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The Reduction of 4-Thiazones and 4-Thiazone-imines, and the Conversion of Triphenyl-4-thiazone to Thiazolium Salts*

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The reduction of 4-thiazones and *N*-acetyl-4-thiazone-imines with sodium borohydride gave thiazolidin-4-ones and 4-acetylaminothiazolidines respectively. Attempts to isomerize 5-alkylidenethiazolidin-4-ones, prepared by the reduction of 5-acyl-4-thiazones, followed by dehydration, to 5-alkyl-4-thiazones were unsuccessful. The ethylation and acetylation of 2, 3, 5-triphenyl-4-thiazone gave the corresponding 4-ethoxy- and 4-acetoxy-thiazolium salts.

A number of 4-thiazone (I: 3, 4-dihydro-4-oxothiazole) and 4-thiazone-imine (II: 3, 4-dihydro-4-iminothiazole) derivatives have been prepared in this laboratory, and their reactions have been investigated.[1] Considering the mode of preparation of these compounds, as well as their reactions, there remains little doubt as to the structural assignment of these compounds. There

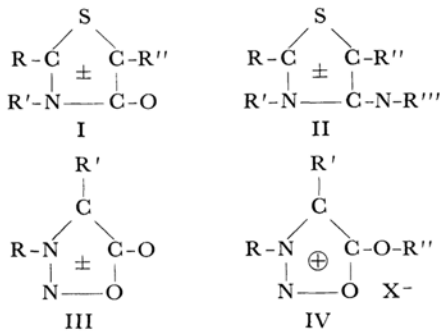
* Studies on meso-ionic compounds. XXVIII. Part XXVII: M. Ohta, H. Kato and T. Kaneko, This Bulletin, **40**, 579 (1967).

1) a) M. Ohta, H. Chosho, C. Shin and K. Ichimura, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **85**, 440 (1964); b) H. Chosho, K. Ichimura and M. Ohta, This Bulletin, **37**, 1670 (1964); c) C. Shin and M. Ohta, *ibid.*, **38**, 1816 (1965); d) M. Ohta, K. Yoshida and S. Sato, *ibid.*, **39**, 1269 (1966).

has been, however, no attempt to convert these compounds to a known ring system. From this point of view, the thiazone ring system is ideal, because the reduction of these compounds may give thiazolidine derivatives which have been well documented. The reduction of thiazones and, thiazone-imines may also be of interest in itself since there have been few reports on the reduction of meso-ionic rings.[2)]

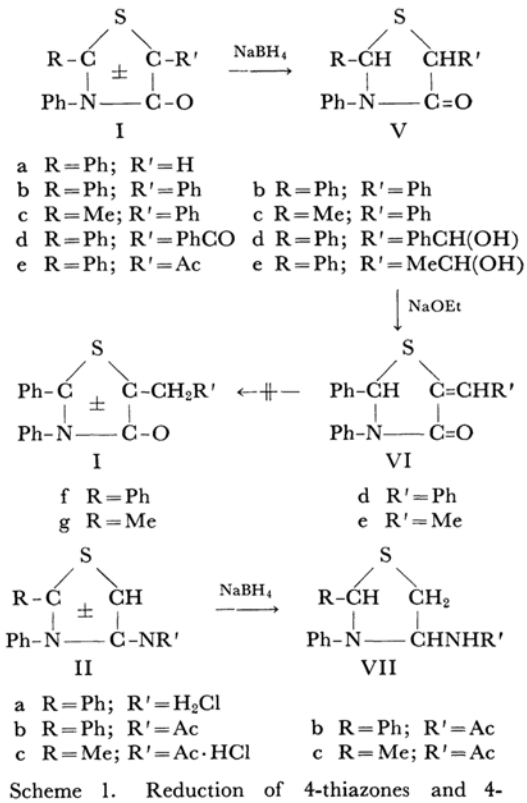
During the course of our studies of 4-thiazones, which, *a priori*, may be regarded as having electronic characteristics similar to those of sydnones, it was noted that the infrared absorptions of the carbonyl groups of this ring system extend over a wide range (1725—1620 cm^{-1}). For example, 2, 3, 5-triphenyl-4-thiazone (Ib) exhibits an infrared carbonyl absorption at 1620 cm^{-1} and is soluble in concentrated hydrochloric acid. These facts suggest that the carbonyl group of this compound is strongly polarized, and that it may be possible to isolate stable salts from such strongly-polarized thiazones. In one phase of our investigation of meso-ionic compounds, we attempted the *O*-alkylation of sydnones (III) in order to convert them to alkoxysydnonium salts (IV). Such attempts with sydnones were, however, unsuccessful.[2)]

The present communication, therefore, is concerned with the reduction of 4-thiazones and 4-thiazone-imines to the corresponding thiazolidine derivatives, and with the conversion of 2, 3, 5-triphenylthiazone to thiazolium salts.



Reduction of 4-Thiazones and 4-Thiazone-imines. The reduction of 2, 3-diphenyl-4-thiazone (Ia) by lithium aluminum hydride gave only a resinous product, and the treatment of Ia with sodium borohydride gave the starting material. It was found, however, that when thiazones with a phenyl or an acyl substituent on the 5-position (Ib—e) were treated with sodium borohydride, they were readily hydrogenated to give the corresponding thiazolidin-4-ones (Vb—e). The reduction product from 2, 3, 5-triphenyl-4-thiazone was identical with 2, 3, 5-triphenylthiazolidin-4-one (Vb), which was prepared from benzaniline and α-mercaptophenylacetic acid. The treatment of carbomethoxymethyl *N*-phenylthiobenzimidate or 2, 3-diphenylthiazone (Ia) with benzoic anhydride gave 2, 3-diphenyl-5-benzoyl-4-thiazone (Id). The reduction of Id with sodium borohydride gave 2, 3-diphenyl-5-(α-hydroxybenzyl)thiazolidin-4-one (Vd), which, when heated with sodium ethoxide in benzene, gave a dehydrated product. This product was identical with 2, 3-diphenyl-5-benzylidenethiazolidin-4-one (VId), which was prepared from 2, 3-diphenylthiazolidin-4-one and benzaldehyde by the method of Brown *et al.*[3)] Similarly, 2, 3-diphenyl-5-acetyl-4-thiazone (Ie) was reduced by sodium borohydride to 2, 3-diphenyl-5-(α-hydroxyethyl)-thiazolidin-4-one (Ve), which was then dehydrated by sodium ethoxide to the 5-ethylidene derivative VIe. From the above results, it is now evident that 4-thiazones have a thiazole-ring skeleton.

The catalytic and sodium borohydride reduction of 2, 3-diphenyl-4-thiazone-imine hydrochloride (IIa) was attempted in this laboratory, but the reaction products could not be purified. When *N*-acetyl-2, 3-diphenyl-4-thiazone-imine (IIb) or



Scheme 1. Reduction of 4-thiazones and 4-thiazone-imines.

2) See for example, M. Ohta and H. Kato, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **86**, 661 (1965).

3) F. C. Brown. R. S. Jones and M. Kent *Can. J. Chem.*, **41**, 817 (1963).

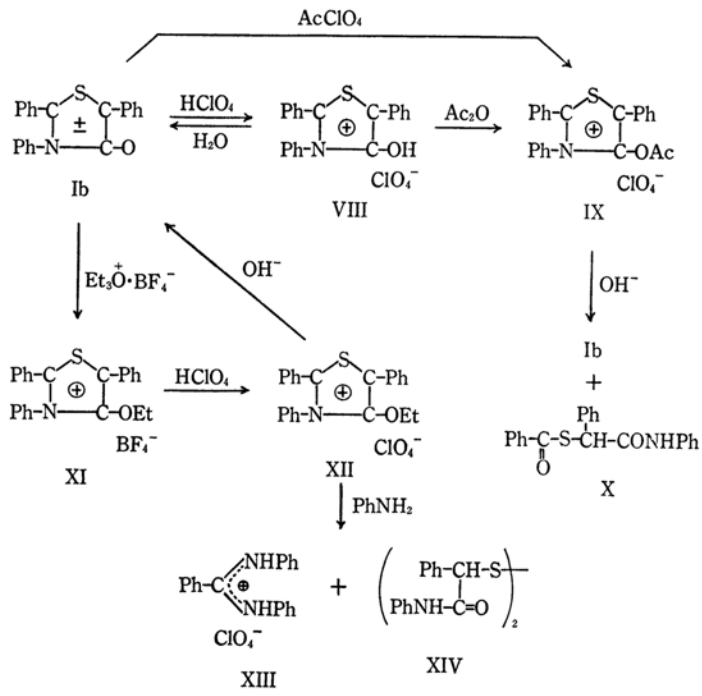
its hydrochloride was treated with sodium borohydride, a crystalline product could be isolated; the elemental analyses and infrared spectrum of this product suggest that the structure of this compound is 2, 3-diphenyl-4-acetylaminothiazolidine (VIIb). A similar treatment of the 2-methyl-3-phenyl derivative (IIc) which had been prepared by the acetylation of 2-methyl-3-phenyl-4-thiazoneimine hydrochloride gave the corresponding 4-acetylaminothiazolidine (VIIc).

The thiazolidin-4-ones (V) may be converted back to the corresponding 4-thiazones (I) if they undergo 2, 5-dehydration; our preliminary experiment showed that when 2, 4, 5-triphenylthiazolidin-4-one (Vb) was heated with sulfur at 200°C, such a dehydration indeed took place to give 2, 3, 5-triphenyl-4-thiazone, though in a very low yield. Such a mode of dehydrogenation to form a meso-ionic compound is being studied further in this laboratory.

The 5-alkylidenethiazolidin-4-ones VI may isomerize to the corresponding 5-alkyl-4-thiazones (I) if there is a considerable gain in the delocalization energy in going from the thiazolidinones to the thiazones. There is even the possibility that the presumed alkylidenethiazolidinone, obtained as has been described earlier, might have already been isomerized to the corresponding thiazone (I). The NMR spectrum of the 2, 3-diphenyl-5-ethylidene derivative VIe, however, exhibits a quartet-doublet pattern at τ 3.33 and 8.20, corresponding to one and four protons respectively; this is corroborative of the ethylidene structure VIe. We tried to effect this isomerization by treating the 5-benzylidene derivative VId with sodium hydride, triphenylmethyl perchlorate, triethyloxonium fluoroborate, and acetyl perchlorate. All such attempts were fruitless, however; all resulted in the recovery of the starting material.

Conversion of 2, 3, 5-Triphenyl-4-thiazone to Thiazolium Salts. The addition of perchloric acid to 2, 3, 5,-triphenyl-4-thiazone (Ib) afforded colorless crystals of 2, 3, 5-triphenyl-4-hydroxythiazolium perchlorate (VIII). The perchlorate VIII regenerated Ib when treated with water or amines. The reaction of the perchlorate VIII and acetic anhydride gave 2, 3, 5-triphenyl-4-acetoxythiazolium perchlorate (IX). The same acetoxythiazolium perchlorate, IX, was formed quantitatively when 2, 3, 5-triphenyl-4-thiazone was treated with acetyl perchlorate. The treatment of IX with aqueous sodium carbonate gave Ib and a compound which may be identifies as α-(benzoylthio)phenylacetanilide (X) on the basis of the elemental analyses and the similarity of its infrared spectrum to that of (benzoylthio)acetanilide. The fact that (benzoylthio)acetanilide is formed by the reaction of thiobenzanilide and bromoacetic acid, probably *via* a cyclic intermediate,[1a] lends support to this structural assignment.

Although 2, 3, 5-triphenyl-4-thiazone (Ib) could not be benzylated with benzyl bromide, triethyloxonium fluoroborate converted Ib to 2, 3, 5-triphenyl-4-ethoxythiazolium fluoroborate (XI),



Scheme 2. Thiazolium salts derived from triphenyl-4-thiazone.

TABLE 1. INFRARED AND ULTRAVIOLET ABSORPTIONS OF 4-THIAZONES AND RELATED COMPOUNDS

Compound	λ_{max} (mμ) (log ε)	$\nu_{C=O}$, cm^{-1}
2, 3, 5-Triphenyl-4-thiazone (Ib)	453 (4.15)	1620
2, 3, 5-Triphenyl-4-hydroxythiazolium perchlorate (VIII)	348 (4.00)	
2, 3, 5-Triphenyl-4-acetoxythiazolium perchlorate (IX)	337 (4.17)	
2, 3, 5-Triphenyl-4-ethoxythiazolium perchlorate (XII)	254 (4.09)	
	344 (4.15)	
2, 3, 5-Triphenylthiazolium perchlorate (XV)	256 (4.14)	
	336 (4.18)	
2, 5-Diphenyl-3-benzyl-4-thiazone		1625
3, 5-Diphenyl-2-methyl-4-thiazone (Ic)	224s (4.01)	1710
2, 3-Diphenyl-4-thiazone (Ia)	310 (2.32)	1725
2, 3-Diphenyl-5-benzoyl-4-thiazone (Id)		1670
2, 3-Diphenyl-5-acetyl-4-thiazone (Ie)		1650
2, 3-Diphenylthiazolidin-4-one		1670
2, 3, 5-Triphenylthiazolidin-4-one (Vb)		1670
3, 5-Diphenyl-2-methylthiazolidin-4-one (Vc)		1670

which was then converted to the corresponding perchlorate XII by perchloric acid. The NMR spectrum of the fluoroborate exhibits a triplet-quartet pattern of the ethyl group at τ 9.05 and 5.95, corresponding to three and two protons respectively, thus lending support to the structure XI. The ethoxythiazolium perchlorate XII is a rather stable compound, hydrolysis to Ib taking place sluggishly even when it was heated with aqueous sodium carbonate.

We have been interested in preparing *N*-alkyl or *N*-aryl derivatives of 4-thiazone-imine, but attempts at preparing such compounds by the direct alkylation of 4-thiazone-imine hydrochloride, or by the ring closure of cyanomethyl *N*-phenylthiobenzimidate, were unsuccessful. In an attempt at converting the 4-ethoxythiazolium salt to the corresponding 4-thiazone-imine by reaction with amines, XII was treated with aniline, piperidine, or diethylamine, but no reaction took place at room temperature and the starting material was recovered unchanged. When XII was heated with an excess of aniline at 100°C, a reaction did take place, but instead of the expected *N*-phenyl-4-thiazone-imine, the products actually isolated were *N*, *N'*-diphenylbenzamidine perchlorate (XIII) and a compound tentatively identified as di(phenylacetanilide)-α-disulfide (XIV).

The infrared carbonyl absorptions and ultraviolet absorption maxima of some thiazones and related compounds are listed in Table 1. 2, 3, 5-Triphenylthiazolium perchlorate (XV), which was required for purposes of comparison, was prepared by the reaction of thiobenzanilide and α-bromophenylacetaldehyde, followed by treatment with perchloric acid. The absorption maximum and intensity of 2, 3, 5-triphenyl-4-acetoxythiazolium perchlorate (IX) are almost identical with those of 2, 3, 5-triphenylthiazolium perchlorate (XV), and the absorption maxima of the 4-hydroxy and 4-ethoxy derivatives VIII and XII are shifted to wavelengths longer by *ca.* 10 mμ compared with IX and XV, which have virtually the same intensity. An almost identical relationship can be found with benzene and diphenyl derivatives with the same substituents (H, OH, OEt and OAc).[4] The absorption maximum of 2, 3, 4-triphenyl-4-thiazone (Ib) is shifted by *ca.* 110 mμ compared with that of the thiazolium salt VIII, suggesting that the exocyclic oxygen of Ib strongly participates in the chromophor. Such a large red shift in going from the salts to the parent substances has been observed in the cases of β-pyridones[5] and β-pyrones.[6] The appearance of the carbonyl absorption of 2, 3, 5-triphenylthiazone at a lower frequency region (1620 cm^{-1}) is quite analogous with the cases of pyrones and tropones; these spectral data, coupled with its basicity, suggest a considerable polarization of the carbonyl group of 2, 3, 5-triphenyl-4-thiazone. From the observation described above, it may safely be concluded that 2, 3, 5-triphenyl-4-thiazone is a typical heterocyclic betaine. Other 4-thiazone derivatives which may be classified in this betaine sub-group are 2, 5-diphenyl-3-benzyl-, 2, 3-diphenyl-5-benzoyl-, and 2, 3-diphenyl-5-acetyl-4-thiazone, all of which are highly colored, show basicity, and exhibit a carbonyl absorption in a relatively low frequency region. On the other hand, 2, 3-diphenyl- and 3, 5-diphenyl-2-methyl-4-thiazone show quite different properties. They are insoluble in strong mineral acids, show only an end-absorption in their ultraviolet spectra, and show a high-frequency

4) K. Hirayama, "Jikken Kagaku Koza," Vol. I, Part 1, ed. by M. Kotake, Maruzen Co., Tokyo (1957), pp. 151, 191.
5) S. F. Mason, *J. Chem. Soc.*, **1957**, 5010; **1959**, 1253.
6) G. Suld and C. C. Price, *J. Am. Chem. Soc.*, **83**, 1770 (1961).

carbonyl absorption; the carbonyl absorption appears higher than that of 2, 3-diphenylthiazolidin-4-one.

It is interesting to note that the nature of the substituents on the 4-thiazone ring affects the electronic structure of these compounds conspicuously. The reason for this notable phenomenon still remains to be elucidated.

Experimental

All melting points were taken on a micro hot stage, and are not corrected. The infrared spectra were taken on KBr tablets. The NMR spectra were taken with a JEOLCO Model C-60 (60 megacycles) on a deuterochloroform solution containing tetramethylsilane as the internal standard.

2, 3, 5 - Triphenylthiazolidin - 4 - on (Vb). a) A suspension of 1 g of 2, 3, 5-triphenyl-4-thiazone and 0.2 g of sodium borohydride in 40 m*l* of ethanol was refluxed for fifteen minutes. After cooling, the excess hydride was decomposed with 1 m*l* of 10% acetic acid, and the solvent was distilled off under reduced pressure to give 0.95 g of a white crystalline solid. Recrystallization from methanol gave colorless prisms melting at 138—139.5°C. This compound was identical with the specimen of 2, 3, 5-triphenylthiazolidin-4-one prepared by the method b) described below. λ_{max}^{EtOH} end-absorption. $\nu_{C=O}$ 1695m; 1670s cm^{-1}.

Found: C, 76.15; H, 5.27; N, 4.14%. Calcd for $C_{21}H_{17}NOS$: C, 76.13; H, 5.14; N, 4.23%.

b) A solution of 1.4 g of α-mercaptophenylacetic acid and 0.7 g of benzalaniline in 30 m*l* of toluene was refluxed for three hours. The toluene was then distilled off under reduced pressure, and 10 m*l* of ether was added to the residue. The crystals which slowly separated out were recrystallized from methanol to give 0.4 g of colorless prisms melting at 138—139°C.

3, 5-Diphenyl-2-methylthiazolidin-4-one (Vc). A similar treatment of 1 g of 3, 5-diphenyl-2-methyl-4-thiazone with sodium borohydride gave 0.9 g of colorless needles (from ethanol) melting at 110—135°C.[7] λ_{max}^{EtOH} end-absorption with a shoulder at 224 mμ (log ε 4.01). $\nu_{C=O}$ 1670 cm^{-1}.

Found: C, 71.69; H, 5.91; N, 5.26%. Calcd for $C_{16}H_{15}NOS$: C, 71.36; H, 5.61; N, 5.20%.

2, 3-Diphenyl-5-benzoyl-4-thiazone (Id). a) Triethylamine (40 m*l*) was added to a solution of 30 g of thiobenzanilide and 20 g of bromoacetic acid in 150 m*l* of benzene. After being allowed to stand overnight, the crystals of triethylamine hydrobromide were filtered off and the solvent was distilled under reduced pressure to give a pale yellow, oily material. A mixture of this oily substance and 15 g of benzoic anhydride was heated at 85°C for five hours; then 200 m*l* of methanol were added to the mixture, and the resulting solution was refluxed for three hours. The mixture was concentrated to dryness under reduced pressure, and the residue was washed with two 200 m*l* portions of hexane and allowed to stand overnight with a small amount of methanol to give 8 g of orange needles melting at 246—248°C. Recrystallization, first from chloroform-ether and then from ethyl cellosolve, gave 5.8 g of orange needles, mp 252.5—253°C. λ_{max}^{EtOH} 280 mμ (log ε 4.09); 417 mμ (log ε 4.21); $\nu_{C=O}$ 1670: 1385 cm^{-1}.

Found: C, 73.81; H, 4.35; N, 3.69%. Calcd for $C_{22}H_{15}NO_2S$: C, 73.94; H, 4.23; N, 3.92%.

b) A mixture of 0.5 g of 2, 3-diphenyl-4-thiazone, 2 g of benzoic anhydride, and 1 m*l* of pyridine was heated on a water bath for four hours. Methanol (10 m*l*) was added to the mixture, and the resulting mixture was refluxed for two hours; it was then concentrated to dryness under reduced pressure. The treatment of the residue by essentially the same method as has been described above gave 0.1 g of orange needles; mp 250—252°C, undepressed on admixture with the sample of 2, 3-diphenyl-5-benzoyl-4-thiazone prepared by the method a).

2, 3-Diphenyl-5-(α-hydroxybenzyl)thiazolidin-4-one (Vd). A suspension of 0.5 g of 2, 3-diphenyl-5-benzoyl-4-thiazone and 0.1 g of sodium borohydride in 20 m*l* of ethanol was refluxed for ten minutes. After cooling, 1 m*l* of acetic acid was added, and the solvent was removed under reduced pressure. An oily substance separated out when water was added to the residue. It was taken up in benzene, the benzene extract was concentrated, and ether was added to give 0.1 g of colorless crystals. Recrystallization from benzene and then from methanol afforded colorless prisms; mp 209.5—210.5°C. λ_{max}^{EtOH} end-absorption. $\nu_{C=O}$ 1675s; ν_{OH} 3400m cm^{-1}.

Found: C, 72.94; H, 5.35; N, 3.80%. Calcd for $C_{22}H_{19}NO_2S$: C, 73.11; H, 5.30; N, 3.88%.

2, 3-Diphenyl-5-benzylidenethiazolidin-4-one (VId). A mixture of 18 mg of 2, 3-diphenyl-5-(α-hydroxybenzyl)thiazolidin-4-one, 7 mg of sodium ethoxide, and 2 m*l* of benzene was refluxed for fifteen minutes. After cooling, the mixture was washed with 1 m*l* of water containing a droplet of acetic acid. The benzene was then removed under reduced pressure, and the residue was triturated with ether and recrystallized from ethyl cellosolve to give 15 mg of pale yellow prisms; mp 189—190.5°C, undepressed on admixture with an authentic specimen.[3] The two samples had identical infrared spectra.

2, 3-Diphenyl-5-(α-hydroxyethyl)thiazolidin-4-one. (Ve). A solution of 0.2 g of sodium borohydride in 20 m*l* of ethanol was added to a suspension of 1 g of 2, 3-diphenyl-5-acetyl-4-thiazone in 20 m*l* of ethanol, and the mixture was stirred for one hour. Acetic acid (1 m*l*) was then added, the solvent was removed under reduced pressure, and ether was added to the residue. The colorless crystals which separated out slowly were collected (0.15 g) and recrystallized from benzene-hexane to give colorless needles, mp 181—183°C. λ_{max}^{EtOH} end-absorption. ν_{OH} 3430 m; $\nu_{C=O}$ 1670s cm^{-1}.

Found: C, 68.33; H, 5.88; N, 4.60%. Calcd for $C_{17}H_{17}NO_2S$: C, 68.21; H, 5.73; N, 4.68%.

2, 3 - Diphenyl - 5 - ethylidenethiazolidin - 4 - one (VIe). Crude oily 2, 3-diphenyl-5-(α-hydroxyethyl)-thiazolidin-4-one (Ve), prepared from 2 g of 2, 3-diphenyl-5-acetyl-4-thiazone, was dissolved in 50 m*l* of benzene; the solution was then refluxed with 0.45 g of sodium ethoxide for fifteen minutes. After cooling, it was washed with 50 m*l* of water containing 5 m*l* of

7) Repeated recrystallization did not give a sharp melting point. This is presumably due to the existence of stereoisomers.

acetic acid. On standing, 0.85 g of colorless needles separated out. Recrystallization from ethyl cellosolve gave colorless needles melting at 206—207°C. λ_{max}^{EtOH} 270 mμ (log ε 4.08). $\nu_{C=O}$ 1670s; $\nu_{C=C}$ 1630m cm^{-1}. NMR: ($CDCl_3$) τ 2.7—2.9 (10H, multiplet); 3.33 (1H, quartet); 8.20 (3H, doublet).

Found: C, 72.55; H, 5.53; N, 5.08%. Calcd for $C_{17}H_{15}NOS$: C, 72.58; H, 5.37; N, 4.98%.

***N*-Acetyl-2-methyl-3-phenyl-4-thiazone-imine Hydrochloride (IIc).** A suspension of 4 g of 2-methyl-3-phenyl-4-thiazone-imine hydrochloride in 25 m*l* of acetic anhydride and a small amount of boron trifluoride etherate was heated on a water bath for four hours. The solvent was then removed under reduced pressure, and acetone was added to the residue. The crystals which separated out were recrystallized from ethanol-ether to give 3.5 g of colorless needles, mp 214—218°C (decomp.). ν_{NH} 3100; $\nu_{C=O}$ 1704 cm^{-1}.

Found: C, 53.42; H, 4.92; N, 10.74%. Calcd for $C_{12}H_{13}N_2OSCl$: C, 53.63; N, 4.84; N, 10.43%.

2, 3-Diphenyl-4-acetaminothiazolidine (VIIb). a) To a stirred solution of 0.5 g of *N*-acetyl-2, 3-diphenyl-4-thiazone-imine hydrochloride in 10 m*l* of ethanol there was added a solution of 0.3 g of sodium borohydride in 15 m*l* of ethanol. After an hour, the excess hydride was decomposed by 10% aqueous acetic acid and the solvent was removed under reduced pressure. The residue was triturated with water and then recrystallized from methanol to give 0.45 g of colorless powder, mp 194—195°C. ν_{NH} 3300; $\nu_{C=O}$ 1650 cm^{-1}.

Found: C, 68.51; H, 6.35; N, 9.49%. Calcd for $C_{17}H_{18}N_2OS$: C, 68.44; H, 6.08; N, 9.39%.

b) From 0.5 g of *N*-acetyl-2, 3-diphenyl-4-thiazone-imine, 0.5 g of VIIb was similarly obtained.

2-Methyl-3-phenyl-4-acetaminothiazolidine (VIIc). *N*-Acetyl-2-methyl-3-phenyl-4-thiazone-imine hydrochloride (0.6 g) was treated with sodium borohydride by essentially the same method as has been described above, giving 0.5 g of colorless leaflets, mp 163—164°C.

Found: C, 61.39; H, 7.03; N, 11.78%. Calcd for $C_{12}H_{16}N_2OS$: C, 61.00; H, 6.83; N, 11.86%.

Dehydrogenation of 2,3,5-Triphenylthiazolidin-4-one (Vb) with Sulfur. A mixture of 100 mg of 2, 3, 4-triphenylthiazolidin-4-one and 400 mg of sulfur was heated at 200°C for fifteen minutes. The mixture was then dissolved in carbon disulfide, and the solution was eluted on an alumina column. The red substance which was adsorbed on alumina was extracted with chloroform, the extract was concentrated, and the red residue was recrystallized from ethanol to give a very small amount of red needles. The infrared spectrum of this substance was identical with that of 2, 3, 5-triphenyl-4-thiazone.

Attempted Isomerization of 2, 3-Diphenyl-5-benzylidenethiazolidin-4-one (VId). 2, 3-Diphenyl-5-benzylidenethiazolidin-4-one was recovered almost quantitatively when:

a) it was refluxed with sodium hydride in toluene for one hour;

b) it was refluxed with triphenylmethyl perchlorate in acetonitrile for five hours, or when

c) it was refluxed with triethyloxonium fluoroborate in dichloromethane for eight hours. The mixture was quenched with water in each case.

2, 3, 5-Triphenyl-4-hydroxythiazolium Perchlorate (VIII). To a suspension of 0.64 g of 2, 3, 5-triphenyl-4-thiazone (Ib) in 10 m*l* of acetone, there was added 0.2 m*l* of 70% perchloric acid. The red color of the suspension gradually faded, and there resulted a yellow solution. The acetone was distilled off, and water was removed from the residue by three azeotropic distillations with dichloromethane. The residue was then dissolved in dichloromethane and precipitated by the addition of ether to give 0.5 g of yellow crystals. They were recrystallized, first from dichloromethane-ether and then from dichloromethane-hexane, to give yellow needles, mp 169—170.5°C.

Found: C, 58.38; H, 3.97; N, 3.32%. Calcd for $C_{21}H_{16}NO_5SCl$: C, 58.60; H, 3.72; N, 3.26%.

When an acetone solution of VIII was treated with water or with an amine, Ib was obtained quantitatively.

2, 3, 5-Triphenyl-4-acetoxythiazolium Perchlorate (IX). a) A suspension of 0.9 g of 2, 3, 5-triphenyl-4-hydroxythiazolium perchlorate in 10 m*l* of acetic anhydride was warmed on a water bath for fifteen minutes. The crystals of VIII dissolved and new crystals separated out. The recrystallization of the crystals from acetonitrile-ether gave colorless needles, mp 181—183°C.

Found: C, 58.39; H, 4.04; N, 3.19%. Calcd for $C_{23}H_{19}NO_6SCl$: C, 58.54; H, 3.82; N, 2.97%.

b) The same compound, IX, could be obtained quantitatively by the addition of acetyl perchlorate (prepared from 0.2 m*l* of perchloric acid and 2 m*l* of acetic anhydride) to a suspension of 0.64 g of 2, 3, 5-triphenyl-4-thiazone in 8 m*l* of acetic anhydride.

Hydrolysis of 2, 3, 5-Triphenyl-4-acetoxythiazolium Perchlorate. A solution of 0.11 g of sodium carbonate in 2 m*l* of water was added to a solution of 0.47 g of 2, 3, 5-triphenyl-4-acetoxythiazolium perchlorate in 10 m*l* of acetonitrile, after which the mixture was warmed on a water bath for five minutes. When the mixture was then cooled, 0.12 g of red crystals separated out. The melting point and the infrared spectrum of this compound were identical with those of 2, 3, 5-triphenyl-4-thiazone. On addition of 10 m*l* of water to the mother liquor, 0.2 g of colorless needles separated out; mp 167—169°C after one recrystallization from methanol. The infrared spectrum of this compound was quite similar to that of α-(benzoylthio)-acetanilide.

Found: C, 72.75; H, 5.34; N, 4.63%. Calcd for $C_{21}H_{17}NO_2S$: C, 72.61; H, 4.94; N, 4.03%.

2, 3, 5-Triphenyl-4-ethoxythiazolium Fluoroborate (XI). A mixture of 1.9 g of triethyloxonium fluoroborate and 3 g of 2, 3, 5-triphenyl-4-thiazone in 20 m*l* of dichloromethane was stirred for one and a half hours. The pale yellow crystals which separated out on the addition of 50 m*l* of ether were recrystallized, first from dichloromethane-ether and then from dichloromethane-hexane, to give 3.7 g of colorless crystals melting at 178.5—180.5°C.

Found: N, 3.57%. Calcd for $C_{23}H_{20}NOSBF_4$: N, 3.14%.

2, 3, 5-Triphenyl-4-ethoxythiazolium Perchlorate (XII). 2, 3, 5-Triphenyl-4-ethoxythiazolium fluoroborate (0.6 g) was dissolved by warming in 50 m*l* of acetone containing 0.15 m*l* of 70% perchloric acid. The mixture was then concentrated to half of its original volume, and ether was added. The crystals which

separated out (0.45 g) were recrystallized from acetone-ether to give 0.45 g of colorless needles melting at 195—197°C.

Found: C, 60.21; H, 4.60; N, 3.29%. Calcd for $C_{23}H_{20}NO_5SCl$: C, 60.31; H, 4.40; N, 3.06%.

Hydrolysis of 2, 3, 5-Triphenyl-4-ethoxythiazolium Perchlorate (XII). To a solution of 0.46 g of XII in 10 m*l* of acetonitrile, a solution of 0.11 g of sodium carbonate in 2 m*l* of water was added; the mixture was then refluxed for one hour. After cooling, 0.07 g of 2, 3, 5-triphenyl-4-thiazone separated out. Water was added to the filtrate, and the solution was extracted twice with 20 m*l* portions of dichloromethane. The extract was concentrated, and the residue was recrystallized from ethanol to give 0.1 g of XII.

Reaction of 2, 3, 5-Triphenyl-4-ethoxythiazolium Perchlorate with Amines. a) When 2, 3, 5-triphenyl-4-ethoxythiazolium perchlorate was treated overnight with an equivalent or an excess amount of aniline, piperidine, or dimethylamine at room temperature, the starting material was quantitatively recovered.

b) A solution of 0.5 g of 2, 3, 5-triphenyl-4-ethoxythiazolium perchlorate in 4 m*l* of aniline was heated on a boiling water bath for two hours. After cooling, ether was added; the crystals which separated out were collected to give 0.4 g of very hygroscopic, colorless needles. The infrared spectrum of this compound was identical with that of *N, N'*-diphenylbenzamidine perchlorate (XIII).

When the mother liquor of the above-described experiment was allowed to stand for a longer period of time, another precipitate (0.15 g) separated out. Recrystallization from ethanol afforded colorless needles melting at 249—251°C.

Found: C, 69.01; H, 5.23; N, 6.52%. Calcd for $C_{28}H_{24}N_2O_2S_2$ (XIV): C, 69.41; H, 4.99; N, 5.78%.

2, 3, 5-Triphenylthiazolium Perchlorate (XV). A solution of 1 g of thiobenzanilide and 1 g of α-bromophenylacetaldehyde in 10 m*l* of ethyl acetate was refluxed for thirty minutes. The brown oily material which separated out was collected by decantation and dissolved in 10 m*l* of ethanol, and 0.5 m*l* of 70% perchloric acid was added to this solution. There gradually separated out 0.25 g of colorless needles, which were recrystallized from acetone-ether to give colorless needles, mp 224—226°C.

Found: C, 60.95; H, 3.63; N, 3.11%. Calcd for $C_{21}H_{16}NO_4SCl$: C, 60.94; H, 3.90; N, 3.38%.