A New Route to 1,4-Dihydro-1,2,4,5-tetrazines via Stabilized Sulfuranes

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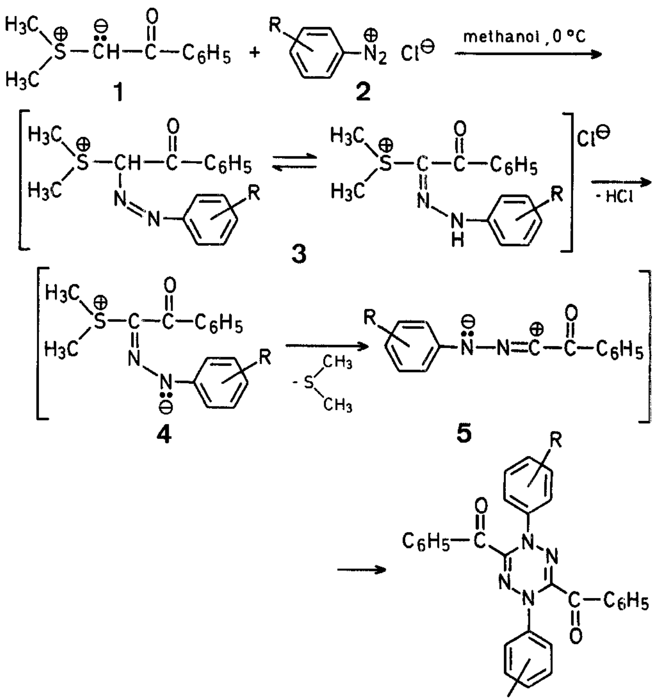
N-Phenacylpyridinium[1,2] and triphenylarsonium bromides[3] are known to react with arenediazonium salts in the presence of sodium acetate in methanol at 0 °C to give 1,4-dihydro-1,2,4,5-tetrazines. The reaction proceeds via 1,3-dipolar dimerization of an intermediate nitrilimine which is, in turn, formed by attack of the carbanion of the *in situ* generated ylid on the diazonium cation. The reaction is facilitated by the fact that the onium ion is a good leaving group. In view of the ability of dialkylsulfonio groups to act as excellent leaving groups, we investigated a similar synthesis of 1,4-dihydro-1,2,4,5-tetrazines (**6**) using phenacylidenedimethylsulfurane (**1**) in place of pyridinium or arsonium bromides. Sulfuranes of the type **1** have hitherto been used in a variety of syntheses, e.g., of epoxides[4], aziridines[5], cyclopropanes[6], and pyridines[7].

Our synthesis of the dihydrotetrazines **6** consists of the reaction of phenacylidenedimethylsulfurane (**1**) with an equimolar amount of an arenediazonium salt **2** in methanol at 0 °C. The reaction presumably proceeds via the intermediacy of the species **3** which is transformed into the nitrilimine **5** which in turn dimerizes to give the dihydrotetrazin **6**; the yields of **6** are 52–78%.

Our method using sulfurane **1** is carried out under mild conditions and gives better yields of 1,4-dihydro-1,2,4,5-tetrazines than are obtained by the pyridinium or arsonium salt methods[1,2,3].



The structure of compounds **6** was established by microanalyses, physical, and spectral data.

1,4-Diaryl-3,6-dibenzoyl-1,4-dihydro-1,2,4,5-tetrazines (6); General Procedure:

A solution of phenacylidenedimethylsulfurane[7] (**1**; 1.8 g, 10 mmol) in methanol (50 ml) is added dropwise to a freshly prepared solution of the diazonium salt (**2**; 10 mmol) at 0 °C during 30 min with stirring. The mixture is kept in an ice bath for a further 2 h. The solid which separates is recrystallized from ethanol.

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Table. 1,4-Diaryl-3,6-dibenzoyl-1,4-dihydro-1,2,4,5-tetrazines (**6**) prepared

6	R	Yield [%]	m.p.[a] [°C]		M.S.[b] *m/e* (M$^+$) (calculated)	I.R.[c] (Nujol) ν [cm^{-1}] (C=O$_{\text{stretching}}$)	^{1}H-N.M.R.[d] (CDCl$_3$/TMS$_{\text{int}}$) δ [ppm]
			found	reported[3]			
a	H	71	195–196°	196°	443 (444.5)	1670	6.8–8.4 (m, 20 H$_{\text{arom}}$)
b	4-CH$_3$	52	147–148°	148°		1670	2.1 (s, 6 H, —CH$_3$); 6.08–8.2 (m, 18 H$_{\text{arom}}$)
c	4-Cl	78	200–201°	202°		1650	6.0–8.1 (m, 18 H$_{\text{arom}}$)
d	4-NO$_2$	70	217–218°	217°	534 (534.5)	1640	6.4–8.6 (m, 18 H$_{\text{arom}}$)
e	4-Br	72	186–187°	188°		1660	6.2–8.2 (m, 18 H$_{\text{arom}}$)
f	4-OCH$_3$	68	163–164°	163°	504 (504.5)	1640	2.92 (s, 6 H, OCH$_3$); 6.0–8.2 (m, 18 H$_{\text{arom}}$)

[a] Melting points were determined using a Gallenkamp apparatus and are uncorrected. The microanalyses were in good accord with the calculated values: C, ±0.07; H, ±0.07; N, ±0.08.

[b] Recorded on Varian Mat Spectrometer.

[c] Recorded on a Perkin Elmer Infracord instrument.

[d] Recorded on Varian A-60 Spectrometer.

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