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2-ARYL-1,2,3-THIADIAZOLIUM SALTS

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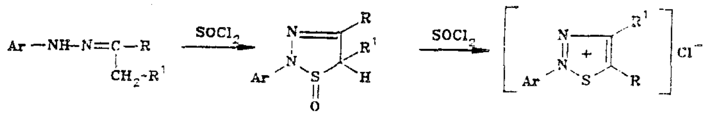
When arylhydrazones of α-methyleneketones are treated with thionyl chloride they form 2-aryl-1,2,3-thiadiazolium chlorides in high yield, via the intermediate 1,2,3-thiadiazol-3-ine 1-oxides. The effect of substituents on the course of the cyclization was investigated.

The reaction of acyl- and arenesulfonylhydrazones of α-methyleneketones with thionyl chloride gives 1,2,3-thiadiazoles; at the same time acyl- or arenesulfonyl groups are split off [1]. The final products are formed via the intermediate 1-oxides [2].

We have found that α-methyleneketone arylhydrazones containing electron-acceptor substituents in the aromatic nucleus of the hydrazine segment form 2-aryl-1,2,3-thiadiazolium (III) salts when boiled with thionyl chloride. When such groups are not present, as, e.g., in the case of acetophenone phenylhydrazone the reaction is extremely vigorous even at low temperature and produces a resinous reaction mass.



Ia-k IIh,k IIIa-j

a-e, h-k Ar=4-NO$_2$C$_6$H$_4$, f Ar=2-NO$_2$C$_6$H$_4$, g Ar=2,4-(NO$_2$)$_2$C$_6$H$_3$; a,e-g R=C$_6$H$_5$, b R=4-CH$_3$OC$_6$H$_4$, c R=CH$_2$C$_6$H$_5$, d R=4-CH$_3$(3-NO$_2$)C$_6$H$_3$, h R=2,5-Br$_2$C$_6$H$_3$, j R=C$_2$H$_5$, k R=4-NO$_2$C$_6$H$_4$; i R—R^1=(CH$_2$)$_4$; a R^1=C$_2$H$_5$, b-h,j,k R^1=H

In the case of p-nitrophenyl methyl ketone p-nitrophenylhydrazone (Ik) the reaction stops at the formation of 1,2,3-thiadiazol-3-ine 1-oxide (IIk), which is not converted to a salt even after boiling for many hours in thionyl chloride. Probably the electron-acceptor substituents in the aromatic nucleus of the ketone segment hinder the conversion of the intermediate 1-oxide to a 1,2,3-thiadiazolium salt. In the case of 2,5-dibromophenyl ketone p-nitrophenylhydrazone (Ih), reaction in thionyl chloride without heating gives the respective 1-oxide (IIh), which is converted to salt (IIIh) when boiled in thionyl chloride. Increasing the donor capability of substituent R accelerates cyclization and salt formation, so that in the case of hydrazones Ii,j the reactions proceed without heating.

In the IR spectra of the 1,2,3-thiadiazolium salts the NO$_2$ bands are very strong. Although it is known that 4-aryl-1,2,3-thiadiazoles have characteristic bands in the form of a doublet at 1470-1480 cm^{-1}, assigned to the vibrations of the five-membered heterocyclic ring [3], in this case they are overlapped by the nitro absorption. The IR spectra of 1,2,3-thiadiazol-3-ine 1-oxides (IIh, k) lack NH bands; this repudiates the 1,2,3-thiadiazol-4-ine structure assigned by Hurd and Mori [1] to the products of the reaction of ketone acylhydrazones and thionyl chloride. The intense C=N band at 1670-1660 cm^{-1} confirms the structure of 1,2,3-thiadiazol-3-ine 1-oxide.

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TABLE 1. Properties of 1,2,3-Thiadiazol-3-ine 1-Oxide (IIh, k) and 2-Aryl-1,2,3-thiadiazolium Salts (IIIa-j)

Compound	mp, °C (with decomp.)	Empirical formula	Yield, %	Compound	mp, °C (with decomp.)	Empirical formula	Yield, %
IIh	197	$C_{14}H_9Br_2N_3O_3S$	26	IIIe	215	$C_{14}H_{10}ClN_3O_2S$	47
IIk	273	$C_{14}H_{10}N_4O_5S$	27	IIIf	119	$C_{14}H_{10}ClN_3O_2S$	93
IIIa	204	$C_{16}H_{14}ClN_3O_2S$	81	IIIg	127	$C_{14}H_9ClN_4O_4S$	75
IIIb	173	$C_{15}H_{12}ClN_3O_3S$	92	IIIh	199	$C_{14}H_8Br_2ClN_3O_2S$	78
IIIc	144	$C_{15}H_{12}ClN_3O_2S$	74	IIIi	234	$C_{12}H_{12}ClN_3O_6S$	52
IIId	182	$C_{15}H_{11}ClN_4O_4S$	82	IIIj	206	$C_{10}H_{10}ClN_3O_6S$	60

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*Compound (IIh) crystallized from acetic acid; (IIIa-j), from DMSO.

EXPERIMENTAL

IR spectra were obtained with a UR-20 instrument in KBr tablets. The purity of the synthesized compounds was verified by TLC with Silufol UV-20 plates and chloforom eluent. Development was in UV light with iodine vapor.

Properties of compounds (I) and (II) are shown in Table 1. The contents of C, H, N, and Br agreed with those calculated.

α-Methyleneketone arylhydrazones were obtained by a known procedure, by boiling equimolar amounts of hydrazine and ketone in alcohol [4, p. 156].

Hydrazones not described here were obtained similarly.

<u>3-Nitro-4-methylacetophenone p-Nitrophenylhydrazone (Id, $C_{15}H_{14}N_4O_4$).</u> Yield 83%, mp 227°C.

<u>2,5-Dibromoacetophenonone p-Nitrophenylhydrazone (Ih, $C_{14}H_{11}Br_2N_3O_2$).</u> YIeld 78%, mp 194-195°C.

<u>p-Nitroacetophenone p-Nitrophenylhydrazone (Ik, $C_{14}H_{12}N_4O_4$).</u> Yield 83%, mp 260°C.

<u>2-Aryl-1,2,3-thiadiazolium Salts (IIIa-j).</u> α-Methyleneketone hydrazone (0.1 mole) was boiled for 1 h in 150 ml of thionyl chloride. Excess thionyl chloride was distilled off. The residue was filtered off and washed on the filter with chloroform. In the case of (IIIi, j) the hydrazone was dissolved in thionyl chloride at room temperature; after 15 min the precipitate was filtered off, washed with chloroform, dissolved in 100 ml of water, and treated with 10 ml of 30% perchloric acid. The perchlorate precipitate was filtered off. All the salts obtained were recrystallized from acetic acid.

<u>1,2,3-Thiadiazol-3-ine 1-Oxide (IIh, k).</u> The α-aminoketone hydrazone, 0.1 mole, was dissolved in thionyl chloride at room temperature. After 20 min the precipitate was filtered off and recrystallized from the appropriate solvent. IR spectrum of (IIh): 1662 (C=N), 1318 cm^{-1} (S=O); (IIk): 1675 (C=N), 1310 cm^{-1}(S=O).

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