Reactions of Heterocycles with Thiophosgene. Part IV.[1] β,4-Dichloro-2-isothiocyanatocinnamaldehyde, a Product from 4,7-Dichloroquinoline

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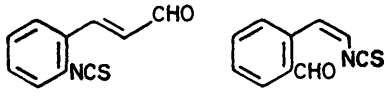
4,7-Dichloroquinoline undergoes ring scission on reaction with thiophosgene and barium carbonate. The resulting β-chloroisothiocyanatocinnamaldehyde [(6) or (7)] reacts with a wide variety of nucleophiles to give 2-substituted 4-formylmethylene-4*H*-3,1-benzothiazines. Some reactions of the 2-morpholinobenzothiazine (13) are described.

EARLIER studies[2] on the reaction of thiophosgene with quinoline and isoquinoline had shown that in the presence of base (hydroxide ion), fission of the heterocyclic ring took place to give the *o*-isothiocyanato-*trans*-cinnamaldehyde (1) and *o*-(*cis*-isothiocyanatovinyl)benzaldehyde (2), respectively. These *ortho*-difunctional

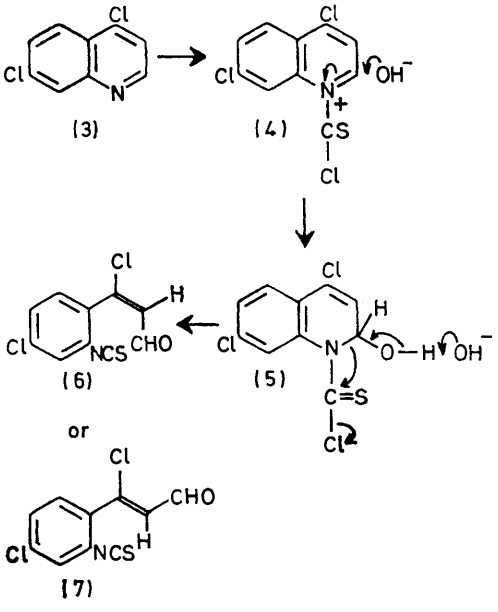


(1) (2)

benzene derivatives offer an interesting source of intermediates for the formation of novel heterocyclic compounds. We have now continued these studies with 4-substituted quinolines.

4,7-Dichloroquinoline (3), an intermediate used in the manufacture of the antimalarial chloroquine,[3] reacted smoothly with thiophosgene and alkali ($BaCO_3$) in methylene chloride–water[4] and yielded (58%) the isothiocyanate (6) as a reasonably stable compound, $\nu_{max.}$ 2000 (NCS) and 1670 cm^{-1} (conj. CHO), τ 0·46 (d, J 7·5 Hz, =CH·C*H*O) and 3·36 (d, J 7·5 Hz, =C*H*·CHO). We were unable to determine the configuration of the olefin [(6) or (7)] from n.m.r. data.

Some Reactions of β,4-*Dichloro*-2-*isothiocyanatocinnamaldehyde* [(6) or (7)].—The isothiocyanate group in this compound reacted readily with a wide variety of nucleophiles; however we were not able in any case to isolate the thioamide (8); instead ring closure took place to yield the substituted benzothiazine (9). Primary and secondary amines reacted to give, in general, compounds (9; R = NR^1R^2). The morpholine derivative (13) was shown to have the stereochemistry indicated by the nuclear Overhauser effect between the exocyclic vinyl proton and the 5-H. The i.r. spectra of the aminobenzothiazines generally showed $\nu_{max.}$ *ca.* 1650 cm^{-1}



(conj. CHO), and the n.m.r. spectra showed the aldehyde proton signal as a doublet (J 4 Hz) at τ *ca.* 0·1 coupled to the vinyl proton (d, J 4 Hz) at τ *ca.* 3·2.

2-Aminopyridine yielded the expected product (17) together with 4,7-dichloroquinoline. β-Aminoethanol

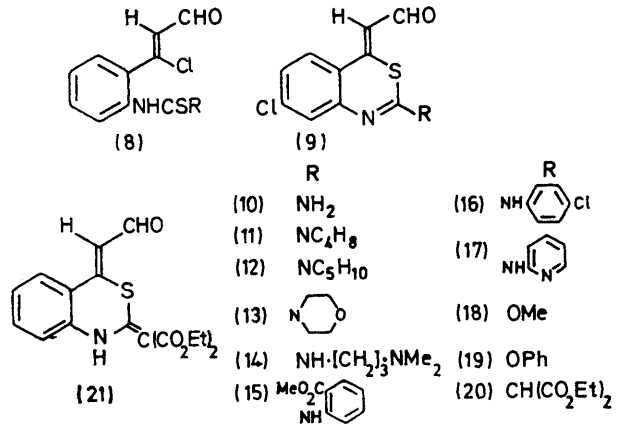
[1] Part III, F. T. Boyle and R. Hull, *J.C.S. Perkin I*, 1974, 1541.

[2] R. Hull, *J. Chem. Soc.* (*C*), 1968, 1777.

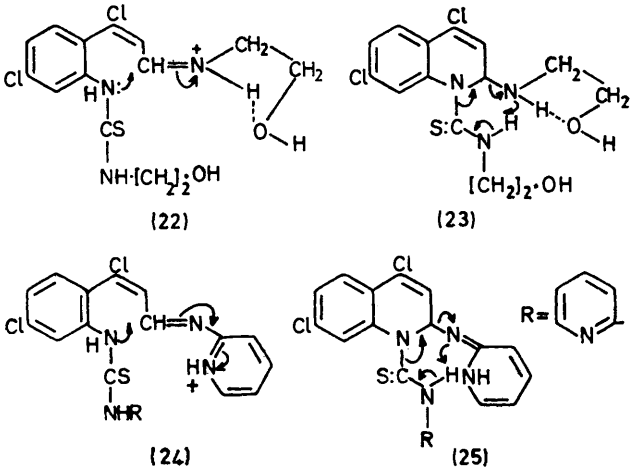
[3] A. R. Surrey and H. F. Hammer, *J. Amer. Chem. Soc.*, 1946, **69**, 113.

[4] F. D. Popp, W. Blount, and P. Melvin, *J. Org. Chem.*, 1961, **26**, 4930.

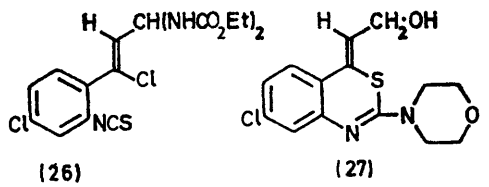
reacted in an anomalous fashion: in this case the only product was 4,7-dichloroquinoline, isolated in 57% yield. Presumably in this reaction some stabilisation of the iminium group is set up by the stereochemically favourable position of the oxygen atom of the ethanolamine, as shown in (22) and (23) (contribution by Dr. P. N. Edwards of this Department). 2-Aminopyridine presumably forms, in part, a species of type (24) ⟶ (25) to account for some formation of 4,7-dichloroquinoline.

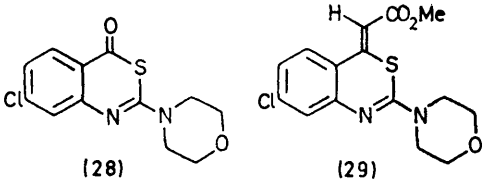


Methanol and phenol reacted normally with the isothiocyanate (6/7) in the presence of alkali and yielded the corresponding 2-methoxy- (18) and phenoxy- (19) derivatives, respectively. Reaction of diethyl sodiomalonate with the isothiocyanate (6/7) in dimethylformamide gave an ester which we regard as having the exomethylene structure (21) rather than the tautomeric structure (20). The n.m.r. spectrum showed the NH signal as a singlet at τ 3·1. Ethyl carbamate, in the presence of acid, reacted with the aldehyde (6/7) to yield the bisurethane (26).



The formyl group in the benzothiazine (13) yielded an oxime and a semicarbazone under standard conditions. The related alcohol (27) was obtained by reduction of the aldehyde (13) with sodium borohydride or lithium aluminium hydride. Oxidation of the aldehyde (13) with potassium permanganate in acetone gave the benzothiazinone (28), $\nu_{max.}$ 1665 cm^{-1} (thiolactone C=O). By the method of Corey and his co-workers,[5] treatment of the aldehyde (13) with active manganese dioxide and hydrogen cyanide in methanol gave the ester (29) in very low yield, $\nu_{max.}$ 1690 cm^{-1} ($\alpha\beta$-unsat. ester), M^+ 338 (1 × Cl). The compound was not sufficiently soluble for a satisfactory n.m.r. spectrum to be obtained.





[5] E. J. Corey, N. W. Gilman, and B. E. Ganem, *J. Amer. Chem. Soc.*, 1968, **90**, 5616.

EXPERIMENTAL

N.m.r. spectra were measured with a Perkin-Elmer R-12 or Varian A-60 (60 MHz) or HA-100 (100 MHz) instrument. Low resolution mass spectra were determined with a Hitachi RMU-6E and high resolution mass spectra with an A.E.I. MS9 or A.E.I. MS 902 S spectrometer.

β,4,Dichloro-2-isothiocyanatocinnamaldehyde [(6) or (7)].—Thiophosgene (45 ml) in methylene chloride (180 ml) was added dropwise over 30 min to a vigorously stirred suspension of barium carbonate (88 g) in water (360 ml) and 4,7-dichloroquinoline (89 g) in methylene chloride (360 ml) at 0°. The mixture was stirred for 4 h at 0° then overnight at room temperature and filtered through a pad of Supercel. The methylene chloride layer was separated and washed successively with water, 2N-hydrochloric acid, and water, then dried and concentrated to a brown oil which solidified on cooling. Crystallisation from light petroleum (b.p. 60—80°) gave the *aldehyde* (68 g, 58%) as pale yellow needles, m.p. 59—61° (Found: C, 46·9; H, 2·3; N, 5·2. $C_{10}H_5Cl_2NOS$ requires C, 46·5; H, 1·9; N, 5·4%), $\nu_{max.}$ (Nujol) 2000br (NCS) and 1670 cm^{-1} (C=O), τ ($CDCl_3$) 0·46 (1H, d, *J* 7·5 Hz, CHO), 2·65 (3H, s, aromatic), and 3·36 (1H, d, *J* 7·5 Hz, vinylic).

2-Amino-7-chloro-4-formylmethylene-4H-3,1-benzothiazine (10).—Aqueous ammonia (*d* 0·88; 1·5 ml) was added to a stirred solution of β,4-dichloro-2-isothiocyanatocinnamaldehyde (1·5 g) in ethyl acetate (25 ml). After ½ h the precipitate formed was filtered off, washed with water, and crystallised from aqueous dimethylformamide to give the *aminobenzothiazine* (1·0 g) as mustard yellow needles, m.p. >300° (Found: C, 50·1; H, 3·1; N, 11·4. $C_{10}H_7ClN_2OS$ requires C, 50·2; H, 2·9; N, 11·7%), $\nu_{max.}$ 3200br (NH), 1670, and 1640 cm^{-1} (C=O?), M^+ 238 (1 × Cl).

7-Chloro-4-formylmethylene-2-(pyrrolidin-1-yl)-4H-3,1-benzothiazine (11).—Pyrrolidine (0·3 g) in ethyl acetate (5 ml) was added to a stirred solution of β,4-dichloro-2-isothiocyanatocinnamaldehyde (0·5 g) in ethyl acetate

(10 ml). After 3 h the supernatant was decanted from a residual red oil and evaporated to yield an orange solid, which was crystallised from cyclohexane to give the *benzothiazine* as yellow needles, m.p. 145—146° (Found: C, 57·2; H, 4·4; N, 9·2. $C_{14}H_{13}ClN_2OS$ requires C, 57·4; H, 4·4; N, 9·6%), $\nu_{max.}$ (Nujol) 1650 cm^{-1} (C=O), M^+ 292 (1 × Cl).

7-Chloro-4-formylmethylene-2-morpholino-4H-3,1-benzothiazine (13).—β,4-Dichloro-2-isothiocyanatocinnamaldehyde (1·04 g) in ethyl acetate (10 ml) was added with stirring to morpholine (0·68 g) in ethyl acetate (5 ml) at room temperature. After 15 min the mixture was filtered and the residue (morpholine hydrochloride) was washed with ethyl acetate (20 ml). The filtrate was concentrated to yield a yellow solid which was triturated with aqueous 2N-acetic acid, filtered off, and dried. Crystallisation from cyclohexane gave the *benzothiazine* (0·65 g, 52%) as yellow needles, m.p. 163—164° (Found: C, 54·4; H, 4·3; N, 8·7. $C_{14}H_{13}ClN_2O_2S$ requires C, 54·4; H, 4·2; N, 9·0%), $\nu_{max.}$ (Nujol) 1650 cm^{-1} (C=O), τ ($CDCl_3$) 0·17 (1H, d, *J* 4 Hz, CHO), 2·43 (1H, d, *J* 9 Hz, 5-H), 2·81 (1H, d, *J* 2 Hz, 8-H), 3·00 (1H, dd, *J* 9 and 2 Hz, 6-H), 3·24 (1H, d, *J* 4 Hz, vinylic), and 6·28 (8H, s, morpholine), M^+ 308 (1 × Cl). The *semicarbazone* crystallised from benzene as yellow needles, m.p. 210° (decomp.) (Found: C, 49·6; H, 4·6; N, 19·2. $C_{15}H_{16}ClN_5O_2S$ requires C, 49·2; H, 4·4; N, 19·2%). The *oxime* crystallised from methanol as yellow needles, m.p. 188—189° (Found: C, 51·7; H, 4·4; N, 12·9. $C_{14}H_{14}ClN_3O_2S$ requires C, 52·0; H, 4·3; N, 13·0%). Similarly was obtained, from piperidine *7-chloro-4-formylmethylene-2-piperidino-4H-3,1-benzothiazine* as yellow needles, m.p. 127—128° [from light petroleum (b.p. 60—80°)] (Found: C, 58·4; H, 5·2; N, 9·4. $C_{15}H_{15}ClN_2OS$ requires C, 58·7; H, 4·9; N, 9·1%), $\nu_{max.}$ (Nujol) 1650 cm^{-1} (C=O), τ ($CDCl_3$) 0·10 (1H, d, *J* 4 Hz, CHO), 2·3—3·1 (3H, m, aromatic), 3·24 (1H, d, *J* 4 Hz, vinylic), and 6·2 and 8·3 (10H, 2 × s, br, piperidine).

7-Chloro-2-(γ-dimethylaminopropylamino)-4-formylmethylene-4H-3,1-benzothiazine (14).—3-Dimethylaminopropylamine (0·2 g) in ethyl acetate (5 ml) was added to a stirred solution of β,4-dichloro-2-isothiocyanatocinnamaldehyde (0·5 g) in ethyl acetate (10 ml). Next day the solution was evaporated and the residue basified with dilute aqueous sodium hydroxide. The mixture was extracted with ether and the extract was dried and concentrated. Crystallisation of the residue (0·5 g) from cyclohexane gave the *benzothiazine* as orange prismatic needles, m.p. 118—119° (Found: C, 56·1; H, 5·8; N, 12·5. $C_{15}H_{18}ClN_3OS$ requires C, 55·9; H, 5·6; N, 12·1%), $\nu_{max.}$ (Nujol) 1630 cm^{-1} (C=O), τ ($CDCl_3$) 0·20 (1H, d, *J* 4 Hz, CHO), 2·50 (1H, d, *J* 9 Hz, 5-H), 2·83 (1H, d, *J* 2 Hz, 8-H), 3·08 (1H, dd, *J* 9 and 2 Hz, 6-H), 3·30 (1H, d, *J* 4 Hz, vinylic), 6·47 (2H, t, *J* 7 Hz, CH_2), 7·61 (2H, t, *J* 7 Hz, CH_2), 7·79 (6H, s, Me_2N), and 8·30 (2H, m, CH_2), M^+ 323 (1 × Cl).

7-Chloro-4-formylmethylene-2-(o-methoxycarbonylanilino)-4H-3,1-benzothiazine (15).—β,4-Dichloro-2-isothiocyanatocinnamaldehyde (3·9 g), methyl anthranilate (2·2 g), and triethylamine (1·6 g) were stirred in methyl acetate (30 ml) overnight. The precipitate formed was filtered off, washed with water, dried, and crystallised from benzene to give the *benzothiazine* (1·5 g) as yellow needles, sintering at 224°, m.p. 230° (decomp.) (Found: C, 58·4; H, 3·6; N, 7·5. $C_{18}H_{13}ClN_2O_3S$ requires C, 58·0; H, 3·5; N, 7·5%), $\nu_{max.}$ (Nujol) 1680 (ester C=O) and 1650 cm^{-1} (αβ-unsat. CO), M^+ 372 (1 × Cl).

7-Chloro-2-(p-chloroanilino)-4-formylmethylene-4H-3,1-benzothiazine (16).—β,4-Dichloro-2-isothiocyanatocinnamaldehyde (5·2 g) in ethyl acetate (70 ml) was added with stirring to a solution of *p*-chloroaniline (2·55 g) and triethylamine (2·0 g) in ethyl acetate (30 ml). After 30 min the mixture was heated under reflux for 15 min and the *product* (2·4 g) was collected and washed with water. Crystallisation from ethanol gave the *benzothiazine* as yellow needles, m.p. 256° (decomp.) (Found: C, 55·3; H, 3·1; N, 7·7. $C_{16}H_{10}Cl_2N_2OS$ requires C, 55·0; H, 2·85; N, 8·05%).

7-Chloro-4-formylmethylene-2-(2-pyridylamino)-4H-3,1-benzothiazine (17).—2-Aminopyridine (0·4 g) was refluxed with β,4-dichloro-2-isothiocyanatocinnamaldehyde (0·5 g) in ethyl acetate (15 ml) for 2 h. The precipitate formed was filtered off and washed successively with water, 5N-acetic acid, and water, and dried. Crystallisation of the residue from toluene gave the *benzothiazine* as fine yellow needles, m.p. >300° (Found: C, 57·2; H, 3·3; N, 12·8. $C_{15}H_{10}ClN_3OS$ requires C, 57·1; H, 3·1; N, 13·3%), $\nu_{max.}$ (Nujol) 1650 cm^{-1} (C=O), M^+ 315 (1 × Cl). The ethyl acetate filtrate was evaporated and the residue was extracted with boiling light petroleum (b.p. 40—60°). The yellow needles deposited on cooling the extract were recrystallised from light petroleum to give 4,7-dichloroquinoline as needles, m.p. and mixed m.p. with an authentic sample 84—85° (lit.,[6] 86—87°), M^+ 197 (2 × Cl).

Reaction of β,4-Dichloro-2-isothiocyanatocinnamaldehyde with 2-Aminoethanol.—The aldehyde (2·5 g) in ethyl acetate (30 ml) was treated with 2-aminoethanol (1·4 g) in ethyl acetate (10 ml). After ½ h, water was added and the organic layer separated, dried, and evaporated to an orange solid. The solid was extracted with hot cyclohexane and the extract evaporated. The residue was crystallised from light petroleum (b.p. 40—60°) giving 4,7-dichloroquinoline (1·1 g) as white needles, m.p. 85—86° (lit.,[6] 86—87°), identical (mixed m.p., t.l.c., and i.r. spectrum) with an authentic sample.

7-Chloro-4-formylmethylene-2-methoxy-4H-3,1-benzothiazine (18).—Potassium hydroxide (2 g) in methanol (10 ml) was added to a stirred solution of β,4-dichloro-2-isothiocyanatocinnamaldehyde (2·0 g) in methanol (20 ml) at room temperature. After 15 min the orange solution was poured into water (50 ml) and extracted with ether. The aqueous phase was separated and acidified with 2N-hydrochloric acid. The precipitate formed was collected and crystallised from ethanol to give the *benzothiazine* (0·6 g, 30%) as a yellow powder, m.p. 140—142° (Found: C, 52·0; H, 3·1; N, 5·4%; M^+, 252·9949. $C_{11}H_8ClNO_2S$ requires C, 52·0; H, 3·2; N, 5·5%; *M*, 252·9964), $\nu_{max.}$ (Nujol) 1650 cm^{-1} (C=O), τ ($CDCl_3$) 0·14 (1H, d, *J* 3 Hz, CHO), 2·28 (1H, d, *J* 9 Hz, 5-H), 2·60 (1H, d, *J* 2 Hz, 8-H), 2·78 (1H, dd, *J* 9 and 2 Hz, 6-H), 3·11 (1H, d, *J* 3 Hz, vinylic), and 5·97 (3H, s, MeO).

7-Chloro-4-formylmethylene-2-phenoxy-4H-3,1-benzothiazine (19).—Powdered potassium hydroxide (1·0 g) in molten phenol (2·5 g) was added to a stirred solution of β,4-dichloro-2-isothiocyanatocinnamaldehyde (2·0 g) in molten phenol (2·5 g) at 90°. After a few minutes the mass solidified and was triturated with cold aqueous 2N-potassium hydroxide. The residual solid was collected, dried, and crystallised from ethanol–benzene (5 : 1) to give the *benzo-*

[6] N. L. Drake, H. J. Creech, D. Draper, J. A. Gorman, S. Haywood, R. M. Peck, E. Walton, and J. O'Neill van Hook, *J. Amer. Chem. Soc.*, 1946, **68**, 1214.

thiazine (2·0 g, 82%) as a yellow powder, m.p. 179—181° (Found: C, 60·9; H, 3·2; N, 4·4. $C_{16}H_{10}ClNO_2S$ requires C, 60·5; H, 3·1; N, 4·4%), $\nu_{max.}$ (Nujol) 1650 cm^{-1} (C=O), τ ($CDCl_3$) 0·09 (1H, d, *J* 3 Hz, CHO), 2·21 (1H, d, *J* 9 Hz, 5-H), 2·4—2·9 (7H, m, 6-H, 8-H, and PhO), and 2·99 (1H, d, *J* 3 Hz, vinylic).

2-Bis(ethoxycarbonyl)methylene-7-chloro-4-formylmethylene-1,2-dihydro-4H-3,1-benzothiazine (21).—β,4-Dichloro-2-isothiocyanatocinnamaldehyde (2·0 g) in dimethylformamide (10 ml) was added dropwise to a stirred solution of diethyl sodiomalonate [from sodium hydride (0·8 g; 50% dispersion) and diethyl malonate (2·6 ml)] in dimethylformamide (10 ml). After ½ h the deep red solution was diluted with water, acidified with acetic acid, and extracted with chloroform. The extract was washed with aqueous sodium carbonate, dried, and evaporated to a red oil. The oil was extracted with hot cyclohexane and the extract evaporated to yield a yellow solid which crystallised from ethanol to give the *benzothiazine* (0·6 g) as yellow needles, m.p. 139—140° (Found: C, 53·5; H, 4·5; N, 3·5. $C_{17}H_{16}ClNO_5S$ requires C, 53·5; H, 4·2; N, 3·7%), $\nu_{max.}$ (Nujol) 1650br cm^{-1} (C=O), τ ($CDCl_3$) −3·1 (1H, s, NH), −0·1 (1H, d, *J* 6 Hz, CHO), 2·56 (1H, d, *J* 9 Hz, 5-H), 2·93 (1H, d, *J* 2 Hz, 8-H), 3·06 (1H, dd, *J* 9 and 2 Hz, 6-H), 3·47 (1H, d, *J* 6 Hz, vinylic), 5·80 (4H, 2q, 2 × CH_2O), and 8·70 (6H, 2t, 2 × Me), M^+ 381 (1 × Cl).

1-Chloro-1-(4-chloro-2-isothiocyanatophenyl)-3,3-bis(ethoxycarbonylamino)prop-1-ene (26).—β,4-Dichloro-2-isothiocyanatocinnamaldehyde (10·4 g) and ethyl carbamate (7·2 g) were stirred in ethyl acetate (40 ml) with a trace of hydrogen chloride for 12 h. The mixture was diluted with light petroleum (b.p. 60—80°), the precipitate was collected and recrystallised from ethyl acetate to give the *bisurethane* (7·2 g) as white needles, m.p. 164—165° (Found: C, 45·8; H, 3·9; N, 10·0. $C_{16}H_{17}Cl_2N_3O_4S$ requires C, 45·8; H, 4·0; N, 10·0%), $\nu_{max.}$ (Nujol) 3300 (NH), 2100 (NCS), and 1705 cm^{-1} (urethane CO), τ ($CDCl_3$) 2·64 (3H, s, aromatic) 3·15br (2H, d, 2 × NH), 3·57 (1H, d, *J* 10 Hz, vinylic), 4·55 (1H, t, *J* 10 Hz, allylic), 5·90 (4H, q, 2 × $OCH_2{\cdot}CH_3$), and 8·80 (6H, t, 2 × CH_3CH_2O), *m/e* 417 (2 × Cl; M^+), 382 (1 × Cl; *M* − Cl), 344 (2 × Cl; *M* − CO_2Et), and 336 (1 × Cl; 382 − EtOH).

7-Chloro-4-(2-hydroxyethylidene)-2-morpholino-4H-3,1-benzothiazine (27).—Sodium borohydride (0·8 g) was added in portions to a stirred solution of 7-chloro-4-formylmethylene-2-morpholino-4*H*-3,1-benzothiazine (3·0 g) in warm ethanol (600 ml). After ½ h the solution was concentrated to small volume and poured into water. The precipitate formed was extracted into ether and the ether layer was separated, dried, and evaporated. The yellow residue was crystallised from cyclohexane to give the *αβ-unsaturated alcohol* (2·3 g, 76%) as prisms, m.p. 133—135° (Found: C, 54·2; H, 5·0; N, 9·3. $C_{14}H_{15}ClN_2O_2S$ requires C, 54·1; H, 4·8; N, 9·0%), $\nu_{max.}$ (Nujol) 3350 cm^{-1} (OH), τ ($CDCl_3$) 2·9—3·4 (3H, m, aromatic in 1,2,4-substituted benzene), 4·07 (1H, t, *J* 6 Hz, vinylic), 5·90 (2H, d, *J* 6 Hz, CH_2), and 6·55 (8H, s, morpholine).

7-Chloro-2-morpholino-3,1-benzothiazin-4-one (28).—Potassium permanganate (0·6 g) was added in portions to a stirred solution of 7-chloro-4-formylmethylene-2-morpholino-4*H*-3,1-benzothiazine (0·5 g) in acetone. After 12 h at room temperature the excess of oxidant was destroyed with sodium sulphite and acetic acid. The solution was diluted with water and the precipitate formed was collected, dried, and crystallised from cyclohexane, giving the *benzothiazinone* (0·3 g) as cream needles, m.p. 159—160° (Found: C, 51·5; H, 4·4; N, 10·1. $C_{12}H_{11}ClN_2O_2S$ requires C, 51·0; H, 3·9; N, 9·9%), $\nu_{max.}$ (Nujol) 1665 cm^{-1} (thiolactone CO), τ ($CDCl_3$) 2·08 (1H, d, *J* 9 Hz, 5-H), 2·65 (1H, d, *J* 2 Hz, 8-H), 2·90 (1H, dd, *J* 9 and 2 Hz, 6-H), and 6·28 (8H, s, morpholine).

7-Chloro-4-methoxycarbonylmethylene-2-morpholino-4H-3,1-benzothiazine (29).—7-Chloro-4-formylmethylene-2-morpholino-4*H*-3,1-benzothiazine (1·5 g) was suspended in methanol (250 ml) and stirred with sodium cyanide (0·8 g), active manganese dioxide (6·0 g), and acetic acid (0·3 ml) at room temperature for 48 h. The mixture was refluxed briefly and filtered hot. Methanol was evaporated from the filtrate and the residue was chromatographed on alumina. A yellow band running just ahead of the starting material was eluted with chloroform. Evaporation left a solid which was crystallised from cyclohexane to give the *ester* (100 mg) as pale yellow needles, m.p. 225—226° (Found: C, 53·5; H, 4·7; N, 8·1. $C_{15}H_{15}ClN_2O_3S$ requires C, 53·2; H, 4·4; N, 8·3%), $\nu_{max.}$ (Nujol) 1690 cm^{-1} (αβ-unsat. ester), *m/e* 338 (1 × Cl; M^+) and 253 (*M* − C_4H_7NO).

[4/1929 *Received*, 20*th September*, 1974]