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PREPARATION AND REACTION OF N-BENZIMIDOYLSULFILIMINES[1)]

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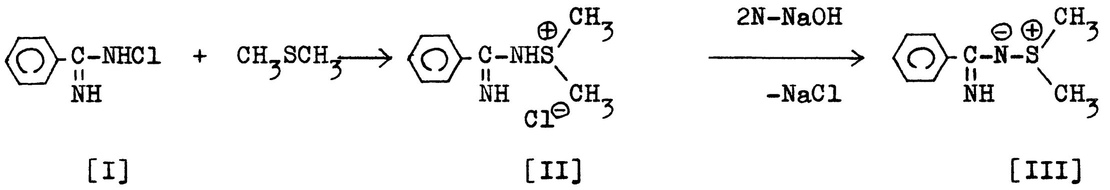
N-Chlorobenzamidine [I] reacted readily with dimethyl sulfide in acetonitrile to form N-benzimidoylaminodimethylsulfonium chloride [II]. Treatment of [II] with sodium hydroxide gave N-benzimidoyl-S,S-dimethylsulfilimine [III] quantitatively. The thermolysis of acyl derivatives of [III] gave rise to 1,2,4-oxadiazoles.

In a continuation of our previous work[2)3)] on the reactions of N-haloamidines, this communication deals with the preparation of sulfonium salt [II] from N-haloamidine and sulfide together with an interesting thermolysis of the acyl derivatives of new type sulfilimine [III] to 1,2,4-oxadiazoles.

Preparation of N-Benzimidoyl-S,S-Dimethylsulfilimine [III]



To a stirred solution of dimethyl sulfide (24 mmol) in acetonitrile (5 ml) was gradually added dropwise a solution of N-chlorobenzamidine (20 mmol) in acetonitrile (5 ml). The temperature was maintained below 15°C during the reaction. After about o.3 hour of continued stirring active chlorine disappeared and sulfonium salt [II] precipitated. [II] was separated by filtration and washed with acetonitrile, 76~84 % yield, mp 183°C. Recrystallization from ethanol gave a pure product, mp 183~183.5°C (Found : C, 49.27 ; H, 5.76 ; N, 12.90 % . Calcd for $C_9H_{13}N_2SCl$: C, 49.88 ; H, 6.05 ; N, 12.93 %). To a stirred solution of [II] (70 mmol) in water-chloroform (20 ml-70 ml) was added 2N sodium hydroxide (50 ml) below

5°C. After the chloroform layer was separated, residual [III] was extracted twice with 15 ml portions of chloroform. The combined extracts were dried (Na_2SO_4), filtered, and evaporated under reduced pressure. The residual needles were washed with ether and separated by filtration under nitrogen atmosphere, yield quant, mp 65~67°C. Recrystallization from chloroform - ether gave a pure sulfilimine [III], mp 67~68°C (Found ; N, 15.70 %. Calcd for $C_9H_{12}N_2S$: N, 15.54 %).

[III] is strong hygroscopic crystals and soluble in water and in usual organic solvent except in ether and in hydrocarbons. [III] is quite stable under reflux in THF for 3 hours but decomposes evolving methyl sulfide under reflux in xylene for 2 hours.

The structures of [II] and [III] were discussed on the basis of spectral data.

In IR spectra$^{4)}$, the C=N stretching vibration of [II] is at 1650 cm^{-1}, while that of [III] is at 1510 cm^{-1}. This shift is analogous to that observed in case of carbonyl group attached to ylid carbon atom or ylid nitrogen atom -----(a).

In UV spectra$^{5)}$, [II] and [III] have the same λmax (239 mμ) but εmax of [III] (11300) is 2100 larger than that of [II] -----(b).

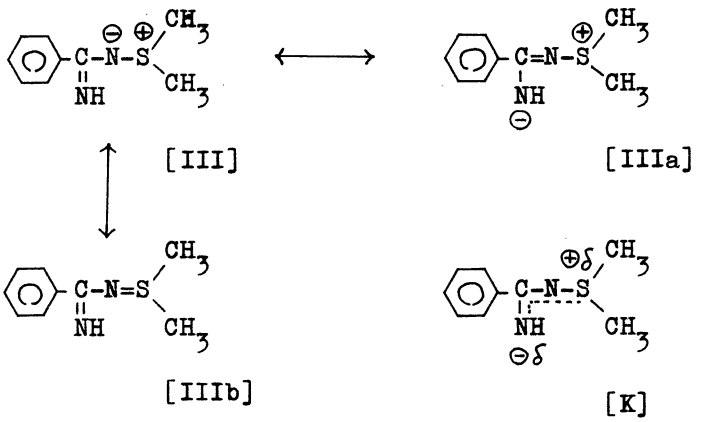
NMR spectra$^{6)}$; [II] : δ = 3.03 (s, $C\underline{H}_3SC\underline{H}_3$) , 9.00 (s, $N\underline{H}$) , 7.40~7.95 (m, $C_6\underline{H}_5$) ;
[III] : δ = 2.74 (s, $C\underline{H}_3SC\underline{H}_3$) , 5.50 (s, $N\underline{H}$) , 7.15~7.95 (m, $C_6\underline{H}_5$)

The resonances of protons to the positively charged sulfur atom and the nitrogen atom are shifted upfield by 0.3 ppm and 3.5 ppm respectively in going from [II] to [III] ----(c).

(a) and (c) suggest that the form [IIIa] is a contributor to the sulfilimine structure.

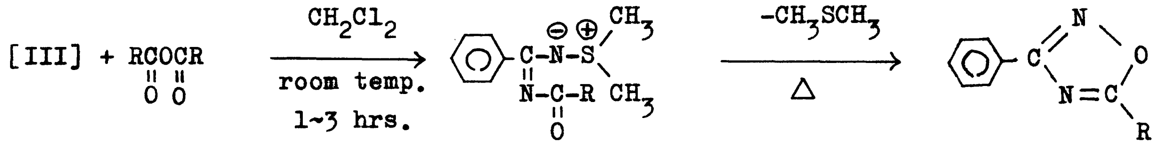
(b) and (c) suggest that the S-N bond possesses partial double bond character due to 2p-3d orbital overlap [IIIb].

The overall structure can be represented by [K].



These resonance forms may contribute to the stabilization of this new sulfilimine.

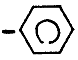
Thermolysis of Acyl Derivatives of [III] —— Formation of 1,2,4-Oxadiazoles



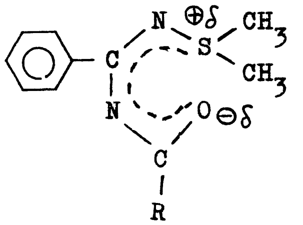
[IV]

Acyl derivatives of [III] were easily prepared by the treatment of [III] with acid anhydride. The results and physical properties are shown in Table I.

Table I. Physical properties of [IV]

Compd	R	Yield (%)	Mp ($^{\circ}$C)	IR Spectra (cm^{-1}) νC=N	IR Spectra (cm^{-1}) νC=O	Anal (Calcd) % C	Anal (Calcd) % H	Anal (Calcd) % N
IV-a	CH$_3$	60	114~116	1600	1620	59.60 (59.43)	6.01 (6.35)	12.51 (12.60)
IV-b		66	188~190	1570	1600	67.36 (67.58)	5.70 (5.67)	9.70 (9.85)
IV-c	CH$_3$-	54	172~173	1550	1590	67.83 (68.43)	6.13 (6.08)	9.10 (9.39)

The C=N absorption of [IV] is at shorter wavelength than that of [III], on the other hand, the C=O absorption is at longer wavelength than normal amide absorption. In consideration of these shifts in IR spectra, the structure of [IV] may be represented by [S].

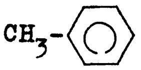


[S]

It was expected that 1,2,4-oxadiazole would be formed by the elimination of methyl sulfide. In fact, heating of [IV-b,c] without solvent in test tubes at about 200°C gave rise to 1,2,4-oxadiazoles. However, [IV-a] gave no corresponding product. The structures of these products were confirmed by elemental analysis and IR spectra.

The results are shown in Table II.

Table II. Formation of 1,2,4-Oxadiazoles

R	Reaction Temp.(°C)	Reaction Time(min.)	Yield (%) (crude product)	Mp (°C)	Anal (Calcd) %		
					C	H	N
	200~210	10	70	108 (108)[7]	75.74 (75.66)	4.56 (4.54)	12.67 (12.60)
	190~200	20	63	121 ~122	76.15 (76.25)	5.08 (5.12)	11.49 (11.86)
CH_3	160	5	0	-	-	-	-

The mechanism for this interesting internal ring formation has not been made clear yet[8].

References

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3) T.Fuchigami and K.Odo, Chem.Lett., 917 (1973).

4) [II] ; νNH 3250, 3100 cm^{-1} . [III] ; νNH 3300 cm^{-1}

5) UV spectra were obtained with a Hitachi 624 spectrophotometer using MeOH as solvent.

6) NMR spectra were obtained with a Hitachi R-24A spectrometer using TMS as internal standard; s-singlet, m-multiplet.
Solvent ; [II] : DMSO-d_6 . [II] : $CDCl_3$

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