valerate and 1-pentanol were collected and compared with authentic samples. 4-Chloro-1-pentanol was cyclized to 2-methyltetrahydrofuran, collected (b.p. 80–81°, $n^{25}D$ 1.4044) and compared with authentic material.

2-Hexyl Hypochlorite.—Products were separated as above. The 2-hexanol and 2-hexanone were collected and identified. The 5-chloro-2-hexanol was cyclized to 2,5-dimethyltetrahydrofuran (b.p. 92–93°, $n^{25}D$ 1.4019) and compared with a known sample.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, THE OHIO STATE UNIVERSITY, COLUMBUS, O., AND THE CENTRAL RESEARCH DEPARTMENT, MINNESOTA MINING AND MANUFACTURING CO., ST. PAUL, MINN.]

Halogenation, Dehydrohalogenation and Dehalogenation of Stilbene Photo-dimers (1,2,3,4-Tetraphenylcyclobutanes)

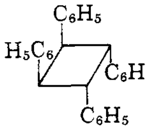
BY HAROLD SHECHTER, WILLIAM J. LINK[1] AND GEORGE V. D. TIERS[2]

RECEIVED DECEMBER 11, 1962

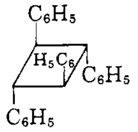
Photo-dimerization of *trans*-stilbene in benzene yields 1,*trans*-2,*trans*-3,*cis*-4-tetraphenylcyclobutane (I) and 1,*trans*-2,*cis*-3,*trans*-4-tetraphenylcyclobutane (II). Reactions of I with N-bromosuccinimide and II with sulfuryl chloride give 1,2,3,4-tetraphenyl-1,3-butadiene (IX). Photo-dimer II is resistant to N-bromosuccinimide. Chlorination of I with sulfuryl chloride produces 1-chloro-1,*trans*-2,*cis*-3,*trans*-4-tetraphenylcyclobutane (VII); reactions of VII with alumina or potassium *t*-butoxide give IX. Photochemical chlorination (2 equiv.) of I results in 1,*trans*-2-dichloro-1,*trans*,2,*cis*-3,*trans*-4-tetraphenylcyclobutane (X). Reactions of X with zinc, phenyllithium, phenylsodium and lithium N,N-diethylamide, respectively, give IX. Chlorination of I, II and IX and subsequent chromatography of the product on alumina yield 3,6-diphenyl-1,2,4,5-dibenzopentalene (XVIII). The stereochemistries of I, II, VII and X were investigated by n.m.r. methods.

In order to obtain information which may contribute to the synthesis of a stabilized cyclobutadiene[3] and/or its possible pseudoaromatic ionic derivatives, the halogenation, dehydrohalogenation and dehalogenation of two photo-dimers of stilbene (isomeric 1,2,3,4-tetraphenylcyclobutanes) have been investigated.

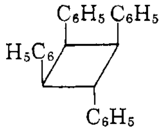
There are four possible isomeric 1,2,3,4-tetraphenylcyclobutanes (I–IV); what are believed to be two of the isomers have been reported previously. Isomer I, 1,*trans*-2,*trans*-3,*cis*-4-tetraphenylcyclobutane, has been obtained by solar (2 years[4a]; 3 days[4b]; no yields were reported) or ultraviolet[4c] (8 days, 7% yield) irradiation of *trans*-stilbene in benzene. The gross structure of the photo-dimer was based on its chemical properties;



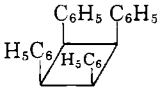
I



II



III



IV

---

[1] (a) Abstracted in part from the Ph.D. dissertation of W. J. Link, The Ohio State University, Columbus, O., March, 1960. (b) This research was supported as indicated: Allied Chemical Corporation Fellow, 1957–1958; General Electric Company Fellow, 1958–1959; National Science Foundation Summer Teaching Fellow, E. I. du Pont Research Fellow, Petroleum Research Fund Fellow 454-A (American Chemical Society) and National Science Foundation Postdoctoral Fellow, 1959–1960.

[2] Central Research Department, Minnesota Mining and Manufacturing Co., 2301 Hudson Rd., St. Paul 19, Minn.

[3] Tetraphenylcyclobutadiene derivatives have been reported by (a) W. Hubel, *et al.*, *J. Inorg. Nucl. Chem.*, **9**, 204 (1959); (b) H. H. Freedman, *J. Am. Chem. Soc.*, **83**, 2194, 2195 (1961); (c) H. H. Freedman, *J. Org. Chem.*, **27**, 2298 (1962); and (d) H. H. Freedman and A. M. Frantz, Jr., Abstr. of 141st Natl. Meeting of the American Chemical Society, 1962, p. 26-O.

[4] (a) G. Ciamician and P. Silber, *Ber.*, **35**, 4128 (1902); (b) H. Stobbe, *ibid.*, **47**, 2701 (1914); (c) M. Pailer and J. Muller, *Monatsh.*, **79**, 615 (1948).

its stereochemistry was determined by crystallographic methods.[5]

An additional source of I and a possible second isomer is based on solar irradiation of aqueous *trans*-4,4′-diamidinostilbene bis-2-hydroxyethanesulfonate to give 1,2,3,4-tetrakis-(4-amidinophenyl)-cyclobutane (photostilbamidine).[6] Photostilbamidine was hydrolyzed to its corresponding tetracarboxylic acid and then decarboxylated to I and to trace amounts of a second isomer, isodistilbene, m.p. 149°.[6] The analyses and molecular weights of I and isodistilbene were similar.[6] There were no chemical nor spectral properties nor a structure initially reported for isodistilbene[6]; a tentative structure, II, was subsequently proposed on the basis of preliminary crystallographic data.[5,7]

In the present study it has been found that ultraviolet photodimerization of *trans*-stilbene in benzene serves as a preparative source ($>15\%$ conversion in 2 months) of I. A second isomer was also obtained, m.p. 149° (2–5% conversion), which corresponds in properties to that reported for isodistilbene.[6] On the basis of present ultraviolet data (I, $\lambda_{\max}$ (ethanol) 261, log ϵ 2.98; isodistilbene, $\lambda_{\max}$ (ethanol) 261, log ϵ 3.02) the assignment of isodistilbene as a 1,2,3,4-tetraphenylcyclobutane appears correct.

A structure for isodistilbene can be assigned and that for I confirmed on the basis of the nuclear magnetic resonance spectra of their aromatic (primarily) and alicyclic protons.[8] Photo-dimer I gave n.m.r. values of 2.95 τ for aromatic protons and 5.60 τ for the α-protons. The τ-values for isodistilbene (II) are 2.79 (aromatic protons) and 6.37 (α-protons); aromatic protons for alkylbenzenes generally exhibit resonance at $\sim$2.7–2.8 τ. These data indicate that the structure of I is correct and in agreement with that found by X-ray analysis. Structure II, 1,*trans*-2,*cis*-3,*trans*-4-tetraphenylcyclobutane, is indicated for isodistilbene; structures III and IV are excluded because they contain *cis vicinal* phenyl rings and thus their aromatic proton resonance spectra should be higher than *ca.* 2.8 τ.

A study was initiated of homolytic substitution of the cyclobutane hydrogen atoms of I. The reagents investigated were N-bromosuccinimide,[9] sulfuryl chloride and chlorine. Many attempts were made to brominate I with N-bromosuccinimide. The solvents and temperatures were varied from refluxing carbon tetrachloride to methylene chloride and chloroform at 0°; initiators were benzoyl peroxide, bis-azoisobutyronitrile or a sunlamp. At the higher temperatures, the only product isolated was 1,2,3,4-tetraphenyl-1,3-butadiene (IX). Subsequent to the present work,[1a] an identical result was reported.[10] When the halogenation was effected in the present investigation under the mildest conditions, only unreacted I and the tetraphenylbutadiene IX were obtained. The infrared spectrum of the crude products from bromination and removal of solvents at low temperature gave no evidence for any substance other than initial I or IX. However, in work-up of certain of the low temperature halogenation experiments, hydrogen bromide was evolved.

It thus appears that bromination of a benzylic position of I occurs and that the intermediate bromide decomposes by elimination of hydrogen bromide to give possibly 1,2,3,4-tetraphenylcyclobutene (VIII).[11] This cyclobutene, if formed, is apparently unstable under the experimental conditions and collapses[12] to its open-chain isomer, 1,2,3,4-tetraphenyl-1,3-butadiene (IX).[11]

Photo-dimer II was resistant to N-bromosuccinimide and benzoyl peroxide in refluxing carbon tetrachloride for relatively long periods (24 hr.); II was recovered essentially quantitatively. The unreactivity of this isomer, in contrast to that of I, may arise from steric factors in that each benzylic hydrogen is shielded by *vicinal* phenyl groups.

The reactions of sulfuryl chloride, a convenient homolytic chlorination agent for benzylic hydrogens,[13] were then investigated with I and II. Photo-dimer II is slowly chlorinated by sulfuryl chloride in refluxing carbon tetrachloride when irradiated with a sunlamp (65% of II was recovered). A solid could not be obtained by various crystallization techniques; the oily product was then chromatographed over alumina and gave 1,2,3,4-tetraphenyl-1,3-butadiene (IX). The initial chlorination product presumably contained chlorotetraphenylcyclobutane (*vide infra*), and subsequent dehydrochlorination[14] and isomerization occurred on the alumina.[11]

Chlorination of I (eq. 1) by sulfuryl chloride initiated by benzoyl peroxide or ultraviolet light occurred readily in refluxing carbon tetrachloride. A monochloride was obtained (46% yield) which gave a positive test with alcoholic silver nitrate but was inert to triethylamine in refluxing ether. Upon chromatography of the monochloride on activated alumina (grade 1) or reaction with potassium *t*-butoxide in refluxing *t*-butyl alcohol (eq. 1), 1,2,3,4-tetraphenyl-1,3-butadiene (IX)[15] was obtained in excellent yields.

Two structures (VI and VII) are theoretically possible for 1-chloro-1,2,3,4-tetraphenylcyclobutane as derived from I; the two arise from the possibility of inversion or retention of the carbon atom being halogenated. In the present chlorinations of I with sulfuryl chloride only one of the two possible monochlorides was found.[16]

The stereochemistry of the 1-chloro-1,2,3,4-tetraphenylcyclobutane (VII) has been established by n.m.r. methods. The monochloride gives a complex spectrum showing a broad plateau at 2.65–2.90 τ, with strong,

---

(5) J. D. Dunitz, *Acta Cryst.*, **2**, 1 (1949).

(6) J. D. Fulton and J. D. Dunitz, *Nature*, **160**, 162 (1947); J. D. Fulton, *Brit. J. Pharmacol.*, **3**, 75 (1948).

(7) (a) Reaction of benzyl chloride and potassium amide in liquid ammonia is reported[7b] to yield a third isomeric 1,2,3,4-tetraphenylcyclobutane, m.p. 149.7°. It has been shown,[7c] however, that this product is 1,2,3,4-tetraphenyl-1-butene; (b) J. Morton, E. Flood and N. Bright, *Can. J. Chem.*, **35**, 1097 (1957); (c) T. S. Cantrell and J. L. Kice, *J. Org. Chem.*, **25**, 447 (1960).

(8) D. Curtin, H. Gruen and B. Shoulders, *Chem. Ind.* (London), 1205 (1958), have shown that the positions of aromatic proton resonance and that for hydrogen atoms alpha to the aromatic rings of *cis*- and *trans*-1,2-diphenylcyclopropanes, 1,2-diphenylcyclopentanes, stilbenes and azobenzenes can be used for assignments of the stereochemistries of these compounds. The chemical shifts for the aromatic protons for a *cis* isomer are always more positive than for the corresponding *trans* isomer. The shifts in the frequencies of hydrogens alpha to a phenyl group are analogous to those for aromatic protons; a proton *cis* to an adjacent phenyl group (the *trans* isomer) gives resonance at a higher field than when it is *trans* (in the *cis* isomer). The more positive values for the chemical shift indicate a greater degree of electronic shielding. It is expected that shielding by the π-electrons of a phenyl ring will be felt more strongly by the nuclei being magnetically probed when they are on the same (*cis*) side of a small alicyclic ring.

(9) 1,1-Difluoro-3-phenylcyclobutane (D. Knutson and M. Vogel, unpublished research; J. Roberts, *Rec. Chem. Prog.*, **17**, 95 (1956)) and 1,2-bis-(bromomethyl)-3,4-diphenylcyclobutane (A. Blomquist and Y. Meinwald, *J. Am. Chem. Soc.*, **81**, 667 (1959)) are brominated at benzylic positions by N-bromosuccinimide.

(10) W. Baker, J. W. Hilpern and J. F. W. McOmie, *J. Chem. Soc.*, 479 (1961).

(11) The over-all chemical changes other than the stereochemical assignments are similar to those of eq. 1.

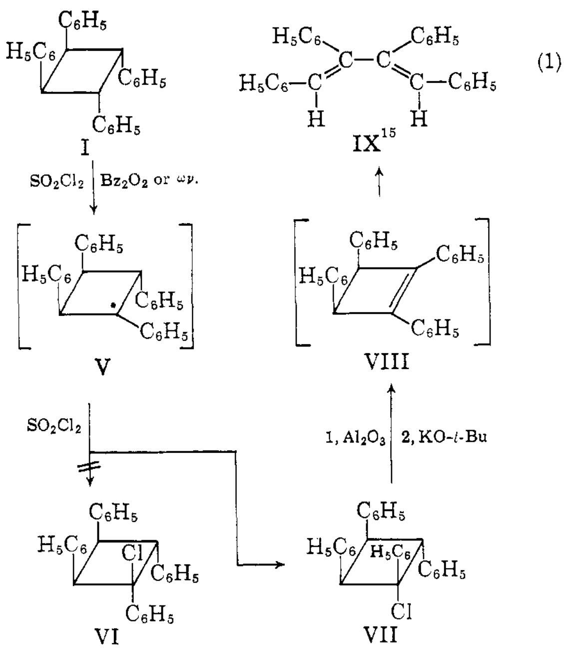
(12) Many examples of isomerization of cyclobutenes to 1,3-butadienes are known; see E. Vogel, *Ann.*, **615**, 14 (1958), and E. Vogel, *Angew. Chem.*, **72**, 4 (1960).

(13) M. Kharasch and H. C. Brown, *J. Am. Chem. Soc.*, **61**, 2142 (1939).

(14) Unsaturated hydrocarbons have been obtained previously on adsorption of hydrohalides on activated alumina: M. Zaoral, *Chem. Listy*, **47**, 1872 (1953); *Chem. Abstr.*, **49**, 966 (1955).

(15) It has been recently reported that 1,2,3,4-tetraphenyl-1,3-butadiene has the *cis,cis* configuration.[3c]

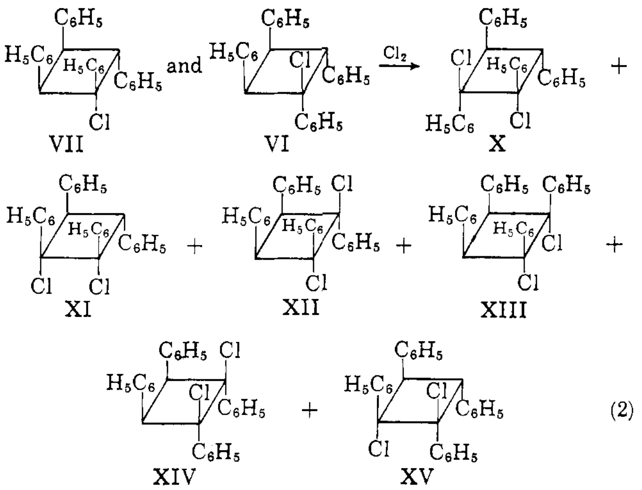
(16) These chlorinations were effected at low conversions to monochloride; the principal product from these experiments was initial I. In a large run in which extensive chlorination occurred, a small amount of an unidentified chloride was obtained which may have been the second isomer.



sharp peaks at 3.05 τ and at the very high value, 3.27 τ, for phenyl protons. The α-protons give a very broad band at *ca.* 5.1 τ. It is thus reasonably certain that an inversion has occurred, presumably at the position on which the chlorine has substituted. The high τ-value for phenyl protons is believed to result from the doubled shielding of the central one of three adjacent phenyl rings on one side of a cyclobutane ring. In reaction of I with sulfuryl chloride, the entering halogen thus prefers to attack from the bottom side of intermediate V. Since the only difference in V for entrance from above or below is a phenyl group at position 3 in the cyclobutane ring, the product isolated, 1-chloro-1,*trans*-2,*cis*-3,*trans*-4-tetraphenylcyclobutane (VII), indicates that *cis*-1,3-interaction of this phenyl group is sufficient to hinder entry from the top. The repulsive effect may be due to steric factors, to participation (though novel) of the intermediate radical with the π-electrons of a phenyl group at position 3 or to some additional effect.[17]

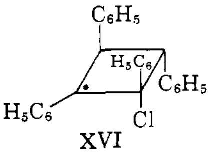
Photo-dimer I was then chlorinated photochemically with excess chlorine in refluxing carbon tetrachloride. The product isolated (>20% yield) upon chromatography over alumina was a dichloro-1,2,3,4-tetraphenylcyclobutane. On refluxing the dichloride in zinc and acetic acid, 1,2,3,4-tetraphenyl-1,3-butadiene (IX) was obtained in 70% yield. The dichloride is therefore a 1,2-dichloro-1,2,3,4-tetraphenylcyclobutane; in its dehalogenation by zinc, the presumed intermediate 1,2,3,4-tetraphenylcyclobutene is unstable with respect to its isomeric butadiene.

In the formation of the 1,2-dichloro-1,2,3,4-tetraphenylcyclobutanes derivable from I, monochlorides VI and VII are the possible reaction intermediates. There are thus six possible dichloro isomers (X–XV) derivable from VI and VII (eq. 2).



The structure proposed for the dichloride is based on n.m.r. data. The n.m.r. spectrum of the 1,2-dichloro-1,2,3,4-tetraphenylcyclobutane is fairly simple; significantly, it is less complicated than that for monochloride VII. It consists of a sharp peak at 2.74 τ and a multiplet at *ca.* 2.57 τ for two types of non-shielded aromatic protons. The sharp peak, presumably for phenyls not α-chlorinated, corresponds well with that for II (2.79 τ). The τ-values are greatly different from that of I (2.95; *cis*-1,2-diphenyls) and especially that of monochloride VII (3.27; *cis*-1,2,3-triphenyls). There is thus no indication of absorption for *cis*-1,2-diphenyl groups in the n.m.r. spectrum of the 1,2-dichloro-1,2,3,4-tetraphenylcyclobutane. The sharp peak at 4.72 τ shows that the two remaining α-protons are equivalent. It appears therefore that a total of two inversions occurred in the dichlorination of I to give a product of the isodistilbene type (II). This conclusion thus leads to structure X, 1,*trans*-2-dichloro-1,*trans*-2,*cis*-3,*trans*-4-tetraphenylcyclobutane, for the dichloride; all other possibilities have *cis*-1,2-diphenyl groups.

Several conclusions can be drawn from the stereochemistry of X. First, the intermediate monochloride *must* have had the same structure, VII, as that isolated from chlorination of I with sulfuryl chloride. Second, an unexpected entry from what appears to be the more sterically-hindered side of the cyclobutane ring in intermediate XVI is required.[18]



XVI

It is to be believed that two *cis*-phenyl rings at ring positions 2 and 4 in XVI will be more effective hindering groups than a chlorine atom at position 2 and a phenyl ring at position 3 if the cyclobutane ring is essentially planar. Perhaps the controlling factor is that the cyclobutane ring is significantly distorted, and thus there is marked shielding (or even participation) at the radical center by the phenyl group at position 3. Such shielding would require entry attack by the chlorinating agent from the opposite side of the cyclobutane ring. Repulsion or even participation of sufficient magnitude by the neighboring chlorine atom, though probably less likely, could also produce the observed stereochemical result.

Finally it is of note that whereas monochloride VII is decomposed by activated alumina, dichloride X is unaffected and may be repeatedly chromatographed over this adsorbent.

A study was made of polychlorination of I by irradiated sulfuryl chloride (1:5 mole ratio) in refluxing carbon tetrachloride. No solids were obtained on manipulation of the product with inert solvents. On

---

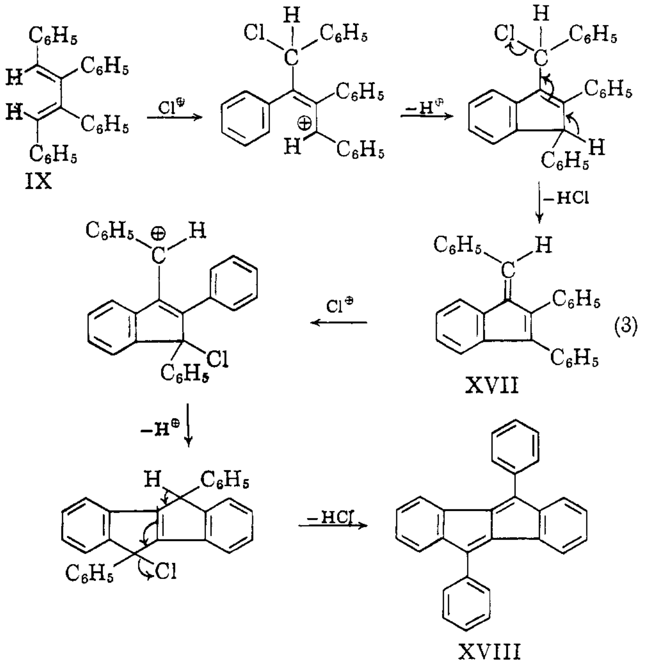
[17] (a) For VII to be formed in major amount, the transition state for reaction must be close to V. (b) The stereochemical result to give VII as the major product is in agreement with observations regarding steric control of base-catalyzed halogenation of 1,3-dinitro-2,4-diphenylcyclobutanes; D. Miller, Ph.D. dissertation, The Ohio State University, 1957. In this work, it was found that the predominant halide results from entrance of halogen at the sterically less-hindered side of the nitronate.

[18] Although all of the products of chlorination of I in this experiment could not be isolated, it is of interest in that with all of the mono- and polychlorinated derivatives possible, X is formed in at least 20% yield.

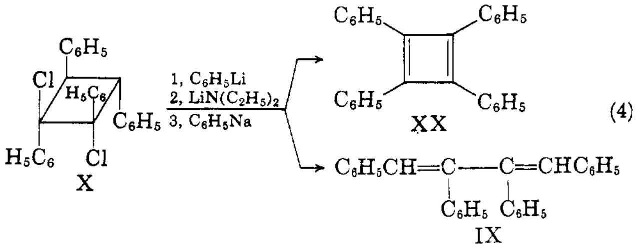
chromatographing the product on activated alumina (activity grade 1), reaction occurred rapidly to give 3,6-diphenyl-1,2,4,5-dibenzopentalene (XVIII, 37% yield; historical name: 9,12-diphenyldiphensuccindadiene-9,11[19]). The structure of XVIIII was confirmed by comparison of its mixture melting point and infrared spectrum with an authentic sample.[20] Reduction of XVIII by zinc and acetic acid gave 3,6-dihydro-3,6-diphenyl-1,2,4,5-dibenzopentalene (historical name: 9, 12-diphenyldiphensuccindene-10[21]); its ultraviolet spectrum was identical with that reported.[21]

The reactions of II with excess irradiated sulfuryl chloride and then of its halogenation product with activated alumina were investigated. Upon following a procedure identical with that for I, the pentalene XVIII was also obtained (34% yield). It was subsequently found that reaction of 1,2,3,4-tetraphenyl-1,3-butadiene (IX) with excess sulfuryl chloride and then with activated alumina also gave pentalene XVIII (28%). The conversion of IX to XVIII provides a clue to the possible paths of formation of XVIII from either I or II by reaction with sulfuryl chloride and activated alumina, respectively.

It is possible that chlorination of the cyclobutane rings of I and II, dehydrochlorination to the cyclobutenes, and ring opening to form 1,2,3,4-tetraphenyl-1,3-butadiene (IX) occurs. Then, formation of pentalene XIX may result from chlorination of the butadiene and subsequent dehydrochlorination of the intermediates. A sequence which will account for formation of the pentalene is illustrated in eq. 3. The processes postulated could occur *via* radicals or other reactive intermediates; possible ionic processes have been represented. Partial support for the general sequence proposed is available since 1-benzal-2,3-diphenylindene (XVII) has been prepared in 80% yield by reaction of bromine with 1,2,3,4-tetraphenyl-1,3-butadiene (IX) in ether or acetic acid.[22]



The synthesis of tetraphenylcyclobutadiene by elimination of two equivalents of hydrogen chloride from X was attempted at 25–30° using phenyllithium or lithium N,N-diethylamide in ether or phenylsodium in pentane as bases (eq. 4). The product isolated (eq. 4) in 93, 95 and 85% yields, respectively, was 1,2,3,4-tetraphenyl-1,3-butadiene (IX). The route by which X is converted to IX has not been established. The bases may effect (1) dehydrochlorination (2 equiv.) of X to cyclobutadiene XX which then abstracts two hydrogen atoms from neighboring molecules[23a]; (2) dehydrochlorination (1 equiv.) of X, subsequent halogen exchange with the base to yield a metalated 1,2,3,4-tetraphenylcyclobutene which isomerizes and protonates to IX; and (3) dechlorination of X to a 1,2,3,4-tetraphenylcyclobutene (VIII) which isomerizes to IX.[23b] Studies of the details of conversion of X to IX are in progress.



Experimental

Photo-dimerization of *trans*-Stilbene.—*trans*-Stilbene (136 g.) dissolved in benzene (1000 ml.) was irradiated in a quartz flask with two external ultraviolet lamps for 2 months. Part of the solvent was removed and replaced by ether and ethanol. After the mixture had been stored at room temperature for 12–14 days, the solid deposited was filtered and washed with ether. The precipitate (36.5 g., 27% conversion) consisted of a mixture of the photo-dimers I and II; *trans*-stilbene was absent. Recrystallization of the solid from ether–ethanol yielded pure I (18 g., m.p. 163°), pure II (5.0 g., m.p. 150°) and mixed dimers. The mixed dimers were retained and continually worked up to give pure I and II; ether was a fair solvent for effecting separation.

The similarity in properties of I and II makes their separation difficult; by photo-dimerization of *trans*-stilbene on relatively large scale and with experience, the method is satisfactory for preparative purposes. In recrystallization of mixtures of the photodimers from benzene–ethanol or ether–ethanol,[24] it was usually possible to obtain a fairly large first crop of pure I. The second crop was usually nearly pure, needing only one or two recrystallizations. The third crop was frequently pure II; successive crops were usually mixtures. After careful, slow crystallization, I and II can be readily distinguished by their crystalline forms. Isomer I separates as colorless prisms; II forms long, hair-fine, colorless needles. It was usually obvious when a precipitate was a mixture of I and II. *trans*-Stilbene, however, crystallizes in a form nearly identical with that of I.[25]

Reaction of I and N-Bromosuccinimide.—(a) N-Bromosuccinimide (1.1 g., 0.006 mole) was added along with a small amount of benzoyl peroxide in carbon tetrachloride (3 ml.) to photo-dimer I (2 g., 0.0055 mole) in carbon tetrachloride (30 ml.). The mixture was refluxed; additional peroxide was added after 0.5 and 1.0 hour. The reaction was followed by observing the amount of succinimide floating at the solvent surface. After 4 hours the mixture was cooled and filtered; the precipitate (succinimide) was completely soluble in water. After removal of a portion of the solvent and addition of ethanol, 1,2,3,4-tetraphenyl-1,3-butadiene (IX, 1.1 g., 56% yield) precipitated on cooling; IX was identified by its melting point (183.5–185°) and by comparison of its mixture melting point and infrared spectrum with those of an authentic sample.[22b]

(b) A solution of I (0.36 g., 0.001 mole) and N-bromosuccinimide (0.18 g., 0.001 mole) in chloroform (15 ml.) was refluxed and irradiated with a 275 watt sunlamp for 20 minutes.

---

(19) K. Brand, *Ber.*, **45**, 3071 (1912).

(20) Kindly provided by Prof. E. D. Bergmann, Tel-Aviv, Israel.

(21) (a) K. Brand and W. Muhl, *J. prakt. Chem.*, [2], **1**, 110 (1925); (b) E. Bergmann, *J. Am. Chem. Soc.*, **75**, 2761 (1953).

(22) (a) A. Orechoff, *Ber.*, **47**, 89 (1914); (b) L. Smith and H. Hoehn, *J. Am. Chem. Soc.*, **63**, 1184 (1941).

(23) (a) M. Avram, C. Nenitzescu and E. Marcis, *Ber.*, **90**, 1857 (1957), have summarized examples in which (triplet) cyclobutadienes appear to remove hydrogen atoms from their environment. (b) Phenyllithium effects dehalogenation of ethylene chlorobromide, ethylene bromide and 1,2-dibromocyclohexane: R. G. Jones and H. Gilman, "Organic Reactions," Vol. VI, John Wiley and Sons, Inc., New York, N. Y., 1951, p. 349.

(24) Distinctive, strong infrared absorption bands[1a] and melting points were used to estimate the purities of various fractions.

(25) Phenanthrene is also produced in small amounts in the photodimerizations. Frequently the crude reaction mixtures were distilled at reduced pressure under nitrogen to remove *cis*- and *trans*-stilbenes and phenanthrene (b.p. 110–170° (2 mm.)); the dark distillation residues were then fractionally crystallized.

Most of the solvent was blown off with dry air. Addition of Skellysolve F gave a precipitate which was washed with water and recrystallized from methylene chloride–Skellysolve F. The infrared spectrum of the product indicated that it was a mixture of I and IX.

(c) Irradiation of a mixture of I (0.36 g.), N-bromosuccinimide (0.18 g., 0.001 mole) and methylene chloride (15 ml.) was effected at 0° under nitrogen with a 250 watt sunlamp. Precipitation of succinimide occurred within 10 minutes. After 1 hour the mixture was washed with water and dried over sodium sulfate, and the solvent blown off with dry air. The infrared spectrum of the product corresponded completely to that of a mixture of IX and I. In a similar experiment effected in chloroform, only IX was isolated as the product.

Attempted Reaction of II and N-Bromosuccinimide.—A solution of photo-dimer II (0.36 g., 0.001 mole), N-bromosuccinimide (0.2 g., 0.0011 mole) and benzoyl peroxide in carbon tetrachloride (10 ml.) was refluxed for 8 hours. After cooling, filtering, and concentrating the mixture, addition of ethanol and cooling resulted in precipitation of initial II (0.35 g.), m.p. 150°. The infrared spectrum of the recovered II was identical with the initial material.

Similar results were obtained on repetition of this experiment and when sunlamp irradiation was used in an effort to initiate bromination.[26]

Reaction of I and Sulfuryl Chloride.—(a) A mixture of photo-dimer I (7.6 g., 0.02 mole), sulfuryl chloride (2.5 ml., 0.032 mole) and benzoyl peroxide (*ca.* 0.1 g.) in carbon tetrachloride (40 ml.) was refluxed 13 hours; additional peroxide (*ca.* 0.1 g.) was added after 4 hours. On manipulation of the mixture with Skellysolve B, I (1.4 g., 18% recovery) and the monochloride VII (3.8 g., 46% yield, 60% conversion) were obtained. Crystallization from methylene chloride–Skellysolve B gave VII as colorless prisms, m.p. 151–152° dec.

Anal. Calcd. for $C_{28}H_{23}Cl$: C, 85.15; H, 5.87; Cl, 8.98. Found: C, 85.21; H, 5.99; Cl, 9.19.

(b) Irradiation (275 watt sunlamp) of I (2.7 g., 0.0075 mole) and sulfuryl chloride (1 ml., 0.012 mole) in refluxing carbon tetrachloride (20 ml.) for 11 hours and crystallization of the products from Skellysolve B gave VII (1.05 g.) in 40% yield.

Reaction of II and Sulfuryl Chloride.—Irradiation (250 watt sunlamp) of a refluxing mixture of photo-dimer II (2.7 g., 0.0075 mole) and sulfuryl chloride (0.8 ml., 0.0099 mole) in carbon tetrachloride (15 ml.) for 11 hours, and chromatography of the concentrated product on alumina, yielded 1,2,3,4-tetraphenyl-1,3-butadiene (IX, 0.7 g., 74% yield) and initial II (1.75 g., 65% recovery).

A similar reaction for 1.25 hours resulted in 91% recovery of II.

Dehydrohalogenation of VII.—(a) Chlorotetraphenylcyclobutane VII (0.2 g., 0.0005 mole) was refluxed 2 hours in *t*-butyl alcohol (20 ml.) containing potassium *t*-butoxide (0.005 mole). The product which formed on cooling was 1,2,3,4 tetraphenyl-1,3-butadiene (IX, 0.15 g., 84% yield based on its infrared spectrum).

(b) Chromatography of VII (0.3 g., 0.0007 mole) over alumina (Woelm, activity grade I) gave IX (0.2 g., 74% yield) on elution.[27]

Reaction of I and Excess Chlorine.—Dry chlorine was bubbled (~1 bubble per second) into a refluxing irradiated (275 watt sunlamp) solution of I (1.7 g., 0.0075 mole) in carbon tetrachloride (15 ml.) for 3 hours. On removal of much of the chloroform and allowing the mixture to stand in Skellysolve B (50 ml.) at 0–5° for 4 days, dichlorotetraphenylcyclobutane X (0.6 g., 19% yield) was obtained. Concentration and chromatography of the residue yielded an unidentified product (0.2 g.). Recrystallization of X from methylene chloride–Skellysolve B yielded large white prisms, m.p. 208.5–210.5°.

Anal. Calcd. for $C_{28}H_{22}Cl_2$: C, 78.30; H, 5.16; Cl, 16.51. Found: C, 78.35; H, 5.10; Cl, 16.47.

Dehalogenation of X.—Small portions of powdered zinc were added to dichlorotetraphenylcyclobutane X (0.86 g., 0.002 mole) suspended in glacial acetic acid (35 ml.) and the mixture was refluxed for 10 hours. The mixture was filtered while hot, the zinc washed with hot acetic acid and the solution allowed to cool. The product isolated was 1,2,3,4-tetraphenyl-1,3-butadiene (IX, 0.5 g., 70% yield), m.p. 182–184°.

3,6-Diphenyl-1,2,4,5-dibenzopentalene (XVIII).—(a) A refluxing mixture of I (1.8 g., 0.005 mole), sulfuryl chloride (2 ml., 0.025 mole) and carbon tetrachloride (25 ml.) was irradiated with a sunlamp (275 watt) for 17 hours. Solid products could not be obtained on replacing the solvent by Skellysolve B and refrigerating the mixture for 10 days. The solvent was removed and the residue placed on a column of alumina (Woelm, activity grade I). On contact with the alumina, the yellow oil produced an orange-red zone accompanied by evolution of heat. On eluting the mixture slowly with Skellysolve B and Skellysolve B–ether solutions, small red crystals were formed on the columns. The product was eluted with benzene, crystallized (0.6 g., 34%) from benzene as dark red needles and from chloroform as bronze plates, and identified as 3,6-diphenyl-1,2,4,5-dibenzopentalene (XVIII), m.p. 254–256°, lit.[19] 259–260°. A mixture melting point with an authentic sample[20] was undepressed.

Reduction of XVIII (0.1 g.) by zinc (1 g.) in refluxing acetic acid (20 ml.) for 3 hours and dilution of the mixture with water gave 3,6-dihydro-3,6-diphenyl-1,2,3,4-dibenzopentalene, m.p. 281–283°, lit.[21] m.p. 285–286°. The ultraviolet absorption spectrum of the reduction product in ethanol was identical with that reported previously.

(b) Photo-dimer II (2.7 g., 0.0075 mole), sulfuryl chloride (3 ml., 0.037 mole) and carbon tetrachloride (25 ml.) were refluxed and irradiated with a 275 watt sunlamp for 23 hours. Removal of the solvent and chromatography of the product as in the previous experiment gave XVIII (1.0 g., 38% yield), m.p. 253–255°.

(c) 1,2,3,4-Tetraphenyl-1,3-butadiene (IX, 1.8 g., 0.005 mole) and sulfuryl chloride (3 ml., 0.037 mole) in carbon tetrachloride (25 ml.) were refluxed and irradiated for 22 hours. Isolation of the product after adsorption on alumina yielded XVIII (0.5 g., 28% yield), m.p. 252–254°.

Dehydrohalogenation of X.—(a) Lithium N,N-diethylamide was prepared by addition of anhydrous diethylamine (3 ml.) to phenyllithium prepared from lithium (0.3 g.) and bromobenzene (3 ml.) in ether (20 ml.) under nitrogen. Dichlorotetraphenylcyclobutane X (0.75 g., 0.00175 mole) was added to the cold solution and the mixture was stirred for 2 hours at 0° and 2 hours at 25–30°. The reaction was quenched by addition of hydrochloric acid (5%). The ether layer was removed, dried over sodium sulfate, and then evaporated in a current of dry air. The product isolated was 1,2,3,4-tetraphenyl-1,3-butadiene (IX, 0.6 g., 95% yield), m.p. 181–183°.

(b) Phenyllithium was prepared from lithium (0.3 g.) and bromobenzene (3 ml.) in ether (20 ml.). Dichlorotetraphenylcyclobutane X(0.65 g., 0.0015 mole) was added and the resulting solution was stirred 2 hours at 0° and 2 hours at room temperature. The reaction mixture was acidified with hydrochloric acid (1%); upon evaporating the ether layer, 1,2,3,4-tetraphenyl-1,3-butadiene (IX, 0.5 g., 93% yield) was obtained, m.p. 182–184°.

(c) Dichlorotetraphenylcyclobutane X (0.65 g., 0.0015 mole) was finely ground and suspended in dry pentane (20 ml.) under nitrogen in a Morton flask. A suspension of sodium phenyl in pentane (5 ml., 0.67 molar, 0.0034 mole) was added. The dark blue color of sodium phenyl disappeared after the reaction mixture had stirred 21 hours. The mixture was filtered and the precipitate washed with methylene chloride. The methylene chloride washings were added to the filtrate. The combined mixture on evaporation gave 1,2,3,4-tetraphenyl-1,3-butadiene (IX, 0.45 g., 85% yield).

N.m.r. Spectra.—A Varian V-4300-2 40,000 mc./sec. instrument was used. The n.m.r. spectra were obtained on 4.0% (w./v.) solutions of I, II and X, and on a 6.0% (w./v.) solution of VII in carbon tetrachloride; the solutions were supersaturated except in the case of I.

---

[26] Attempts to chlorinate I or II with N-chlorosuccinimide in refluxing carbon tetrachloride or chlorobenzene using a sunlamp or bis-azoisobutyronitrile as an initiator were unsuccessful.

[27] Attempted reaction of VII (0.2 g.) and triethylamine (0.2 ml.) in refluxing ether for 19 hours resulted in quantitative recovery of initial material.