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The Photochemical Sulfenylation of Hindered Phenols with Diaryl Disulfides

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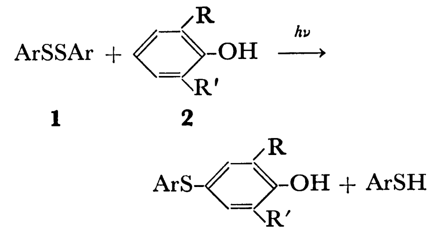
Synopsis. The photochemical reaction of diaryl disulfides with 2,6-disubstituted phenols was investigated. The reaction with highly hindered phenols proceeded appreciably upon irradiation with a high-pressure mercury lamp, giving rise to 4-arylthio-2,6-disubstituted phenols. The reaction was initiated by the homolytic scission of the disulfides.

A previous report[1)] concerning hindered phenols has demonstrated the synthesis of 4-arylthio-2,6-disubstituted phenols in basic media using diaryl disulfides as sulfenylating agents. We wish to report here another simple method of preparing the same sulfides by a photochemical sulfenylation of hindered phenols. The reaction proceeds smoothly and mildly upon the simple irradiation of a solution of diaryl disulfides and hindered phenols in an inert solvent with an ultraviolet lamp.



1 2 3 4 (1)

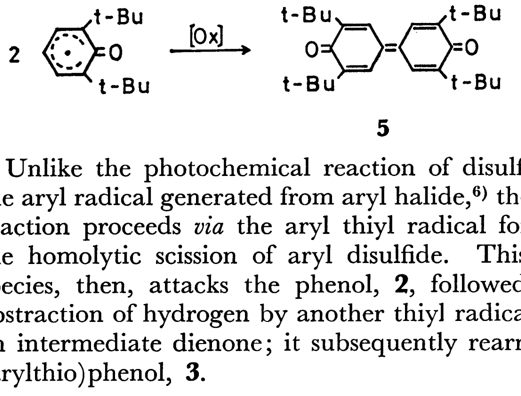
Thus, a solution of diphenyl disulfide (**1**, Ar=C_6H_5) and 2,6-di-*t*-butylphenol (**2**, R=R'=*t*-C_4H_9) in cyclohexane was irradiated with a high-pressure mercury lamp through a Pyrex filter at room temperature for 20 h. 2,6-Di-*t*-butyl-4-(phenylthio)phenol (**3**, Ar=C_6H_5, R=R'=*t*-C_4H_9) was obtained in a 65% yield based on the phenol **2** consumed (GLC). Table 1 summarizes the results of the application of this method to several disulfides and substituted phenols.

In this reaction, solvents with no hydrogen active towards abstraction, such as cyclohexane and benzene, are suitable. Carbon tetrachloride, well-known chain-transfer reagents,[2)] showed itself a good solvent, perhaps by reason of the formation of arenesulfenyl chloride, which subsequently acted as a sulfenylating agent.[3,4)] The yields of **3** were significantly influenced by the substituents (R and R'). A less hindered phenol, 2,6-dimethylphenol, did not afford the corresponding arylthiolated phenol and was recovered quantitatively. The reaction of 2,6-di-*t*-butylphenol with aqueous hexacyanoferrate(III) in the presence of diphenyl disulfide or thiophenol leads to the exclusive formation of a diphenoquinone derivative, **5**,[5)] yielded from the dimerization of the phenoxyl radical, without forming the expected **3**. The radical reaction of **1** and **2** initiated with α,α'-azodiisobutyronitrile also failed.

Table 1. Arylthiophenols from disulfides and phenols

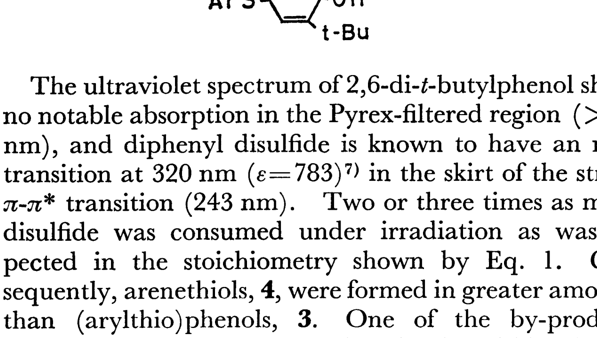
Disulfide (1) Ar	Phenol (2) R	Phenol (2) R'	Solvent	Yield of (Arylthio)phenol (3)	(%)
C_6H_5	*t*-Bu	*t*-Bu	*c*-C_6H_{12}	29	(61)
C_6H_5	*t*-Bu	*t*-Bu	C_6H_6	25	(54)
C_6H_5	*t*-Bu	*t*-Bu	CCl_4	24	(65)
p-$CH_3C_6H_4$	*t*-Bu	*t*-Bu	*c*-C_6H_{12}	28	(61)
p-$CH_3OC_6H_4$	*t*-Bu	*t*-Bu	*c*-C_6H_{12}	10	(69)
p-ClC_6H_4	*t*-Bu	*t*-Bu	C_6H_6	23	(39)
C_6H_5	*t*-Bu	Me	*c*-C_6H_{12}	13	(36)
C_6H_5	*i*-Pr	*i*-Pr	*c*-C_6H_{12}	24	(48)
C_6H_5	Me	Me	*c*-C_6H_{12}	0	(0)

Irradiated for 24 h. The yields are based on the phenols. The yields based on the phenols consumed are shown in parentheses.



5 (2)

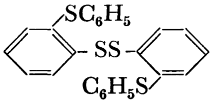
Unlike the photochemical reaction of disulfide with the aryl radical generated from aryl halide,[6)] the present reaction proceeds *via* the aryl thiyl radical formed by the homolytic scission of aryl disulfide. This radical species, then, attacks the phenol, **2**, followed by the abstraction of hydrogen by another thiyl radical to give an intermediate dienone; it subsequently rearranges to (arylthio)phenol, **3**.



(3)

The ultraviolet spectrum of 2,6-di-*t*-butylphenol shows no notable absorption in the Pyrex-filtered region (>300 nm), and diphenyl disulfide is known to have an n-π^* transition at 320 nm (ε=783)[7)] in the skirt of the strong π-π^* transition (243 nm). Two or three times as much disulfide was consumed under irradiation as was expected in the stoichiometry shown by Eq. 1. Consequently, arenethiols, **4**, were formed in greater amounts than (arylthio)phenols, **3**. One of the by-products formed in this reaction was bis[4-(2-phenylthio)phenyl] disulfide (**6**), which was isolated in an 18% yield when equimolar amounts of diphenyl disulfide and 2,6-di-*t*-

butylphenol were irradiated in cyclohexane for 50 h. This disulfide, **6**, is considered to be formed *via* 2-(phenylthio)benzenethiol, a rearranged dimer of the phenylthiyl radical.[8]



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Experimental

*Preparation of 4-Arylthio-2,6-dialkylphenol (**3**).* The following procedure is representative of the preparation of **3**. Diphenyl disulfide (**1**, Ar=C_6H_5, 371 mg) and 2,6-di-*t*-butylphenol (**2**, R=R′=*t*-C_4H_9, 175 mg) were dissolved in cyclohexane (5 ml) and were then, after degassing, irradiated in a Pyrex ampoule with a high-pressure mercury lamp (450 W) for 20 h. The products were analyzed by GLC. Then, the solvent was removed from the reaction mixture under reduced pressure; subsequent column chromatography of the residue on silica gel (eluted by hexane) gave 2,6-di-*t*-butyl-4-(phenylthio)phenol (**3**, Ar=C_6H_5, R=R′=*t*-C_4H_9) in a 57% yield (58 mg) based on the phenol consumed. The conversion of **2** was 38%.

All of the products, (arylthio)phenols (**3**), were identified by a comparison of the mp, GLC, and IR and NMR spectra with those of the authentic sample.[1]

*Bis[4-(2-phenylthio)phenyl] Disulfide (**6**).* When diphenyl disulfide (110 mg) and 2,6-di-*t*-butylphenol (105 mg) in cyclohexane (3 ml) were irradiated using the above procedure, bis[4-(2-phenylthio)phenyl] disulfide (20 mg, 18% based on the **1**) was obtained after column chromatographic separation, along with **3** (Ar=C_6H_5, R=R′=*t*-C_4H_9, 18 mg) and **4** (Ar=C_6H_5, 8 mg). Recrystallization with aqueous ethanol gave pale yellow crystals; mp 118.5—120 °C. MS *m/e*: 434(M^+). IR (Nujol) 1582, 1440, 758, and 693 cm^{-1}. UV (cyclohexane) max: 254 nm (ε 8.2×10^4). Found: C, 66.15; H, 4.38; S, 29.59%. Calcd for $C_{24}H_{18}S_4$: C, 66.31; H, 4.18; S, 29.50%.

References

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