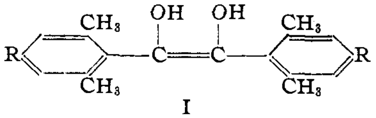
[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Enediols. VI.[1] Stilbenediols from Duril and Isoduril

BY REYNOLD C. FUSON AND S. C. KELTON, JR.

The remarkable stability of the hexamethylstilbenediols (I, R = CH_3)[2] appears to be yet another manifestation of steric hindrance. In an effort to relate this stability to structural features, a number of orienting experiments were undertaken. The most straightforward of these was to determine the influence of the number and position of the methyl groups. The synthesis of the 2,2',6,6'-tetramethylstilbenediols (I, R = H) has already been reported.[3] The present paper deals with similar enediols derived from duril and isoduril. It has been found that these diols possess the same remarkable properties which have been described for enediols derived from mesitil[2] and 2,6-xylil.[3]

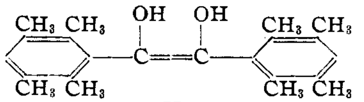


I

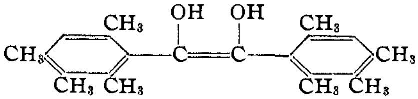
The starting materials in the synthesis of duril and isoduril were 2,3,5,6-tetramethylbenzoic acid and 2,3,4,6-tetramethylbenzoic acid, respectively. These acids had been made previously from the amides[4] but in the present work they were prepared from the corresponding bromides by the Grignard method. This procedure is convenient and has the advantage that it involves no possibility of migration of methyl groups. To obtain satisfactory yields of the Grignard reagent in the synthesis of the 2,3,5,6-tetramethylbenzoic acid the entrainment method of Grignard[5] was employed.

The acids were converted to the acid chlorides which were coupled by the action of the binary mixture, Mg + MgI_2.[6]

The coupling produced in each case a mixture of the expected diketone and an enediol. In the durene series the enediol was isolated and found to be the lower melting (*cis*) form (II). The enediol in the isodurene series (III) was so sensitive to air that it could not be isolated from the reduction mixture.[7] It was produced, however, by the method of Thompson[2b] as modified by Fuson and Horning[1]; hydrogenation of isoduril in methanol and acetic acid gave an almost quantitative yield of the enediol. Attempts to carry out the hydrogenation in low-boiling petroleum ether gave a product which was chiefly isoduroin. Apparently, the enediol underwent ketonization under these conditions. Color tests[8] showed the presence of enediol during the early stages of the hydrogenation.



II



III

The higher-melting (*trans*) enediol in each series was obtained by hydrogenation of the benzil in methanol by the method of Thompson.[2b] When the *trans* enediol from duril was heated in methanolic hydrogen chloride it rearranged to duroin.

The four enediols and the two benzoins were converted to acetates by acetic anhydride. The *cis* and *trans* enediols from isoduril gave the same diacetate. A lower-melting diacetate was obtained by hydrogenation of isoduril in acetic anhydride. This must be the *cis* modification, which means that the one from the *cis* enediol is the *trans* form. Rearrangements of this type have already been observed.[2c,3] The *cis* diacetate in the durene series was also made by hydrogenation of the diketone in acetic anhydride.

Hydrogenation of duril and isoduril at 230° and a hydrogen pressure of 5500 lb. per sq. in. gave the corresponding ethanes when a copper-chromite catalyst was used. In the presence of Raney nickel at 150° and under a hydrogen pres-

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[1] For the preceding communication in this series see Fuson and Horning, THIS JOURNAL, **62**, 2962 (1940).

[2] (a) Fuson and Corse, *ibid.*, **61**, 975 (1939); (b) Thompson, *ibid.*, **61**, 1281 (1939); (c) Fuson, McKeever and Corse, *ibid.*, **62**, 600 (1940).

[3] Fuson, Scott, Horning and McKeever, *ibid.*, **62**, 2091 (1940).

[4] Gattermann, *Ber.*, **32**, 1118 (1899).

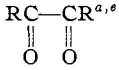
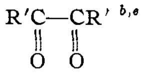
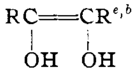
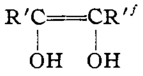
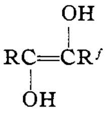
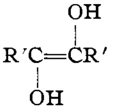
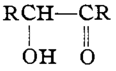
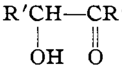
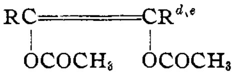
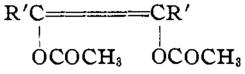
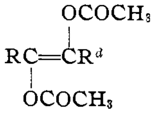
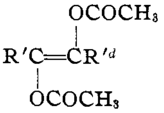
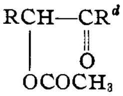
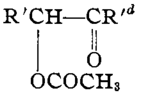
[5] For a leading reference see Smith, Webster and Guss, THIS JOURNAL, **59**, 1078 (1937).

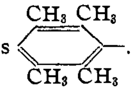
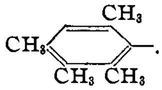
[6] Gomberg and Bachmann, *ibid.*, **49**, 236 (1927).

[7] When a large amount of the reducing agent was employed there was isolated a small amount of a hydrocarbon. It had the composition of diisodurylacetylene and could be converted to 1,2-diisodurylethane by high pressure hydrogenation.

[8] Tillmans, Hirsch and Reinshagen, *Z. Untersuch. Lebensm.*, **56**, 272 (1928).

TABLE I

Compound	Formula	Solvent	M. p., °C.[g]	Analyses, % Calcd. C	Analyses, % Calcd. H	Analyses, % Found C	Analyses, % Found H
Duril ($C_{22}H_{26}O_2$)	 $\mathrm{R}\underset{\mathrm{O}}{\underset{\Vert}{\mathrm{C}}}-\underset{\mathrm{O}}{\underset{\Vert}{\mathrm{C}}}\mathrm{R}^{a,e}$	High-boiling petroleum ether	250–251	81.94	8.13	82.23	8.38
Isoduril ($C_{22}H_{26}O_2$)	 $\mathrm{R'}\underset{\mathrm{O}}{\underset{\Vert}{\mathrm{C}}}-\underset{\mathrm{O}}{\underset{\Vert}{\mathrm{C}}}\mathrm{R'}^{b,e}$	High-boiling petroleum ether	184–184.5	81.94	8.13	81.84	8.40
cis-Enediol from duril ($C_{22}H_{28}O_2$)	 $\mathrm{R}\underset{\mathrm{OH}}{\underset{\vert}{\mathrm{C}}}=\underset{\mathrm{OH}}{\underset{\vert}{\mathrm{C}}}\mathrm{R}^{e,b}$	Ether and low-boiling petroleum ether	167–169[c]	81.44	8.70	81.19	8.70
cis-Enediol from isoduril ($C_{22}H_{28}O_2$)	 $\mathrm{R'}\underset{\mathrm{OH}}{\underset{\vert}{\mathrm{C}}}=\underset{\mathrm{OH}}{\underset{\vert}{\mathrm{C}}}\mathrm{R'}^{f}$	Ether and low-boiling petroleum ether	142–144[c]	81.44	8.70	81.33	8.44
trans-Enediol from duril ($C_{22}H_{28}O_2$)	 $\mathrm{R}\underset{\mathrm{OH}}{\underset{\vert}{\mathrm{C}}}=\overset{\mathrm{OH}}{\overset{\vert}{\mathrm{C}}}\mathrm{R}^{f}$	Ether and low-boiling petroleum ether	214–215[c]	81.44	8.70	81.45	8.78
trans-Enediol from isoduril ($C_{22}H_{28}O_2$)	 $\mathrm{R'}\underset{\mathrm{OH}}{\underset{\vert}{\mathrm{C}}}=\overset{\mathrm{OH}}{\overset{\vert}{\mathrm{C}}}\mathrm{R'}$	Methanol	183–185[c]	81.44	8.70	81.29	8.57
Duroin ($C_{22}H_{28}O_2$)	 $\mathrm{R}\underset{\mathrm{OH}}{\underset{\vert}{\mathrm{CH}}}-\underset{\mathrm{O}}{\underset{\Vert}{\mathrm{C}}}\mathrm{R}$	High-boiling petroleum ether	130–131	81.44	8.70	81.14	8.66
Isoduroin ($C_{22}H_{28}O_2$)	 $\mathrm{R'}\underset{\mathrm{OH}}{\underset{\vert}{\mathrm{CH}}}-\underset{\mathrm{O}}{\underset{\Vert}{\mathrm{C}}}\mathrm{R'}$	Methanol	117–118	81.44	8.70	81.23	8.84
cis-Enediol diacetate from duril ($C_{26}H_{32}O_4$)	 $\mathrm{R}\underset{\mathrm{OCOCH_3}}{\underset{\vert}{\mathrm{C}}}=\underset{\mathrm{OCOCH_3}}{\underset{\vert}{\mathrm{C}}}\mathrm{R}^{d,e}$	Methanol	219–220	76.44	7.90	76.08	8.01
cis-Enediol diacetate from isoduril ($C_{26}H_{32}O_4$)	 $\mathrm{R'}\underset{\mathrm{OCOCH_3}}{\underset{\vert}{\mathrm{C}}}=\underset{\mathrm{OCOCH_3}}{\underset{\vert}{\mathrm{C}}}\mathrm{R'}$	Methanol	161–163	76.44	7.90	76.63	7.94
trans-Enediol diacetate from duril ($C_{26}H_{32}O_4$)	 $\mathrm{R}\underset{\mathrm{OCOCH_3}}{\underset{\vert}{\mathrm{C}}}=\overset{\mathrm{OCOCH_3}}{\overset{\vert}{\mathrm{C}}}\mathrm{R}^{d}$	High-boiling petroleum ether	263–265	76.44	7.90	76.63	8.07
trans-Enediol diacetate from isoduril ($C_{26}H_{32}O_4$)	 $\mathrm{R'}\underset{\mathrm{OCOCH_3}}{\underset{\vert}{\mathrm{C}}}=\overset{\mathrm{OCOCH_3}}{\overset{\vert}{\mathrm{C}}}\mathrm{R'}^{d}$	High-boiling petroleum ether	252–254	76.44	7.90	76.73	8.02
Duroin acetate ($C_{24}H_{30}O_3$)	 $\mathrm{R}\underset{\mathrm{OCOCH_3}}{\underset{\vert}{\mathrm{CH}}}-\underset{\mathrm{O}}{\underset{\Vert}{\mathrm{C}}}\mathrm{R}^{d}$	Methanol	144–145	78.65	8.25	78.91	8.40
Isoduroin acetate ($C_{24}H_{30}O_3$)	 $\mathrm{R'}\underset{\mathrm{OCOCH_3}}{\underset{\vert}{\mathrm{CH}}}-\underset{\mathrm{O}}{\underset{\Vert}{\mathrm{C}}}\mathrm{R'}^{d}$	Methanol	127–129	78.65	8.25	78.48	8.26
Ethane from duril ($C_{22}H_{30}$)	RCH_2CH_2R	High-boiling petroleum ether	235–236	89.73	10.27	89.81	10.50
Ethane from isoduril ($C_{22}H_{30}$)	$R'CH_2CH_2R'$	High-boiling petroleum ether	169–171	89.73	10.27	89.53	10.29

[a] R—represents . [b] R′—represents . [c] The melting point was determined in a nitrogen-filled, sealed capillary. [d] Prepared by boiling the hydroxyl compound with an excess of acetic anhydride for from three to ten hours. [e] The reaction was run in an atmosphere of dry oxygen-free nitrogen. Commercial nitrogen was purified by passing it successively through Fieser's solution, chromous chloride solution, concentrated sulfuric acid and magnesium perchlorate. [f] The product was isolated by performing the necessary manipulations with a nitrogen atmosphere over the solutions. [g] All melting points in this paper have been corrected.

sure of 2600 lb. per sq. in. 1.5 g. of duril gave 0.67 g. of duroin.

Table I gives the melting points and analytical data for the new compounds prepared in this study.

Experimental

2,3,5,6-Tetramethylbenzoic Acid.—From 50 g. of bromodurene, 32.7 g. of ethyl bromide and 16.2 g. of magnesium was obtained 25.5 g. (61%) of the acid; m. p. 179–180° (cor.).[4] The acid chloride was prepared by the action of thionyl chloride; b. p. 105–106° (6 mm.); m. p. 59–60°.

2,3,4,6-Tetramethylbenzoic Acid.—In this synthesis 100 g. of bromoisodurene gave 47.3 g. of the acid; m. p. 164–166°.[4] The acid chloride boiled at 102–103° (3 mm.); $n^{20}\text{D}$ 1.5380; d^{20}_{20} 1.1087.

Summary

Duril and isoduril have been prepared and converted to the corresponding enediols. Each of the latter has been isolated in *cis* and *trans* modifications.

The corresponding benzoins and 1,2-diarylethanes have also been made.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE OHIO STATE UNIVERSITY]

The Relation between the Absorption Spectra and the Chemical Constitution of Dyes. XVI. The Separation of Chromophores in Unsymmetrical Disazo Dyes

BY WALLACE R. BRODE AND JOHN D. PIPER

It was pointed out in a preceding paper[1] that a study of unsymmetrical disazo dyes should yield valuable information concerning the relative influence of the chromophores. In the present paper a spectrophotometric study has been made of a series of such dyes. The intermediates for the two ends, *p*-cresol and dimethylaniline, were chosen because of the markedly different type of absorption bands produced by these intermediates in monoazo and symmetrical disazo dyes. The *p*-cresol dyes, due to their *o*-hydroxy-azo coupling, give a set of double banded maxima quite similar to the β-naphthol type (which is also an *o*-hydroxyazo coupling). The dimethylaniline dyes produce a single intense band which is characteristic of para coupled auxochromes.[2]

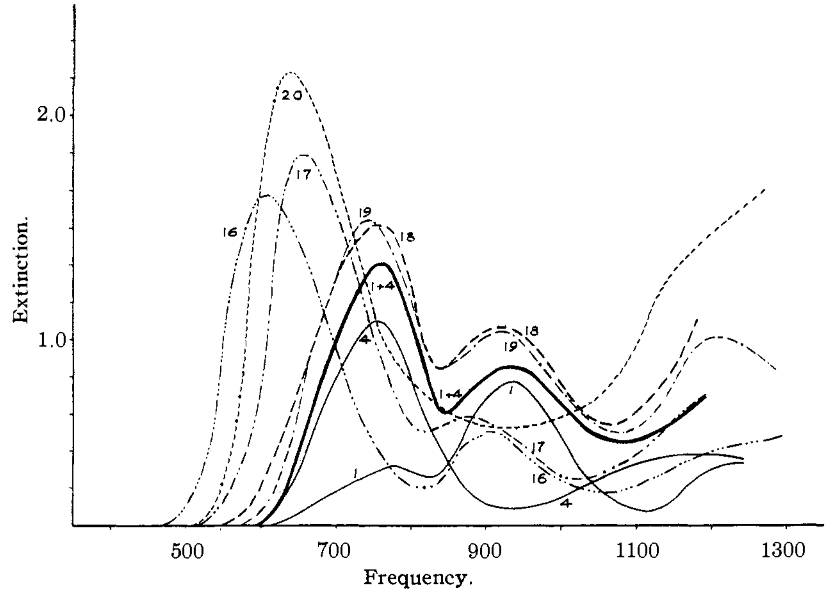

Fig. 1.—Absorption spectra of disazo dyes in 95% ethyl alcohol: dye 1, *o*-phenylazo-*p*-cresol; dye 4, *p*-phenylazodimethylaniline; dyes 16 to 20 as indicated in Table I.

Preparation.—In the preparation of the previously described[1] symmetrical disazo dyes the process of direct

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(1) Piper and Brode, THIS JOURNAL, **57**, 135 (1935).

(2) Brode, *ibid.*, **51**, 1204 (1929).