9,10-DIMETHYL- AND 9,10-DIPHENYL-9,10-DIHYDRO-9,10-ETHANOANTHRACENE BY FRIEDEL–CRAFTS CYCLIALKYLATIONS OF 1,4-DIARYLSUBSTITUTED-1,4-DIOLS

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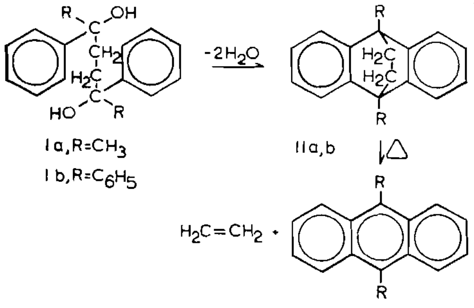
Received November 16, 1964

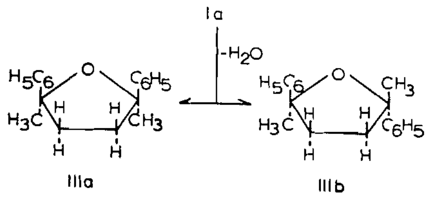
ABSTRACT

The 1,4-diols, 2,5-diphenylhexane-2,5-diol (I*a*), and 1,1,4,4-tetraphenylbutane-1,4-diol (I*b*) were found to undergo intramolecular cyclodehydrations and dehydration yielding 9,10-disubstituted-9,10-dihydro-9,10-ethanoanthracenes, 2,2,5,5-tetrasubstituted-tetrahydrofurans, and 1,1,4,4-tetrasubstituted-1,3-butadienes when treated with hydrogen fluoride or aluminium chloride. No evidence could be found for intermolecular cyclialkylations of added aromatics such as benzene, anisole, or veratrole. Nuclear magnetic resonance spectra of the products are discussed.

RESULTS AND DISCUSSION

A number of 1,4-diols are readily available from either the action of ketones on acetylenic Grignard reagents or the action of Grignard reagents on appropriate diesters. Bruson (1) reported using two such diols in experiments on the cyclialkylation of various aromatic compounds. The present investigation is concerned with the reactions which take place when the diols 2,5-diphenylhexane-2,5-diol (I*a*) and 1,1,4,4-tetraphenylbutane-1,4-diol (I*b*) are used as alkylating agents in Friedel–Crafts cyclialkylations. In particular it was desirable to determine whether these diols would cyclialkylate an added aromatic or whether they would react intramolecularly. Bruson (1) has reported that the diol (I*b*) cyclialkylated *o*-cresol to yield 5,5,8,8-tetraphenyl-3-methyl-5,6,7,8-tetrahydro-2-naphthol but this structure was based only on a carbon and hydrogen analysis.





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[1] *Recipient of a National Research Council Studentship.*

Canadian Journal of Chemistry. Volume 43 (1965)

The treatment of 2,5-diphenylhexane-2,5-diol (I*a*) with anhydrous hydrogen fluoride in the presence or absence of benzene (Table I, Nos. 1 and 2) yielded a four component mixture. The major component (63%) was found to be the new hydrocarbon, 9,10-dimethyl-9,10-dihydro-9,10-ethanoanthracene (II*a*). The assignment of this structure is based on the following evidence. The ultraviolet spectrum was characteristic of an *o*-disubstituted aromatic with bands at 2 720 Å (ϵ = 1 390), 2 650 Å (ϵ = 1 150) and a slight inflection at 2 580 – 2 590 Å. The infrared spectrum showed a strong band at 760 cm^{-1} for *o*-disubstitution. The mass spectrum of the compound II*a* showed a parent mass of 234 with a large fragment mass at 206. This fragment mass is attributed to 9,10-dimethylanthracene formed by the loss of the ethano bridge as ethylene from the parent compound. This was further substantiated by the fact that spectral peaks at masses 26, 27, and 28 were in the proper ratio for ethylene and that 9,10-dimethylanthracene was produced when the compound II*a* was heated with selenium at 275°. A similar loss of an ethano bridge has been reported by Campbell and co-workers (2).

The nuclear magnetic resonance (n.m.r.) spectrum of II*a* (see Table II) showed a symmetrical A_2B_2 multiplet centered at 2.73 p.p.m. assigned to the eight aromatic protons of the two ortho-disubstituted rings. It is of interest to note that the methyl protons absorbed on the low field side (8.04) of the methylene protons (8.34). A Stuart-Briegleb model of II*a* showed that the methyls are positioned approximately in the planes of the two aromatic rings. The methyl protons are thus deshielded by the ring current effect and resonate at lower field than normally expected. This effect is similar to that reported by LeGoff (3) for 2,3,6,7-tetraacetoxy-9,10-dimethyl-9,10-dihydro-9,10-ethanoanthracene. The formation of II*a* apparently takes place by a double intramolecular cyclodehydration of the starting diol as shown in the illustration. The remainder of the reaction mixture from hydrogen fluoride treatment of I*a* consisted of a mixture (32%) of *cis*- and *trans*-2,5-dimethyl-2,5-diphenyltetrahydrofuran (III*a*, *b*).

The reaction of the diol (I*a*) with a molar equivalent of aluminium chloride produced a mixture of 59% compound II*a* and 40% of a mixture of the two isomeric furans (III*a*, *b*) mentioned above (Table I, No. 3). On the other hand, reaction of the diol (I*a*) with a catalytic amount of aluminium chloride (Table I, No. 4) produced a mixture of III*a* and *b* (58% and 42%) which were separated by crystallization and repetitive gas–liquid chromatography (g.l.c.) to yield a solid (m.p. 75–76°) and a liquid. Both compounds showed several strong bands in the infrared at 1 000 – 1 100 cm^{-1} characteristic of the furan ethers, as well as strong bands at 705 and 770 cm^{-1} indicating monosubstituted aromatics. On this basis the components were thought to be the isomeric *cis*- and *trans*-2,5-dimethyl-2,5-diphenyltetrahydrofurans. These have been reported previously by Kotlyarevskii and co-workers (4).

The n.m.r. spectra of these compounds (Table II) confirmed their structures to be the *cis*- and *trans*-furan derivatives. The solid isomer showed a singlet at 8.48 p.p.m. assigned to the two methyl groups. The methylene protons absorbed in a well-defined A_2B_2 symmetrical multiplet* centered at 7.83 and the aromatic protons absorbed in a complex multiplet centered near 2.66. The liquid isomer showed a singlet at 8.42 for the methyls, a singlet at 7.77 for the methylenes,* and a complex multiplet centered near 2.75 assigned to the aromatic protons.

The treatment of 1,1,4,4-tetraphenylbutane-1,4-diol (I*b*) with anhydrous hydrogen fluoride in the presence or absence of benzene gave a high yield of the new hydrocarbon,

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**This difference in the methylene absorption readily distinguished the two isomers. The determination of the configuration of the isomers by n.m.r. spectroscopy is under investigation and will be reported separately.*

TABLE I

Cyclodehydration reactions

No.	Reactants (mole)	Catalyst (mole)	Solvent*	Time, h	Products	% yield
1	2,5-Diphenylhexane-2,5-diol (I*a*)(0.010)	HF (0.48)	Benzene	16	Dimethylethanoanthracene (II*a*) Dimethyldiphenyltetrahydrofurans (III*a*,*b*)	63 32
2	I*a* (0.010)	HF (0.48)	CCl_4	16	II*a* III*a*,*b*	68 —
3	I*a* (0.010)	$AlCl_3$ (0.01)	Benzene	23	II*a* III*a*,*b*	59 40
4	I*a* (0.010)	$AlCl_3$ (0.00075)	Benzene	48	III*a*,*b*	100
5	1,1,4,4-tetraphenylbutane-1,4-diol (I*b*)(0.005)	HF (0.50)	Benzene	24	Diphenylethanoanthracene (II*b*)	100
6	I*b* (0.005)	HF (0.50)	—	24	II*b*	94
7	I*b* (0.01)	$AlCl_3$ (0.01)	Benzene	24	II*b* 1,1,4,4-Tetraphenylbutadiene (IV)	14 30
8	I*b* (0.005)	$AlCl_3$ (0.00075)	Benzene	19	IV Tetraphenyltetrahydrofuran(?)	
9	I*b* (0.02)+*o*-cresol (0.09)	$AlCl_3$ (0.06)	*n*-Hexane	15	II*b* IV	70 —
10	I*b* (0.005)+veratrole (0.022)	$AlCl_3$ (0.015)	Petroleum ether	92	IV	—

*Reactions in hydrogen fluoride were carried out at room temperature; those catalyzed by $AlCl_3$, at reflux temperatures of the solvents. For other details see Experimental.

TABLE II

Nuclear magnetic resonance spectral data

Compound	Chemical shifts		Multiplicity	Relative areas	Assignments
II*a*	8.38*	(4.22)†	Singlet	3.9	2×—CH_2—
	8.04	(3.88)	Singlet	5.7	2×—CH_2
	2.73	(−1.45)	Symmetrical multiplet (A_2B_2)	8.0	Ortho-disubstitution
II*b*		(3.74)†	Singlet	4.0	2×—CH_2—
		(−1.07)	Symmetrical multiplet (A_2B_2)	7.5	Ortho-disubstitution
		(−1.72)	Complex multiplet	10	2×C_6H_5
III (m.p. 75–76°)	8.48		Singlet	6.0	2×—CH_3
	7.83		Symmetrical multiplet (A_2B_2)	4.0	2×—CH_2—
	2.66		Complex multiplet	9.7	2×C_6H_5
III (liquid)	8.42		Singlet	5.9	2×—CH_3
	7.77		Singlet	4.0	2×—CH_2
	2.75		Complex multiplet	10.1	2×C_6H_5
Tetraphenyl-1,3-butadiene IV		(−1.00)†	Singlet	2.1	2×C=C—H
		(−1.35)	Singlet	10.0	2×C_6H_5—
		(−1.54)	Singlet	10.0	2×C_6H_5—
9,10-Diphenylanthracene	2.40		Symmetrical multiplet (A_2B_2)	9‡	9,10-Substituted anthracene
	2.37		Singlet	10‡	2×C_6H_5

*τ values determined in CCl_4.
†Values in parentheses are chemical shifts relative to tetrachloroethane (τ = 5.95) and were recorded in the solvent at 146°.
‡Integrations were approximate due to overlap of bands.

9,10-diphenyl-9,10-dihydro-9,10-ethanoanthracene (II*b*) (Table I, Nos. 5 and 6). The assignment of this structure was based on the following physical and chemical evidence. The ultraviolet spectrum of II*b* gave bands at 2 710 Å (ϵ = 746), 2 642 Å (ϵ = 1 130), and 2 580 – 2 590 Å (ϵ = 1 140). The infrared spectrum showed strong bands at 745 cm^{-1} attributed to *o*-disubstitution and at 707 and 767 cm^{-1} attributed to monosubstitution. The mass spectrum indicated a parent mass at mass 358 with a large fragment mass at 330. This is consistent with the proposed structure. The mass of 330 is due to 9,10-diphenylanthracene produced by the loss of the ethano bridge from the original II*b*. Hydrocarbon II*b* was not soluble in the usual solvents for n.m.r. spectroscopy at room temperature. However, its spectrum was determined at elevated temperatures in tetrachloroethane and this spectrum (see Table II) confirmed the suggested structure.

The singlet at 3.74 (chemical shift from tetrachloroethane) was assigned to the two methylene groups. Under high resolution, the band at −1.07 was resolved into an A_2B_2-type of symmetrical multiplet which could therefore be assigned to the two ortho-disubstituted rings. The two monosubstituted rings absorbed in a complex multiplet in the region near −1.72. Further supporting evidence for this structure was obtained by the thermal decomposition of II*b* yielding 9,10-diphenylanthracene and ethylene which was identified by gas–solid chromatography. The 9,10-diphenylanthracene was identified by its ultraviolet spectrum (see Experimental) and n.m.r. spectrum. The latter showed a symmetrical A_2B_2 multiplet expected of a 9,10-disubstituted anthracene (see Table II). The phenyl protons absorbed as a singlet at 2.37 p.p.m.

The reaction of the diol (I*b*) with a molar equivalent of aluminium chloride (Table I, No. 7) yielded only 14% II*b* with a larger quantity of 1,1,4,4-tetraphenyl-1,3-butadiene (IV). The latter was identified by spectral analyses (see Table II). Reaction of I*b* with a catalytic amount of aluminium chloride yielded what was apparently a mixture of the

1,3-butadiene (IV) and 2,2,5,5-tetraphenyltetrahydrofuran (No. 8). This mixture was previously reported by Wasserman and Kloetzel (5) as a mixture with a narrow melting range in the vicinity of 160° which was difficult to separate.

The reaction of the diol (I*b*) with *o*-cresol and aluminium chloride (Table I, No. 9) yielded no phenolic reaction product. The products isolated were 70% crude compound II*b* and the 1,3-butadiene (IV). A similar reaction with veratrole (Table I, No. 10) yielded only the 1,3-butadiene (IV). The report by Bruson (1) that *o*-cresol and the diol I*b* yielded 5,5,8,8-tetraphenyl-3-methyl-5,6,7,8-tetrahydro-2-naphthol is open to question. It is most likely that the compound isolated (m.p. 330–332°) was the ethanoanthracene (II*b*) described in this paper.

It is apparent that 1,4-diaryl-1,4-diols such as I*a* and I*b* undergo intramolecular dehydrations exclusively. They fail to alkylate added aromatics under a variety of conditions. With hydrogen fluoride or molar equivalents of aluminium chloride as catalysts, the predominate reaction was a double aromatic intramolecular cyclodehydration. This provided a synthesis of the 9,10-disubstituted-9,10-dihydro-9,10-ethanoanthracenes. Because of the availability of various diols, the convenience of the cyclodehydration, and high yields obtainable, this reaction will be useful in future syntheses of such bridged hydrocarbons.

EXPERIMENTAL

Apparatus and Methods

The ultraviolet spectra were recorded on a Beckman DK-2 Ratio Recording Spectrophotometer. The infrared spectra were recorded on a Perkin–Elmer Model 137 "Infracord" spectrophotometer. Gas–liquid chromatography analyses were carried out on an F & M Model 500 Programmed Temperature Gas Chromatograph equipped with a dual column attachment. Silicone Gum Rubber on Chromosorb P was used as the column material for all high boiling liquids and solids. The mass spectrometer analyses were determined at an independent laboratory. The n.m.r. spectra were recorded on a Varian A-60 spectrometer equipped with a variable temperature probe. Melting points were determined on a Fisher-Johns melting point apparatus equipped with a microscope or a Thomas Hoover "Unimelt" capillary melting point apparatus. Reactions with anhydrous hydrogen fluoride were carried out in a 12 in. stainless steel MD Test Tube Reactor equipped with stainless steel gaskets made by Autoclave Engineers Inc. Samples of pure components for analyses were obtained by gas–liquid chromatography.

Reagents

The 2,5-diphenylhexane-2,5-diol was a gift of the Air Reduction Chemical Co. It was approximately an equal mixture of the two possible diastereoisomers and was used as such. The 1,1,4,4-tetraphenylbutane-1,4-diol (m.p. 203–205°) was prepared by the procedure of Wasserman and Kloetzel (5).

Reaction of 2,5-Diphenylhexane-2,5-diol (Ia) with Hydrogen Fluoride

(a) With Benzene as Solvent

Benzene (15 ml) and 2,5-diphenylhexane-2,5-diol (2.70 g, 0.010 mole) were placed in the reaction tube and it was cooled below 10° in an ice bath. The hydrogen fluoride (9.5 g) was added from a commercial cylinder and the tube was sealed and stirred for 16 h at room temperature. The tube was then cooled to below 10° and opened. The contents were poured onto crushed ice and the organic material extracted with petroleum ether. After the extract was washed free of acid with sodium carbonate and water, it was dried over sodium sulfate. Distillation of the solvent yielded a solid. Gas–liquid chromatography indicated a four component mixture, the respective components being 63, 18, 14, and 4% of the mixture. Chromatography of this product from petroleum ether on alumina and recrystallization of the solid fractions from ethanol yielded a crystalline solid, m.p. 126–128°. The ultraviolet spectrum gave bands at 2 720 Å (ϵ = 1 390), 2 650 Å (ϵ = 1 150), and an inflection at 2 580 – 2 590 Å. The infrared spectrum showed a strong band at 760 cm^{-1}. The mass spectrum of the compound indicated a parent mass of 234, with a large fragment mass at 206. Peaks were also observed at masses 26, 27, and 28 in the proper ratio for ethylene. The n.m.r. spectrum of this compound (II*a*) is outlined in Table II.

Anal. Calcd. for $C_{18}H_{18}$: C, 92.26 H, 7.74. Found: C, 92.08, 92.18; H, 7.72, 7.80.

(b) With Carbon Tetrachloride as Solvent

The reaction was repeated using 10 ml of carbon tetrachloride as solvent in place of benzene. The petroleum ether extract yielded 2.54 g of product which was found to be a similar mixture to that obtained in (*a*). Chromatography on alumina as above yielded a crystalline solid (68%) which was identical with that obtained above.

Thermal Decomposition of 9,10-Dimethyl-9,10-dihydro-9,10-ethanoanthracene (IIa)

Selenium (0.50 g) and compound II*a* (0.25 g) were ground together and the mixture was heated in a nitrate bath at 275° for 30 h. Crystals which sublimed were periodically returned to the flask. The cooled mixture was shaken with benzene and decolorizing carbon and then filtered. Distillation of the benzene yielded 0.20 g of solid. Chromatography from benzene on alumina and sublimation of the fractions *in vacuo* yielded a yellow crystalline solid. The ultraviolet spectrum of this gave bands at 3 980 Å (log = ϵ 3.91), 3 780 Å (log ϵ = 3.90), 3 580 Å (log ϵ = 3.64), 3 410 Å (log ϵ = 3.29), 3 260 Å (log ϵ = 2.98), 2 610 Å (log ϵ = 5.21), and 2 530 Å (log ϵ = 4.87). This was identified as 9,10-dimethylanthracene by comparison with the spectrum recorded by Jones (6) and with the tabulation of the main absorption bands which were as follows: 3 980 Å (log ϵ = 3.99), 3 780 Å (log ϵ = 4.00), 3 570 Å (log ϵ = 3.77), 3 410 Å (log ϵ = 3.43), 3 260 Å (log ϵ = 3.03), 2 600 Å (log ϵ = 5.24).

Reactions of 2,5-Diphenylhexane-2,5-diol (Ia) with Aluminium Chloride in the Presence of Benzene

(a) With a Molar Equivalent of Catalyst

Benzene (7.8 g, 0.1 mole) and the diol (I*a*) (2.70 g, 0.01 mole) were mixed and 1.33 g (0.01 mole) of aluminium chloride was added over 10 min. The reaction was vigorous with the evolution of a great deal of hydrogen chloride. Water cooling was used to moderate the reaction. After 1 h at room temperature and 22 h refluxing, the mixture was hydrolyzed on crushed ice. Extraction with ether yielded 2.07 g of a semisolid. Gas–liquid chromatography showed that 59% of the semisolid was compound II*a* while 40% of it was a mixture of the two isomeric substituted tetrahydrofurans (III*a* and *b*).

(b) With a Catalytic Amount of Catalyst. Separation of cis and trans-2,5-Dimethyl-2,5-diphenyltetrahydrofuran (IIIa and b)

Benzene (7.8 g, 0.1 mole), the diol (I*a*) (2.70 g, 0.01 mole), and aluminium chloride (0.10 g, 0.00075 mole) were mixed and refluxed for $12\frac{1}{2}$ h and let stand for 36 h at room temperature. The mixture was then hydrolyzed on ice, extracted with benzene, treated as usual to remove acid, and then freed from benzene by distillation. Gas–liquid chromatography of the residue indicated two components representing 58 and 42% of the mixture respectively and with the same retention time as the minor components obtained in the reaction described above. On standing, part of the liquid crystallized. Filtration of the crystals and recrystallization from ethanol yielded a solid, m.p. 75–76°. The major component of the residual liquid was collected as a liquid by repetitive gas–liquid chromatographic fractionation of small samples of the mixture. Both the crystals and the liquid showed several strong bands in the infrared between 1 000 and 1 100 cm^{-1} characteristic of the furan ethers. Bands at 705 and 770 cm^{-1} indicated monosubstituted aromatics. The n.m.r. spectra of the solid and the liquid are outlined in Table II.

Reactions of 1,1,4,4-Tetraphenylbutane-1,4-diol (Ib) with Hydrogen Fluoride

(a) With Benzene as Solvent

Hydrogen fluoride (10 g) was condensed in the cooled tube. The 1,1,4,4-tetraphenylbutane-1,4-diol (1.97 g, 0.005 mole) was added in small quantities and 5 ml of benzene was added dropwise. The tube was sealed and stirred for 24 h at room temperature. The tube was cooled, then opened, and the contents were poured on ice. A solid was observed that apparently would not dissolve in either benzene or chloroform. It was collected by filtration and a total of approximately 1.8 g of crude solid obtained. Sublimation under high vacuum at 220° yielded a solid, m.p. 312° (II*b*) with decomposition. The ultraviolet spectrum gave bands at 2 710 Å (ϵ = 746), 2 642 Å (ϵ = 1 130), and 2 580 – 2 590 Å (ϵ = 1 140). The infrared spectrum showed strong bands at 767 and 707 cm^{-1} attributed to monosubstitution and 745 cm^{-1} attributed to *o*-disubstitution. Mass spectral analysis indicated a parent mass of 358. There was a strong peak for a fragment mass of 330.

Anal. Calcd. for $C_{28}H_{22}$: C, 93.81; H, 6.19. Found: C, 93.91, 94.07; H, 6.08, 6.14.

(b) In the Absence of Solvent

The reaction was repeated using no solvent. After the reaction mixture had been stirred for 24 h, the tube was opened as usual. The contents of the tube was solid. This solid was added to water to remove adhering acid and was collected by filtration to yield 1.68 g (a 94% yield) of solid, m.p. 309–310° with decomposition. The ultraviolet spectrum was identical to the product from (*a*).

Thermal Decomposition of 9,10-Diphenyl-9,10-dihydro-9,10-ethanoanthracene (IIb)

The compound II*b* (0.25 g) was heated at 315° for 20 min in an atmosphere of nitrogen. Samples of the off-gas from the decomposition were analyzed by gas–solid chromatography on a silica gel column. The major component was found to be ethylene by comparison of retention time with that of an authentic sample. The residual solid was sublimed *in vacuo* to yield a crystalline solid, m.p. 252–254° (lit. (7) 9,10-diphenylanthracene, m.p. 250–252°). The ultraviolet spectrum showed bands at 3 920 Å (log ϵ = 4.14), 3 720 Å (log ϵ = 4.15), 3 540 Å (log ϵ = 3.87), 3 370 Å (log ϵ = 3.73), 2 585 Å (log ϵ = 5.27), and 2 260 Å (log ϵ = 4.48). This was essentially identical with the spectrum of 9,10-diphenylanthracene reported by Jones (6).

Anal. Calcd. for $C_{26}H_{18}$: C, 94.51; H, 5.49. Found: C, 94.51, 94.42; H, 5.67, 5.66.

Reactions of 1,1,4,4-Tetraphenylbutane-1,4-diol (Ib) with Aluminium Chloride in the Presence of Benzene

(a) With a Molar Equivalent of Catalyst

Benzene (7.80 g, 0.1 mole) and the diol (I*b*) (3.94 g, 0.01 mole) were mixed and 1.33 g (0.01 mole) of aluminium chloride was added over 10 min. After 1 h at room temperature and 23 h reflux, the mixture was hydrolyzed on ice and chloroform added. The insoluble solid which formed was collected and after recrystallization from dioxane yielded 0.51 g of II*b*.

From the chloroform-soluble material there was obtained 1.1 g of a solid, m.p. 190–204°. Two recrystallizations from benzene yielded crystals of m.p. 205–207° (hot stage) and 202.5–203.5° (capillary). The infrared spectrum (in Nujol and KBr) showed strong bands near 700 and 770 cm^{-1} attributed to monosubstituted aromatic absorption. There was no hydroxyl absorption. The ultraviolet spectrum had strong broad absorption at 2 480 Å and 3 460 Å consistent with the spectrum of 1,1,4,4-tetraphenylbutadiene (IV) illustrated in the literature (8). The n.m.r. spectrum of IV (see Table II) was also consistent with this structure. The reported melting point for IV was 202.5–203.5° (5).

(b) With a Catalytic Amount of Catalyst

A mixture of benzene (7.8 g, 0.1 mole), the diol (I*b*) (1.82 g, 0.005 mole), and aluminium chloride (0.10 g, 0.00075 mole) were stirred and refluxed for 19 h. The mixture was hydrolyzed on ice and the benzene was allowed to evaporate. The solid which separated was collected by filtration (m.p. 140–165°). Crystallization from ethanol–benzene yielded crystals of m.p. 162–165°. The ultraviolet spectrum of this solid gave broad bands at 3 420 – 3 460 Å and 2 490 – 2 500 Å characteristic of the 1,3-butadiene (IV). The infrared spectrum gave strong bands between 1 000 and 1 100 cm^{-1} indicative of ether absorption. An attempt was made to separate the mixture following the procedure of Wasserman (5) but no pure compounds were obtained.

Reaction of 1,1,4,4-Tetraphenylbutane-1,4-diol (Ib) with Aluminium Chloride

(a) In the Presence of o-Cresol

Following the procedure of Bruson (1), aluminium chloride (8.0 g, 0.06 mole) was suspended in 100 ml of *n*-hexane. The diol (I*b*) (8.0 g, 0.02 mole) and *o*-cresol (10 g, 0.09 mole) were added all at once. After refluxing for 15 h, the mixture was hydrolyzed on 200 ml of 1:4 mixture of hydrochloric acid and water. On treatment with *n*-hexane, there was obtained 5.0 g of insoluble solid which was identified as diphenylethanoanthracene (70%) by its melting point and ultraviolet spectrum. Distillation of the *n*-hexane yielded a mixture of a solid and a liquid. This was found by gas–liquid chromatography to be a mixture of unreacted *o*-cresol and a smaller amount of tetraphenylbutadiene (IV).

(b) In the Presence of Veratrole

A similar reaction was carried out with 3.10 g (0.022 mole) of veratrole, 2.00 g (0.005 mole) of the diol (I*b*), and 2.00 g (0.015 mole) of aluminium chloride. After refluxing for 92 h in 25 ml of low boiling petroleum ether, the mixture was hydrolyzed on ice and extracted with benzene. This product was found to be a mixture of the diene (IV) and veratrole with no compound II*b* or other alkylation product detectable.

ACKNOWLEDGMENTS

The authors thank Dr. A. G. McInnes of the National Research Council, Halifax, Nova Scotia, for recording the n.m.r. spectra of the dimethyl diphenyltetrahydrofurans. Financial assistance from the National Research Council is also gratefully acknowledged. The Varian A-60 n.m.r. spectrometer was purchased with funds from a National Research Council Major Equipment Grant.

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