BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 40 2854—2859 (1967)

Reaction of 2-Benzimidazolinethione with Dimethylsulfoxide and Acetyl Chloride

Kentaro ANZAI and Saburo SUZUKI

The Institute of Physical and Chemical Research, Yamato-machi, Saitama

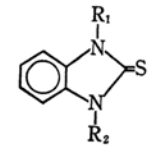
(Received April 18, 1967)

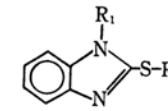
Dimethyl sulfoxide (DMSO) and acetyl chloride reacted with 2-benzimidazolinethione (I), converting the latter compound to its thiomethoxymethyl and methylenebis derivatives. From the reaction mixture the following compounds were isolated: 1, 3-dithiomethoxymethyl-2-benzimidazolinethione (VII), 1, 1'-methylenebis-3-thiomethoxymethyl-2-benzimidazolinethione (VIII), 1-thiomethoxymethyl-2-benzimidazolinethione (IX), 1, 1'-methylenebis-2-benzimidazolinethione (XIII), and 2-(methylenesulfonium)benzimidazolide (XIV). The mechanism for the formation of these compounds will be discussed. The reaction of 2-benzoxazolinethione (XX) with DMSO and acetyl chloride yielded, besides its thiomethoxymethyl and methylenebis derivatives, 1-hydroxymethylbenzoxazolone (XXIII); the mechanism for the exchange of the sulfur in XX with the oxygen will also be discussed. *N*-Alkyl derivatives of I could be distinguished from *S*-alkyl derivatives by their ultraviolet spectra.

It is known that the reaction of aromatic compounds with DMSO and Lewis acids gives thiomethoxy as well as thiomethoxymethyl derivatives. Phenols reacted with DMSO and dry hydrogen chloride to produce dimethylhydroxyarylsulfonium chlorides, $ArS^+Me_2Cl^-$, which were, upon hydrolysis, converted to methyl hydroxyaryl thioethers, ArSMe.[1] The addition of acetyl chloride or monochloromethyl ether to a DMSO solution of uracil converted the latter compound to 5-thiomethoxyuracil.[2] The reaction of pyridine with DMSO and dicyclohexylcarbodiimide yielded *N*-thiomethoxymethylpyridinium chloride,[3] and a similar reaction converted testosterone to 17-*O*-(thiomethoxymethyl) testosterone.[4] Styrene and naphthalene were converted to methyl cinnamyl sulfide and α-thiomethoxymethylnaphthalene respectively with DMSO and sulfuric acid.[5]

The present paper will deal with the reaction of 2-benzimidazolinethione (I) with DMSO and acetyl chloride.

It is known[6] that the alkylation of I with methyl iodide yields, depending upon the reaction conditions, alkyl derivatives of 2-benzimidazolinethione (*e.g.*, II and III) and those of 2-benzimidazolethiol (*e.g.*, V and VI). We found that a distinction can be made between these two types of compounds by their ultraviolet spectra (Fig. 1). We also found that its derivatives have sometimes been carelessly described as having thiol structures; *e.g.*, 1-methyl-2-benzimidazolinethione (II) was uncorrectly described as 1-methyl-2-benzimidazolethiol (IV) by the investigator who synthesized it.[6] The ultraviolet spectrum of I clearly shows that it is a thione in methanol; we also found that the change in the solvent does not alter I to the thiol form. Though 2-thiomethoxybenzimidazole (V) and 1-methyl-2-thiomethoxybenzimidazole (VI) are basic and dissolve in 10% HCl, I, II, and 1,3-dimethyl-2-benzimidazolinethione (III) show no basicity.





I $R_1=H$, $R_2=H$ IV $R_1=CH_3$, $R_2=H$
II $R_1=H$, $R_2=CH_3$ V $R_1=H$, $R_2=CH_3$
III $R_1=CH_3$, $R_2=CH_3$ VI $R_1=CH_3$, $R_2=CH_3$

To a DMSO solution of I acetyl chloride was added, while the temperature was kept at 50—60°C, and then the reaction mixture was extracted with ethyl acetate. Thin-layer chromatography on silicic acid (Fig. 2) has shown the presence of at least six UV positive compounds in the extract. The column chromatography on silicic acid, using a mixture of benzene and ethyl acetate (19 : 1) as the developer led to success in isolating three major products; they were identified as 1, 3-dithiomethoxymethyl-2-benzimidazolinethione (VII),

1) E. Goethals and P. de Radzitzky, *Bull. Soc. Chim. Belges*, **73**, 546 (1964).
2) K. Anzai and S. Suzuki, *Agr. Biol. Chem. (Japan)*, **30**, 597 (1966).
3) K. E. Pfitzner and J. G. Moffatt, *J. Am. Chem. Soc.*, **87**, 5661 (1965).
4) K. E. Pfitzner and J. G. Moffatt, *ibid.*, **87**, 5670 (1965).
5) R. Oda and Y. Hayashi, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **87**, 291 (1966).
6) K. Futaki, *Yakugaku Zasshi (J. Pharm. Soc. Japan)*, **74**, 1365 (1954).

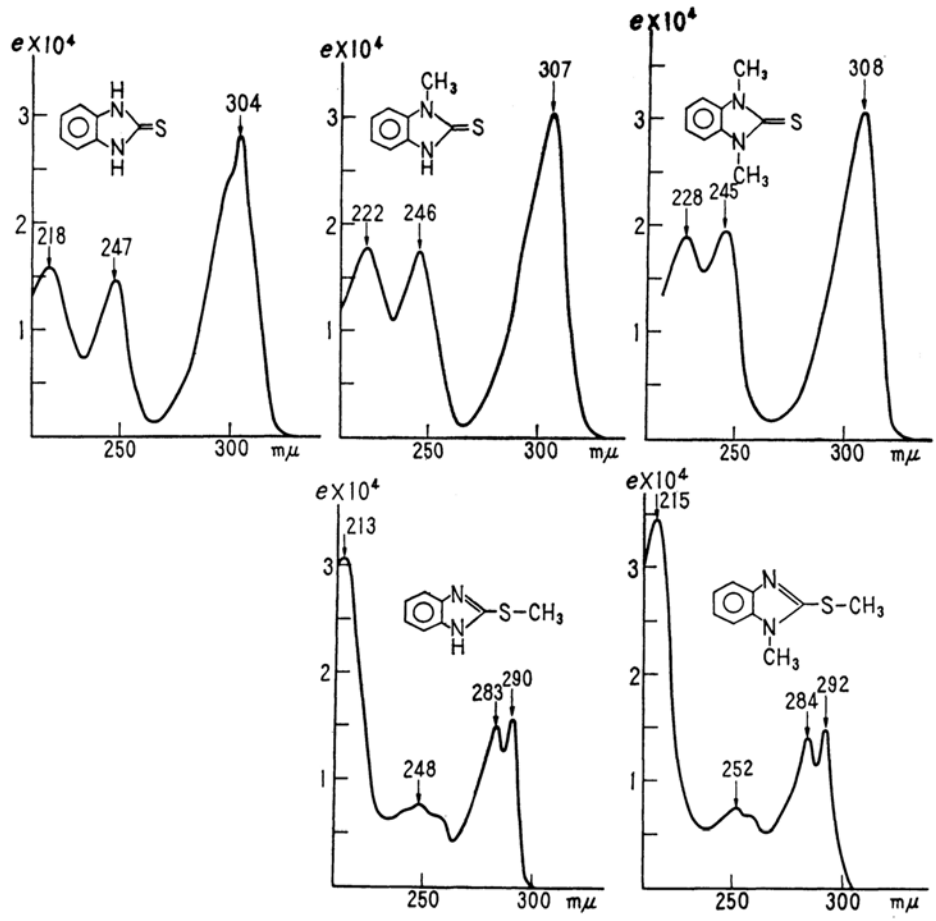


Fig. 1. UV spectra of 2-benzimidazolinethione and its methyl derivatives, methanol, 10 mcg/ml.

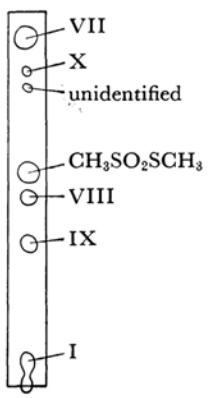
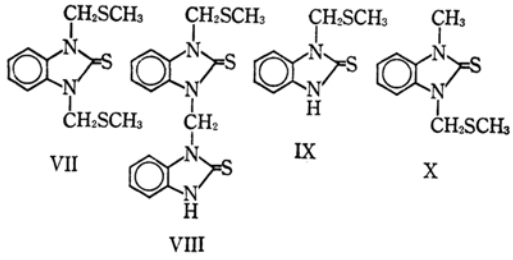


Fig. 2. Reaction products of 2-benzimidazolinethione with DMSO and CH_3COCl: TLC on silicic acid; benzene 19, ethyl acetate 1.



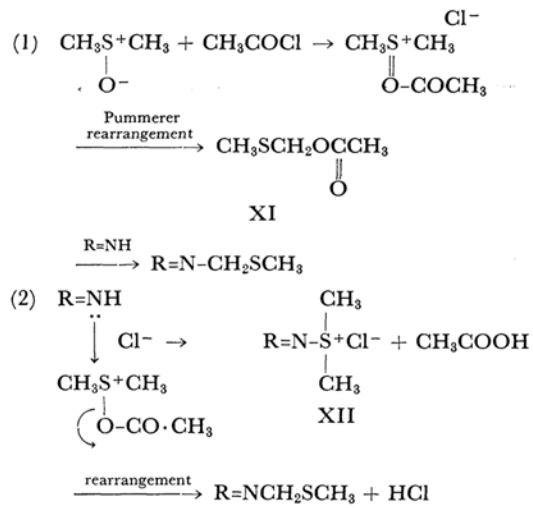
1, 1′-methylenebis-3-thiomethoxymethyl-2-benzimidazolinethione (VIII), and 1-thiomethoxymethyl-2-benzimidazolinethione (IX).

The ultraviolet spectra of these compounds show that they are not *S*-substituted 2-benzimidazolethiols. The NMR spectra are also consistent with the proposed structures, and the infrared spectrum of each compound shows a band at about 750 cm^{-1} which can be ascribed to *O*-substituted benzenes. The N-H stretching frequency at 3150 cm^{-1} in I is still clearly observed in IX, but can hardly be observed in VIII and can no longer be observed in VII. The unreacted I was also recovered when eluted with a higher ratio of ethyl acetate to benzene.

Though we were not successful in isolating the minor component eluted soon after VII, thin-layer chromatography on silicic acid using several

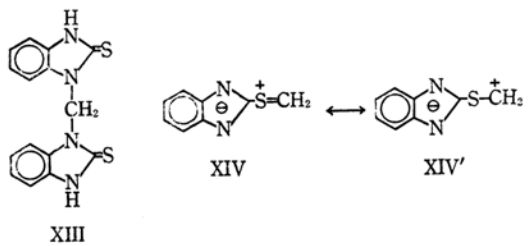
solvent systems has suggested that the compound is 1-methyl-3-thiomethoxymethyl-2-benzimidazolinethione (X), which can also be synthesized by another route (*see below*). Though the other minor component has not yet been identified because of our failure to obtain an analytical sample even after repeated attempts at chromatography, the ultraviolet spectrum suggests that it is a 1, 3-disubstituted 2-benzimidazolinethione.

The introduction of the thiomethoxymethyl group with DMSO and acetyl chloride can reasonably be explained by one of the following two paths:



We were unsuccessful in our attempt to synthesize VII or IX by the reaction of I with α-methoxydimethyl sulfide[7] (XI) and sulfuric acid, using dimethylformamide as a solvent. Moreover, the occurrence of sulfonium compounds,[1] thiomethoxy,[2] and thiomethoxymethyl[3-5] derivatives, depending upon the reactants, upon reactions with DMSO and Lewis acids can reasonably be explained by postulating, in each case, intermediates analogous to the sulfonium XII.

When the reaction was carried out at a lower temperature (below 30°C), other products, which were insoluble in ethyl acetate and extractable with butanol, were obtained. The butanol extract, after the solvent had been evaporated and extracted with benzene in order to remove VII, VIII, and IX, was submitted to alumina chromatography, using a mixture of benzene and methanol (19 : 1) as the developer. Two compounds were isolated, though in low yields; the one which was eluted second was identified as 1, 1'-methylenebis-2-benzimidazolinethione (XIII).



The other compound is hardly soluble in water and organic solvents other than dimethylformamide and DMSO, and it easily crystallized during chromatography. The fact that the solubility in water increases upon the addition of either acid or alkali

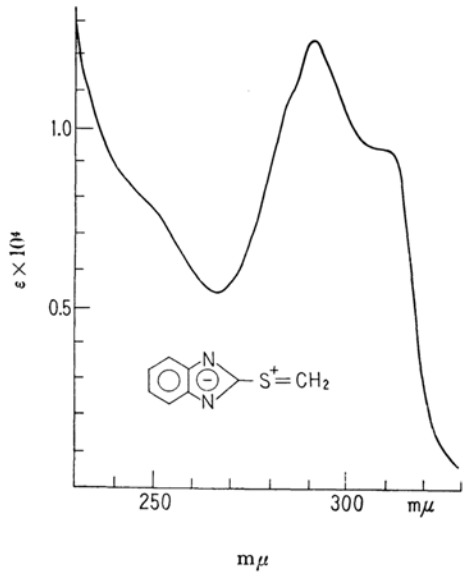
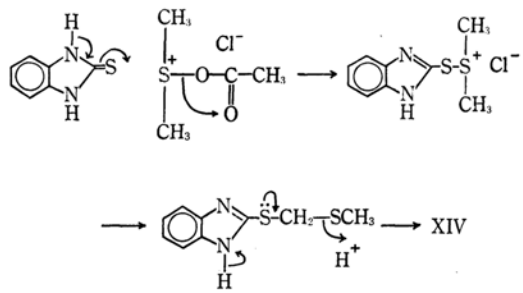


Fig. 3. UV spectrum of 2-(methylenesulfonium) benzimidazolide, methanol.

suggests that it is an amphoteric compound or a zwitter ion. The molecular formula, $C_8H_6N_2S$, shows that only one carbon and one hydrogen atom were added to I; the ultraviolet spectrum (Fig. 3) is quite different from those of I and its alkyl derivatives (Fig. 1), suggesting that the chromophore itself is altered. These data, as well as the NMR spectrum, which shows signals at δ6.17 (2H, singlet) and at δ6.95—7.75 (4H, complex), indicate that the compound is 2-(methylenesulfonium) benzimidazolide (XIV). The formation of XIV can reasonably be explained by the mechanism shown below:



7) L. Horner and P. Kaiser, *Ann. Chem.*, **626**, 19 (1959).

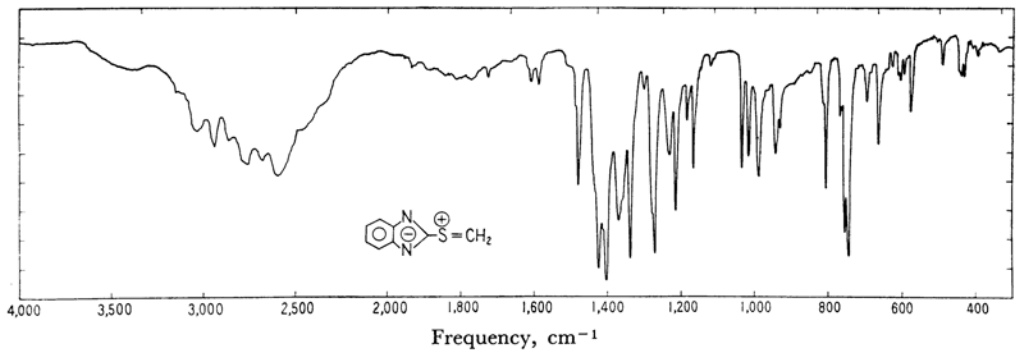
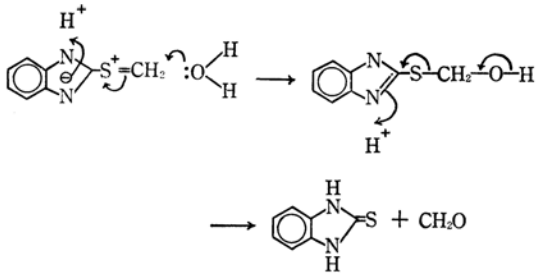


Fig. 4. IR spectrum of 2-(methylenesulfonium)benzimidazolide, solid.

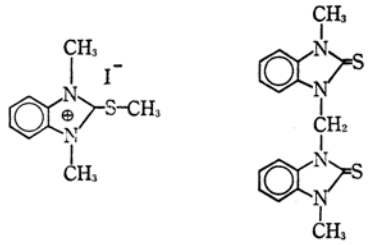
The infrared spectrum (Fig. 4) shows no absorption in the region of N–H stretching, and the band at 745 cm^{-1} can be ascribed to an *O*-substituted benzene. The C–H stretching region shows a characteristic feature: though the absorption at 3040 cm^{-1} can be ascribed to aromatic C–H stretching, the broad absorptions between 2940 and 2600 cm^{-1} are unusual in aliphatic C–H stretching. It is probable that a resonance form, XIV', contributes to the shift of the C–H band to a lower frequency.

Though it is stable in response to alkali, XIV is easily decomposed by acid into I, thus liberating formaldehyde.



It may be because of its susceptibility to acid that XIV could no more be isolated from the reaction mixture when the reaction was carried out at a higher temperature (50—60°C).

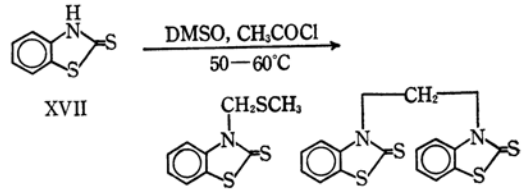
Though the presence of some reaction intermediates with $-S^+=CH_2$ groups has been postulated by some investigators,[8-11] the synthesis of stable methylenesulfonium compounds has not yet been repoted, nor is there any known zwitter ion containing a benzimidazolide anion. Both the benzimidazolide anion in XIV and the benzimidazolium cation in, *e. g.*, 1, 3-dimethyl-2-methylthiobenzimidazolium iodide[9] (XV), may be considered to contain the 6π-electron sextet in the heterocyclic rings.



XV XVI

The reaction of 1-methyl-2-benzimidazolinethione (II) with DMSO and acetyl chloride yielded 1-methyl-3-thiomethoxymethyl-2-benzimidazolinethione (X) and 1, 1'-methylenebis-3, 3'-dimethyl-2-benzimidazolinethione (XVI); they were also separated with column chromatography on silicic acid.

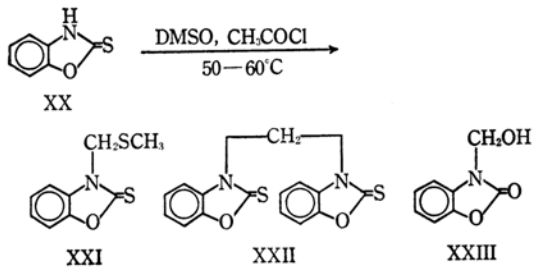
Under similar conditions 2-benzothiazolinethione-(XVII) was converted to 1-thiomethoxymethyl-2-benzothiazolinethione (XVIII) and 1, 1'-methylenebis-2-benzothiazolinethione (XIX).



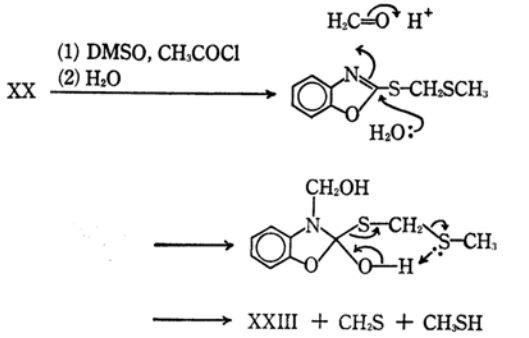
XVII XVIII XIX

Though the reaction of 2-benzoxazolinethione (XX) with DMSO and acetyl chloride yielded, as might be expected, 1-thiomethoxymethyl-2-benzoxazolinethione (XXI) and 1, 1'-methylenebis-2-benzoxazolinethione (XXII), the major product, after the hydrolysis of the reaction mixture, was found to be 1-hydroxymethyl benzoxazolone (XXIII), which can also be synthesized by other route (See Exp. Section).

8) W. E. Parham and S. H. Groen, *J. Org. Chem.*, **30**, 3181 (1965).
9) J. L. Kice, B. R. Toth, D. C. Hampton and J. F. Barbour, *ibid.*, **31**, 848 (1966).
10) B. H. Klanderman, *ibid.*, **30**, 2469 (1965).
11) J. L. Kice and E. H. Morkved, *J. Am. Chem. Soc.*, **85**, 3472 (1963).



The following mechanism can probably best explain the exchange of the sulfur in XX with the oxygen:



The formation of formaldehyde in the reaction mixture of DMSO and acetyl chloride has already been reported.[2]

Experimental

1, 3 - Dithiomethoxymethyl - 2 - benzimidazolinethione (VII), 1, 1'-Methylenebis -3 - thiomethoxymethyl-2-benzimidazolinethione (VIII), and 1-Thiomethoxymethyl-2-benzimidazolinethione (IX). Into a solution of 7.5 g of 2-benzimidazolinethione (I) in 100 m*l* of DMSO, 50 g of acetyl chloride were dropped with stirring. A vigorous exothermal reaction started, the temperature being kept at 50—60°C in an ice-water bath. After the acetyl chloride had been consumed, the mixture was further stirred and the temperature was kept at 50—60°C for 1 hr. A volatile fraction, consisting mainly of methyl sulfide and methyl disulfide, was distilled off into a dry ice - acetone bath. Water was added, and the aqueous solution was extracted with ethyl acetate. TLC of the ethyl acetate extract on silicic acid showed at least seven $KMnO_4$-positive spots when developed with a mixture of ethyl acetate and benzene (1 : 19): R_f 0.92, 0.83, 0.79, 0.57, 0.50, 0.37, 0.07. R_f 0.57 was found to correspond to methyl methanethiolsulfonate.

The ethyl acetate extract was, after it had been washed with water, condensed; methyl methanethiolsulfonate, a product of the reaction, was removed by vacuum distillation; bp 111—113°C at 3 mmHg. The residue was submitted to column chromatography on silicic acid (3×60 cm), using a mixture of ethyl acetate and benzene (1 : 19) as the developer. After repeated attempts at chromatography, three major products, corresponding to R_f 0.92, 0.50 and 0.37, were isolated; they were found to be homogenous by TLC. The unreacted I was eluted by increasing the ratio of ethyl acetate to benzene (1 : 4).

1, 3 - Dithiomethoxymethyl - 2 - benzimidazolinethione (VII), corresponding to R_f 0.92, was crystallized from carbon tetrachloride; yield 1.5 g; mp 124—127°C: λ_{max}^{MeOH} 311 (ε 30600), 252 (ε 11600), 226 mμ (ε 24700): NMR(CCl_4) δ 2.18 (2 $-SC\underline{H}_3$), δ 5.42 (2 $=NC\underline{H}_2S-$), δ 7.2($C_6\underline{H}_4-$).

Found: C, 48.95; H, 5.15: N, 10.49%. Calcd for $C_{11}H_{14}N_2S_3$: C, 48.85; H, 5.22; N, 10.36%.

Crystallizing from alcohols gave alcohol adducts, which gave no reliable analytical data.

1, 1'- Methylenebis -3- thiomethoxymethyl -2 - benzimidazolinethione (VIII), corresponding to R_f 0.50, was hardly soluble in water or in most organic solvents; the crystals separated during chromatography, when recrystallized from dimethylformamide and ethanol, or dimethylformamide and water, yielded 600 mg; mp 289—295°C: λ_{max}^{MeOH} 310 (ε 49400), 300 (ε 46800), 248 (ε 23900), 223 mμ (ε 37800): NMR (DMSO-d), δ 2.20 ($-SC\underline{H}_3$), δ 5.70 ($-NC\underline{H}_2S-$), δ 6.95 ($-NC\underline{H}_2N-$), δ 7.2($2C_6\underline{H}_4-$ and $=N\underline{H}$)

Found: C, 54.55; H, 4.31; N, 15.36; S, 25.75%. Calcd for $C_{17}H_{16}N_4S_3$: C, 54.81; H, 4.33; N, 15.04; S, 25.82%.

1-Thiomethoxymethyl-2-benzimidazolinethione (IX), corresponding to R_f 0.37, was soluble in most organic solvents and was crystallized from benzene and ligroin; yield 800 mg; mp 186—187°C: λ_{max}^{MeOH} 308 (ε 31500), 248 (ε 12600), 223 mμ (ε 22400): NMR(DMSO-d), δ 2.18 ($-SC\underline{H}_3$), δ 5.52 ($-SC\underline{H}_2S-$), δ 7.27 ($C_6\underline{H}_4-$ and $=N\underline{H}$).

Found: C, 51.79; H, 4.89; N, 13.49; S, 30.25%. Calcd for $C_9H_{10}N_2S_2$: C, 51.39; H, 4.79; N, 13.32; S, 30.49%.

2-(Methylenesulfonium) Benzimidazolide (XIV) and 1, 1' - Methylenebis -2 - benzimidazolinethione (XIII). Into a solution of 1.5 g of I in 20 m*l* of DMSO, 10 g of acetyl chloride were dropped with stirring, while the temperature was so kept as not to exceed 30°C. After the volatile matters had been distilled off, the residue was repeatedly extracted with 50 m*l* portions of butanol; the butanol layer was, after having been washed with a small amount of water, evaporated *in vacuo*. After being extracted with benzene to remove VII, VIII, IX, X, and the other compounds soluble in organic solvents, the residue was submitted to alumina chromatography, using a mixture of methanol and benzene (1 : 19) as the developer. Two products were isolated.

2 - (Methylenesulfonium) benzimidazolide (XIV), eluted first, was actually insoluble in water and in most organic solvents other than dimethylformamide and DMSO, and crystals separated during chromatography. An increase in the solubility in water was observed upon the addition of either hydrochloric acid or sodium hydroxide; when the substance was recrystallized from dimethylformamide and methanol, the yield was 320 mg (20%); mp 268—269°C: λ_{max}^{MeOH} 312 (ε 9800, shoulder), 290 mμ (ε 13800); NMR (DMSO-d), δ 6.16 ($-S^+=C\underline{H}_2$), δ 6.95—7.75 ($C_6\underline{H}_4-$).

Found: C, 58.40; H, 3.75; N, 17.15; S, 19.72%. Calcd for $C_8H_6N_3S$: C, 59.22; H, 3.73; N, 17.27; S, 19.77%.

When 1, 1'- methylenebis - 2 - benzimidazolinethione

(XIII) was crystallized from ethanol, the yield was 150 mg; double mp 226°C and above 320°C: λ_{max}^{MeOH} 308 (*e* 30000), 297 (*e* 27700), 243 mμ (*e* 18000): NMR (DMSO-d), δ 6.25 (=N-C$\underline{H}_2$-N=), δ 6.8—7.8 (2 C$_6\underline{H}_4$- and 2=N$\underline{H}$).

Found: C, 57.36; H, 3.78; N, 17.90; S, 20.24%. Calcd for $C_{15}H_{12}N_4S_2$: C, 57.66; H, 3.87; N, 17.94; S, 20.53%.

Acid Hydrolysis of 2-(Methylenesulfonium) Benzimidazolide (XIV). Five milliliters of 2 N HCl were added to a solution of 10 mg of XIV in 0.5 m*l* of DMSO, and the solution was heated on a steam bath for 30 min. After it had been extracted with ethyl acetate, the solvent layer was washed with water and evaporated to dryness. When the residue was crystallized from methanol and acetone, the yield was 5 mg. The infrared spectrum was found to be identical with that of an authentic sample of I.

The acid hydrolysate was neutralized, and I and the unreacted XIV were removed by extraction with butanol. When 10 m*l* of a 0.4% aqueous solution of dimedone was added and the solution was left in a refrigerator overnight, methylenebismethone was crystallized; yield 3 mg. Without XIV no formation of formaldehyde was detected under comparable conditions.

1-Methyl-3-thiomethoxymethyl-2-benzimidazolinethione (X) and 1, 1′-Methylenebis-3, 3′-dimethyl-2-benzimidazolinethione (XVI). Ten grams of acetyl chloride were added to a solution of 740 mg of 1-methyl-2-benzimidazolinethione (II) in 20 m*l* of DMSO, the temperature being kept at 50—60°C. The reaction mixture was then treated in a way similar to that used in the reaction of I with DMSO and acetyl chloride. The ethyl acetate extract of the reaction mixture was applied to column (2×40 cm) chromatography on silicic acid, using a mixture of ethyl acetate and benzene (1 : 19) as the developer. Two products were isolated.

1-Methyl-3-thiomethoxymethyl-2-benzimidazolinethione (X), eluted first, was crystallized from benzene and ligroin; yield 220 mg; mp 118—120°C: λ_{max}^{MeOH} 309 (*e* 30100), 248 (*e* 13900), 228 mμ (*e* 21800): NMR ($CDCl_3$) δ 2.25 (-SC$\underline{H}_3$), δ 3.78 (-NC$\underline{H}_3$), δ 5.50 (=NC$\underline{H}_2$S-), δ, 7.2(C$_6\underline{H}_4$-).

Found: C, 54.20; H, 5.20; N, 12.86; S. 28.02%. Calcd for $C_{10}H_{12}N_2S_2$: C, 53.53; H, 5.39; N, 12.49; S, 28.58%.

1, 1′-Methylenebis-3, 3′-dimethyl-2-benzimidazolinethione (XVI) was crystallized from benzene; yield 20 mg; mp 217—219°C: λ_{max}^{MeOH} 310 (*e* 30000), 300 (*e* 27900), 255 mμ (*e* 8700, shoulder).

Found: C, 59.80; H, 4.30; N, 15.71; S, 18.64%. Calcd for $C_{17}H_{16}N_4S_2$: C, 59.97; H, 4.74; N, 16.46; S, 18.84%.

The unreacted II was eluted from the column with further development, and 120 mg of II were recovered.

1-Thiomethoxymethyl-2-benzothiazolinethione (XVIII) and 1, 1′-Methylenebis-2-benzothiazolinethione (XIX). The reaction of 1 g of 2-benzothiazolinethione (XVII) with 20 m*l* of DMSO and 10 m*l* of acetyl chloride was carried out at 50—60°C under conditions similar to those used in the reaction of I with DMSO and acetyl chloride. The reaction mixture was then extracted with ethyl acetate; TLC on silicic acid showed two UV-positive spots (R_f 0.85 and 0.78) when developed with a mixture of benzene and ethyl acetate (19 : 1). The XVIII and XIX compounds were separated with adsorption-column chromatography on silicic acid (2.5×55 cm), using benzene as the developer; XVIII was eluted first. After it had been crystallized from benzene and ligroin, the yield of XVIII was 200 mg; mp 144—147°C: λ_{max}^{MeOH} 328 (*e* 27200), 230 mμ (*e* 19700).

Found: C, 48.28; H, 3.70; N, 6.46; S, 41.6%. Calcd for $C_9H_9NS_3$: C, 47.54; H, 3.99; N, 6.16; S, 42.31%.

After repeated attempts at the chromatography of the eluate containing XIX, the compound was crystallized from benzene and ligroin; yield 50 mg; mp 171—172°C: λ_{max}^{MeOH} 320 (*e* 15800), 272 (*e* 21400), 223 mμ (*e* 43500).

Found: C, 51.70; H, 2.66; N, 7.79; S, 36.82%. Calcd for $C_{15}H_{10}N_2S_4$: C, 51.99; H, 2.91; N, 8.09; S, 37.01%.

1-Thiomethoxymethyl-2-benzoxazolinethione (XXI), 1, 1′-Methylenebis-2-benzoxazolinethione (XXII) and 1-Hydroxymethylbenzoxazolone (XXIII). One gram of 2-benzoxazolinethione (XX) was treated as has been described in the preceding section. The reaction mixture was then extracted with ethyl acetate; TLC on silicic acid showed UV-positive spots at R_f 0.85, 0.76, 0.28, and 0.09, spots which were found to correspond to XXI, XXII, the unreacted XX, and XXIII respectively. These compounds were isolated by column chromatography on silicic acid (2.5×55 cm), XXI and XXII being eluted with benzene, and XXIII, with a mixture of ethyl acetate and benzene (1 : 5).

After it had been recrystallized from benzene and ligroin, the yield of XXI was 20 mg; mp 146—147°C: λ_{max}^{MeOH} 302 (*e* 27900), 258 mμ (*e* 8500).

Found: C, 51.10; H, 4.44; N, 6.55%. Calcd for $C_9H_9NOS_2$: C, 51.12; H, 4.29; N, 6.63%.

The yield of XXII was 20 mg, after it had been recrystallized from benzene and ligroin; mp 159—160°C: λ_{max}^{MeOH} 298 (*e* 27800), 285 (*e* 26600), 278 (*e* 20900), 249 mμ (*e* 17800).

Found: C, 56.94; H, 3.01; N, 8.47; S, 20.14%. Calcd for $C_{15}H_{10}N_2O_2S_2$: C, 57.30; H, 3.21; N, 8.91; S. 20.40%.

The yield of XXIII was 150 mg, after it had been recrystallized from ethyl acetate; mp 103—110°C: λ_{max}^{MeOH} 273 (*e* 5500), 226 mμ (*e* 11700).

Found: C, 58.13; H, 4.08; N, 8.42%. Calcd for $C_8H_7NO_3$: C, 58.18; H, 4.27; N, 8.48%.

1-Hydroxymethylbenzoxazolone (XXIII) was prepared by another route. A solution of 1 g of benzoxazolone in 20 m*l* of ethanol and 5 m*l* of 37% aqueous formalin were mixed and then left at room temperature for 48 hr. After the solvent was evaporated to dryness, the residue was crystallized from ethyl acetate; yield 1 g. The infrared spectra of the two samples of XXIII were found to be identical.