acetic anhydride was allowed to stand at room temperature overnight. After addition of 0.21 g. (2.5 mmol.) of sodium acetate the solvents were removed *in vacuo*. The residue was collected in ether and the ether was filtered and evaporated. The residual oil crystallized from acetone at −80°; m.p. 50–56° (0.30 g., 57%). After crystallization from methanol VIII melted at 71–74°. Further crystallization from the same solvent gave a sample melting at 74.5–75.5°.

Anal. Calcd. for $C_{29}H_{48}O_2$: C, 81.25; H, 11.29. Found: C, 80.98; H, 11.31.

The test for unsaturation with tetranitromethane was positive. When the diols VII was allowed to stand in pyridine–acetic anhydride overnight, only unchanged VII was recovered.

Cyclic sulfite ester IX *of* VIIa. A solution of 1.20 g. of diol VII in 45 ml. of benzene with 1 ml. of thionyl chloride and 3 drops of pyridine was allowed to stand 2 hr. at room temperature. Removal of the solvents *in vacuo* gave a dark brown tar. From an ethanol extract of the tar a pale yellow oil was obtained which was chromatographed on 50 g. of silica. The benzene eluate weighed 0.130 g. and melted at 136–139°. Several crystallizations from methanol-acetone and finally from acetone gave a sample of IX melting at 139–141.5°.

Anal. Calcd. for $C_{27}H_{46}O_3S$: C, 71.95; H, 10.29. Found: C, 72.42; H, 10.17.

Treatment of IX with alcoholic potassium hydroxide regenerated the diol VIIa.

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Structure of a Supposed Tetraphenylcyclobutane

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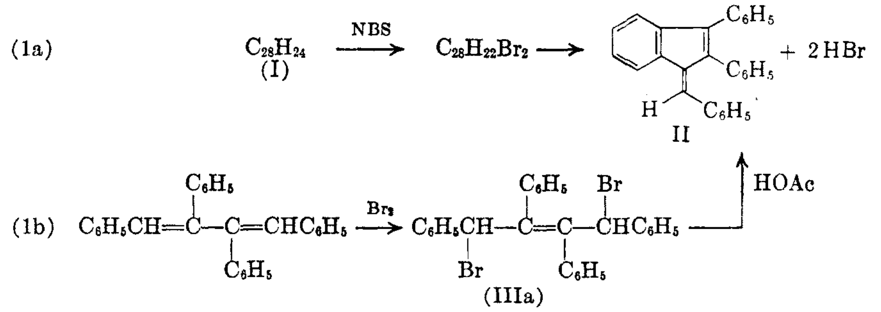
Recently Morton, Flood, and Bright[1] reported the isolation of a hydrocarbon $C_{28}H_{24}$ (I) which they believed to be a previously unreported isomer of 1,2,3,4-tetraphenylcyclobutane. We were interested in investigating the reaction of such cyclobutanes with *N*-bromosuccinimide, and by chance, we happened to choose their compound for study rather than the other previously reported isomers.[2,3]



Compound I readily underwent reaction with two moles of *N*-bromosuccinimide in refluxing carbon tetrachloride to yield a very labile dibromide which decomposed on further refluxing of the solution to afford hydrogen bromide and a brilliant yellow hydrocarbon, $C_{28}H_{20}$ (II). II was obtained in about 40% yield and was shown to be 1-benzylidene-2,3-diphenylindene by comparison with an authentic sample of this benzofulvene prepared from tetraphenylbutadiene by the usual route[4] (Eq. 1b). Although this result (Eq. 1a) is not mechanistically incompatible with the formulation of I as a tetraphenylcyclobutane, as witness Eq. 2, some question arose concerning the structure of I when we learned from Dr. Emil White[5] that the other isomers[2,3] of 1,2,3,4-tetraphenylcyclobutane do not behave in this fashion.

The reported[6] m.p. of one of the geometric isomers of 1,2,3,4-tetraphenyl-1-butene is the same as that of I, and since treatment of this tetraphenylbutene with two moles of N-bromosuccinimide might be expected to give the dibromide (III) which yields II on decomposition, we synthesized[6] a sample of this olefin for comparison with I. The synthetic sample of 1,2,3,4-tetraphenyl-1-butene was identical in every respect with I. It is thus clear that I is one of the geometric isomers of 1,2,3,4-tetraphenyl-1-butene rather than a tetraphenylcyclobutane.

Morton, Flood, and Bright[1] isolated I (15%) as a by-product of the formation of stilbene (80%) from the reaction of benzyl chloride with excess potassium amide in liquid ammonia. It seems possible that I may arise from some such side reaction as 3:

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(1) J. M. Morton, E. A. Flood, and N. F. H. Bright, *Can. J. Chem.*, **35**, 1097 (1957).

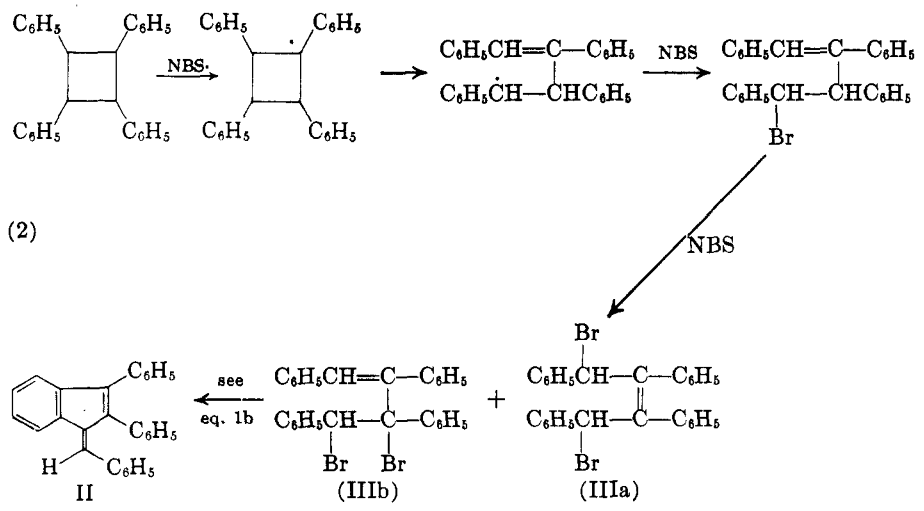
(2) M. Pailer and U. Müller, *Monatsh.*, **79**, 615 (1948).

(3) J. D. Fulton and J. D. Dunitz, *Nature*, **160**, 161 (1947).

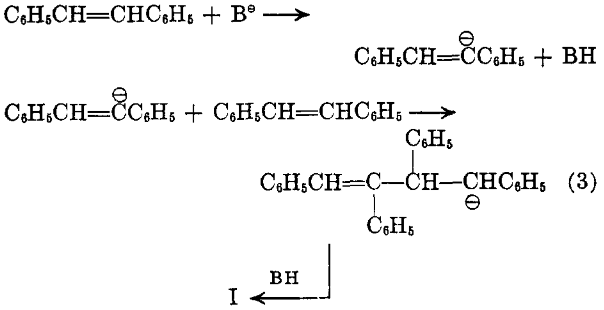
(4) A. Orechoff, *Ber.*, **47**, 89 (1914).

(5) E. H. White, private communication.

(6) E. Bergmann, D. Winter, and W. Schreiber, *Ann.*, **500**, 122 (1933).



(2)



$$C_6H_5CH{=}CHC_6H_5 + B^{\ominus} \longrightarrow C_6H_5CH{=}\overset{\ominus}{C}C_6H_5 + BH$$

$$C_6H_5CH{=}\overset{\ominus}{C}C_6H_5 + C_6H_5CH{=}CHC_6H_5 \longrightarrow C_6H_5CH{=}\underset{C_6H_5}{C}{-}\overset{C_6H_5}{C}H{-}\underset{\ominus}{C}HC_6H_5 \quad (3)$$

$$\mathrm{I} \xleftarrow{BH}$$

EXPERIMENTAL

Preparation of I. The reaction of benzyl chloride with excess potassium amide was carried out in the manner described by Morton, Flood, and Bright.[1] We found it less tedious to separate I from the majority of the stilbene formed by fractional sublimation rather than fractional crystallization as used by the Canadian authors. Sublimation of 5-g. batches of the hydrocarbon mixture at 0.5 mm. (furnace temp., 130°) removed the major portion of the stilbene. Recrystallization of the partially purified I so obtained from ethanol gave pure I, m.p. 149–150° (lit.[1] 149–150°). The ultraviolet absorption spectrum of I in isooctane showed $\lambda_{max} = 260$ mμ (log ϵ, 4.19).[7]

Reaction of I *with N-bromosuccinimide.* In 20 ml. of carbon tetrachloride was dissolved 1.50 g. of I, 1.50 g. of *N*-bromosuccinimide, and about 20 mg. of benzoyl peroxide. The solution was refluxed for 6 hr. under nitrogen. A slow stream of nitrogen was passed through the solution during the reaction, and the exit tube of the condenser was connected to a trap containing acidic aqueous silver nitrate. No hydrogen bromide was evolved during the first hour of reflux, but after about 1.5 hr. hydrogen bromide began to be evolved. At the end of 5 hr. hydrogen bromide evolution had ceased. At the end of the reflux period the solution was cooled, the succinimide removed by filtration, and the solvent removed under reduced pressure. The viscous residue was chromatographed on 80 g. of acid-washed alumina. Elution with 2:1 hexane-benzene gave 0.92 g. of orange solid. Recrystallization of this material from benzene-hexane gave 0.59 g. (40%) of II, m.p. 172–173°. An additional recrystallization gave purer II, brilliant yellow needles, m.p. 176–177°.

Anal. Calcd. for $C_{28}H_{20}$: C, 94.34; H, 5.66. Mol. wt. 356. Found: C, 94.17; H, 5.80. Mol. wt. (Signer) 360. Ultraviolet absorption spectrum in isooctane: λ_{max} 332 mμ, 286 mμ, 240 mμ (log ϵ 4.03, 4.32, 4.38).

In another experiment the solution was refluxed for only 1 hr. instead of 6. The solution was then cooled, the succinimide filtered off, and the solvent removed under reduced pressure. The semisolid residue was recrystallized from hexane-benzene, pale yellow needles, m.p. 153° (dec.). Analysis for bromine indicated this rather labile substance was a dibromide (although apparently not entirely pure since the analysis showed somewhat less than the calculated amount of bromine). Refluxing a solution of this dibromide in toluene for 1 hr. gave a quantitative conversion to II.

Preparation of 1-benzylidene-2,3-diphenylindene and comparison with II. 1,2,3,4-Tetraphenyl-1,3-butadiene, prepared by the method of Smith and Hoehn,[8] was brominated to give III, and III was subsequently cyclized to 1-benzylidene-2,3-diphenylindene by the procedures described by Orechoff.[4] After recrystallization the benzofulvene melted at 183–184°. The infrared and ultraviolet absorption spectra of this authentic sample of 1-benzylidene-2,3-diphenylindene were identical with those of II. The slightly lower melting point of II (176–177°) is apparently due to the presence of an impurity in the benzofulvene prepared by the *N*-bromosuccinimide route, since a mixture of II and authentic 1-benzylidene-2,3-diphenylindene also melted at 176–177°. This fact together with the identity of the spectra seems to establish clearly that II and 1-benzylidene-2,3-diphenylindene are indeed the same compound.

Preparation of 1,2,3,4-tetraphenyl-1-butene and comparison with I. A sample of the 150°-melting isomer of this olefin was prepared by the method described by Bergmann, Winter, and Schreiber.[6] This involves the addition of benzylmagnesium chloride to α-benzyldesoxybenzoin, followed by dehydration of the resulting carbinol. The 150°-isomer is separated from the other olefins formed by fractional crystallization. It was recrystallized from ethanol, m.p. 148–149°, mixed m.p. with I, 148–149°. The infrared spectra of I and the tetraphenylbutene were completely superimposable as were the ultraviolet absorption spectra. It is thus definite that Morton *et al.*'s tetraphenylcyclobutane (I) is in fact one of the geometric isomers of 1,2,3,4-tetraphenyl-1-butene.

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(7) The identity of the ultraviolet spectra of I as prepared by us and as reported by Morton *et al.*[1] leaves no doubt that despite our slightly different method of purification we are dealing with the same compound. The Canadian authors mentioned that the extinction coefficient for I seemed anomalously high for a tetraphenylcyclobutane. On the other hand it is perfectly reasonable for a tetraphenylbutene. The position of the λ_{max} for I (260 mμ) is undoubtedly due to the fact that coplanarity of the phenyl groups is sterically prevented in both the geometric isomers of 1,2,3,4-tetraphenyl-1-butene.

(8) L. I. Smith and H. H. Hoehn, *J. Am. Chem. Soc.*, **63**, 1184 (1941).

The α-benzyldesoxybenzoin required in the above synthesis was prepared by alkylation of desoxybenzoin with benzyl chloride in the presence of sodamide in liquid ammonia using the general procedure developed by Hauser[9] for such alkylations.

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[9] C. R. Hauser and T. M. Harris, *J. Am. Chem. Soc.*, **81**, 1161 (1959).

Diels-Alder Reactions with Dihydronaphthalenes[1]

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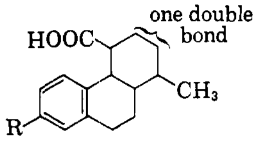
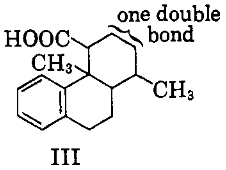
It had been shown that 1,2-dihydronaphthalene reacts with 2,4-hexadienoic acid (sorbic acid) to give a phenanthrene derivative I in 18% yield.[2] This reaction has now been extended to 7-methoxy-1,2-dihydronaphthalene and 1-methyl-3,4-dihydronaphthalene. In both cases the Diels-Alder reaction with 2,4-hexadienoic acid gave low yields of noncrystalline gums. These two products were shown to be primarily structures II and III respectively by degradation of II to 1-methyl-7-methoxyphenanthrene and III to 1-methylphenanthrene. The crude products may have been mixtures of isomers. The position of the double bond was not determined.



I. R = H
II. R = CH₃O



III

The structural isomer formed in these reactions is analogous to that formed when 2,4-hexadienoic acid reacts with styrene and its derivatives.[2] In all of these reactions, the number two carbon atom of 2,4-hexadienoic acid bonds to the α-carbon of the phenylolefin system and the number five carbon atom bonds to the β-carbon of the phenylolefin.

EXPERIMENTAL

7-Methoxy-1,2-dihydronaphthalene plus 2,4-hexadienoic acid. 7-Methoxy-1,2-dihydronaphthalene was prepared by the following sequence: β-Naphthol was hydrogenated to 1,2,3,4-tetrahydro-6-hydroxynaphthalene by the method of Stork.[3] The conversion to the methyl ether was effected with methyl sulfate.[4] Oxidation with lead tetraacetate and thermal removal of acetic acid gave 7-methoxy-1,2-dihydronaphthalene.[5]

7-Methoxy-1,2-dihydronaphthalene was treated with 2,4-hexadienoic acid in a manner similar to that used with 1,2-dihydronaphthalene.[2] Dimethylaniline was added to the extent of one-fourth the total weight of the reactants and 2% by weight of hydroquinone was also added. An atmosphere of carbon dioxide was employed. Variation in the ratio of reactants from equimolar to 1:2 and 2:1 seemed to have little effect. Raising the temperature of the reaction from 140° to 190° increased the yield of distillable product from 6 to 12.5% and lowered the yield of acidic copolymer from 35 to 12%. The runs were held at these temperatures for 100 to 150 hr.

The product II was collected as a hard, yellow gum, b.p. 150–200° (1 mm.). The neutral equivalent was 274, which agrees with 272 which is that calculated for $C_{17}H_{20}O_3$.

The carbon skeleton of the adduct was indicated by its degradation to 1-methyl-7-methoxyphenanthrene. A mixture of 0.95 g. of adduct and 0.4 g. of 10% palladium-carbon catalyst was heated for 20 min. at 300–315° in a carbon dioxide atmosphere. The crude product was dissolved in acetone and the catalyst was removed by filtration. The acetone was replaced by benzene and the solution washed with aqueous alkali. After evaporative distillation and recrystallization of the distillate from methanol, 40 mg. (5%) of white plates, m.p. 134–135°, were isolated. The melting point was not depressed when mixed with an authentic sample of 1-methyl-7-methoxyphenanthrene.[6]

1-Methyl-3,4-dihydronaphthalene plus 2,4-hexadienoic acid. 1-Methyl-3,4-dihydronaphthalene was prepared by the method of English and Cavaglieri.[7]

A mixture of 35 g. of this compound, 22.4 g. of 2,4-hexandienoic acid, 5 ml. of dimethylaniline, and 1.5 g. of hydroquinone was heated at 190° for 100 hr. in a carbon dioxide atmosphere. An ether solution of the reaction mixture was extracted with 5% potassium hydroxide solution and the aqueous extract precipitated with dilute hydrochloric acid. Evaporative distillation of the precipitated acid at 170–210° (1 mm.) gave 6.2 g. (12%) of distillate and 6.4 g. (12.5%) of acidic copolymer. The distillate was a hard yellow, acidic gum and is believed to possess structure III. The position of the double bond is uncertain.

The carbon skeleton of III was indicated by its degradation to 1-methylphenanthrene. The experimental conditions were identical with those used in the degradation of II to 1-methyl-7-methoxyphenanthrene. The yield of 1-methylphenanthrene, m.p. 117–119°, was 30%. The melting point was not depressed when mixed with an authentic sample of 1-methylphenanthrene and the identity was further checked by preparation of the picrate, m.p. 134–137°.

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[1] Grateful acknowledgment is made for the support of this research by the Bristol Laboratories Inc., Syracuse, N. Y.

[2] N. Deno, *J. Am. Chem. Soc.*, **72**, 4057 (1950).

[3] G. Stork, *J. Am. Chem. Soc.*, **69**, 576 (1947).

[4] V. C. Burnop, G. M. Elliot, and R. P. Linstead, *J. Chem. Soc.*, 727 (1940).

[5] W. S. Johnson, J. M. Anderson, and W. E. Shelberg, *J. Am. Chem. Soc.*, **66**, 218 (1944).

[6] This sample was kindly supplied by Dr. Andre S. Dreiding of the Detroit Institute for Cancer Research.

[7] J. English, Jr., and G. Cavaglieri, *J. Am. Chem. Soc.*, **65**, 1085 (1943).

Preparation of Some Bicyclic Nitriles by the Diels-Alder Reaction

MEYER SCHWARZ AND MILLARD MAIENTHAL

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As part of a program to relate the dielectric properties of some nitriles to their structures it