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Studies on Mesoionic Compounds. VIII.[1] Some Reactions of the Mesoionic 4-Amino-1,2,4-triazolium-3-thiolate System[2]

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N-Acylaminorhodanine (II) reacted with hydrazine hydrate to afford the mesoionic 4-amino-1,2,4-triazolium-3-thiolate (I). Reactions of I with methyl iodide, sodium nitrite, and acylating agents were investigated. Acylation of I gave diacyl derivatives (VII and VIII), and alkaline hydrolysis of these compounds afforded monoacyl derivatives (IX and X). The monoacyl compounds (IX—XI) were derivatived to aminimides (XII—XIV) by treatment with methyl iodide and alkali.

Keywords——mesoionic compound; 1,2,4-triazole; acylation; methiodide; aminimide

The synthesis of 4-amino-1,5-diphenyl-1,2,4-triazolium-3-thiolate (Ia) was first reported by Lazaris *et al.* in 1972.[4] Recently Ollis *et al.*[5] described a similar synthesis of the same ring system (I) (Chart 1). Among various five-membered mesoionic compounds,[6] the synthesis of derivatives possessing an electron-releasing substituent such as amino, alkoxyl, and hydroxyl groups has not been described, except for a few examples of sydnone and sydnone imine compounds.[7] Therefore, compound (I), having primary amino group, is almost unique. We now report some reactions of I.

When triethylammonium 3-acyldithiocarbazates were treated with chloroacetic acid, the rhodanine derivatives (II) were isolated. The mesoionic compound (I) was also obtained by reactions of II with hydrazine hydrate. However, similar reactions of II with substituted hydrazine compounds such as phenylhydrazine resulted in the formation of many complex materials. The compound (I) was very stable to acid and alkali. These compounds were characterized as the benzylidene derivatives by treatment with benzaldehyde.[4,5] The action of nitrous acid on the compound (I) gave the disulfide (III); the claim[4] that the triazolethione (IV) is formed in this reaction was incorrect.[5] Actually, lithium aluminum hydride reduction of the product of the above reaction gave IV. Oxidation of IV with iodine[5,8] afforded III in high yield. On the other hand, in the infrared (IR) spectra of I strong absorption bands were observed at 1400—1380 cm^{-1}, which were attributed to thione stretching.[9] Furthermore, the presence of an exocyclic sulfur atom was confirmed, as with many other thione-type

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[6] Recent reviews in this area include: *a*) M. Ohta and H. Kato, "Nonbenzenoid Aromatics," Vol. 1, ed. by J.P. Snyder, Academic Press, New York, 1969, p. 117; *b*) W.D. Ollis and C.A. Ramsden, "Advances in Heterocyclic Chemistry," Vol. 19, ed. by A.R. Katritzky and A.J. Boulton, Academic Press, New York, 1976, p. 1.

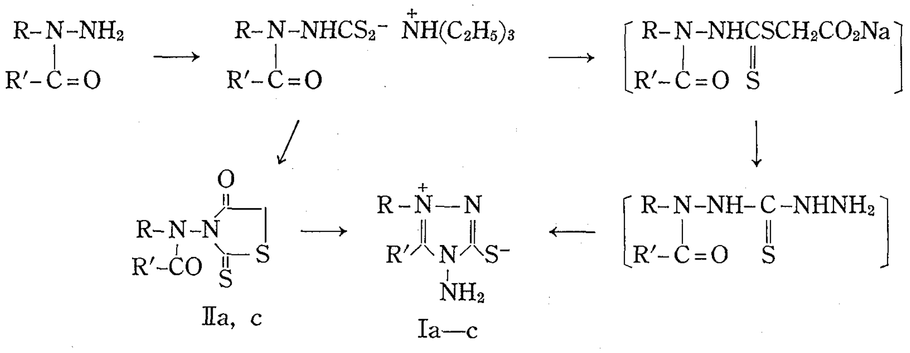
[7] *a*) K. Masuda, S. Kishimoto, and T. Kaneko, *Oyo Yakuri*, **2**, 280 (1968); *b*) M. Götz and K. Grozinger, *J. Heterocycl. Chem.*, **7**, 123 (1970); *c*) *Idem.*, *Tetrahedron*, **27**, 4449 (1971); *d*) M. Götz, K. Grozinger, and J.T. Oliver, *J. Med. Chem.*, **16**, 671 (1973).

[8] E. Fromm and A. Trnka, *Ann.*, **442**, 150 (1925).

[9] M. Ohta, H. Kato, and T. Kaneko, *Bull. Chem. Soc. Jpn.*, **40**, 579 (1967).

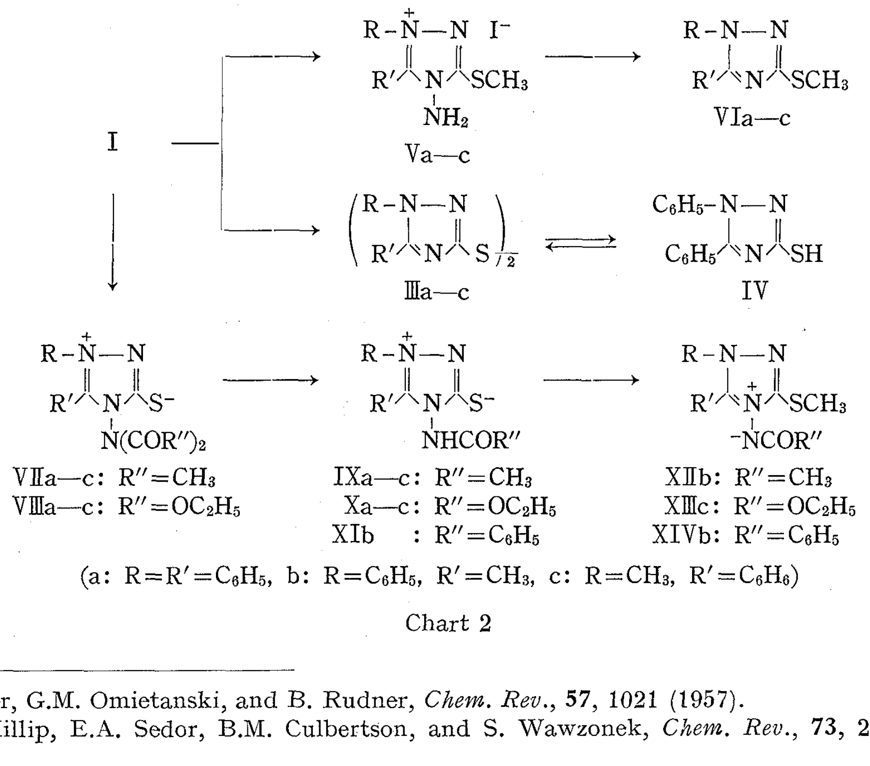
mesoionic compounds, by methylation with methyl iodide to give the methiodide (V). Heating of V in morpholine or piperidine gave a mixture of the original mesoionic compound (I) and the deaminated triazole derivative (VI). The formation of VI was due to pyrolysis of the quaternary salt.[10] Thus, only VI was obtained on refluxing of V at high temperature (in pyridine, dioxane or toluene).

On the acylation of I, reactions using an excess (more than two equivalents) of acetic anhydride and ethyl chloroformate gave the corresponding diacyl derivatives (VII and VIII), respectively. When an equimolar amount or a small excess of these acylating agents was used, a mixture of the monoacyl and diacyl derivatives was formed. In the case of benzoylation, however, only the monobenzoyl compound (XI) was obtained. The diacyl compounds (VII and VIII) were easily hydrolyzed by dilute alkaline solution at room temperature to afford the corresponding monoacyl compounds (IX and X). These monoacyl derivatives (IX—XI) could be derivatized to the aminimides[11] (XII—XIV) on treatment with methyl iodide followed by alkali. In the IR spectra of the compounds (XII—XIV), the absorptions of carbonyl stretchings appeared in a lower frequency region than those of the mesoionic monoacyl compounds (IX—XI) by 110—150 cm^{-1}. Nuclear magnetic resonance (NMR) and



(a: $R=R'=C_6H_5$, b: $R=C_6H_5$, $R'=CH_3$, c: $R=CH_3$, $R'=C_6H_5$)

Chart 1



(a: $R=R'=C_6H_5$, b: $R=C_6H_5$, $R'=CH_3$, c: $R=CH_3$, $R'=C_6H_6$)

Chart 2

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10) H.H. Sisler, G.M. Omietanski, and B. Rudner, *Chem. Rev.*, **57**, 1021 (1957).
11) W.J. McKillip, E.A. Sedor, B.M. Culbertson, and S. Wawzonek, *Chem. Rev.*, **73**, 255 (1973).

mass spectral data also supported the formation of the compounds (XII—XIV). These aminimides did not react with dipolarophiles such as dimethyl acetylenedicarboxylate, and on thermolysis gave VI.

Experimental[12]

4-Amino-1,2,4-triazolium-3-thiolates (I)——Using the reported method,[4,5] the compounds (Ia—c) were prepared in the following way. An aqueous solution of equimolar amounts of triethylammonium 3-acyldithiocarbazate (prepared from N′-phenylbenzhydrazide,[13] N′-phenylacethydrazide,[14] or N′-methylbenzhydrazide[15] by treatment with NEt_3 and CS_2 in EtOH) and sodium chloroacetate was heated with an excess of $N_2H_4 \cdot H_2O$ on a steam bath for 1.5 hr. After cooling, the resulting precipitates were collected and recrystallized to give I.

Ia: Pale yellow needles, mp 225—226° (MeOH) (lit.[4]) mp 215—216°). IR ν_{max}^{KBr} cm^{-1}: 3200, 3160, 1390. UV λ_{max}^{EtOH} nm (log ε): 247 (4.45), 318 (3.57). MS *m/e*: 268 (M^+). *Anal.* Calcd. for $C_{14}H_{12}N_4S$: C, 62.66; H, 4.51; N, 20.88. Found: C, 62.85; H, 4.22; N, 21.02.

Ib: Colorless plates, mp 220—223° (MeOH). IR ν_{max}^{KBr} cm^{-1}: 3190, 3150, 1380. UV λ_{max}^{EtOH} nm (log ε): 242 (4.29), 280 (3.59). NMR ($CDCl_3$) δ: 2.7 (3H, s, Me), 5.0—6.0 (2H, broad peak, NH_2), 7.3 (5H, s, C_6H_5). MS *m/e*: 206 (M^+). *Anal.* Calcd. for $C_9H_{10}N_4S$: C, 52.40; H, 4.89; N, 27.17. Found: C, 52.44; H, 4.92; N, 26.88.

Ic: Colorless leaflets, mp 211—213° (MeOH). IR ν_{max}^{KBr} cm^{-1}: 3200, 3120, 1400. UV λ_{max}^{EtOH} nm: 235, 300. MS *m/e*: 206 (M^+). *Anal.* Calcd. for $C_9H_{10}N_4S$: C, 52.40; H, 4.89; N, 27.17. Found: C, 52.34; H, 4.71; N, 27.12.

Preparation of the Compounds (I) from the Rhodanine Derivatives (II)——A solution of triethylammonium 3-benzoyl-3-phenyldithiocarbazata (4.6 g) and sodium chloroacetate (1.6 g) in water (20 ml) was acidified with 10% HCl, and warmed on a water bath for 10 min. Extraction with $CHCl_3$ and usual work-up of the extract gave 2.43 g (63%) of yellow cubes of IIa, mp 182—185° (MeOH). IR ν_{max}^{KBr} cm^{-1}: 1750, 1680. NMR ($CDCl_3$) δ: 4.0 (2H, s, CH_2), 7.0—7.6 (10H, m, $2\times C_6H_5$). MS *m/e*: 328 (M^+). *Anal.* Calcd. for $C_{16}H_{12}N_2OS_2$: C, 58.52; H, 3.68; N, 8.53. Found: C, 58.81; H, 3.49; N, 8.74.

A mixture of IIa (100 mg) and 80% $N_2H_4 \cdot H_2O$ (30 mg) in water (5 ml) was heated on a steam bath for 2 hr. The precipitates were collected and recrystallized from MeOH to give 20 mg (25%) of Ia, mp 229—230°. This compound was identical with Ia obtained in the above procedure by comparison of the IR spectra.

In the same way, IIc was obtained in 82% yield as a yellow oil. IR ν_{max}^{film} cm^{-1}: 1760, 1680. The compound (Ic) was prepared from IIc in the same way in 46% yield, mp 210—213° (MeOH).

Di-3-(1,2,4-triazolyl) Disulfides (III)——$NaNO_2$ (250 mg) was added portionwise to a suspension of the compound (Ia) (870 mg) in concd. HCl (10 ml) at 0—5° with stirring. The mixture was stirred for 1 hr, then diluted with water and extracted with $CHCl_3$. The extract was worked up as usual to give 390 mg (48%) of the disulfide (IIIa), colorless prisms, mp 187—188° (lit.[5]) mp 178°). NMR ($CDCl_3$) δ: 7.5 (s). MS *m/e*: 504 (M^+). *Anal.* Calcd. for $C_{28}H_{20}N_6S_2$: C, 66.64; H, 4.00; N, 16.66. Found: C, 66.71; H, 3.95; N, 16.95.

IIIb and IIIc were similarly obtained in 87% and 42% yield, respectively.

IIIb: Colorless oil, bp 200° (0.6 mmHg, bath temp.), which crystallized on standing, mp 82—86°. NMR ($CDCl_3$) δ: 2.4 (6H, s, $2\times$Me), 7.3 (10H, s, $2\times C_6H_5$). MS *m/e*: 380 (M^+). *Anal.* Calcd. for $C_{18}H_{16}N_6S_2$: C, 56.82; H, 4.24; N, 22.09. Found: C, 57.09; H, 4.05; N, 21.93.

IIIc: Colorless sticks, mp 106—108° (isopropyl alcohol). NMR ($CDCl_3$) δ: 3.9 (6H, s, $2\times$Me), 7.2—7.8 (10H, m, $2\times C_6H_5$). MS *m/e*: 380 (M^+). *Anal.* Calcd. for $C_{18}H_{16}N_6S_2$: C, 56.82; H, 4.24; H, 22.09. Found: C, 56.96; H, 4.03; N, 21.89.

Reduction of the Disulfide (IIIa) with $LiAlH_4$——A solution of IIIa (504 mg) in tetrahydrofuran (6 ml) was added to a cooled suspension of $LiAlH_4$ (40 mg) in tetrahydrofuran (4 ml) with stirring. The mixture was stirred for 15 min. After the addition of ice-water, the mixture was adjusted to pH 5 with 10% HCl and extracted with $CHCl_3$. The extract was worked up as usual to yield 380 mg (75%) of IV, colorless needles, mp 187—190° (benzene) (lit.[8]) mp 188°). IR ν_{max}^{KBr} cm^{-1}: 2600, 1370. This product was methylated with MeI and K_2CO_3 to afford the methylthio derivative (96% yield), mp 104—105°, which was identical with the compound (VIa) by comparison of the IR spectra.

Oxidation of the Compound (IV) to IIIa——A mixture of IV (100 mg) and I_2 (64 mg) (dissolved in a small amount of aqueous KI) in 5% NaOH (0.5 ml) was stirred at room temperature for 5 hr. Extraction

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[12] All melting points are uncorrected. IR spectra were recorded on a JASCO IRA-1 spectrophotometer, and UV spectra were measured with a Hitachi 124 spectrophotometer. NMR spectra were obtained with a JEOL JNM-PMX-60 spectrometer with tetramethylsilane as an internal standard. Mass spectra (MS) were obtained with a JEOL JMS-01SG instrument.

[13] O. Widman, *Ber.*, **26**, 945 (1893).

[14] R. Behrend and W. Reinsberg, *Ann.*, **377**, 189 (1910).

[15] A. Michaelis and E. Hadanck, *Ber.*, **41**, 3885 (1908).

with $CHCl_3$ and usual work-up of the extract gave 86 mg (86.3%) of IIIa, colorless needles, mp 186—187° (isopropyl alcohol). The IR spectrum of this product was identical with that of an authentic sample of IIIa.

3-Methylthio-1,2,4-triazoles (VI)——A mixture of the amino derivative (I) and a large excess of MeI in MeOH was stirred at room temperature for 1 hr. Concentration gave the methiodide (V) quantitatively. Va: colorless oil. NMR ($CDCl_3$) δ: 2.6 (3H, s, SMe), 6.0 (2H, s, NH_2), 7.0—8.0 (5H, m, C_6H_5), 7.4 (5H, s, C_6H_5). Vb: Colorless needles, mp 166—167° (dec.). IR ν_{max}^{KBr} cm^{-1}: 3300, 3260. NMR (CD_3OD) δ: 2.7 (3H, s, SMe), 2.75 (3H, s, Me), 7.6 (5H, s, C_6H_5). Vc: Pale yellow oil. IR ν_{max}^{film} cm^{-1}: 3240, 3150. NMR ($CDCl_3$) δ: 2.65 (3H, s, SMe), 3.9 (3H, s, NMe), 6.05 (2H, broad peak, NH_2), 7.3—8.2 (5H, m, C_6H_5).

A mixture of Va (1.6 g) and pyridine (5 ml) was refluxed for 1.5 hr. After concentration, the residue was dissolved in $CHCl_3$ and washed with water. The $CHCl_3$ solution was passed through a column of SiO_2 (Merck, 70—230 mesh) (5 g). Removal of the eluent by evaporation gave 860 mg (82%) of VIa, pale yellow prisms, mp 103—105° (*n*-hexane–benzene). NMR ($CDCl_3$) δ: 2.7 (3H, s, SMe), 7.4 (10H, s, $2\times C_6H_5$). *Anal.* Calcd. for $C_{15}H_{13}N_3S$: C, 67.39; H, 4.90; N, 15.72. Found: C, 67.58; H, 4.94; N, 15.53.

Similarly, 38 mg (37%) of VIb was obtained from Vb (167 mg) and pyridine (1.5 ml), and 155 mg (39%) of VIc was obtained from Vc (697 mg) and pyridine (2 ml). VIb: Colorless oil, bp 180—190° (0.1 mmHg, bath temp.). NMR ($CDCl_3$) δ: 2.5 (3H, s, Me), 2.6 (3H, s, Me), 7.5 (5H, s, C_6H_5). MS *m/e*: 205 (M^+). *Anal.* Calcd. for $C_{10}H_{11}N_3S$: C, 55.93; H, 5.74; N, 21.74. Found: C, 56.03; H, 5.65; N, 21.72. VIc: Colorless crystals, bp 140—160° (0.05 mmHg, bath temp.), mp 52—55°. NMR ($CDCl_3$) δ: 2.6 (3H, s, SMe), 3.85 (3H, s, NMe), 7.2—7.7 (5H, m, C_6H_5). *Anal.* Calcd. for $C_{10}H_{11}N_3S$: C, 55.93; H, 5.74; N, 21.74. Found: C, 56.18; H, 5.78; N, 21.61.

4-(N,N-Diacetylamino)-1,2,4-triazolium-3-thiolates (VII)——A mixture of the amino derivative (Ia—c) (1 mmol), Ac_2O (2 ml) and AcOH (2 ml) was heated on an oil bath at 55—60° for 1—2 hr. After dilution with water the mixture was extracted with $CHCl_3$. The extract was worked up as usual to give the diacetyl derivative (VIIa—c). VIIa: 120 mg (34%), colorless prisms, mp 168—171° (EtOH–$CHCl_3$). IR ν_{max}^{KBr} cm^{-1}: 1730, 1360. UV λ_{max}^{EtOH} nm (log ε): 249 (4.38), 330 (3.61). NMR ($CDCl_3$) δ: 2.5 (6H, s, $2\times$COMe), 7.1—7.8 (10H, m, $2\times C_6H_5$). MS *m/e*: 352 (M^+). *Anal.* Calcd. for $C_{18}H_{16}N_4O_2S$: C, 61.34; H, 4.58; N, 15.90. Found: C, 61.50; H, 4.69; N, 15.67. VIIb: 170 mg (59%), colorless prisms, mp 180—182° (EtOH–$CHCl_3$). IR ν_{max}^{KBr} cm^{-1}: 1750, 1720, 1360. UV λ_{max}^{EtOH} nm (log ε): 250 (4.31), 290 (3.43). NMR ($CDCl_3$) δ: 2.5 (9H, s, $2\times$COMe+Me), 7.5 (5H, s, C_6H_5). MS *m/e*: 290 (M^+). *Anal.* Calcd. for $C_{13}H_{14}N_4O_2S$: C, 53.78; H, 4.86; N, 19.30. Found: C, 53.51; H, 4.84; N, 19.04. VIIc: 140 mg (48%), colorless sticks, mp 162—165° (isopropyl alcohol). IR ν_{max}^{KBr} cm^{-1}: 1740, 1720, 1370. NMR ($CDCl_3$) δ: 2.4 (6H, s, $2\times$COMe), 3.9 (3H, s, NMe), 7.2—7.8 (5H, m, C_6H_5). *Anal.* Calcd. for $C_{13}H_{14}N_4O_2S$: C, 53.78; H, 4.86; N, 19.30. Found: C, 53.99; H, 4.86; N, 19.30. Found: C, 53.99; H, 4.61; N, 19.20.

4-Acetamido-1,2,4-triazolium-3-thiolates (IX)——A mixture of VIIa—c (1 mmol) and 10% NaOH (3 ml) was stirred at room temperature for 30 min. After acidification with 10% HCl, the mixture was extracted with $CHCl_3$. The extract was worked up as usual to give IXa—c. IXa: 267 mg (86%), colorless prisms, mp 275—278° (EtOH–$CHCl_3$). IR ν_{max}^{KBr} cm^{-1}: 1720, 1380. UV λ_{max}^{EtOH} nm (log ε): 250 (4.42). NMR ($CDCl_3$) δ: 2.0 (3H, s, COMe), 7.2 (5H, s, C_6H_5), 7.2—7.7 (5H, m, C_6H_5), 10.6 (1H, s, CONH). *Anal.* Calcd. for $C_{16}H_{14}N_4OS$: C, 61.92; H, 4.55; N, 18.05. Found: C, 62.03; H, 4.39; N, 17.88. IXb: 145 mg (58%), colorless needles, mp 246—249° (EtOH). IR ν_{max}^{KBr} cm^{-1}: 3100, 1710, 1390. UV λ_{max}^{EtOH} nm (log ε): 248 (4.28), 285 (3.46). NMR ($CDCl_3$) δ: 2.2 (3H, s, COMe), 2.5 (3H, s, Me), 7.5 (5H, s, C_6H_5), 10.2—11.1 (1H, broad peak, CONH). MS *m/e*: 248 (M^+). *Anal.* Calcd. for $C_{11}H_{12}N_4OS$: C, 53.20; H, 4.87; N, 22.57. Found: C, 52.90; H, 4.78; N, 22.54. IXc: 156 mg (63%), colorless plates, mp 232—235° (isopropyl alcohol). IR ν_{max}^{KBr} cm^{-1}: 3160, 1710, 1360. NMR ($CDCl_3$) δ: 2.05 (3H, s, COMe), 3.8 (3H, s, NMe), 7.6 (5H, s, C_6H_5), 10.7—11.1 (1H, broad peak, CONH). *Anal.* Calcd. for $C_{11}H_{12}N_4OS$: C, 53.20; H, 4.87; N, 22.57. Found: C, 53.45; H, 4.91; N, 22.30.

4-(N,N-Diethoxycarbonylamino)-1,2,4-triazolium-3-thiolates (VIII) and 4-Ethoxycarbonylamino-1,2,4-triazolium-3-thiolates (X)——a) A mixture of Ia (536 mg) and ethyl chloroformate (543 mg) in $CHCl_3$ (10 ml) was refluxed for 3 hr. After cooling, the mixture was washed with water and evaporated to give 750 mg (91%) of VIIIa as a pale yellow oil. Distillation of this product caused considerable decomposition. IR ν_{max}^{film} cm^{-1}: 1780, 1740, 1370. NMR ($CDCl_3$) δ: 1.3 (6H, t, $J=7$ Hz, $2\times$Me), 4.4 (4H, q, $J=7$ Hz, $2\times CH_2$), 7.2—7.8 (10H, m, $2\times C_6H_5$). The crude VIIIa (670 mg) was dissolved in EtOH (10 ml) and 5% NaOH (3 ml) was added. The mixture was stirred at room temperature for 30 min. After concentration, the residue was diluted with water, acidified with 10% HCl, and extracted with $CHCl_3$. The extract was worked up as usual to give 340 mg (61.5%) of Xa, colorless needles, mp 199—201° (isopropyl alcohol). IR ν_{max}^{KBr} cm^{-1}: 3160, 1750, 1370. UV λ_{max}^{EtOH} nm (log ε): 251 (4.41). NMR ($CDCl_3$) δ: 1.2 (3H, t, $J=7$ Hz, Me), 4.2 (2H, q, $J=7$ Hz, CH_2), 7.0—7.7 (10H, m, $2\times C_6H_5$), 8.9 (1H, s, CONH). *Anal.* Calcd. for $C_{17}H_{16}N_4O_2S$: C, 59.98; H, 4.72; N, 16.46. Found: C, 59.79; H, 4.73; N, 16.24.

b) A mixture of Ib (2.1 g) and ethyl chloroformate (2.7 g) in $CHCl_3$ (20 ml) was refluxed for 2 hr. The mixture was worked up as above to give 2.8 g (80%) of VIIIb, colorless plates, mp 133—135° (dec.) (AcOEt). IR ν_{max}^{KBr} cm^{-1}: 1780, 1760, 1390. UV λ_{max}^{EtOH} nm (log ε): 250 (4.31). NMR ($CDCl_3$) δ: 1.3 (6H, t, $J=7$ Hz, $2\times$Me), 2.6 (3H, s, Me), 4.4 (4H, q, $J=7$ Hz, $2\times CH_2$), 7.5 (5H, s, C_6H_5). *Anal.* Calcd. for $C_{15}H_{18}N_4O_4S$: C, 51.41; H, 5.18; N, 15.99. Found: C, 51.24; H, 5.17; N, 15.96.

Treatment of VIIIb (700 mg) with 5% NaOH (3 ml) in EtOH (5 ml) as in procedure a) gave 370 mg (65%) of Xb, colorless cubes, mp 190—192° (EtOH–benzene). IR $\nu_{\max}^{\text{KBr}}$ cm^{-1}: 3320, 1750, 1380. UV $\lambda_{\max}^{\text{EtOH}}$ nm (log ε): 248 (4.29). NMR ($CDCl_3$) δ: 1.3 (3H, t, J=7 Hz, Me), 2.6 (3H, s, Me), 4.25 (2H, q, J=7 Hz, CH_2), 7.4 (5H, s, C_6H_5), 9.15 (1H, s, CONH). *Anal.* Calcd. for $C_{12}H_{14}N_4O_2S$: C, 51.78; H, 5.07; N, 20.13. Found: C, 51.62; H, 5.06; N, 19.85.

c) Similarly, 1.58 g (90%) of VIIIc was obtained from Ic (1 g) and ethyl chloroformate (1.74 g) as a pale yellow oil. IR $\nu_{\max}^{\text{film}}$ cm^{-1}: 1780, 1740, 1370. NMR ($CDCl_3$) δ: 1.3 (6H, t, J=7 Hz, 2×Me), 3.85 (3H, s, NMe), 4.4 (4H, q, J=7 Hz, 2×CH_2), 7.3—7.8 (5H, m, C_6H_5). On treatment with 5% NaOH (5 ml) in the same way, VIIIc (700 mg) gave 475 mg (85%) of Xc, colorless sticks, mp 94—96° (isopropyl alcohol). IR $\nu_{\max}^{\text{KBr}}$ cm^{-1}: 3200, 1740, 1370. UV $\lambda_{\max}^{\text{EtOH}}$ nm (log ε): 247 (4.27), 309 (3.59). NMR ($CDCl_3$) δ: 1.25 (3H, t, J=7 Hz, Me), 3.85 (3H, s, NMe), 4.2 (2H, q, J=7 Hz, CH_2), 7.7 (5H, s, C_6H_5), 9.3 (1H, s, CONH). *Anal.* Calcd. for $C_{12}H_{14}N_4O_2S$: C, 51.78; H, 5.07; N, 20.13. Found: C, 51.50; H, 5.24; N, 20.14.

4-Benzamido-5-methyl-1-phenyl-1,2,4-triazolium-3-thiolate (XIb)——A solution of benzoyl chloride (281 mg) in $CHCl_3$ (2 ml) was added to a cooled solution of Ib (412 mg) in $CHCl_3$ (10 ml), and the mixture was stirred at room temperature for 7 hr. The mixture was extracted with 10% K_2CO_3, and the aqueous extract was acidified with 10% HCl. Extraction with $CHCl_3$ and usual work-up of the extract gave 425 mg (68.5%) of XIb, colorless needles, mp 180—182° (isopropyl alcohol). IR $\nu_{\max}^{\text{KBr}}$ cm^{-1}: 3400, 3200, 1690, 1380. NMR ($CDCl_3$) δ: 2.6 (3H, s, Me), 7.0—8.2 (10H, m, 2×C_6H_5), 11.4 (1H, broad peak, CONH). *Anal.* Calcd. for $C_{16}H_{14}N_4OS$: C, 61.91; H, 4.55; N, 18.05. Found: C, 61.75; H, 4.56; N, 17.83.

5-Methyl-3-methylthio-1-phenyl-1H-1,2,4-triazolium 4-Acetylimine (XIIb)——A mixture of IXb (375 mg) and MeI (1 ml) in $CHCl_3$ (6 ml) was stirred at room temperature for 1 hr. The mixture was then shaken with saturated aqueous $NaHCO_3$. The $CHCl_3$ solution was worked up as usual to give 288 mg (73%) of XIIb, colorless cubes, mp 165—169° (benzene). IR $\nu_{\max}^{\text{KBr}}$ cm^{-1}: 1570. NMR ($CDCl_3$) δ: 2.1 (3H, s, COMe), 2.65 (3H, s, SMe), 2.7 (3H, s, Me), 7.6 (5H, s, C_6H_5). *Anal.* Calcd. for $C_{12}H_{14}N_4OS$: C, 54.94; H, 5.38; N, 21.36. Found: C, 54.65; H, 5.42; N, 21.44.

1-Methyl-3-methylthio-5-phenyl-1H-1,2,4-triazolium 4-Ethoxycarbonylimine (XIIIc)——A mixture of Xc (2.0 g) and MeI (1.5 g) in $CHCl_3$ (10 ml) was stirred at room temperature for 30 min. The mixture was worked up as above to give 1.56 g (74%) of XIIIc, colorless prisms, mp 137—140° (benzene). IR $\nu_{\max}^{\text{KBr}}$ cm^{-1}: 1630. UV $\lambda_{\max}^{\text{EtOH}}$ nm (log ε): 228 (4.18), 254 (3.98). NMR ($CDCl_3$) δ: 1.15 (3H, t, J=7 Hz, Me), 2.6 (3H, s, SMe), 3.9 (3H, s, NMe), 4.0 (2H, q, J=7 Hz, CH_2), 7.6 (5H, s, C_6H_5). MS *m/e*: 292 (M^+). *Anal.* Calcd. for $C_{13}H_{16}N_4O_2S$: C, 53.40; H, 5.52; N, 19.17. Found: C, 53.14; H, 5.49; N, 19.16.

5-Methyl-3-methylthio-1-phenyl-1H-1,2,4-triazolium 4-Benzoylimine (XIVb)——A mixture of XIb (620 mg) and MeI (1 ml) in $CHCl_3$ (10 ml) was stirred at room temperature for 30 min. Treatment of the mixture with $NaHCO_3$ as described above gave 583 mg (90%) of XIVb as a colorless viscous oil. IR $\nu_{\max}^{\text{KBr}}$ cm^{-1}: 1540. NMR ($CDCl_3$) δ: 2.6 (6H, s, 2×Me), 7.1—7.6 (3H, m, arom.), 7.5 (5H, s, C_6H_5), 7.95—8.2 (2H, m, arom.). MS *m/e*: 324 (M^+). Picrate of XIVb: yellow leaflets, mp 198—199° (isopropyl alcohol). *Anal.* Calcd. for $C_{17}H_{16}N_3OS \cdot C_6H_3N_3O_7$: C, 51.20; H, 3.55; N, 15.58. Found: C, 51.04; H, 3.62; N, 15.69.

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