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The alkaline decomposition of *o*-phthalaldehyde di-*p*-toluenesulfonylhydrazone

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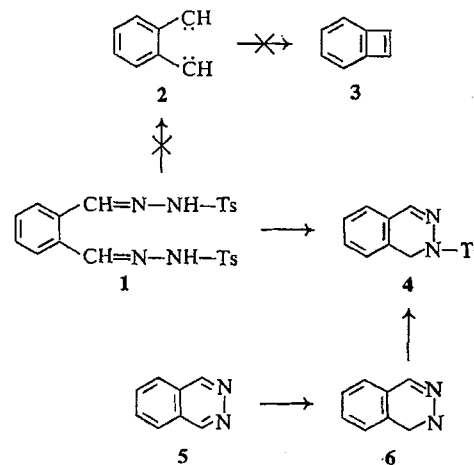
The Bamford-Stevens reaction of *o*-phthalaldehyde di-*p*-toluenesulfonylhydrazone gives *N*-(3,4-dihydrophthalazinyl)-*p*-tolylsulfone. The product is synthesized by an independent method.

The alkaline decomposition of tosylhydrazones³ of aldehydes and ketones has been extensively used for the synthesis of olefins (1) and some novel cyclic compounds (2).

The Bamford-Stevens reaction of benzaldehyde tosylhydrazone (1a, 1c) under aprotic conditions (3) yields an aryl carbene which dimerizes to *trans*-stilbene in high yield. Very little is known about the alkaline decomposition of ditosylhydrazones (1a) under aprotic conditions. The ditosylhydrazone of *o*-phthalaldehyde (1) could yield a dicarbenoid (4) species (2) and hence benzocyclobutadiene (3) (5) or some interesting unsaturated macrocyclic compounds.

o-Phthalaldehyde ditosylhydrazone (1) was prepared by mixing *o*-phthalaldehyde and *p*-toluenesulfonylhydrazine in a 1:2 ratio in ethanol. The use of acetic acid as solvent (6) gave a colored solution. Heating a solution of 1 in dimethyl formamide at 120°, or in diethyl Carbitol at 160°, with either sodium methoxide or sodium hydride gave *N*-(3,4-dihydrophthalazinyl) *p*-tolylsulfone (4) in 5-30% yield, as the only new substance isolated.⁴ No products derived from benzocyclobutadiene (3) (5) could be detected in the reaction product. Cava and Stein (7) have obtained a similar product by the reaction of

phthalaldehydic acid tosylhydrazone with excess acetyl chloride in methanol.



The product 4 was also synthesized by the method of Lemal and Fry (8). Phthalazine (5) was reduced with lithium aluminium hydride to 3,4-dihydrophthalazine (6), and the crude product was treated directly with *p*-toluenesulfonyl chloride in freshly distilled sulfolane and triethylamine.

Dornow and Bartsch (1b) have reported the formation of sulfones from diazoalkanes and aldehyde tosylhydrazones and hence the conversion of 1 to 4 is not surprising. A likely precursor of 4 may involve a monocarbene resulting from loss of one tosylhydrazone group

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³Tosyl = Ts = *p*-toluenesulfonyl.

⁴Ditolyldisulfide and sodium *p*-tolylsulfinate were also formed as side products (see refs. 1c, 9).

from **1** with subsequent carbene insertion to the N-H bond of the remaining tosylhydrazone. The intervention of a protonated diazo compound even under "aprotic" conditions (8, 9) cannot be excluded.

Experimental

Melting points were taken on a Kofler microscope hot-stage and are corrected. Infrared spectra were obtained as KBr discs on a Unicam SP-200 spectrophotometer. Infrared values (ν) are given in cm^{-1} . Nuclear magnetic resonance (n.m.r.) spectra were recorded on a Varian Associates HA-100 spectrometer with tetramethyl silane as an internal standard and deuteriochloroform as solvent. Ultraviolet spectra were obtained in ethanol on a Cary model 14 spectrophotometer. The mass spectra were taken on an A.E.I. MS9 double-focusing mass spectrometer. Woelm alumina (activity II-III) was used for column chromatography.

o-Phthalaldehyde Ditosylhydrazone (**1**)

To 2.3 g of *p*-toluenesulfonylhydrazone in 10 ml of warm absolute ethanol was added 0.8 g of *o*-phthalaldehyde in 3 ml of absolute ethanol. The solution was heated to reflux for a few minutes and allowed to stand at room temperature for 3 h. The solid was filtered to give 2.7 g (96%) of **1**, m.p. 151–152° (decomp.). The mass spectrum did not give a parent ion (the unusual splitting pattern of tosylhydrazones is well known (10); n.m.r. (τ), 7.58 s (six protons, Ar-CH), 1.8–3.0 m (complex multiplet which includes aromatic H, CH=N, and NH protons); ν 3300; 3100 (NH), 1640 (C=N), 1595, 1560 (aromatic), 1335, 1165 (SO₂); λ_{max} 225 m μ (ϵ 28 800), 290 (8650).

Anal. Calcd. for C₂₂H₂₂N₄O₄S₂: C, 56.17; H, 4.71; N, 11.91. Found: C, 56.30; H, 5.32; N, 11.81.

Alkaline Decomposition of *o*-Phthalaldehyde Ditosylhydrazone (**1**)

A solution of **1** (2.35 g, 5 mmoles) in 20 ml of dimethyl formamide was added to 0.24 g (10 mmoles) of sodium hydride⁵ in 5 ml of dimethyl formamide at 5°. After being stirred for 1 h, the solution was immersed in an oil bath at 120°. After 5 min at this temperature, nitrogen evolution had ceased. The reaction mixture was filtered, the filtrate was extracted into ether, and washed six times with water. The semi-crystalline residue was chromatographed to give 300 mg (21%) of a crystalline compound m.p. 169–171° in the 1:1 pentane:ether fractions. Recrystallization from ether-pentane gave product **4**, m.p. 171–173°. The mass spectrum gave a parent ion at *m/e* 286, as well as large peaks at *m/e* 285, 155, and 130, which would be consistent with structure **4**; n.m.r. (τ) 7.56 s (Ar-CH), 5.54 s (CH₂-N), 2.0–3.0 (eight aromatic protons); ν 3450 br (NH), 1600 (aromatic), 1370, 1180 s (SO₂); λ_{max} 222 m μ (ϵ 22 100), 290 (9030).

Anal. Calcd. for C₁₅H₁₄N₂O₂S: C, 62.93; H, 4.93; N, 9.79. Found: C, 62.80; H, 5.32; N, 9.97.

In a similar reaction in which only one equivalent of sodium hydride was used, the product **4** was obtained in 14% yield. When the reaction was carried out in dry diethyl Carbitol at 160° with two equivalents of sodium

methoxide, only a 6% yield of **4** was obtained. All the reactions were carefully examined by thin-layer chromatography for hydrocarbon components, but none could be detected.

Alternative Synthesis of *N*-(3,4-Dihydrophthalazinyl)-*p*-tolylsulfone (**4**)

To a stirred slurry of lithium aluminium hydride (0.38 g, 10 mmoles) in 10 ml of ether under nitrogen, was added dropwise a solution of 1.3 g (10 mmoles) of phthalazine (**5**) in 20 ml of tetrahydrofuran. The mixture was then refluxed for 8 h. Water (1 ml) was added and the mixture was filtered through a filter cel-magnesium sulfate pad. The solvent was removed under reduced pressure. Thin-layer chromatography and elution of the product with ether showed mainly one spot (R_f , 0.8; phthalazine R_f , 0.05). One half of the product (**6**) was dissolved in 17.5 ml of freshly distilled sulfolane, and 0.8 ml (5 mmoles) of triethylamine and 950 mg (5 mmoles) of *p*-toluenesulfonylchloride were added. The solution was heated at 140–150° for 1.5 h, cooled, and then extracted with ether. The resulting oil on chromatography in the 1:1 pentane-ether fractions gave 100 mg of **4**, m.p. 172–174°, undepressed upon admixture with the product obtained above; mass spectrum was identical to that obtained previously.

Anal. Calcd. for C₁₅H₁₄N₂O₂S: C, 62.93; H, 4.93; N, 9.79. Found: C, 62.70; H, 4.93; N, 10.20.

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⁵The sodium hydride was freed from mineral oil by washing with dry pentane.