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Formation of 5-Phenyltetrazole from N^2-Benzoyl-N^4-(phenylsulfonyl)benzohydrazide Hydrazone

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Synopsis. 5-Phenyltetrazole is obtained in a moderate yield by the mercury(II) oxide oxidation of the title hydrazidine prepared from *N*-(phenylsulfonyl)benzohydrazonoyl chloride and benzohydrazide. The tetrazole formation is interpreted in terms of an intramolecular S_N2 type process of the intermediate formazan with the removal of benzenesulfinic acid. In the absence of oxidizing agents, the hydrazidine gives 2,5-diphenyl-1,3,4-oxadiazole and 3,5-diphenyl-4-phenylsulfonylamino-4*H*-1,2,4-triazole.

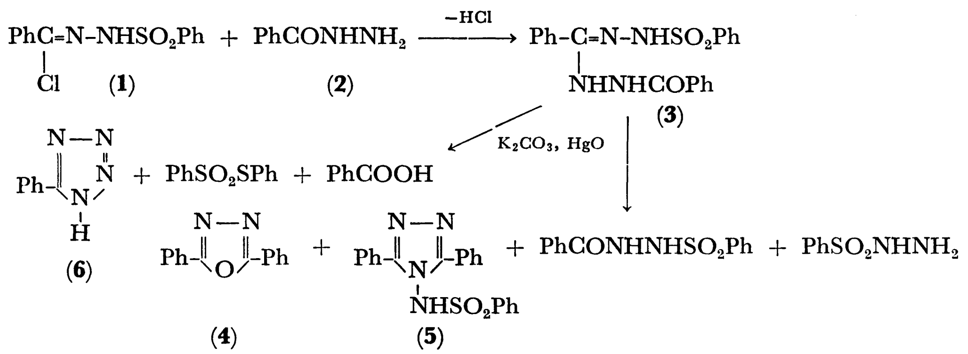
In a previous paper[1] we reported a method for preparing 2,5-disubstituted tetrazoles by the reaction of *N*-(phenylsulfonyl)benzohydrazonoyl chloride(**1**) with arylhydrazines, in which the hydrazines act as a nucleophile in the initial reaction step. This method using hydrazine is, however, not applicable to the preparation of 5-monosubstituted tetrazoles, since hydrazine acts as a base to lead to the formation of 3,6-diphenyl-1,4-bis(phenylsulfonyl)-1,4-dihydro-1,2,4,5-tetrazine. The present paper deals with the formation of 5-phenyltetrazole and other two azoles from **1** and benzohydrazide(**2**).

When a solution of **1** and two equivalent amounts of **2** in THF was stirred for 18—20 h at room temperature, the reaction mixture turned slightly acidic with the precipitation of benzohydrazide hydrochloride. Work-up gave N^2-benzoyl-N^4-(phenylsulfonyl)benzohydrazide hydrazone(**3**) or its tautomer in 92% yield together with a trace amount of 2,5-diphenyl-1,3,4-oxadiazole(**4**) and 3,5-diphenyl-4-phenylsulfonylamino-4*H*-1,2,4-triazole(**5**).

The hydrazidine(**3**) afforded 5-phenyltetrazole(**6**) in 56% yield along with *S*-phenyl benzenethiosulfonate and benzoic acid, when treated with mercury(II) oxide (yellow)–potassium carbonate.[2] With potassium carbonate alone,[3] the yield of **6** decreased to 32%.

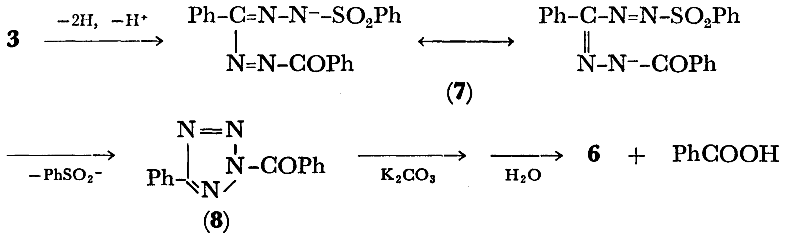
The recrystallization of **3** from methanol or THF–hexane resulted in a partial conversion of **3** into **4**, and at higher temperature the formation of **5** from **3** was also observed. Heating compound **3** at its melting point without solvent gave **5** almost quantitatively. Prolonged stirring or refluxing the mixture of **1** and **2** in THF, without the isolation of **3** formed intermediately, brought about an increase in the yields of **4** and **5** along with the formation of benzenesulfonohydrazide and 1-benzoyl-2-phenylsulfonylhydrazine (see Experimental section).

The sequence of reactions is summarized as follows (Scheme 1):



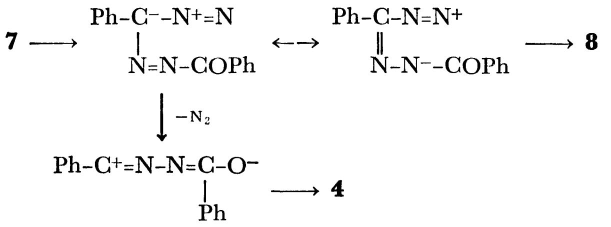
Scheme 1.

The formation of **6** from **3** can be formulated as follows (Scheme 2):[4]



Scheme 2.

For the step **7**→**8**, two mechanisms are possible: one involves the Bamford-Stevens type α-elimination of benzenesulfinic acid followed by the 1,5-dipolar cyclization of the resulting (benzoylazo)diazomethane(Scheme 3), and the other an intramolecular S_N2 type displacement of benzenesulfinate ion by the benzoylamino-anion part of **7**.



Scheme 3.

However, the azodiazomethane is also the source of **4**[5] as shown in Scheme 3. From the fact that **4** could not be obtained in this tetrazole-formation reaction, the direct displacement mechanism may be reasonable.[6] The precursor of the *S*-phenyl benzenethiosulfonate is benzenesulfinic acid[8] removed from **7**.

The formation of **4** and **5** can be easily explained in terms of an intramolecular cyclization of **3** with the removal of benzenesulfonohydrazide and water, respectively. 1-Benzoyl-2-phenylsulfonylhydrazine should be the hydrolyzed product of **3**.

Experimental

Melting points were determined with a Yanagimoto micromelting point apparatus Model MP-S3 and are uncorrected. The microanalysis was performed on a Perkin-Elmer elemental analyzer Model 240, and the IR spectra were recorded with a JASCO DS-301 spectrometer. The products were identified by means of their analytical and spectral data and by comparison with authentic specimens prepared by other synthetic methods.

Preparation of N^2-*Benzoyl*-N^4-*(phenylsulfonyl)benzohydrazide Hydrazone (**3**).* A solution of **1**[1] (10 mmol) and **2**(20 mmol) in THF (40 ml) was stirred for 18—20 h at room temperature. After the removal of precipitated benzohydrazide hydrochloride by filtration, the filtrate was concentrated below 40 °C and extracted with chloroform. The chloroform extract was washed with water, dried(Na_2SO_4), and then concentrated, giving fairly pure **3**(92%) as an amorphous solid, which was purified by recrystallization from methanol or by re-precipitation from THF-hexane, mp 205—207 °C (dec).[9] IR(KBr, cm^{-1}):[10] 3270, 3205(ν_{NH}); 1640(ν_{CO}); 1300(asym ν_{SO_2}); 1162(sym ν_{SO_2}). Found: C, 61.01; H, 4.49; N, 14.45%. Calcd for $C_{20}H_{18}N_4O_3S$: C, 60.90; H, 4.60; N, 14.20%.

*Oxidation of **3** with Mercury(II) Oxide(yellow).* A mixture of **3**(0.395 g, 1 mmol), HgO(0.324 g, 1.5 mmol), K_2CO_3 (0.4 g, 3 mmol), $CaSO_4$(0.4 g, 3 mmol), and dioxane(15 ml) was stirred for 20 h at room temperature. The reaction mixture was filtered and washed with dioxane(20 ml), and then with water(50 ml). The filtrate combined with the washings(dioxane) was concentrated to give crude *S*-phenyl benzenethiosulfonate(0.096 g), which was purified by recrystallization from ethanol, mp 43—44 °C(lit,[11] 45 °C). The water-washings were acidified with dil. HCl, saturated with NaCl, and then extracted with ether. Chromatographic treatment (silica gel, benzene-ethanol) of the ether extract gave benzoic acid(0.072 g, 59%) and **6**(0.075 g, 56%): Mp 213—214 °C (dec)(lit,[5a] 214—215 °C, dec).

*Oxadiazole(**4**) and Aminotriazole (**5**).* A THF solution of **1** and **2**(1 : 2 mole ratio) was refluxed for 4 h or stirred for 5 d at room temperature. The resulting precipitates were separated by filtration and washed with water, giving almost pure **5**: mp 312—315 °C(dec)(acetone).[12]

The THF layer was concentrated, extracted with chloroform, and washed with water, After the removal of the solvent, the residue was chromatographed(silica gel, benzene-ether-ethanol), giving **4** (mp 138—139 °C; lit,[5a] 137—138 °C), 1-benzoyl-2-phenylsulfonylhydrazine(mp 197—198 °C; lit,[13] 199 °C), and benzenesulfonohydrazide, which was confirmed as acetone phenylsulfonylhydrazone: Mp 143—144 °C. IR(KBr, cm^{-1}): 3189(ν_{NH}); 1332, 1162(ν_{SO_2}). Found: C, 51.04; H, 5.71; N, 13.04%. Cacld for $C_9H_{12}N_2O_2S$: C, 50.94; H, 5.70; N, 13.20%. The results are summarized in Table 1.

TABLE 1. OXADIAZOLE(**4**) AND AMINOTRIAZOLE(**5**)

Reaction Conditions[a]	Yield(%) of products[b]			
	4	5	$PhCONHNHSO_2Ph$	$PhSO_2NHNH_2$
I	37	30	27	26
II	40	13	32	40

a) I: Refluxing for 4 h. II: Stirring for 5 d at room temperature. b) Yield as mole per cent based on **1**.

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References

1) S. Ito, Y. Tanaka, and A. Kakehi, *Bull. Chem. Soc. Jpn.*, **49**, 762 (1976).

2) No formation of **4** and **5** was observed in this case.

3) The mixture(in dioxane) was stirred for 5 d.

4) In the absence of mercury(II) oxide, the oxidation of **3** to formazan proceeds probably *via* the autoxidation with atmospheric oxygen catalyzed by potassium carbonate.

5) a) R. Huisgen, J. Sauer, H. J. Sturm, and J. H. Markgraf, *Chem. Ber.*, **93**, 2106 (1960).
b) R. M. Herbst, *J. Org. Chem.*, **26**, 2372 (1961).

6) This intramolecular displacement process may be well represented by the interaction of the lone-pair orbital of the benzoylazo α-nitrogen(or the benzoylamino nitrogen) with the σ^* orbital of the $PhSO_2$-N bond in the planar quasi-aromatic configuration of **7**.[1,7]

7) S. Ito, Y. Tanaka, A. Kakehi, and K. Kondo, *Bull. Chem. Soc. Jpn.*, **49**, 1920 (1976).

8) J. L. Kice and K. W. Bowers, *J. Am. Chem. Soc.*, **84**, 605 (1962).

9) Compound **3** alters to **5** without complete melting when heated gradually, while it shows its clear melting point, giving **5**, when placed on a pre-heated metal plate.

10) Absorption peaks of the crystalline **3**. Compound **3** in the amorphous state exhibits absorption peaks at 3275^{sh}, 3252(ν_{NH}), 1609(ν_{CO}), 1330(asym ν_{SO_2}), and 1166(sym ν_{SO_2}): This difference is probably due to the tautomerism or the molecular association.

11) E. Knoevenagel and A. Römer, *Ber.*, **56B**, 215 (1923).

12) S. Ito, Y. Tanaka, A. Kakehi, and T. Matsuno, *Bull. Chem. Soc. Jpn.*, **50**, 327 (1978).

13) P. Grammaticakis, *Bull. Soc. Chim. Fr.*, **1953**, 86.