21317-45-3; dicyclohexylammonium S-(4-methylphenyl)phosphorothioate, 21317-46-4.

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The Reaction of Phenols with Ethyl Azodicarboxylate

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The thermal reaction of some 2,4-, 2,6-, and 2,4,6-substituted phenols with ethyl azodicarboxylate has been studied. In general, both C–C coupling products derived from the phenoxy radicals as well as coupling products from the phenoxy and the hydrazodicarboxylate radicals are formed. The latter compounds were independently prepared by the acid-catalyzed addition of ethyl azodicarboxylate to the phenols. 2,4,6-Tri-*t*-butylphenol reacts with ethyl azodicarboxylate under surprisingly mild conditions with loss of a 2-*t*-butyl group to yield 1-(2-hydroxy-3,5-di-*t*-butyl)phenyl 1,2-ethyl hydrazodicarboxylate. No reaction is observed between azodicarboxylate and phenols of high oxidation potential such as 2-chloro-, 2,6-dichloro-, 2,6-dinitro-, or 2-chloro-6-phenylphenol.

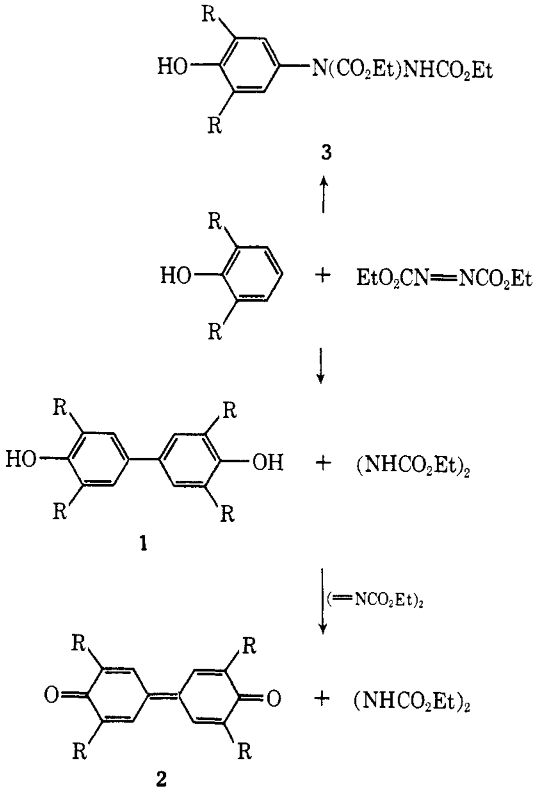
Azo-disubstituted compounds possessing electron-withdrawing substituents, among which azodicarboxylates are the most readily available, are known to show a strong tendency to abstract hydrogen atoms from suitable donors. Alcohols,[1-3] mercaptans,[3] hydrazo compounds,[3] and hydroquinones[4] are readily oxidized by ethyl azodicarboxylate to the corresponding carbonyl compounds, disulfides, azo compounds, and quinones, respectively. Other compounds possessing labile hydrogens such as benzylic hydrocarbons,[5] aldehydes,[6a] or formates[6] react with azodicarboxylates to give the coupling products of the resulting carbon and hydrazo radicals.[7]

$$R'H + RN{=}NR \longrightarrow R'NR\text{-}NHR$$

Azo esters might then be expected to be good oxidizing agents for phenols. However, no report of such reactions has been made, although the reaction of phenols with a large number of oxidizing agents has been studied intensively.[8] Huisgen and coworkers[5] described the use of phenols as inhibitors in the radical addition of azo esters to hydrocarbons, but did not characterize any of the products derived from the phenols. The oxidation of phenols with ethyl azodicarboxylate was therefore examined.

2,6-Disubstituted Phenols.—Phenols of low oxidation potentials such as the 2,6-dialkyl-substituted compounds readily reacted with ethyl azodicarboxylate to yield the C–C coupling products (**1** and/or **2**) derived from the phenoxy radicals as well as the addition products (**3**) of the azo ester to phenols (Scheme I).

SCHEME I



1a, **2a**, **3a**, R = CH_3
1b, **2b**, **3b**, R = $C(CH_3)_3$

As the low solubility of 3,3′,5,5′-tetramethyldiphenoquinone (**2a**) makes the determination of this compound rather easy, the reaction of 2,6-dimethylphenol was studied in some detail (Table I). Oxidation with azo ester proceeded slowly at room temperature, but with a remarkable rate at 50° (Table I, runs 12–15, 1–3). Equimolar amounts of phenol and azo ester gave a 50% yield of the diphenoquinone and an equimolar amount of ethyl hydrazodicarboxylate when the reaction was carried out at a high concentration of the reactants. With increasing dilution, the amount of diphenoquinone formed decreased (runs 1, 10, 11) and more of the 4,4′-dihydroxybiphenyl (**1a**) and the addition product

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[1] G. O. Schenck and H. Formanek, *Angew. Chem.*, **70**, 505 (1958).

[2] R. C. Cookson, I. D. R. Stevens, and C. T. Watts, *Chem. Comm.*, 259 (1965).

[3] F. Yoneda, K. Suzuki, and Y. Nitta, *J. Amer. Chem. Soc.*, **88**, 2328 (1966).

[4] O. Diels and P. Fritsche, *Chem. Ber.*, **44**, 3018 (1911).

[5] R. Huisgen, F. Jakob, W. Siegel, and A. Cadus, *Ann. Chem.*, **590**, 1 (1954).

[6] (a) K. Alder and T. Noble, *Chem. Ber.*, **76**, 54 (1943); (b) R. Huisgen and F. Jakob, *Ann. Chem.*, **590**, 37 (1954).

[7] Addition products may also be formed *via* a concerted mechanism; see W. A. Thaler and B. Franzus, *J. Org. Chem.*, **29**, 2226 (1964), and references cited therein.

[8] (a) V. V. Ershov, A. A. Volod'kin and G. N. Bogdanov, *Russ. Chem. Rev.*, **32**, 75 (1963); (b) H. Musso, *Angew. Chem.*, **75**, 965 (1963); (c) K. U. Ingold, *Chem. Rev.*, **61**, 563 (1961); (d) "Oxidative Coopling of Phenols," W. I. Taylor and A. R. Battersby, Ed., Marcel Dekker, Inc., New York, N. Y., 1967.

TABLE I

OXIDATIVE DIMERIZATION OF 2,4-DIMETHYLPHENOL WITH ETHYL AZODICARBOXYLATE

No.	Moles of ester/ mole of phenol[a]	Solvent, ml	Temp, °C	Time, hr	Yield of quinone, %	Moles of $(NHR)_2$/ mole of quinone
1	1.0	CCl_4, 15	90	6	50	*b*
2	1.0	CCl_4, 15	90	9	50	1.1
3	1.0	CCl_4, 15	90	18	50	1.1
5	1.0	C_6H_6, 15	90	21	46	1.1
6	2.4	CCl_4, 10	90	6	50	1.1
7	2.4	CCl_4, 10	90	16	50	1.1[c]
8	2.4	CCl_4, 10	90	16	46	1.1
9	4.0	None	90	6	50	1.2
10	1.0	CCl_4, 40	90	48	34	1.7
11	2.0	CCl_4, 100	90	6	11	*b*
12	1.5	CCl_4, 15	RT	24	0	0
13	1.5	CCl_4, 15	RT	48	4	1.0
14	1.0	CCl_4, 25	RT	288	33	1.3
15	1.5	CCl_4, 15	50	48	43	1.1

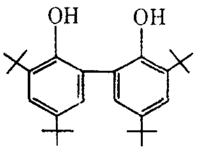
[a] 0.025 mol of phenol was used in each experiment. [b] Not determined. [c] 100 mg of benzoylperoxide was initially added.

3a was formed. The yield of diphenoquinone was not raised above 50% of theory when a larger than equimolar amount of azo ester to phenol was employed (runs 1–9). Obviously, the addition of the hydrazo radicals NHRNR· to the phenoxy radicals competes successfully with dimerization of the phenoxy radicals. The addition products **3a** and **3b** were isolated from the reaction mixtures by chromatography of the diphenoquinone mother liquors. Pure materials were obtained only in low yields since separation of the addition products from the hydrazo ester was not complete and since the substituted hydrazo esters **3a** and **3b** did not easily crystallize. Their structures were readily established on the basis of their elemental analyses, molecular weights, infrared and nmr data, and independent syntheses, which were achieved in analogy to other electrophilic substitution reactions of azo esters[9,10] by treatment of ethyl azodicarboxylate with strong acids in the presence of the aromatic compounds. The reaction with (excess) 2,6-dimethylphenol, for example, gave **3a** in 90% yield.

Other 2,6-disubstituted phenols such as 2,6-di-*t*-butyl-, 2,6-diphenyl-, or 2,6-dimethoxyphenol gave comparable yields of the corresponding diphenoquinones. No reaction was observed, however, between ethyl azodicarboxylate and 2,6-disubstituted phenols of higher oxidation potentials such as 2,6-dinitro-, 2,6-dichloro-, or 2-chloro-4-phenylphenol.

2,4-Di-*t*-butylphenol.—When heated with ethyl azodicarboxylate at 90°, 2,4-di-butylphenol gave 60% 2,2′-dihydroxy-3,3′,5,5′-tetra-*t*-butyldiphenyl (**4**) which was identified by comparison with an authentic[11] sample, prepared by oxidation of 2,4-di-*t*-butylphenol with potassium ferricyanate. Two minor products were isolated from the reaction. One was shown to be the addition product **5**, which was independently prepared by the acid-catalyzed reaction of ethyl azodicarboxylate with 2,4-di-*t*-butylphenol. The second product proved to be a cyclic urethan derived from **5** by loss of ethanol. It was independently obtained in quantitative yield by heating **5** in the presence of acid or base (see Experimental Section). Attempts to prepare the (2-hydroxy-3,4-di-*t*-butyl)phenylhydrazine from **5** were not successful. Treatment of **5** with strong alkali led to the formation of 2,4-di-*t*-butylphenol and 2,4-di-*t*-butyl-6-aminophenol.[12]

2,4,6-Trisubstituted Phenols.—2,4,6-Tri-*t*-butylphenol reacted slowly with ethyl azodicarboxylate at 60° to give a single product which proved to be identical with **5**, the addition product of ethyl azodicarboxylate to 2,4-di-*t*-butylphenol. Formation of **5** from 2,4,6-tri-*t*-butylphenol may be rationalized by coupling of the hydrazo with the phenoxy radical to give the cyclohexadienone **7**, followed by loss of a *t*-butyl group (Scheme II).



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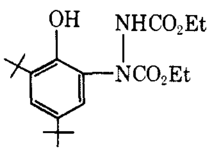
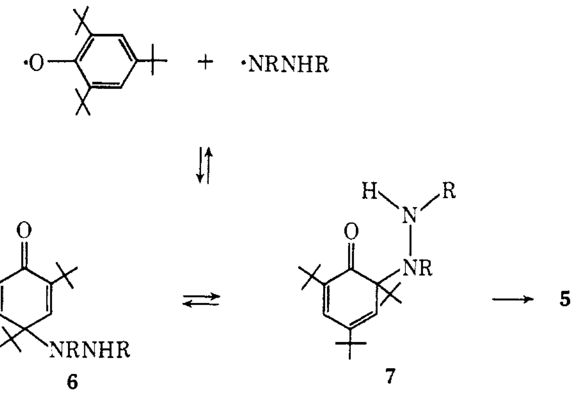


5

SCHEME II



Rearomatization of cyclohexadienones by loss of alkyl groups or other suitable substituents is a known process.[13] However, such reactions usually occur under rather stringent conditions with regard to temperature and pH. This suggests that an intramolecularly facilitated elimination may occur in the reaction with the azo ester. The product **6**, resulting from a coupling in the 4 position was not found under the reaction conditions. Formation of the dienones **6** and **7** may well be reversible (Scheme II); both the dissociation[14a,b] and the rearrangement[13e,14c,d] of cyclohexadienones have been observed. Alternatively, the exclusive formation of **5** may be explained by assuming that the oxidation occurs *via* a concerted mechanism.[15]

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[9] For pertinent literature, see ref 5 and 10.

[10] H. Zollinger, "Diazo and Azo Compounds," Interscience Publishers, New York, N. Y., 1961, p 286.

[11] E. Müller, R. Mayer, B. Narr, A. Rieker, and K. Scheffler, *Ann. Chem.* **645**, 25 (1961).

[12] The phenol probably is derived from the reaction of the phenyldiimide with base: P. C. Huang and E. M. Kosower, *J. Amer. Chem. Soc.*, **89**, 3910 (1967).

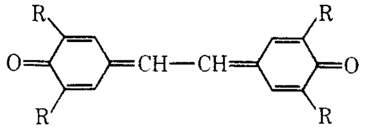
[13] (a) G. H. Stillson and J. B. Fishel, British Patent 591,547 (1947); (b) H. E. Albert and W. C. Sears, *J. Amer. Chem. Soc.*, **76**, 4979 (1954); (c) K. Ley and E. Müller, *Chem. Ber.*, **89**, 1402 (1956); (d) D. M. W. Anderson and J. L. Duncan, *Chem. Ind.* (London), 457 (1959); (e) R. A. Bowie and G. R. Bedford, *Tetrahedron Lett.*, 5471 (1968).

[14] (a) E. Müller, A. Rieker, R. Meyer, and K. Scheffler, *Ann. Chem.*, **645**, 36 (1961); (b) H. D. Becker, *J. Org. Chem.*, **30**, 982 (1965); (c) H. R. Gersmann and A. F. Bickel, *J. Chem. Soc.*, 2711 (1959); (d) L. Denivelle and R. Fort, *Compt. Rend.*, **240**, 2423 (1955).

[15] For a discussion of such a mechanism, see ref 8c and 16.

[16] C. Walling and R. B. Hodgdon, *J. Amer. Chem. Soc.*, **80**, 228 (1958).

The oxidation of mesitol (**8**, 2,4,6-trimethylphenol) with 1 mol of ethyl azodicarboxylate gave 3,3′,5,5′-tetra-*t*-butylstilbene-4,4′quinone (**10a**) in 31% yield[17] and the adduct **11a** (18%).



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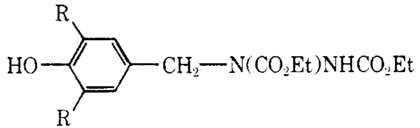

11

10a, 11a, R = CH_3

10b, 11b, R = $C(CH_3)_3$

Only a trace of the stilbenequinone **10b** and a 37% yield[17] of the hydrazo ester **11b** were isolated from the reaction of 2,6-di-*t*-butyl-4-methylphenol (**11**). In addition, a compound $C_{36}H_{54}O_6N_2$ containing one moiety of the stilbenequinone and one moiety of the azo ester was formed in low yield.

Products previously obtained in the oxidation of **9** were 1,2-di(3,5-di-*t*-butyl-4-hydroxy)phenylethane and **10b**.[18] It was shown[19] that these products are not derived from the benzyl radicals (formed by rearrangement of the phenoxy radicals) but rather by dimerization of 3,6-di-*t*-butyl-1,4-quinone methide. Since quinone methides are known to undergo addition reactions with a variety of nucleophiles,[20] the formation of **11a** and **11b** is best rationalized by the addition of the hydrazo ester to the quinone methides derived from **8** and **9**, respectively.

Experimental Section

Thermal Reaction of Ethyl Azodicarboxylate with Phenols. 2,6-Dimethylphenol.—A solution of 6.11 g (50 mmol) of 2,6-dimethylphenol and 8.8 g (50 mmol) of ethyl azodicarboxylate[21] in 15 ml of carbon tetrachloride was heated under nitrogen in an oil bath kept at 85°. The precipitate which had been formed was filtered, washed with a little carbon tetrachloride and petroleum ether, and refluxed with three 40-ml portions of absolute methanol to leave 3.0 g (50%) of **3,3′,5,5′-tetramethyldiphenoquinone** (**2a**), mp and mmp 200–205°. The infrared spectrum of the diphenoquinone was identical with the spectrum of an authentic[22] sample. The methanolic mother liquor was brought to dryness *in vacuo* and the residue was refluxed with little carbon tetrachloride, cooled, filtered, washed with carbon tetrachloride and petroleum ether, and dried to give 4.82 g of ethyl hydroazodicarboxylate, mp and mmp 131–134°.

The carbon tetrachloride filtrate from the reaction mixture was brought to dryness *in vacuo* and the residue was chromatographed over aluminum oxide with petroleum ether, benzene, chloroform, and chloroform-methanol. Elution gave **1-(4-hydroxy-3,5-dimethyl)phenyl-1,2-ethyl hydrazodicarboxylate** (**3a**) of mp 125–130° which was identical with the compound prepared by the acid-catalyzed addition of ethyl azodicarboxylate to 2,6-dimethylphenol (see below). Elution of **3a** was followed by that of ethyl hydrazodicarboxylate. Reactions between azo ester and 2,6-dimethylphenol that were carried out at higher dilution also gave the **quinhydrone of 2a**, mp 187° (independently prepared from equimolar quantities of 1 and 2) as well as 1a, mp 220–224°, which was identified by comparison with an authentic sample.[22]

2,6-Di-*t*-butylphenol.—A solution of 4.13 g (20 mmol) of 2,6-di-*t*-butylphenol and 7.0 g (40 mmol) of ethyl azodicarboxylate in 10 ml of carbon tetrachloride was heated under nitrogen at 90° bath temperature for 18 hr. The reaction mixture was cooled to −10° and the precipitate which formed was filtered and washed with 20 ml of carbon tetrachloride and 150 ml of petroleum ether to leave 2.48 g of ethyl hydrazodicarboxylate, mp 133°. The wash liquors were concentrated *in vacuo* and the **3,3′,5,5′-tetra-*t*-butyldiphenoquinone** (**2b**) was allowed to crystallize: yield 2.15 g (53%); mp 244°, lit.[23] mp 242–244°. Chromatography of the residue over aluminum oxide gave **1-(4-hydroxy-3,5-di-*t*-butyl)phenyl 1,2-ethyl hydrazodicarboxylate** (**3b**), mp 140° (from petroleum ether–carbon tetrachloride), which was identical with the compound prepared by the acid-catalyzed addition of ethyl azodicarboxylate to 2,6-di-*t*-butylphenol.

2,6-Diphenylphenol.—A solution of 3.0 g (12.5 mmol) of 2,6-diphenylphenol and 3.27 g (19 mmol) of ethyl azodicarboxylate in 15 ml of carbon tetrachloride was heated under nitrogen at 90° bath temperature for 21 hr. The reaction mixture was cooled; the precipitate was filtered, washed with carbon tetrachloride and petroleum ether, and refluxed with two 40-ml portions of absolute methanol to leave 0.67 g of **3,3′,5,5′-tetraphenyldiphenoquinone** (**2**, R = C_6H_5), mp 269°, lit[24] mp 270°. Concentration of the carbon tetrachloride solution gave another 0.163 g (0.896 g, 30%). The methanolic mother liquor was brought to dryness *in vacuo* and the residue was refluxed with a little carbon tetrachloride, cooled, and filtered to yield 0.670 g of ethyl hydrazodicarboxylate, mp and mmp 132–133°.

2,6-Dimethoxyphenol.—A solution of 3.85 g (25 mmol) of 2,6-dimethoxyphenol and 6.53 g (37.5 mmol) of ethyl azodicarboxylate in 15 ml of carbon tetrachloride was heated under nitrogen at 90° bath temperature for 15 hr. Work-up as described for 2,6-dimethylphenol gave 2.77 g of hydrazo ester and 1.23 g (34%) of **3,3′,5′,5′-tetramethoxydiphenoquinone** (**2**, R = OCH_3) as a violet, crystalline powder.

Attempted Reaction of 2,6-Dinitrophenol.—A solution of 4.20 g (25 mmol) of 2,6-dinitrophenol and 6.53 g (37.5 mmol) of ethyl azodicarboxylate in 15 ml of carbon tetrachloride was heated under nitrogen at 90° for 12 hr. Cooling of the reaction mixture gave 3.27 g of unreacted phenol. The mother liquor was concentrated and the residue was distilled *in vacuo* to afford 5.97 g (91.5%) of unreacted azo ester, bp 50–70° (0.03 mm). The distillation residue gave another 0.445 g of 2,6-dinitrophenol (3.72 g, 88%). Similarly, no reaction was observed between 2,6-dichloro- and 2-chloro-4-phenylphenol and ethyl azodicarboxylate.

2,4-Di-*t*-butylphenol.—A solution of 10.3 g (50 mmol) of 2,4-di-*t*-butylphenol and 8.7 g (50 mmol) of ethyl azodicarboxylate in 20 ml carbon tetrachloride was heated under nitrogen at 90° bath temperature for 6 hr. The mixture was cooled to −10° and the precipitate was filtered, washed with carbon tetrachloride and petroleum ether, and dried to afford 3.41 g of ethyl hydrazodicarboxylate, which had mp and mmp 130°. The combined carbon tetrachloride and petroleum ether liquors were concentrated *in vacuo*. The resulting crystalline residue was treated with acetonitrile, filtered, and washed with little acetonitrile to afford 5.78 g of **2,2′-dihydroxy-3,3′,5,5′-tetra-*t*-butyldiphenyl** (**4**), mp 193–196.5°. The recrystallized material of mp 197–198° (from methanol–acetonitrile) was identical with an authentic sample.[11] Concentration of the acetonitrile mother liquors gave another 0.63 g of **4** (6.41 g, 68%) and 1.25 g of **1-(2-hydroxy-3,5-di-*t*-butyl)phenyl-1,2-ethyl hydrazodicarboxylate** (**5**), mp 185–186°, which was identical with the compound prepared by acid-catalyzed addition of ethyl azodicarboxylate to 2,4-di-*t*-butylphenol (see below).

2,4,6-Trimethylphenol (Mesitol).—A solution of 6.80 g (50 mmol) of mesitol and 10.44 g (66 mmol) of ethyl azodicarboxylate in 100 ml of carbon tetrachloride was heated under nitrogen at 90° for 9 hr. The reaction mixture was cooled; the precipitate

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[17] Yields are based on crystalline material obtained from column chromatography.

[18] C. D. Cook, *J. Org. Chem.*, **18**, 261 (1953), and earlier papers cited therein.

[19] (a) G. M. Coppinger, *J. Amer. Chem. Soc.*, **86**, 4385 (1964); (b) R. H. Bauer and G. M. Coppinger, *Tetrahedron*, **19**, 1201 (1963); (c) R. Magnusson, *Acta Chem. Scand.*, **20**, 2211 (1966).

[20] (a) L. J. Filar and S. Winstein, *Tetrahedron Lett.*, No. 24, 9 (1960); (b) H. D. Becker, *J. Org. Chem.*, **32**, 4093 (1967).

[21] N. Rabjohn, "Organic Syntheses," Coll. Vol. III, John Wiley & Sons, New York, N. Y., 1955, p 375.

[22] Courtesy of Dr. A. S. Hay.

[23] K. Ley, E. Müller, R. Mayer, and K. Scheffler, *Chem. Ber.*, **91**, 2670 (1958).

[24] J. Plesek, *Chem. Listy*, **50**, 252 (1956).

(9.13 g) was filtered, washed with petroleum ether, and extracted with two 75-ml portions of refluxing ethanol to leave 2.10 g (31%) of **3,3′,5,5′-tetra-*t*-butyl-stilbenequinone (10a)**, violet needles from dimethyl sulfoxide. Concentration of the ethanolic mother liquor gave 5.83 g of ethyl hydrazodicarboxylate, which had mp and mmp 130–132°. The carbon tetrachloride mother liquor was concentrated and chromatographed over alumina to give a little unreacted phenol and 2.7 g (17.5%) of **1-(3,5-dimethyl-4-hydroxyl)benzyl-1,2-ethyl hydrazodicarboxylate (11a)**: mp 88–90° (from carbon tetrachloride); ir ($CHCl_3$) 3600 (OH), 3400 (NH), 1755 and 1710 (COOR), and 1490 cm^{-1} (phenyl); nmr ($CDCl_3$) at τ 3.15 (s, 2 H), 4.09 (s, NH, 1 H), 5.49 (s, $ArCH_2$, 2 H), 5.82 and 5.85 (quartets, 4 H), 7.82 (s, $ArCH_3$, 6 H), 8.76 and 8.80 (triplets, 6 H).

Anal. Calcd for $C_{15}H_{22}N_2O_5$: C, 58.05; H, 7.15; N, 9.03; mol wt, 310.34. Found: C, 58.22; H, 7.16; N, 9.15; mol wt, 309.

2,4,6-Tri-*t*-butylphenol.—A solution of 13.10 g (0.05 mol) of 2,4,6-tri-*t*-butylphenol and 10.44 g (0.06 mol) of ethyl azodicarboxylate in 125 ml of benzene was heated under nitrogen at 90° for 115 hr. The solution was cooled and the solvent evaporated *in vacuo*. The residue was treated with petroleum ether, filtered, washed with more petroleum ether, and dried to afford 8.27 g (75%, based on consumed phenol) of crude **1-(2-hydroxy-3,5-di-*t*-butyl)phenyl-1,2-ethyl hydrazodicarboxylate (5)**, mp 130–170°. After one crystallization from ethanol, the melting point was 815°. The product was identical with the compound obtained from the acid-catalyzed addition of ethyl azodicarboxylate to 2,4-di-*t*-butylphenol (see below).

Anal. Calcd for $C_{20}H_{32}N_2O_5$: C, 63.13; H, 8.48; N, 7.36. Found: C, 62.80; H, 81.10; N, 7.30.

The petroleum ether mother liquor was chromatographed over aluminum oxide. Petroleum ether eluted 5.03 g of unreacted phenol. The benzene eluate gave 0.25 g of the cyclic urethan of mp 147°, which was identical with the product prepared from the adduct of ethyl azodicarboxylate to 2,4-di-*t*-butylphenol (see below). Elution with chloroform afforded 0.62 g of ethyl hydrazodicarboxylate, mp and mmp 130–132°.

2,6-Di-*t*-butyl-4-methylphenol.—A solution of 11.02 g (50 mmol) of 2,5-di-*t*-butyl-4-methylphenol and 9.0 g (52 mmol) of ethyl azodicarboxylate in 80 ml of benzene was heated under nitrogen at 90° for 25 hr. Evaporation of the solvent and treatment of the residue with petroleum ether left 1.86 g of ethyl hydrazodicarboxylate, which had mp and mmp 130–132°. The petroleum ether soluble material was chromatographed over aluminum oxide. Elution with petroleum ether–benzene gave 0.740 g (4.9%) of a compound of mp 205° (from ethanol); ir ($CHCl_3$) no OH or NH, 1710 (COOR), 1725 (sh), 1660, and 1642 cm^{-1}.

Anal. Calcd for $C_{36}H_{54}N_2O_6$: C, 70.78; H, 8.91, N, 4.59; mol wt, 610.8. Found: C, 70.66, 70.80; H, 8.84, 8.75; N, 4.77; mol wt, 595.

Further elution with benzene gave 7.35 g (37%) of **1-(3,5-di-*t*-butyl-4-hydroxy)benzyl-1,2-ethyl hydrazodicarboxylate (11b)**: mp 92–94° (from cyclohexane); ir ($CHCl_3$) 3630 (OH), 3405 (NH), 1745 and 1710 cm^{-1} (COOR); nmr ($CDCl_3$) at τ 2.91 (s, 2 H), 3.18 and 4.70 (singlets, OH and NH, 2 H), 5.41 (s, 2 H) 5.82 and 5.83 (quartets, 4 H), 8.56 (s), and 8.78 (triplets, total of 24 H). Elution with chloroform and chloroform–ethanol finally gave 0.66 g of ethyl hydrazodicarboxylate, mp and mmp 130–132°.

Acid-Catalyzed Addition of Ethyl Azodicarboxylate to 2,6-Dimethylphenol.—To a solution of 12.0 g (100 mmol) of 2,6-dimethylphenol, dissolved in 30 ml of anhydrous ether which had been saturated with hydrogen chloride gas at 0°, was added dropwise with ice cooling 8.8 g (50 mmol) of ethyl azodicarboxylate in 50 ml of carbon tetrachloride. After the mixture stirred overnight, 50 ml of petroleum ether were added. The precipitate was filtered, washed with carbon tetrachloride and petroleum ether, and dried to afford 12.8 g (87%) of **1-(3,5-dimethyl-4-hydroxy)phenyl-1,2-ethyl hydrazodicarboxylate (3a)**: mp 134° (from chloroform or ethanol); ir (KBr) 3455 (OH), 3303 (NH), 1715, 1700, and 1255 cm^{-1} (COOR); nmr (100 Mc, acetone-d_6) at τ 1.25 (s, br, NH, 1 H), 2.39 (s, OH, 1 H), 2.98 (s, ArH, 2 H), 5.89 (one quartet, 4 H), 7.82 (s, $ArCH_3$, 6 H), 8.80 and 8.83 (two triplets, 6 H).

Anal. Calcd for $C_{14}H_{20}N_2O_5$: C, 56.74; H, 6.80, N, 9.45; mol wt, 296.3. Found: C, 56.77; H, 6.92; N, 9.46; mol wt, 296.

Acid-Catalyzed Addition of Ethyl Azodicarboxylate to 2,4-Di-*t*-butylphenol.—To a solution of 10.3 g (50 mmol) of 2,4-di-*t*-butylphenol, dissolved in 25 ml of ether that had been saturated with hydrogen chloride gas at 0° was added with cooling and stirring 5.0 g (29 mmol) of ethyl azodicarboxylate in 40 ml of carbon tetrachloride. The solution was stirred overnight and then brought to dryness *in vacuo*. The crystalline residue was titurated with petroleum ether and dried to afford 8.22 g (75%) of **1-(2-hydroxy-3,5-di-*t*-butyl)phenyl-1,2-ethyl hydrazodicarboxylate (5)**: mp 186°; ir ($CHCl_3$) 3260 (OH, NH), 2963 (CH_3), 1726 and 1692 (COOR), 1595 (CH_3), 1270 and 1245 cm^{-1} (COOR); nmr (acetone-d_6, 100 Mc) at τ 0.90 (s, NH), 1.10 (s, OH), 2.70 (d, 1 H), 2.90 (d, 1 H), 5.80 (q, 2 H), 5.90 (q, 2 H), 8.61 (s), and 8.75 (s, total of 18 H). The compound was identical with the product from the thermal reaction of 2,4-di-*t*-butyl- or 2,4,6-tri-*t*-butylphenol with ethyl azodicarboxylate.

Anal. Calcd for $C_{20}H_{32}N_2O_5$: C, 63.13; H, 8.48; N, 7.36; mol wt, 382.5. Found: C, 62.90; H, 8.53; N, 7.45; mol wt, 372.

Cyclization of 5.—A solution of 2.0 g of **5** in 50 ml of triethylamine was refluxed under nitrogen for 8 hr. The mixture was cooled and the solvent evaporated *in vacuo* to leave a slightly yellow residue which crystallized readily when titurated with petroleum ether to leave 1.50 g (86%) of colorless crystals, mp 147–148° (from carbon tetrachloride–petroleum ether). The same product was obtained by treatment of **5** with piperidine at reflux, with 5% ethanolic potassium hydroxide solution at 30°, with lead dioxide in benzene at 30°, or with a trace of *p*-toluolsulfonic acid in refluxing toluene. Spectroscopic data follow: ir ($CHCl_3$) 3395 and 3350 (NH), 1785 (–OCON–), 1755 (COOR), 1635 and 1605 cm^{-1} (C_6H_5); nmr (acetone-d_6) at τ 2.85 (d), 2.98 (d), 5.75 (q), 8.67 (s), 8.75 (t).

Anal. Calcd for $C_{18}H_{26}N_2O_4$: C, 64.65; H, 7.84; N, 8.38; mol wt, 334.4. Found: C, 64.48; H, 7.87; N, 8.17; mol wt, 330.

Disproportionation of 5 by Alkali.—A solution of 10.0 g of **5** in 65 ml of 25% sodium hydroxide solution and 150 ml of 95% ethanol was refluxed under nitrogen for 3 hr. The color of the solution changed from red to dark brown and finally to light yellow during this time. It rapidly turned dark when exposed to air. After cooling, the solvent was evaporated *in vacuo* and the residue was treated with water and ether until two clear layers were obtained. The ethareal solution was extracted with brine and dried ($MgSO_4$). Evaporation of the ether *in vacuo* left a residue which partly crystallized when treated with petroleum ether. The petroleum ether layer gave a residue that was distilled to afford 2.0 g of 2,4-di-*t*-butylphenol, identified by its ir spectrum. The crystals that had not dissolved in petroleum ether were collected and dried to afford 2.87 g of **2,4-di-*t*-butyl-6-aminophenol** as colorless crystals, mp 169° (from carbon tetrachloride–petroleum ether), lit.[25] mp 166–168°. Spectroscopic data follow: ir ($CHCl_3$) 3615 (OH), 3400 and 3320 (NH), 1605 cm^{-1} (NH, C_6H_5); nmr (acetone-d_6) at τ 3.37 (m, 2 H), 8.68 (2), and 8.75 (s, total of 18 H).

Anal. Calcd for $C_{14}H_{23}NO$: C, 75.97; H, 10.47; N, 6.33; mol wt, 221.3. Found: C, 75.94; H, 10.39; N, 6.30; mol wt, 222.

Registry No.—**3a**, 21736-35-6; **3b**, 21736-36-7; **5**, 21736-37-8; **11a**, 21736-38-9; **11b**, 21736-39-0; 2,4-di-*t*-butyl-6-aminophenol, 1643-39-6; ethyl azodicarboxylate, 1972-28-7; 2,6-dimethylphenol, 576-26-1; 2,6-di-*t*-butylphenol, 128-39-2; 2,6-diphenylphenol, 2432-11-3; 2,6-dimethoxyphenol, 91-10-1; 2,4-di-*t*-butylphenol, 96-76-4; 2,4,6-trimethylphenol, 527-60-6; 2,4,6-tri-*t*-butylphenol, 732-26-3; 2,6-di-*t*-butyl-4-methylphenol, 128-37-0.

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(25) German Patent 1,104,522; see also H. Haeussler and H. Jadamus, *Chem. Ber.*, **97**, 3051 (1964).