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Oxidation of *p*-Tolyl Triphenylmethylhydrazo Sulfone[1]

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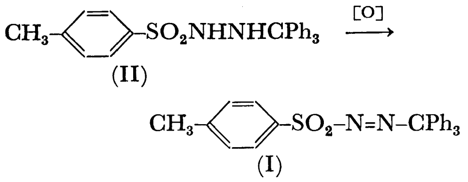
In order to synthesize and study the decomposition of *p*-tolyl triphenylmethylazo sulfone, *p*-tolyl triphenylmethylhydrazo sulfone was oxidized by various oxidizing agents. Although it was oxidized fairly easily by mercury(II) oxide or potassium permanganate, the azo compound formed was unstable and decomposed immediately with evolution of nitrogen. The main products were *p*-tolyl triphenylmethyl sulfone and *p*-tolyl *p'*-benzhydrylphenyl sulfone; both are ascribable to the recombination of *p*-toluenesulfonyl and triphenylmethyl radicals.

Aryl arylazo sulfones yield aryl and arenesulfonyl radicals upon irradiation of light[2] or upon thermolyses in neutral or basic media.[3,4] They yield aryl cations when they are decomposed in acidic media.[5,6]

All the azosulfones studied so far by various investigators are aryl azosulfones, and the decompositions of alkyl azosulfones have not been investigated yet. In an attempt to understand the chemistry of alkyl azosulfones, the synthesis of *p*-tolyl triphenylmethylazo sulfone(I) has been investigated. I is expected to decompose at fairly low temperatures, since both the trityl and *p*-tosyl radicals are resonance-stabilized radicals.

Results and Discussion

Aryl triphenylmethylazo sulfones are not described in the literature. In order to synthesize I, oxidation of *p*-tolyl triphenylmethylhydrazo sulfone (II) was attempted.



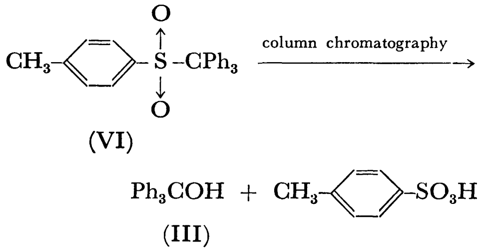
(II)

(I)

Although II was oxidized fairly easily by such oxidizing agents as yellow mercury(II) oxide, manganese(IV) oxide, potassium permanganate or bromine, nitrogen was evolved simultaneously, and I could not be isolated.

Oxidation with mercury(II) oxide in benzene did not take place appreciably at room temperature, but proceeded smoothly at the boiling point of the solvent. When the products were subjected to column chromatography on Florisil, the main product was triphenylmethyl alcohol(III) (75% yield). When the oxidation was carried out in air, triphenylmethyl peroxide (IV) was found in 20 mol% yield. Under nitrogen, formation of IV was suppressed, and triphenylmethane (V) was found in 1.5 mol% yield. Mercury(II) *p*-toluenesulfonate precipitated and amounted to 20 mol%. Almost no *p*-toluenesulfinate was contained in the salt which precipitated. When *p*-toluenesulfinic acid was treated with mercury(II) oxide in benzene, the main product was mercury(II) *p*-toluenesulfinate and very little mercury(II) *p*-toluenesulfonate was found; this finding shows that the mercury(II) *p*-toluenesulfonate formed upon oxidation of II is not ascribable to the oxidation of *p*-toluenesulfinic acid which is a possible intermediate.

When the products of oxidation of II with mercury(II) oxide in benzene were not subjected to column chromatography but separated by recrystallizations, the yield of III was only 35% and *p*-tolyl triphenylmethyl sulfonte(VI) was found in 50% yield. A separate experiment showed that on a Florisil, alumina or silica gel column VI was quantitatively converted to III (another main product was *p*-toluenesulfonic acid). Therefore, VI must be one of the main products of oxidation of II in benzene.



(VI)

(III)

Since aryl arylazo sulfones undergo heterolysis in acidic media and homolysis in neutral or basic media, it is possible that the decomposition of I produced by oxidation of II is influenced by *p*-toluenesulfonic acid formed as a product. Therefore, II was oxidized with mercury(II) oxide in benzene in the presence of triethylamine (1.5 mol/mol of II). The products isolated by column chromatography were III (44 mol%), V (22 mol%), *p*-benzhydrylphenyl *p'*-tolyl sulfone (VII) (24 mol%) and triethylammonium *p*-toluenesulfonate (23 mol%). These products are quite different from those found in the absence of triethylamine.

When II was oxidized by mercury(II) oxide in pyridine, the oxidation proceeds even at about 30 °C. Nitrogen was evolved in an almost quantitative yield, and the products isolated by column chromatography were III (42—47 mol%), V (7—8 mol%), and VII (25—30 mol%). When the oxidation was carried out in air, IV was found in a small yield (3.6 mol%) in addition to the products described above. When the oxidation products were analyzed by NMR

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[1] Organic Sulfur Compounds. Part XLI.

[2] M. Kobayashi, S. Fujii, and H. Minato, This Bulletin, **45**, 2039 (1972).

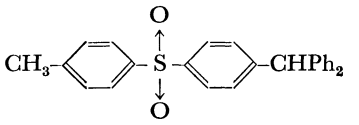
[3] M. Kobayashi, H. Minato, M. Kojima, and N. Kamigata, *ibid.*, **44**, 2501 (1971).

[4] M. Kojima, H. Minato, and M. Kobayashi, *ibid.*, **45**, 2032 (1972).

[5] M. Kobayashi, H. Minato, and N. Kobori, *ibid.*, **43**, 219 (1970).

[6] N. Kamigata, M. Kobayashi, and H. Minato, *ibid.*, **45**, 2047 (1972).

before the column-chromatographic separation, VI and VII were found in 20 and 30 mol% yields, respectively. Therefore, about a half of the total yield of III (after the column chromatography) is ascribable to the hydrolysis of VI during the chromatography, but the other half must have been formed as such directly by the oxidation of II. Since VI does not isomerize to VII even when VI was treated with pyridine, VII must be a primary reaction product.



(VII)

When powdery MgO was used as a base instead of an amine, VI was formed in 50—65% yield and the yield of VII was only 2 mol%. Other products were V (1.5 mol%) and IV (oxidation in air) (10 mol%).

In the oxidation in benzene, no products ascribed to the reactions with benzene were found under varied conditions.

When II was oxidized with potassium permanganate in acetonitrile, oxidation proceeded smoothly and nitrogen was evolved almost quantitatively. The products were III (65 mol%), VI (trace) and an unidentified sulfone (30 wt%; the IR spectrum resembles that of VII but its NMR spectrum does not show the methine proton).

When II was oxidized with manganese(IV) oxide in acetonitrile, oxidation proceeded slowly at room temperature, and it took 10 days before the evolution of nitrogen ceased (70 mol%). The reaction mixture was extracted with an $NaHCO_3$ solution. *p*-Toluenesulfonic acid (49 mol%) was obtained from the aqueous extract, and the evaporation of the organic layer gave almost pure III. The yields of the sulfones (VI or VII) were negligibly small.

Oxidation of II with bromine in acetonitrile proceeded rapidly at room temperature with evolution of nitrogen (90 mol%). When the reaction mixture was diluted with water, extracted with chloroform and the extract was evaporated, almost pure III was obtained. No sulfone (VI or VII) was found.

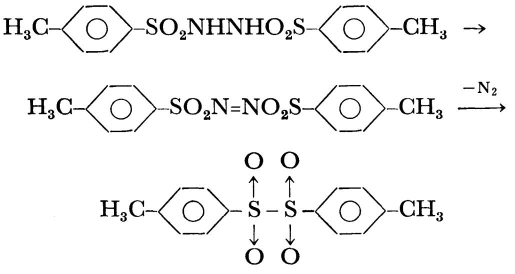
The experimental results described above show that II can readily be oxidized to I but I is very unstable and decomposes with evolution of nitrogen.

Formation of IV shows that triphenylmethyl radical was present and the decomposition of I is homolytic. Sulfone VI is formed by the combination of triphenylmethyl and *p*-tosyl radicals. Since triphenylmethyl radicals are fairly stable, they diffuse out of solvent cage, and form IV upon reaction with oxygen. Part of triphenylmethyl radicals are further oxidized by excess oxidizing agent to III. Part of *p*-tosyl radicals are further oxidized by excess oxidizing agents to *p*-tosyloxy radicals, and then to *p*-toluenesulfonic acid.

Bromine is known to be an efficient radical-scavenger, as exemplified by the efficient trapping of α-cyanoisopropyl radical by bromine in the decomposition of azoisobutyronitrile. Therefore, when II was oxidized with bromine, all the triphenylmethyl radicals were probably converted to triphenylmethyl bromide, which was then hydrolyzed to III. *p*-Tosyl radicals were probably converted to *p*-tosyl bromide, which was then hydrolyzed to *p*-toluenesulfonic acid.

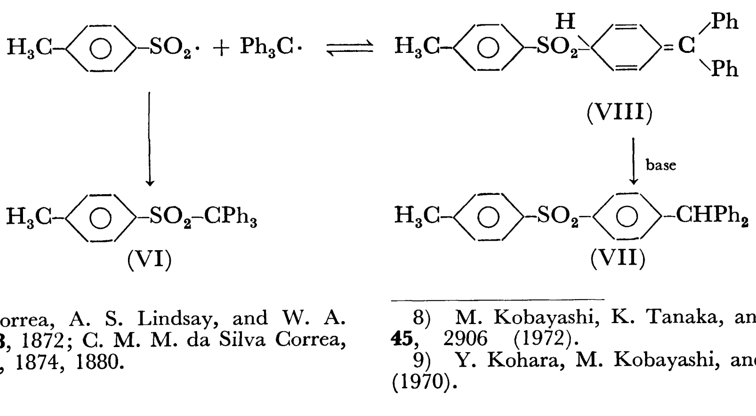
The absence of the products ascribed to the reactions with benzene can be explained in terms of the small reactivity of the resonance-stabilized triphenylmethyl and *p*-toluenesulfonyl radicals. The arenesulfonyl radicals produced by the decomposition of arenesulfonyl iodides did not react with aromatic solvents.[7] Part of the arenesulfonyl radicals formed by the photolysis of aryl α-disulfones attacked aromatic solvents, but the yields of the aromatic substitution products were low.[8]

The oxidation of *N,N′*-diarenesulfonylhydrazine gave the corresponding diimide, which immediately decomposed. The main products were α-disulfone (by recombination in cage), thiolsulfonate and sulfonic acid.[9]



Arenesulfonyl radicals formed in this system also did not react with solvent molecules (benzene, tetrachloroethylene, anisole, *etc*).

The oxidation of II with HgO in the presence of base yielded VII. Formation of VII can be explained by addition of *p*-tosyl radical at a *para* position of triphenylmethyl radical.



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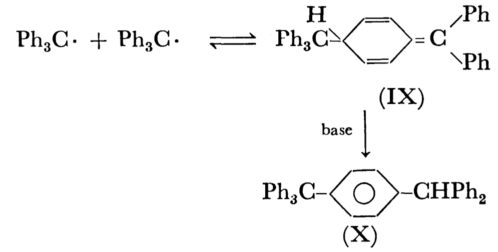
[7] C. M. M. da Silva Correa, A. S. Lindsay, and W. A. Waters, *J. Chem. Soc.*, *C*, **1968**, 1872; C. M. M. da Silva Correa, and W. A. Waters, *ibid.*, **1968**, 1874, 1880.

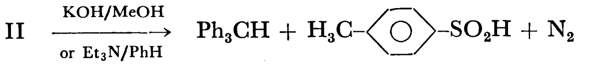
[8] M. Kobayashi, K. Tanaka, and H. Minato, This Bulletin, **45**, 2906 (1972).

[9] Y. Kohara, M. Kobayashi, and H. Minato, *ibid.*, **43**, 2933 (1970).

VII is formed only when a strong base is present. These finding can be rationalized by assuming that the formation of VIII is reversible and VIII is converted to VII by prototropy catalyzed by base. In the absence of base, VIII redissociates to triphenylmethyl and *p*-tosyl radicals, which recombine and form VI. Formation of VIII from triphenylmethyl and *p*-tosyl radicals is analogous to the formation of the Gomberg trityl(IX) from two triphenylmethyl radicals.[10] It is known that IX isomerizes to X with a basic catalyst.[11]



Formation of much triphenylmethane in the HgO-oxidation of II in the presence of triethylamine could be ascribed to abstraction of hydrogen of the amine with triphenylmethyl radical. However, a separate experiment showed that in the presence of a strong base II is converted to triphenylmethane, *p*-toluenesulfinic acid and nitrogen. Therefore, this base-catalyzed decomposition of II appears to be the better explanation for the formation of triphenylmethane in the HgO-base-oxidation of II.



$$\mathrm{II}\ \xrightarrow[\text{or }Et_3N/PhH]{KOH/MeOH}\ Ph_3CH + H_3C\text{-}C_6H_4\text{-}SO_2H + N_2$$

When such stronger oxidizing agents as manganese (IV) oxide were used, the radical pair formed by the decomposition of I were probably further oxidized on the surface of the solid oxidizing agents, and therefore no sulfones were found.

Experimental

Materials. Pyridine and triethylamine were purified by the usual procedures. Yellow mercury(II) oxide was used as received. Manganese(IV) oxide was that used for elemental analyses.

Synthesis of p-*Tolyl Triphenylmethylhydrazo Sulfone(II).* Triphenylmethyl chloride (2.8 g) was added to a chloroform (60 ml) solution of *p*-tosylhydrazine (2.8 g). After 2 hr refluxing, the *p*-tosylhydrazine hydrochloride which precipitated was filtered, and the filtrate was evaporated. Recrystallization of the residue from ethanol gave pure II; mp 136 °C (decomp); yield, 1.6 g (37%). IR, 1160, 1308, 1325 (S–O), 3230, 3280 (N–H) cm^{-1}. NMR, δ, 2.45(s), 4.10(b), 4.95(s), 7.20(m). Found: C, 72.66; H, 5.47%. Calcd for $C_{26}H_{24}O_2N_2S$: C, 72.87; H, 5.64%.

Oxidation of II. The results are summarized in Table 1. Typical examples are shown below.

a) Oxidation of II with HgO in Benzene. A mixture of II (1.290 g, 3.0 mmol), yellow mercury(II) oxide (0.683 g, 3.16 mmol), anhydrous sodium sulfate (1.2 g) and benzene (50 ml) was stirred with a magnetic stirrer at 70 °C. The yellow color of mercury(II) oxide disappeared, and nitrogen was evolved. The mixture was filtered, and the filtrate was evaporated. Crystallization of the residue from benzene–ether yielded crystals of VI (0.618 g, 1.55 mmol; mp 171 °C (lit, 173 °C)) first, and then those of III (0.273 g, 1.05 mmol; mp 160—161 °C(lit, 164.2 °C). They were identified by their IR and NMR spectra.

TABLE 1. PRODUCTS OF OXIDATION OF $TsNHNHCPh_3$ WITH HgO

Run	Reactants (mmol)		Solvent	Others	Separation method
	$TsNHNHCPh_3$	HgO			
1	3.00	3.16	PhH	—	Recryst. from Et_2O–PhH
2	6.10	30	PhH	Et_3N 10 mmol	Florisil column
3	4.96	10.2	Py	—	Florisil column
4	5.71	6.95	Py	under N_2	Florisil column
5	5.32	6.35	Py	—	Florisil column
6	2.18	2.18	PhH	MgO 21.8 mmol under N_2	Florisil column
7	2.00	4.80	PhH	—	Florisil column

Run	Products, mmol (mol%)						
	TsOH	Ph_3CH	$(Ph_3CO)_2$	Ph_3COH	$TsCPh_3$	$TsC_6H_4CHPh_2$	Unknown sulfone
1	—	—	—	1.05 (35.0)	1.55 (51.7)	—	—
2	1.43 (23.4)	1.35 (22.0)	—	2.74 (45.7)	(a)	1.5 (23.4)	—
3	—	—	0.18 (7.2)	2.16 (43.4)	(a)	1.5 (30.2)	23.5 wt%
4	—	0.46 (8.0)	—	2.7 (47.2)	(a)	1.41 (24.8)	20.4 wt%
5	—	0.38 (7.1)	0.15 (5.6)	2.23 (42.0)	(20)[b]	1.68 (31.6)	(10)[b]
6	—	0.33 (1.5)	0.11 (9.7)	1.43 (66.1)	—	—	—
7	—	—	0.23 (22)	1.52 (76.0)	—	—	—

a) Hydrolyzed during chromatography. b) Determined by NMR.

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[10] H. Lankamp, W. Th. Nanta, and C. MacLean, *Tetrahedron Lett.*, **1968**, 249.

[11] R. D. Guthrie and G. R. Weisman, *Chem. Commun.*, **1969**, 1316.

b) Oxidation of II with HgO in the Presence of Triethylamine. Triethylamine (1.0 g, 10 mmol) and mercury(II) oxide (6.487 g, 30.0 mmol) were added to a benzene solution (100 ml) of II(2.609 g, 6.10 mmol), and the mixture was refluxed for 2 hr. It was filtered, and the filtrate was washed with water, dried and then concentrated. Florisil column chromatography of the residue yielded V (0.328 g, 1.35 mmol), III (0.712 g, 2.74 mmol) and VII (0.600 g, 1.5 mmol). The addition of S-benzylisothiourea hydrochloride to the aqueous washings gave crystals of *p*-toluenesulfonate (0.483 g, 1.43 mmol). VII, mp 158 °C; IR; 1150, 1300, 1320 cm^{-1}(S–O); NMR($CDCl_3$), δ, 2.36(s, 3H), 5.55(s, 1H), 6.95~7.89 (m, 18 H); Found: C, 78.19; H, 5.58; S, 8.72%. Calcd for $C_{26}H_{22}O_2S$: C, 78.37; H, 5.57; S, 8.05%.

c) Oxidation of II with HgO in Pyridine. A mixture of II (3.420 g, 8.0 mmol), pyridine (40 ml) and mercury-(II) oxide (2.07 g, 9.6 mmol) was stirred at 60—70 °C. After the evolution of gas ceased, the mixture was filtered, and the pyridine was removed by vacuum distillation of the filtrate. The residue was found to contain VI and VII in a 7 : 10 ratio from its NMR spectrum($CDCl_3$). When the residue was subjected to Florisil column chromatography, V (7.1 mol%), IV (2.8 mol%), III (42 mol%), and VII (32 mol%) were isolated. Therefore, the amount of VI present before the chromatography can be calculated as 22 mol% ($32\times7/10$).

Reaction between II and Triethylamine. A mixture of II (0.838 g, 1.96 mmoles), triethylamine (1.0 g) and benzene (50 ml) was refluxed for 18 hr. When it was washed with aq Na_2CO_3 and the organic layer was concentrated, V was obtained; 0.460 g, 1.91 mmoles (98 mol%). When the aqueous layer was concentrated and S-benzylisothiourea hydrochloride was added, *p*-toluenesulfinate salt was obtained; 0.423 g, 1.31 mmol.