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Thermolysis of α-Azidoacetcphenone Phenylsulfonylhydrazones. A New Preparative Route to 4-Aryl-1H-1,2,3-triazoles[1)]

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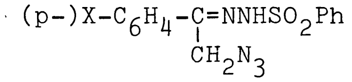
Thermolysis of α-azidoacetophenone phenylsulfonylhydrazones gave 4-aryl-1H-1,2,3-triazoles in good yields. The reaction proceeds probably via the elimination of benzenesulfinic acid from 4-aryl-2-phenylsulfonyltriazolines formed intermediately.

Reactions of arylsulfonylhydrazone derivatives involving the release of arenesulfinate, e.g., the Bamford-Stevens[2)] and its related reactions,[3)] may be attractive from the synthetic point of view. In the present paper, we would like to communicate a new preparative route to 4-aryl-1H-1,2,3-triazoles (2) from α-azidoacetophenone phenylsulfonylhydrazones (1) via the elimination of benzenesulfinic acid. Concerning azidoketone hydrazones, the formation of 1,2,4-triazines from acylhydrazones has been recently reported.[4)]

Azidoketone sulfonylhydrazones 1 were prepared by the reaction of the corresponding α-bromoacetophenone phenylsulfonylhydrazones[5)] with sodium azide in DMF (Table 1).

Table 1. α-Azidoacetophenone Sulfonylhydrazones (1)



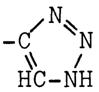
$$(p\text{-})X\text{-}C_6H_4\text{-}\underset{CH_2N_3}{\underset{|}{C}}\text{=NNHSO}_2\text{Ph}$$

Hydrazone[a)]	X	Yield/%[b)]	Mp/°C(dec.)[c)]
1a	H	94	88 – 91
1b	Br	94	120 – 121
1c	Cl	92	114 – 115
1d	NO_2	82	131 – 132
1e	Me	92	107 – 109
1f	Ph	90	190 – 192
1g	Ph-N=N	82	121 – 122

a) Satisfactory analytical data (± 0.3% for C, H, N) and reasonable spectral data were obtained for all compounds. b) Isolated yield. c) Uncorrected. Chloroform was used for recrystallization: in order to avoid decomposition, compounds 2 were dissolved into the solvent as at a low temperature as possible and precipitated in a refrigerator.

Thermolysis of 1 led to the triazole formation accompanied by the liberation of nitrogen and benzenesulfinic acid: a 5-mmol portion (1.577 g) of **1a** was heated for 2 h in dry benzene (50 ml) under reflux. After cooling and the removal of solvent, the resulting residue was chromatographed on a silica-gel column (2.0 cm x 15 cm, eluent: a hexane-benzene-ether system) to give 4-phenyl-1H-1,2,3-triazole (**2a**: 0.694 g, 4.78 mmol, 96%), along with S-phenyl benzenethiosulfonate (0.351 g, 1.4 mmol). Compounds **1b–f** were treated in the same manner to give the corresponding triazoles (**2b–f**), whereas **1g** underwent the transformation into triazole **2g** at an elevated temperature (in toluene under reflux for 30 min). The results are summarized in Table 2.

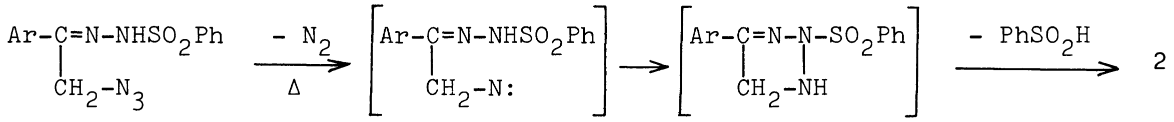
Table 2. 4-Aryl-1H-1,2,3-triazoles (2), (p-)X-C_6H_4-



Triazole (2)[a]	X	Yield/%[b]	Mp/°C[c]
2a	H	96	143 – 145
2b	Br	78	181 – 182
2c	Cl	94	169 – 171
2d	NO_2	79	189 – 191
2e	Me	87	157 – 159
2f	Ph	96	218 – 220
2g	Ph-N=N	71	208 – 210

a) Triazoles **2a–e** are known compounds. All products (**2a–g**) gave reasonable spectral and satisfactory analytical data (± 0.3% for C, H, N). b) Isolated yield. c) Uncorrected. Solvent for recrystallization: $CHCl_3$ (**2a–c**,**g**), MeOH (**2d–f**).

S-Phenyl benzenethiosulfonate should be formed from benzenesulfinic acid by disproportionation;[6)] thus, the triazole formation from 1 can be formulated as follows:



$$\begin{array}{l}\text{Ar-C=N-NHSO}_2\text{Ph}\\ \;\;|\\ \text{CH}_2\text{-N}_3\end{array} \xrightarrow[\Delta]{-\,N_2} \left[\begin{array}{l}\text{Ar-C=N-NHSO}_2\text{Ph}\\ \;\;|\\ \text{CH}_2\text{-N:}\end{array}\right] \longrightarrow \left[\begin{array}{l}\text{Ar-C=N-N-SO}_2\text{Ph}\\ \;\;|\qquad\;|\\ \text{CH}_2\text{-NH}\end{array}\right] \xrightarrow{-\,PhSO_2H} 2$$

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