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The Preparation and Properties of Mesoionic 5-Iminothiazole Derivatives

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Mesoionic 5-iminothiazoles were prepared by the cyclization of *N*-thiobenzoyl-methylaminoacetonitriles with hydrogen chloride or acyl chlorides. The reaction between a 5-aminothiazolium chloride and acyl chlorides, isocyanate, sulfonyl chloride, and nitrous acid gave the corresponding *N*-substituted mesoionic 5-iminothiazole derivatives. The spectral data of these compounds as well as the ready bromination of the ring support the view that this ring system is aromatic.

Although the chemistry of mesoionic thiazole derivatives in general has been widely investigated,[2)] only a single derivative of mesoionic 5-iminothiazole (3,5-dihydro-5-iminothiazole or anhydro 3-substituted 5-aminothiazolium hydroxide) has been described in the literature.[3)] That paper concerns the formation of mesoionic 3-methyl-2,4-diphenyl-5-phenyliminothiazole by the proton-catalyzed rearrangement of mesoionic 1-methyl-2,3,5-triphenylimidazole-4-thione. This rearrangement has been found to be difficult to reproduce and no properties of the mesoionic 5-iminothiazole have been described. Unsuccessful attempts to prepare this ring system by the action of amines on 5-methylmercaptothiazolium salts have been reported earlier.[4)]

The preparation of some 3-substituted 5-aminothiazolium salts by the alkylation of the corresponding 5-aminothiazoles has been described earlier.[5,6)] In one case, even treatment with methyl iodide of 5-acetamido-2-thio-3-isopropylthiazoline in aqueus sodium hydroxide has been studied.[6)] It is reported, however, that this treatment, instead of affording the corresponding mesoionic compound or inner salt, gave the corresponding thiazolium hydroxide.

We wish to report here a more reliable method of

1) To whom inquiries should be addressed.

2) M. Ohta and H. Kato, "Nonbenzenoid Aromatics," ed. by J. P. Snyder, Academic Press, New York (1969), p. 117.

3) R. Huisgen, E. Funke, F. C. Schaeffer, H. Gotthardt, and E. Brunn, *Tetrahedron Lett.*, **1967**, 1809.

4) T. Shiba and H. Kato, This Bulletin, **43**, 3941 (1970).

5) A. H. Cook, I. M. Heilbron, and A. L. Levy, *J. Chem. Soc.*, **1947**, 1594; E. D. Sych and L. P. Umanskaya, *Zh. Obshch. Khim.*, **34**, 2068 (1964); *Chem. Abstr.*, **61**, 10805 (1964).

6) A. H. Cook and S. F. Cox, *J. Chem. Soc.*, **1949**, 2337.

synthesizing mesoionic 5-iminothiazoles, a method promising a wider synthetic applicability, and also some properties of the ring system thus prepared.

Results and Discussion

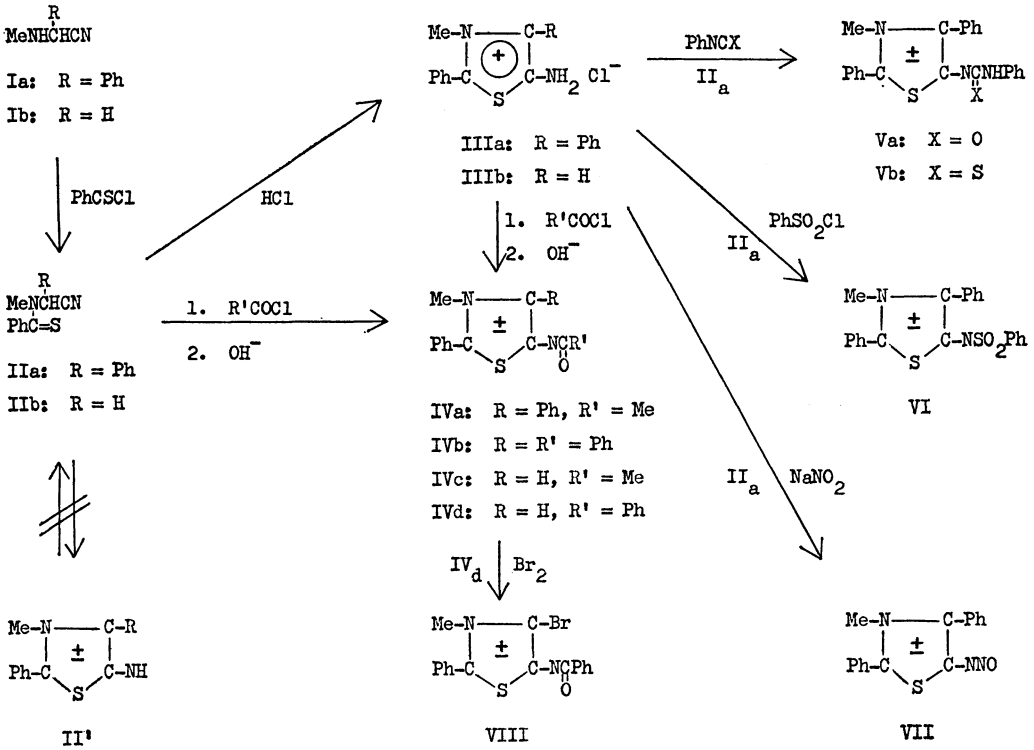
Preparation and Recations. The thiobenzoylation of two acetonitriles, Ia and Ib, gave *N*-thiobenzoylmethylaminoacetonitriles (IIa and IIb). The two nitriles, IIa and IIb, showed only a very weak absorption of a cyano group in the infrared region, suggesting the possibility that II may partly tautomerized to cyclic mesoionic iminothiazoles, II'. However, the lack of any infrared bands assignable to an NH group, and the fact that II did not react with acetic anhydride, eliminate such a possibility.

The treatment of thiobenzoylaminoacetonitriles, IIa and IIb, with hydrogen chloride in aprotic solvents gave 5-aminothiazolium hydrochlorides, IIIa and IIIb, as hygroscopic compounds. The hydrochlorides were characterized by conversion to the corresponding perchlorates and picrates. The structures of these salts were determined by elemental analyses, spectroscopic data, and the reactions to be described below. On heating the hydrochlorides, IIIa and IIIb, with acetyl and benzoyl chloride, the corresponding *N*-acetyl- and *N*-benzoyl-aminothiazolium chlorides, IVa—d,HCl, were formed. Alternatively, the same *N*-acylaminothiazolium chlorides, IVa—d,HCl, were prepared by the reaction of thiobenzoylaminoacetonitriles, IIa and IIb, with acetyl and benzoyl chloride in benzene. The mode of the formation of these compounds is analogous to that of sydnone imines.[7]

The treatment of the salts, IVa—d,HCl, with alkali afforded mesoionic 5-acyliminothiazoles, IVa—d. In a similar manner, the corresponding phenylcarbamoyl- and phenylthiocarbamoyl-iminothiazole, Va and Vb, were prepared by the treatment of 5-amino-3-methyl-2,3,4-diphenylthiazolium chloride (IIIa) with phenyl isocyanate and phenyl isothiocyanate respectively. Thiazolium chloride, IIIa, reacted with benzenesulfonyl chloride in the presence of a base to afford mesoionic 5-benzenesulfonyliminothiazole, VI. By the action of sodium nitrite on IIIa, *N*-nitroso-iminothiazole VII was formed slowly. It was anticipated that the elimination of a molecule of nitrogen from VII, in a fashion analogous to that with *N*-nitroso-sydnone imines,[8] would give the corresponding mesoionic 5-oxothiazole.[2,9] However, both the pyrolysis and photolysis of the *N*-nitroso derivative, VII, in aprotic solvents resulted in a polymer formation, and no nitrogen evolution was observed.

In order to obtain chemical support concerning the aromatic nature of the mesoionic 5-iminothiazole ring, the bromination of IVd was carried out. Bromination took place readily at the 4-position of IVd to afford 4-bromo-5-benzoylimino-3-methyl-2-phenylthiazole VIII. The structure of the bromide was assigned on the basis of elemental analyses, the lack of an NMR signal around τ 2.7, and the lack of an infrared band at 3080 cm^{-1} (*vide infra*).

The hydrochlorides III and acyliminothiazoles IV



Scheme 1. Preparation and Reactions of 5-iminothiazoles

7) H. Kato, M. Hashimoto, and M. Ohta, *Nippon Kagaku Zasshi*, **78**, 707 (1957).

8) L. E. Kholodov and V. G. Yashunskii, *Byul. Izobret Tovarnykh Znakov, No.* **16**, 37 (1965); *Chem. Abstr.*, **64**, 3557 (1966); S. A. Zotova and V. G. Yashunski, *Zh. Organ. Khim.*, **3**, 1889 (1967).

9) A. Lawson and C. E. Searle, *J. Chem. Soc.*, **1957**, 1556; G. C. Barrett and A. R. Khokhar, *J. Chem. Soc., C*, **1969**, 1117.

are quite stable to acid, and were recovered unchanged after having been heated with 10% hydrochloric acid for one hour. It appears that the iminothiazoles have a considerable basicity because the hydrochloride IIIa was unchanged by treatment with aqueous sodium hydrogen carbonate. Even the *N*-acyl derivatives IV readily form hydrochlorides and picrates.

Spectral Properties (Cf. Tables 1 and 2). The large hypsochromic shifts of the ultraviolet absorption maxima of IV at the longest wave length with an increase in the solvent polarity show that they are $n\rightarrow\pi$ transitions; they may also suggest that there is a considerable charge separation between the heterocyclic ring and the exocyclic acylimido group.[10]

The infrared spectra of 5-iminothiazoles unsubstituted at the 4-position show a medium intensity peak at 3100 cm^{-1} (hydrochlorides) or 3080 cm^{-1} (free bases) which may be assigned as the C–H stretching band of the 4-position. None of the free bases of *N*-acyl (IVa—d) and *N*-carbamoyl (Va) derivatives shows an infrared absorption band of the carbonyl group in a region normally expected for an amide group. The infrared spectra of the corresponding salts (IVa—d, HCl, Va,HCl) show an absorption at 1630—1680 cm^{-1}, but this absorption is weaker than that expected for a normal amide carbonyl band. Moreover, they usually show both the absorption bands assignable to a hydroxyl and an ammonium (and/or amino) group.

The NMR signal of the 3-methyl group of mesoionic iminothiazoles, IV, appears at τ 6.05—6.25, a position which is higher by *ca.* 0.2 ppm than that of the corresponding aminothiazolium chlorides, IV,HCl. The signal of the proton at the 4-position of IVc and IVd appears at *ca.* τ 2.7, whereas that of thiazolium hydrochloride, IVc,HCl, is shifted considerably to a lower magnetic field and appears at τ 1.15. This shift of the proton signal with the hydrochloride may partly be due to a solvent effect, because this spectrum had to be taken in a mixture of deuteriochloroform and deuteriodimethyl sulfoxide. In fact, the position of the proton signal of the 4-position of IVb is fairly much dependent upon the solvent employed (Table 2). This shift is probably due to the formation of a hydrogen bond with the solvent.[11] The chemical shift values of the

TABLE 1. ULTRAVIOLET AND INFRARED SPECTRA OF 5-IMINOTHIAZOLE DERIVATIVES

Compound	λ_{max}^{EtOH} (nm) (log ε)	IR (KBr, cm^{-1})[a]
IIIa[b]	250 (4.004)	3420, 3230, 3100, 1670, 1565, 1475, 1360, 1320
	320 (4.021)	
IIIb[c]	350 (4.032)	3210, 3110, 1580, 1515, 1315
IVa,HCl	250 (4.039)	3640, 3240, 2930, 3680—2160, 1660, 1580, 1515, 1480, 1360, 1270
	320 (4.076)	
IVb,HCl	230 (4.356)	3600—2200,1630, 1580, 1480, 1280
	325 (4.170)	
IVc,HCl	240 (3.908)	3660—3200, 3100, 2900—2500, 2790, 2750, 2710, 2610, 1660, 1580, 1530, 1355, 1285
	318 (4.083)	
IVd,HCl	230 (4.233)	3650—2500, 2930, 1750,1650, 1580, 1520, 1304
	320 (4.164)	
Va,HCl		3660—2500, 1680,1580, 1550, 1485, 1300, 1215

	λ_{max}^{EtOH}	Pyridine	Tetrahydrofuran	Cyclohexane[d]	IR (KBr, cm^{-1})[a]
IVa	240 (4.078)			255	1550, 1520, 1450, 1380
	304 (3.868)	325 (3.951)	325 (4.017)	330	
	374 (3.992)	405 (4.067)	410 (4.071)	420	
IVb	228 (4.385)				1580, 1500, 1450, 1430, 1370
	328 (4.051)	340 (4.072)			
	390 (4.232)	435 (4.176)			
IVc	250 (3.987)			257	3080, 1560, 1490, 1470, 1380, 1220
	360 (4.028)	388 (4.102)	394 (4.051)	400	
IVd	287 (3.856)				3080, 1580, 1560, 1490, 1470, 1385, 1340
	372 (4.257)	397 (4.267)			
Va					3260, 1590, 1560, 1450, 1375, 1300

a) Only medium to strong bands between 4000—1200 cm^{-1} are listed. Underlined wave-numbers indicate the strongest bands.
b) UV spectrum was taken on perchlorate.
c) Perchlorate
d) Due to the low solubility in this solvent, extinction coefficients could not be determined.

10) A. E. Gillam and E. S. Stern, "An Introduction to Electronic Absorption Spectroscopy in Organic Chemistry," Edward Arnold, London (1955), P. 260; W. A. Lees and A. Buraway, *Tetrahedron*, **19**, 419 (1963).

11) J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. II, Pergamon Press, Oxford (1966), p. 855; R. F. Smith, J. L. Deutsch, P. A. Almeter, D. S. Johnson, S. M. Roblyer, and T. C. Rosenthal, *J. Heterocycl. Chem.*, **7**, 671 (1970).

Table 2. NMR spectra of 5-iminothiazole derivatives

Compound	2-Ph	3-Me	4-Ph	4-H	5-Substituent
IIIa	2.40—2.60	6.15	2.15—2.40 2.40—2.60	—	4.60—5.10
IIIb[a)b)]	2.33	6.01	—	2.68	—
IVa,HCl	2.15—2.40	6.07	1.82—1.93 2.55—2.70	—	7.70
IVb,HCl	1.98—2.62	6.07	1.98—2.62	—	1.98—2.62
IVc,HCl[a)]	2.30	5.88	—	1.15	7.68
IVa	2.42	6.25	2.30—2.62	—	7.81
IVb[a)]	2.15—2.80	6.12	2.15—2.80	—	2.15—2.80
IVc	2.46	6.05	—	2.68[c)]	7.74
IVd	2.46	6.09	—	2.72	1.65—1.78 2.50—2.65
VIII	2.43	5.98	—	—	1.55—1.73 2.50—2.64

a) Measured as a solution in $CDCl_3$-DMSO-d_6 (1:1)
b) Perchlorate
c) Chemical shifts in other solvents: DMF: 705, dioxane: 731, acetonitrile: 739, acetone: 743, $CDCl_3$-DMSO-d_6 (1:1): 753 Hz downfield from internal TMS.

3-methyl group and the 4-hydrogen atom are those usually encountered with common aromatic azoles[12] and many other mesoionic ring systems.[2]

From the properties of IV described above, one may infer that this ring system shows a certain degree of aromaticity, that there is a considerable charge separation between the ring and the exocyclic acylimido group, and that the acyl group is considerably polarized.

Experimental[13]

The Attempted Proton-catalyzed Isomerization of 1-Methyl-2,3,5-triphenylimidazole-4-thione.[3] *a*) A solution of 1 g of 1-methyl-2,3,5-triphenylimidazole-4-thione (imidazolethione) in 50 m*l* of chloroform was saturated with dry hydrogen chloride with cooling. After stirring for four hours at 20°C, the solvent was distilled off and the colorless residue of the hydrochloride (mp 195—197°) was collected. On treatment with aqueous sodium bicarbonate or even with water, 0.8 g of imidazolethione was recovered.

Imidazolethione was recovered in 75—100% yields, after treatment with bicarbonate or with water, when the chloroform solution was treated with: *b*) a slow stream of hydrogen chloride for fifteen hours at 20—30°C, *c*) with an equivalent amount of hydrogen chloride for five hours or overnight, or *d*) with conc. hydrochloric acid for two hours, or *e*) when a solution of imidazolethione in tetrahydrofuran was treated as has been described in procedure *a*). In every case, the crude hydrochloride or the recovered crude imidazolethione showed no infrared absorption at 1670 cm^{-1}.

1,3-Dimethyl-2,5-diphenylimidazole-4-thione[4] was also recovered unchanged when it was treated by methods similar to those described above.

N-*Thiobenzoyl-α-phenyl-methylaminoacetonitrile (IIa)* Into a solution of 3 g (0.019 mol) of thiobenzoyl chloride in 20 m*l* of triethylamine, there was dropwise added with stirring at 0°C, 2.8 g (0.019 mol) of α-phenyl-methylaminoacetonitrile. After thirty minutes' stirring, the solvent was removed under reduced pressure and the residue was extracted with benzene. The benzene extract was washed with water and dried over sodium sulfate. After the solvent had been distilled off, an oily residue remained; this solidified upon the addition of isopropanol, Recrystallization from isopropanol gave 2 g (54% yield) of yellow prisms melting at 79—81°C. IR: 2230 (CN), 1380, 1068 (C=S); NMR: 7.05 (3H, s, Me), 2.30—2.80 (10H ,m, Ph), 1.55 (1H, s, CH).

Found: C, 71.93; H, 5.32; N, 10.54%. Calcd for $C_{16}H_{14}N_2S$: C, 72.16; H, 5.30; N, 10.52%.

N-*Thiobenzoyl-methylaminoacetonitrile (IIb).* This was prepared in a 50% yield, by a method similar to that described above, from 2 g (0.028 mol) of methylaminoacetonitrile and 4.4 g (0.028 mol) of thiobenzoyl chloride. Colorless needles (from isopropanol); mp 123—124°C. IR: 2240 (CN), 1375, 1084 (C=S); NMR 6.70 (3H, s, Me), 4.92 (2H, s, CH_2), 2.60 (5H, s, Ph).

Found: C, 62.87; H, 5.43; N, 14.53%. Calcd for $C_{10}H_{10}N_2S$: C, 63.15; H, 5.30; N, 14.73%.

5-Amino-3-methyl-2,4-diphenylthiazolium Chloride (IIIa). Hydrogen chloride was saturated to a solution of 1 g of IIa in 40 m*l* of anhydrous ether. The white powder which slowly separated out was recrystallized from ethanol-acetone (2:5) to give 1 g (91% yield) of colorless prisms melting at 206—207°C.

Found: C, 63.32; H, 5.12; N, 9.52%. Calcd for $C_{16}H_{15}N_2SCl$: C, 63.57; H, 4.97; N, 9.27%.

Perchlorate. Colorless prisms [from ethanol-acetone (1:4)]: mp 302—303°C.

Found: C, 52.77; H, 4.05; N, 7.24%. Calcd for $C_{16}H_{16}N_2O_4SCl$; C, 52.48; H, 4.38; N, 7.61%.

Picrate. Yellow needles (from ethanol): mp 200—201.5°C. Found: C, 53.63; H, 3.26; N, 13.81%. Calcd for $C_{22}H_{17}N_5O_7S$: C, 53.33; H, 3.45; N, 14.13%.

5-Amino-3-methyl-2-phenylthiazolium Chloride (IIIb). This was prepared by the saturation of hydrogen chloride in a

12) *Cf. e.g.*, "NMR Spectra Catalog," Vol. I and II, Varian Associates, Palo Alto, Calif, (1962, 1963); H. A. Szymanski and R. E. Yelin, "NMR Band Handbook," IFI/Plenum, New York (1968).

13) The melting points were determined on a micro hot stage, and are not corrected. The ultraviolet spectra were recorded on a Hitachi model ESP-2U spectrophotometer and the infrared spectra were recorded as KBr disks on a Hitachi model EPI-SII spectrophotometer. The NMR spectra were measured using a JEOLCO JNM-4H-100 (100 MHz) spectrometer in deuteriochloroform solutions containing tetramethylsilane as internal standard, and the chemical shifts are given in τ values. The mass spectra were measured at 75 eV using a direct inlet technique.

benzene solution of IIb. Since it was very hygroscopic, it was characterized by converting it to the corresponding perchlorate and picrate. The yields were in the range of 80—95%.

Perchlorate. White prisms; mp 132—133°C. Found: C, 41.52; H, 3.58; N, 9.48%. Calcd for $C_{10}H_{11}N_2O_4SCl$: C, 41.38; H, 3.79; N, 9.65%.

Picrate. Yellow needles (from ethanol); mp 125—126°C. Found: C, 45.98; H, 3,37; N, 16.89%. Calcd for $C_{16}H_{13}N_5O_7S$: C, 45.83; H, 3,13; N, 16.70%.

5-Acetylamino-3-methyl-2,4-diphenylthiazolium Chloride (IVa, HCl). (*a*) A solution of 5 g (0.02 mol) of nitrile IIa and 3.1 g(0.04 mol) of acetyl chloride in 50 m*l* of benzene was allowed to stand for two days at room temperature. The white precipitate was recrystallized from acetone-isopropanol (4:1) to give 4.8 g (70% yield) of fine, colorless needles melting at 207—208°C (dec.).

Found: C, 62.43; H, 5.10; N, 7.72%. Calcd for $C_{18}H_{17}N_2OSCl$: C, 62.69; H, 4.97; N, 8.12%.

(*b*) A mixture of 0.22 g of thiazolium chloride, IIIa, and 3 m*l* of acetyl chloride was heated under reflux on a water bath for two hours. After cooling, the solid precipitate was collected, washed with ether, and recrystallized from acetone-isopropanol (4:1) to give the same product, IVa,HCl, in a 84% yield.

Picrate of IVa. Yellow needles (from ethanol); mp 166—167°C. Found: C, 58.19; H, 3.73; N, 11.42%. Calcd for $C_{29}H_{21}N_5O_8S$: C, 58.09; H, 3.51; N, 11.68%.

5-Acetylimino-3-methyl-2,4-diphenylthiazole (IVa). An aqueous solution of IVa,HCl was made alkaline with sodium hydrogen carbonate and was then extracted with benzene. The benzene extract was dried over sodium sulfate, the solvent was distilled off, and the residue was recrystallized from acetone to give yellow prisms; mp 229—230°C. Mass *m/e* (rel. intensity): 308(33,P), 293 (65, P—Me), 265 (1, P—Ac), 121 (100, PhC=S), 118 (37, PhC=MMe), 77 (43, Ph), 43 (27, Ac).

Found: C, 69.83; H, 5.12; N, 8.80%. Calcd for $C_{18}H_{16}N_2OS$: C, 70.10; H, 5.22; N, 9.08%.

By procedures similar to those described above, the following compounds were prepared.

5-Benzoylamino-3-methyl-2,4-diphenylthiazolium Chloride (IVb, HCl). Colorless prisms [from acetone-ethanol (4:1)]; mp 187—188°C, yield 74%.

Found: C, 67.60; H, 4.68; N, 6.68%. Calcd for $C_{23}H_{19}N_2OSCl$: C, 67.90; H, 4.71; N, 6.89%.

Picrate of IVb. Yellow needles (from ethanol); mp 166—167°C.

Found: C, 58.19; H, 3.73; N, 11.42%. Calcd for $C_{29}H_{21}N_5O_8S$: C, 58.09; H, 3.51; N, 11.68%.

5-Benzoylimino-3-methyl-2,4-diphenylthiazole (IVb). Yellow prisms (from acetone); mp 259—260°C; yield, 82%.

Found: C, 74.79; H, 4.87; N, 7.25%. Calcd for $C_{23}H_{18}N_2OS$: C, 74.58; H, 4.90; N, 7.56%.

5-Acetylamino-3-methyl-2-phenylthiazolium Chloride (IVc,HCl). Colorless prisms (from isopropanol); mp 243—244°C (dec); yield, 87%.

Found: C, 53.36; H, 5.02; N, 10.16%. Calcd for $C_{12}H_{13}N_2OSCl$: C, 53.63; H, 4.88; N, 10.42%.

5-Acetylimino-3-methyl-2-phenylthiazole (IVc). Colorless needles (from acetone); mp 219—220°C; yield, 75%. Mass *m/e* (rel. intensity): 232 (35, P), 217 (100, P—Me), 189 (1, P—Ac), 121 (74, PhC=S), 118 (28, PhC=NMe), 77 (very intense, Ph), 43 (very intense, Ac).

Found: C, 61.92: H, 5.29; N, 12.24%. Calcd for $C_{12}H_{12}N_2OS$: C, 62.06; H, 5.21; N, 12.06%.

5-Benzoylamino-3-methyl-2-phenylthiazolium Chloride (IVd,HCl). Colorless prisms (from isopropanol); mp 237—238°C; yield, 91%.

Found: C, 61.40; H, 4.56; N, 8.24%. Calcd for $C_{17}H_{15}N_2OSCl$: C, 61.72; H, 4.57; N, 8.46%.

5-Benzoylimino-3-methyl-2-phenylthiazole (IVd). Yellow leaflets (from acetone-ethanol); mp 261—262°C; yield, 90%.

Found: C, 69.18; H, 4.74; N, 9.73%. Calcd for $C_{17}H_{14}N_2OS$: C, 69.37; H, 4.80; N, 9.52%.

5-Phenylcarbamoylimino-3-methyl-2,4-diphenylthiazole (Va). This was prepared from IIa and phenyl isocyanate by heating them on a water bath for 2 hr, and then treating them with sodium hydrogen carbonate. Yellow prisms (from acetone-ethanol); mp 245—246°C; yield, 75%.

Found: C, 72.10; H, 4.75; N, 11.17%. Calcd for $C_{23}H_{19}N_3OS$: C, 71.67; H, 4.97; N, 10.90%.

Hydrochloride of Va. White prisms (from acetone); mp 230—231°C (dec.).

Found: C, 65.07; H, 4.52; N, 9.63%. Calcd for $C_{23}H_{20}N_3OSCl$: C, 65.47; H, 4.77; N, 9.95%.

5-Phenylthiocarbamoylimino-3-methyl-2,4-diphenylthiazole (Vb). Yellow leaflets (from aceton-ethanol); mp 241—242°C; yield, 82%.

Found: C, 68.50: H, 4.54; N, 10.10%. Calcd for $C_{23}H_{19}N_3S_2$: C, 68.82; H, 4.77; N, 10.47%.

5-Benzenesulfonylimino-3-methyl-2,4-diphenylthiazole (VI) To a solution of 0.5 g of IIIa in 5 m*l* of water, 0.3 g of benzenesulfonyl chloride and then two molar equivalents of aqueous potassium hydroxide were slowly added with cooling and stirring. The precipitate was recrystallized from ethanol to give 0.25 g (37% yield) of yellow prisms melting at 242—243°C. IR: 1130 (SO_2).

Found: C, 64.76; H, 4.23; N, 6.77%. Calcd for $C_{22}H_{18}N_2O_2S_2$: C, 65.02; H, 4.46; N, 6.89%.

5-Nitrosoimino-3-methyl-2,4-diphenylthiazole (VII). To a cooled solution of 1.0 g of IIIa in 6 m*l* of water, a solution of 0.3 g of sodium nitrite in 4 m*l* of water was added, after which the mixture was allowed to stand for two days at room temperature. The yellow precipitate which slowly separated out was recrystallized from ethanol to give 0.5 g (51% yield) of yellow prisms melting at 187—188°C (dec.). IR: 1110, 1190 (N–O–?).

Found: C, 64.85; H, 4.51; N, 13.99%. Calcd for $C_{16}H_{13}N_3OS$: C, 65.08; H, 4.44; N, 14.23%.

5-Benzoylamino-4-bromo-3-methyl-2-phenylthiazolium Bromide (VIII,HBr). To a suspension of 0.5 g of IVd in 20 m*l* of ether, 0.1 m*l* of bromine was added with stirring and cooling. After twenty minutes, the newly-formed precipitate was recrystallized from ethanol to give 0.5 g (80% yield) of white prisms melting at 184—185°C (dec.). IR: 3340, 1660, 1570, 1455, 1305, 1270.

Found: C, 44.60; H, 2.94; N, 5.96%. Calcd for $C_{17}H_{14}N_2OSBr_2$: C, 44.96; H, 3.11; N, 6.17%.

The Free Base VIII was formed by the treatment of the hydrobromide with aqueous sodium hydrogen carbonate. Yellow prisms (from ethanol); mp 235—236°C. IR: 1460, 1380.

Found: C, 54.84; H, 3.31; N, 7.22%. Calcd for $C_{17}H_{13}N_2OSBr$: C, 54.71; H, 3.51; N, 7.51%.

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