The Reaction of α-Haloketones with *N*-Alkyl Benzothiazolium Salts

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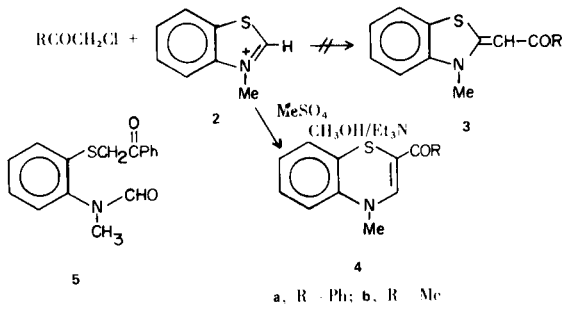
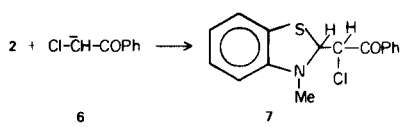
Phenacyl chloride (**1a**) reacts with the 3-methylbenzothiazolium quaternary salt (**2**) to give 4-methyl-2-benzoyl-4*H*-1,4-benzothiazine (**4a**). A mechanism is discussed. Secondary α-haloketones give benzothiazolines. Merocyanine dyes are formed by the reaction of **2** with carbanions. It is shown that **2** functions as a hydride ion abstractor in the formation of merocyanine dyes.

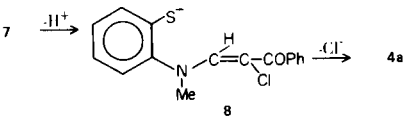
Our interest in the synthesis of aroylmethylene benzothiazolines prompted us to examine the reaction between phenacyl chloride (**1a**) and the 3-methylbenzothiazolium quaternary salt **2**. When the reaction was carried out in methanol using triethylamine as condensing agent, the product was not the expected benzothiazoline, **3a** (1), but the isomeric benzothiazine derivative, **4a** (2). A similar compound (**4b**) is obtained when chloroacetone (**1b**) is used in place of **1a**. The thiazine (**4a**) was previously ob-



tained by base-catalyzed ring closure of **5** (3). When the above reaction was carried out at low temperature, using isopropanol as solvent, a thermally unstable product (**7**) was obtained. The structure **7** was assigned on the basis of uv and nmr spectra and elemental analysis, and was presumably formed by addition of the carbanion **6** to **2**:

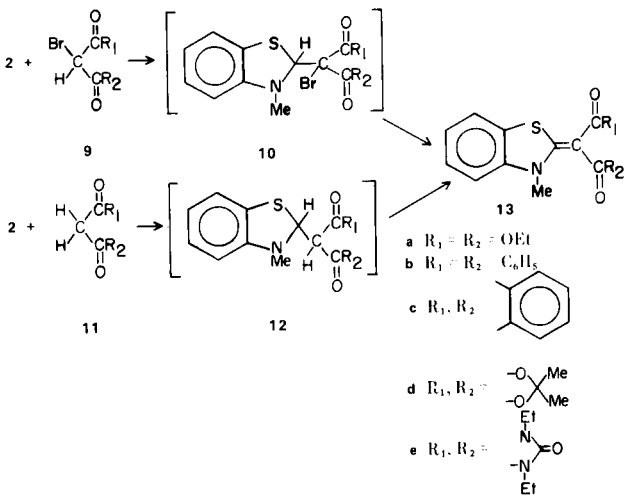


The intermediate (**7**) is readily transformed by heat into **4a**. It is proposed that this transformation occurs *via* deprotonation and ring opening, followed by intramolecular displacement of chlorine:

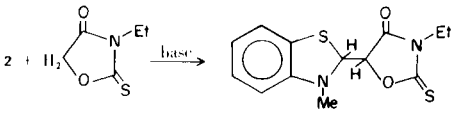


The deprotonation of **7** to give **8** may be self-catalyzed by the basic amine function.

Support for the above mechanism is found in the observation that a benzothiazoline derivative is obtained in cases where the intermediate analogous to **7** has no hydrogen atom on the carbon atom adjacent to the carbonyl function, as in the reaction of **2** with diethyl bromomalonate (**9a**) to give the merocyanine **13a**. Intermediates **10a-e**



are analogous to compounds obtained by Metzger *et al.* (4a), by the addition of halogen-free carbanions to **2**. Thus reaction of equimolar quantities of **14** and **2** leads to the dihydro compound **15**. However, the only products isolated when **11b-e** were allowed to react with **2** under the same conditions were the merocyanines **13b-e**.



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In addition, when 2 moles of **2** were allowed to react with 1 mole of **11c**, the yield of **13c** was raised from 41% to 96%. Apparently, in some cases, **2** is capable of oxidizing the dihydro compound to the corresponding merocyanine (4b). Attempts to oxidize **15** to **16** under these conditions were not successful, but **2** underwent an oxidative transformation to the spiro compound **17** (5). The dye **16** was obtained from **14** and 3-methyl-2-methylthiobenzothiazolium *p*-toluenesulfonate.

16 17

EXPERIMENTAL

The nmr spectra were measured on a Varian A60 spectrometer. The chemical shifts are given in δ values using TMS as internal standard.

2-(α-Chlorophenacyl)-3-methylbenzothiazoline (**7**).

A mixture of 1.04 g. (0.004 mole) of 3-methylbenzothiazolium methosulfate, 0.61 g. (0.004 mole) of phenacyl chloride, and 6 ml. of 2-propanol was cooled to ice-bath temperature and 0.40 g. (0.004 mole) of triethylamine was added. The mixture was stirred without further cooling until a clear solution was obtained. The solution was chilled for about ¼ hour and the vessel scratched to initiate crystallization. The solid that separated was collected and washed with a little 2-propanol, then with ligroin (30-60°), and dried. The yield of pale yellow crystals was 0.43 g. (36%); ir (potassium bromide): 1690 cm^{-1} (C=O); nmr (benzene-d_6): δ = 2.70 (s, 3H, *N*-methyl), 5.32 (AB quartet, 2H, methine protons, J = 9 Hz), 6.3-7.8 (m, 9H, aromatic).

Anal. Calcd. for $C_{16}H_{14}ClNOS$: C, 63.3; H, 4.6; Cl, 11.7; N, 4.6; S, 10.6. Found: C, 63.4; H, 4.6; Cl, 11.7; N, 4.5; S, 10.6.

4-Methyl-2-benzoyl-4*H*-1,4-benzothiazine (**4a**).

(a) A solution of 15.5 g. (0.1 mole) of phenacyl chloride in 100 ml. of methanol was added at a rapid drop rate to 3-methylbenzothiazolium methosulfate (**2**) (20 g., 0.0767 mole) and 25 ml. of triethylamine in 100 ml. of methanol. After the addition was complete, the reaction mixture was warmed to 60° for 0.5 hour and poured into 1 liter of cold water. The solid that separated was filtered and dried, yield, 20 g., 97%. After recrystallization from pyridine-methanol, 13 g. (65%) of **4a** was obtained, m.p. 164°; lit. (3) 162°; ir (potassium bromide): identical with that of an authentic sample; λ max (acetonitrile): 314 (4,800), 455 (5,000); nmr: δ 3.1 (S, 3H, *N*-methyl), 6.4-8 D (m, 10H, aromatic and vinylic protons).

(b) A solution of 0.5 g. of **7** in 10 ml. of 2-propanol was refluxed for 1 minute and allowed to cool slowly to room temperature. After 2 hours, the orange crystals that separated were collected and washed with a little 2-propanol to give 0.26 g. of **4a**.

4-Methyl-2-acetyl-4*H*-1,4-benzothiazine (**4b**).

Prepared as **4a**, method A, yield 68%, m.p. (methanol) 130-132°; nmr: δ 2.8 (S, 3H, $CH_3C{=}O$), 3.15 (S, 3H, *N*-methyl), 6.1-7.7 (m, 5H, aromatic and vinylic protons).

Anal. Calcd. for $C_{11}H_{11}NOS$: C, 64.4; H, 5.4; N, 6.8; S, 15.6. Found: C, 64.3; H, 5.4; N, 6.9; S, 16.0.

2-Benzoylmethylene-3-methylbenzothiazoline (**3a**).

A solution of 7.34 g. (0.02 mole) of 2,3-dimethylbenzothiazolium *p*-toluenesulfonate and 3.0 ml. (0.02 mole) of benzoyl chloride in 15 ml. of dry pyridine was heated on the steam bath for 1 hour. Methanol (45 ml.) was added to the hot pyridine solution. After cooling, the product was collected and crystallized from pyridine-methanol, yield 3.5 g., 65%, m.p. 180° (lit. (1) m.p. 181°); λ max (acetonitrile): 385 (38,000).

2-Acetylmethylene-3-methylbenzothiazoline (**3b**).

Prepared as the above compound, yield 59%, m.p. (methanol) 161°.

Anal. Calcd. for $C_{11}H_{11}NOS$: C, 64.4; H, 5.4; S, 15.6. Found: C, 64.3; H, 5.3; S, 15.5.

2-(1,3-dioxoindanylidene)-3-methylbenzothiazoline (**13c**).

Method A.

A solution of 2.45 g. (0.01 mole) of 3-methylbenzothiazolium methosulfate and 2.3 g. (0.01 mole) 2-bromo-1,3-indandione in 15 ml. of acetonitrile containing 5 ml. of triethylamine was heated under reflux for 2 hours. After cooling, the product was collected and crystallized from pyridine-methanol to give 2.3 g. (78%) of **13c**, m.p. 220°; (mol. wt. by mass spectroscopy 293); λ max (acetonitrile): 379 (48,000).

Anal. Calcd. for $C_{17}H_{11}NSO_4$: C, 69.8; H, 3.8; S, 10.9. Found: C, 69.5; H, 3.6; S, 10.5.

Method B.

A solution of 4.90 g. (0.02 mole) of **2** and 1.5 g. (0.01 mole) of 1,3-indandione in 25 ml. of hot methanol was treated with 5 ml. of triethylamine and heated at reflux for 1.5 hours. The product, 2.8 g. (96%), was collected and crystallized from pyridine-methanol to give 2.4 g. (83%) of **13c**, m.p. 220°. When equimolar quantities of components were used in the above reaction, a 41% yield of **13c** was obtained.

Method C.

A solution of 3.7 g. of 2-methylthio-3-methylbenzothiazolium *p*-toluenesulfonate (0.01 mole) and 2.0 g. (0.014 mole) of indandione in 35 ml. of ethyl alcohol containing 4.0 ml. of triethylamine was heated to reflux for 2 hours. The reaction mixture solidified. After cooling, the product was collected by filtration and crystallized from pyridine/methanol, yield 63%.

2-(Dibenzoylmethylene)-3-methylbenzothiazoline (**13b**).

Prepared by method A from 2-bromodibenzoylmethane and **2**, yield 74%, m.p. 250° from pyridine-methanol (lit. (1) 250°).

Prepared by method C from 2-methylthio-3-methylbenzothiazolium *p*-toluenesulfonate, yield 64%.

3-Ethyl-5-(3-methyl-2-benzothiazolinylidene)-2-thioxo-oxazolidin-4-one (**16**).

Prepared by method C from 3-ethyl-2-thioxo-oxazolidin-4-one, yield 73%.

Anal. Calcd. for $C_{13}H_{12}N_2S_2O_2$: C, 53.4; H, 4.1; S, 21.9. Found: C, 53.3; H, 4.0; S, 22.0. Mol. wt. by mass spectroscopy 292.

2-Di(ethoxycarbonyl)methylene-3-methylbenzothiazoline (**13a**).

Prepared by method A from diethyl bromomalonate and **2**, yield 29%, m.p. (2-propanol) 113-115° (lit. (6) m.p. 120°).

2-(2,2-Dimethyl-4,6-dioxodioxan-5-ylidene)-3-methylbenzothiazoline (**13d**).

Prepared by method B, yield 72%, m.p. 215° from pyridine-methanol.

Anal. Calcd. for $C_{14}H_{13}NSO_4$: C, 57.7; H, 4.5; N, 4.8. Found: C, 57.4; H, 4.3; N, 4.8. Mol. wt. 291 by mass spectroscopy.

The use of two equivalents of **2** to one of **14** results in the formation of the spirane **17**, m.p. 203° (lit. (5c) 205°). Mol. wt. by mass spectroscopy 286.

1,3-Diethyl-5-(3-methyl-2-benzothiazolidinylidene)barbituric Acid (**13e**).

Prepared by method A from 5-bromo-1,3-diethylbarbituric acid and **2**, yield 67%, m.p. (pyridine/methanol) 231°.

Anal. Calcd. for $C_{16}H_{17}N_3SO_3$: C, 58.0; H, 5.1; N, 12.7. Found: C, 58.1; H, 5.2; N, 12.7.

Also prepared by method B in 82% yield.

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