water. The products were extracted with ether and separated by fractional crystallization from hexane or preparative thin-layer chromatography. The conversion was quantitative. The following products were isolated: 1.4 g (55%) 6-nitro-2,4-di(tert-butyl)phenol (III), mp 62-63°C [1] and 1.7 g (42%) 4,4′,6,6′-tetra(tert-butyl)-2,2′-bisphenol (V), mp 185-186°C [2].

Nitration of 2,6-Di(tert-butyl)phenol (II). Analogously, 0.01 mole (II) gave 1.46 g (58%) 4-nitro-2,6-di(tert-butyl)phenol (IV), mp 153-154°C [3] and 0.6 g (30%) 2,2′,6,6′-tetra(tert-butyl)para-diphenoquinone (VI), mp 245-246°C [5].

Nitration of 6-XCH_2-2,4-di(tert-butyl)phenols (X = OH, OCH_3, and $N(CH_3)_2$). Analogously to (I), 0.01 mole substrate gave 96-98% (III), mp 62-63°C.

Nitration of 4-XCH_2-2,6-di(tert-butyl)phenols. Analogously to (I), 0.01 mole starting phenol gave (IV) in 94% yield, mp 153-154°C.

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METALLATION AND FUNCTIONALIZATION OF o-SULFONYLDI- AND o-SULFONYLTRIARYLCARBINOLS. UNEXPECTEDLY FACILE CYCLIZATION OF TERT-BUTYLSULFONYLCARBINOL INTO A SULTINE

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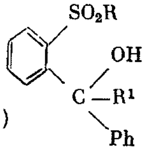
UDC 542.91:547.568.1+
547.544.3:547.253.4

The lithiation of o-sulfonyltriphenylcarbinols proceeds in the ortho position relative to the sulfonyl group, as indicated by formation of the corresponding carboxylic acids upon the action of CO_2. Unusual facility was found for the loss of the tert-butyl group in 2-(tert-butylsulfonyl)-3-diphenylhydroxymethylbenzoic acid in acid media to give the corresponding sultine.

The ortho orienting effect of the sulfonyl group in metallation by BuLi permits us to obtain o-sulfonylbenzaldehydes, which are the starting reagents in the synthesis of stable benzonitrile oxides [1, 2].

In order to obtain new functionally substituted benzaldehydes, we studied the direction of the metallation of o-sulfonylcarbinols (Ia)-(Ic), which were obtained by the functionalization of the corresponding o-Li-phenylsulfones [3, 4].



(I)

$R = R^1 = Ph$ (a); $R = Ph$, $R^1 = H$ (b); $R = CMe_3$, $R^1 = Ph$ (c).

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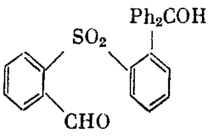
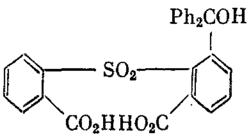
The action of excess BuLi and then DMF on sulfone (Ia) gave a mixture containing monoaldehyde (IIa) in addition to starting (Ia). The structure of (IIa) was indicated by its PMR spectrum but it could not be isolated as a pure compound. Analogous treatment of sulfone (Ib) gave a mixture of several formyl derivatives, which could not be separated or identified, while sulfone (Ic) virtually did not react under these conditions.

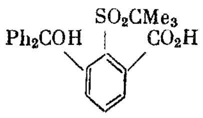
The carboxylation of the lithium derivatives in the case of (Ib) gave dicarboxylic acid (IIb) in 76% yield, while monoacid (IIc) was obtained in 43% yield from (C).



(IIa)



(IIb)

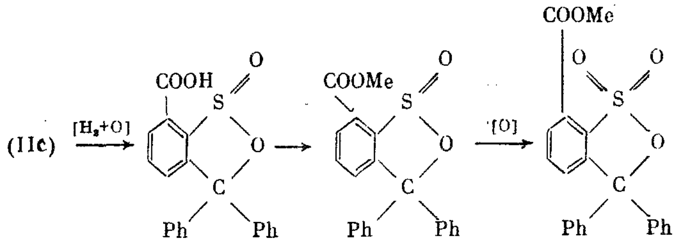


(IIc)

The discrepancy between the results of the carboxylation and formylation is apparently related to the different volumes of the electrophiles attacking the sterically-hindered carbanions [1].

Thus, the metallation of sulfonylcarbinols (I) in all cases proceeds in the ortho position relative to the sulfonyl group although the hydroxymethyl substituent also may have an ortho-orienting effect on this process [5].

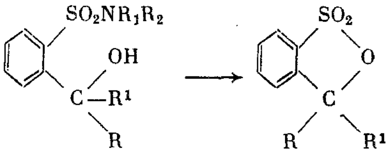
An unusual transformation with the loss of tert-butyl alcohol and intramolecular cyclization with the formation of sultine (IIIc) was observed upon maintaining (IIc) in aqueous hydrochloric acid. The thermal transformation of (IIc) proceeds analogously. Gas liberation was observed after fusion of the acid on further heating along with solidification of the melt, which then melts as sultine (IIIc).



(IIIc) (IVc) (Vc)

The structures of (IIc), (IIIc), and their methyl esters (VIc) and (IVc) were indicated by spectral data. The PMR spectrum of acid (IIc) and ester (VIc) has a singlet for the carbinol hydroxyl protons at 6.50 ppm along with three aromatic proton signals and singlet for the tert-butyl group protons at 1.60 ppm. Both these signals are lacking in the PMR spectrum of sultine (IVc). The IR spectrum of (VIc) has a hydroxyl band at 3400 cm^{-1}, while this band is lacking in the spectrum of ester (IVc). Chemical evidence for the structure of (IVc) and the presence of a sulfide sulfur atom in this compound is found in its oxidation to sultone (Vc).

Starting sulfonylcarbinol (Ic) under the same conditions does not undergo cyclization. This transformation is apparently related to the steric "pressure" of the adjacent carboxyl group on the tert-butylsulfonyl group. Cases have been reported of the cyclization of sulfamides having a carbinol residue in the position ortho to the sulfamoyl group, for example, the thermal [6] and acid-catalyzed cyclodeamination of sulfamides to give sultones [7, 8]. The reaction rate in this case increases with increasing volume of substituent R. Such facile decomposition of sultones in acid media is unknown to us.



Cleavage of the stronger C—S bond and reduction of the sulfonyl group to a sulfinyl group upon cyclization are significant features in our cyclization.

Elimination of a hydroxyl group with formation of a stable triarylcarbonium cation occurs in the first step in the presence of acid with subsequent transformations according to the following scheme:

TABLE 1. Characteristics of Compounds Synthesized

Compound	Yield, %	Mp, °C	Molecular mass, M^+	Chemical formula, calc. mol. mass	$\frac{\text{Found}}{\text{Calculated}}$, %		
					C	H	S
(Ic)	62	195,5–196	380	$C_{23}H_{24}O_3S$ 380,5	$\frac{72,61}{72,59}$	$\frac{6,48}{6,35}$	$\frac{8,26}{8,42}$
(IIb)	76	227–228	–	$C_{21}H_{16}O_7S$ 412,4	$\frac{61,20}{61,16}$	$\frac{4,10}{3,91}$	$\frac{7,53}{7,77}$
(IIIb)	–	130–132	440	$C_{23}H_{20}O_7S$ 440,4	$\frac{62,66}{62,71}$	$\frac{4,70}{4,57}$	$\frac{7,38}{7,27}$
(IIc)	43	184–186 * 256–258	–	$C_{24}H_{24}O_5S$ 424,5	$\frac{67,71}{67,90}$	$\frac{5,91}{5,70}$	$\frac{7,32}{7,55}$
(VIc)	–	166–167	438	$C_{25}H_{26}O_5S$ 438,5	$\frac{68,78}{68,47}$	$\frac{6,18}{5,98}$	$\frac{7,02}{7,31}$
(IIIc)	42	259–260	–	$C_{20}H_{14}O_4S$ 350,4	$\frac{68,94}{68,55}$	$\frac{4,31}{4,02}$	$\frac{8,83}{9,15}$
(IVc)	–	165–166,5	364	$C_{21}H_{16}O_4S$ 364,4	$\frac{68,99}{69,21}$	$\frac{4,54}{4,42}$	$\frac{8,47}{8,80}$
(Vc)	95	174,5–176	380	$C_{21}H_{16}O_5S$ 380,4	$\frac{65,98}{66,30}$	$\frac{4,41}{4,24}$	$\frac{8,33}{8,43}$

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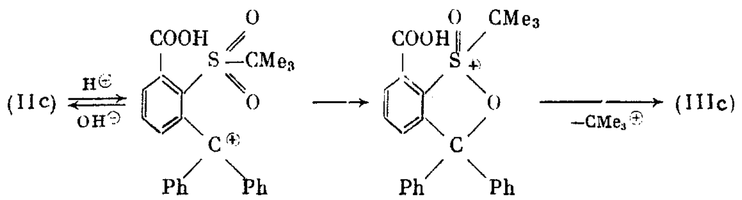
*This compound has two melting points, see above.



We should note that sulfonyl oxygen atoms are capable of nucleophilic attack on a carbocation [9]. This general scheme does not exclude intermediate one-electron transfer steps, especially under thermal conditions.

This cyclization holds definite synthetic interest since it is the only pathway to o-substituted sultines and sultones. Attempts to effect the direct metallation of sultone did not give the desired results.

EXPERIMENTAL

The melting points were taken on a Boetius block. The mass spectra were taken on a Varian MAT CH-6 mass spectrometer at 70 eV. The ionization chamber temperature was 50-150°C. The PMR spectra were taken on a Bruker WM-250 spectrometer at 250 MHz relative to TMS. The IR spectra were taken on a Perkin–Elmer 577 spectrometer at 400-400 cm^{-1}.

tert-Butyl-[o-(1-hydroxy-1,1-diphenylmethyl)phenyl]sulfone (Ic). A sample of 30.5 ml (60 mmoles) ethereal n-BuLi was added with stirring over 20 min to a solution of 9.9 g (50 mmoles) tert-butylphenylsulfone [10] in 190 ml absolute ether at -30°C in an argon atmosphere. The mixture was stirred for 40 min at -30°C and for 1 h at 20°C. A solution of 9.10 g (50 mmoles) benzophenone in 30 ml abs. ether was added dropwise to the mixture cooled to -60°C, stirred for 1 h at 20°C, and left overnight. After the addition of water, the precipitate was filtered off, washed with water and ether, and dried. IR spectrum (ν, cm^{-1}): 1290, 1160 (SO_2), 3400 (OH). PMR spectrum in $(CD_3)_2CO$ (δ, ppm): 1.38 s (9H, 3Me), 6.82-6.92 m (1H, H^3), 6.92 s (1H, OH), 7.02-7.16 m (5H, Ph), 7.20-7.30 m (5H, Ph), 7.51-7.70 m (2H, H^4, H^5), 8.10-8.21 m (1H, H^6). The yields, physical constants, and analysis results are given in Table 1.

2-(1-Hydroxy-1,1-diphenylmethyl)phenylsulfonylbenzaldehyde (IIa). A sample of 24 ml (50 mmoles) ethereal n-BuLi was added to a suspension of 4 g (10 mmoles) sulfone (Ia) [3] in 40 ml abs. ether and 10 ml abs. benzene at 0°C under argon and stirred for 2 h. A sample of 5 ml (70 mmoles) DMF in 10 ml abs. ether was added at -70°C and brought to 20°C. The mixture was poured into 10% hydrochloric acid. The precipitate formed was filtered off, washed with water, and dried. IR spectrum (ν, cm^{-1}): 1700 (C=O), 1160, 1310 (SO_2), 3400 (OH). PMR spectrum in $CDCl_3$ (δ, ppm, J, Hz): 6.70 s (1H, OH), 6.85 d.d (1H, $H^{3'}$, J = 7.5, J = 1.5), 6.97-7.78 m (4H, H^4, $H^{4'}$, H^5, $H^{5'}$), 7.10-7.78 m (10H, 2Ph), 7.92-8.07 m (2H, H^6, $H^{6'}$), 8.26 d.d (1H, H^3), 10.50 s (1H, CHO).

6-(1-Hydroxy)benzyldiphenylsulfone-2,2'-dicarboxylic Acid (IIb). A sample of 20 ml (36 mmoles) ethereal n-BuLi was added to a solution of 1.94 g (6 mmoles) sulfone (Ib) [4] in 25 ml abs. ether under argon at 0°C, stirred for 2 h, and poured onto dry ice in ether. The mixture was brought to 20°C and poured into water. The aqueous layer was separated, washed with ether, and acidified. The precipitate formed was filtered off, washed with water, and dried. IR spectrum (ν, cm^{-1}): 1700, 1720 (C=O), 1310, 1160 (SO_2), 3400 (OH). PMR spectrum of (IIb) in $(CD_3)_2CO$ (δ, ppm, J, Hz): 5.00 s (1H, CH), 6.65 s (1H, OH), 7.10-7.22 m (5H, Ph), 7.70-7.82 m (6H, H^3, $H^{3'}$, H^4, $H^{4'}$, H^5, $H^{5'}$), 7.95 d.d (1H, H^6, J = 7.5, J = 1.5). PMR spectrum of (IIIb) in $(CD_3)_2CO$ (δ, ppm, J, Hz): 3.78 s, 3.82 s (6H, $2CO_2Me$), 5.00 s (1H, CH), 6.63 s (1H, OH), 7.10-7.22 m (5H, Ph), 7.53-7.72 m (4H, H^4, $H^{4'}$, H^5, $H^{5'}$), 7.77-7.83 m (2H, H^3, $H^{3'}$), 7.85 d.d (1H, $H^{6'}$, J = 7.5, J = 1.5). The yields, physical constants, and analysis results for acid (IIb) and its dimethyl ester (IIIb) are given in Table 1.

2-tert-Butylsulfonyl-3-(1-hydroxy-1,1-diphenylmethyl)benzoic Acid (IIc). A sample of 8.7 ml (14 mmoles) ethereal n-BuLi was added to a solution of 1.33 g (3.5 mmoles) sulfone (Ic) in 25 ml dry THF under argon at -70°C, stirred for 1 h, poured onto dry ice in ether, and left overnight. Water was added. The aqueous layer was separated and washed with ether. THF was distilled off in a rotary evaporator and the aqueous solution was acidified by the addition of hydrochloric acid. The precipitate formed was filtered off, washed with water, and dried. IR spectrum (ν, cm^{-1}): 1700 (C=O), 1320, 1155 (SO_2), 3400 (OH). PMR spectrum of (IIc) in $(CD_3)_2CO$ (δ, ppm): 1.60 s (9H, 3Me), 6.50 s (1H, OH), 7.03-7.13 m (5H, Ph), 7.29-7.39 m (5H, Ph), 7.54-7.67 m (3H, H^4, H^5, H^6). PMR spectrum of (VIc) in $(CD_3)_2CO$ (δ, ppm): 1.60 s (9H, 3Me), 3.88 s (3H, CO_2Me), 6.50 s (1H, OH), 7.04-7.13 m (5H, Ph), 7.27-7.38 m (5H, Ph), 7.55-7.63 m (3H, H^4, H^5, H^6). The yields, physical constants, and analysis data for acid (IIc) and its methyl ester (VIc) are given in Table 1.

3,3-Diphenyl-3H-2,1-benzoxathiol-1-oxide-7-carboxylic acid (IIIc) was obtained analogously to (IIc). However, after acidification of the aqueous layer, the product was maintained in acid media for 15-17 h. IR spectrum (ν, cm^{-1}): 1720 (C=O), 3050 (CO_2H). PMR spectrum of (IIIc) in $(CD_3)_2CO$ (δ, ppm): 7.20-7.51 m (10H, 2Ph), 7.86-7.90 m (2H, H^4, H^5), 8.18-8.26 m (1H, H^6). PMR spectrum of (IVc) in CD_2Cl_2 (δ, ppm, J, Hz): 4.02 s (3H, CO_2Me), 7.15-7.45 m (10H, 2Ph), 7.60-7.75 m (2H, H^4, H^5), 8.17 d.d (1H, H^6, J = 7.5, J = 1.5). The yields, physical constants, and analysis data for acid (IIIc) and its methyl ester (IVc) are given in Table 1.

Methyl Ester of 3,3-Diphenyl-3H-2,1-benzoxathiol-1,1-dioxide-7-carboxylic Acid (Vc). A sample of 5 ml acetic acid in 3 ml water was added to 0.20 g (0.54 mmole) sultine (IVc), heated for 3 h at 100°C, and two thirds of the solvent was distilled off. The precipitate formed was filtered off, washed with water, and dried. IR spectrum (ν, cm^{-1}): 1720 (C=O), 1285, 1160 (SO_2). PMR spectrum in $(CD_3)_2CO$ (δ, ppm): 4.00 s (3H, CO_2Me), 7.17-7.50 m (10H, 2Ph), 7.83-7.89 m (2H, H^4, H^5), 8.16-8.22 m (1H, H^6). The yield, physical constants, and analysis data for (Vc) are given in Table 1.

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PHOTOLYSIS OF 2-DIALKYLAMINO-3-METHYL-1,4-NAPHTHOQUINONES

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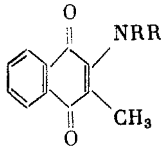
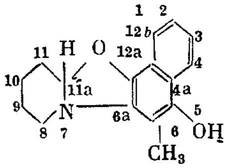
The photolysis of 2-dialkylamino-1,4-naphthoquinones is significantly more efficient when a methyl group is at C^3. The quantum yields are 2-6 times greater than for 2-dialkylaminonaphthoquinones lacking a methyl group. 2-Monoalkylamino-1,4-naphthoquinones also undergo photochemical dealkylation.

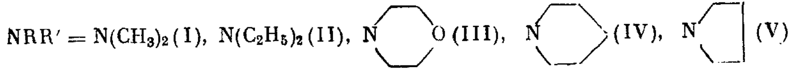
1,4-Naphthoquinone derivatives containing a dialkylamino group at C^2 have found use as light-sensitive components in silverless photographic films [1, 2]. Our previous quantitative study of the photolysis of a series of such compounds showed that the efficiency of their photoconversion under the same conditions is a function primarily of the nature of the amine residue, while the effect of substituents such as chlorine and the methoxy group at C^3 of the quinone system is slight [3, 4]. In a continuation of a study on the effect of substituents on the photolysis efficiency, we investigated the photolysis of 2-dialkylamino-1,4-naphthoquinones (I)-(V), containing a methyl group capable of participating in photochemical reactions [5, 6] in the quinoid part of the molecule.



(I)—(V)



(IVA)



A long-wavelength maximum in the vicinity of 460 nm is found in the UV spectrum of analogs of (I)-(V) lacking a methyl group. A bathochromic shift of about 40 nm is observed upon the introduction of a methyl group at C^3 in a 2-dialkylamino-1,4-naphthoquinone. Such a shift in the long-wavelength maximum has been noted for 3-chloro- [3] and 3-methoxy-2-dialkylamino-1,4-naphthoquinone [4]. The nature of change in the electronic absorption spectra of (I)-(V) during photolysis (Fig. 1) is analogous to that observed for 2-dialkylaminonaphthoquinones studied in our previous work [3, 4] and entails a decrease in optical density in the vicinity of 500 nm and appearance of a band at ~340 nm. The existence of isosbestic points indicates a single photoreaction. First-order kinetics were found for this photochemical reaction. These findings indicate that the photochemical reaction of 2-dialkylamino-1,4-naphthoquinones leads to the formation of unstable naphthdihydrooxazoles analogously to the proposal of Fokin [7] and demonstrated in our previous work on the photolysis of 2-dialkylamino-3-methoxynaphthoquinones using ^1H and ^{13}C NMR spectroscopy [8].

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