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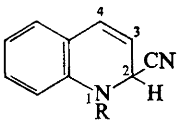
Reissert Compounds. The Reaction of Some Thiocarbonyl Chlorides with Quinoline, Isoquinoline, and Pyridine

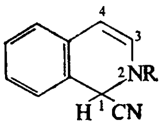
By **R. Hull**, Imperial Chemical Industries Limited, Pharmaceuticals Division, Alderley Park, Macclesfield, Cheshire

Certain alkyl- and aryl-oxythiocarbonyl chlorides with potassium cyanide and quinoline or isoquinoline yield Reissert compounds (1 and 2; R = CS·OEt and CS·OPh). The marked deshielding influence of the thiocarbonyl over the corresponding carbonyl derivatives is noted in the n.m.r. spectra. Attempts to extend the reaction with thiophosgene were unsuccessful. Instead, *o*-isothiocyanato-*trans*-cinnamaldehyde (5) and 3-oxoimidazo[1,5,-*a*]-quinoline (6) were obtained from quinoline, thiophosgene, and potassium cyanide. Higher yields of the aldehyde resulted on replacement of cyanide by hydroxide ion. The *cis*-isomer of *o*-isothiocyanatocinnamaldehyde (12) was obtained when barium carbonate was used as base. Similar isothiocyanato-formyl ring-fission products (13), (20), and (21) have been obtained from isoquinoline and pyridine. A di-isoquinolino-1,3,5-oxadiazine (16) was also obtained in the isoquinoline reaction.

Reissert compounds have been obtained from a wide variety of aliphatic and aromatic acid halides, anhydrides,[1] or sulphonyl chlorides[2] with quinolines, isoquinolines, and potassium cyanide.

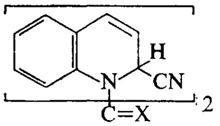
We have now observed that a similar reaction occurs with certain thiocarbonyl chlorides (*e.g.* ethoxythiocarbonyl[3] and phenoxythiocarbonyl[4] chlorides), quinoline or isoquinoline, and potassium cyanide in methylene dichloride–water,[5] to yield compounds of types (1 and 2; R = CS·OEt and CS·OPh) respectively.

(1)




(2)

N.m.r. spectra of the esters (1; R = CS·OEt) and (2; R = CS·OEt) showed the C-2 proton of (1; R = CS·OEt) and the C-1 proton of (2; R = CS·OEt) to be hidden under the aromatic region (τ 2·35—2·85 and 2·55—2·95 respectively). For comparison we prepared the corresponding ethoxycarbonyl derivatives (1; R = CO_2Et) and (2; R = CO_2Et) by reaction of ethyl chloroformate and potassium cyanide with quinoline and isoquinoline, respectively, by the usual procedure. The C-2 proton of (1; R = CO_2Et) was now observed as a doublet at τ 3·85 and the C-1 proton of (2; R = CO_2Et) as a broadened singlet at 3·65 (possible splitting into a doublet due to long range coupling with H-3 as reported by Chhabra, Kershaw, and Uff[6] in related Reissert compounds). The changes in deshielding influences brought about by substitution of thiocarbonyl for carbonyl groups were also observed on the C-3 proton of the dihydroisoquinolines (2; R = CS·OEt) and (2; R = CO_2Et) (see Experimental). Similar observations have been noted in other systems.[7]



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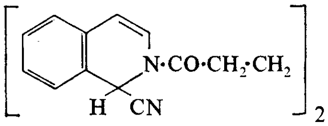

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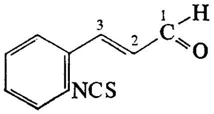
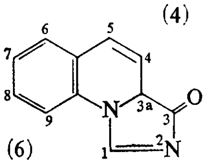


(5)



(6)

Attempts were then made to prepare the Reissert compound (3; X = S). Although 'bis-Reissert' compounds of type (4) have been described,[1] the simpler derivatives (3; X = O or S) appear to be novel. Reaction of quinoline with thiophosgene and potassium cyanide in methylene dichloride–water gave, however, mainly two products, (5) in 4% yield, and (6) in 22% yield, which were separated by preparative thin-layer chromatography. The evidence for the structures proposed is described below. Elemental analysis of

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[1] F. D. Popp and A. Soto, *J. Chem. Soc.*, 1963, 1760.

[2] J. M. Wefer, A. Catala, and F. D. Popp, *J. Org. Chem.*, 1965, **30**, 3075.

[3] M. Delepine, *Bull. Soc. chim. France*, 1911, (4), **9**, 901.

[4] H. Rivier, *Bull. Soc. chim. France*, 1906, (3), **35**, 837.

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

[6] S. R. Chhabra, J. R. Kershaw, and B. C. Uff, *Tetrahedron Letters*, 1967, 3199.

[7] P. L. Southwick, J. A. Fitzgerald, and G. E. Milliman, *Tetrahedron Letters*, 1965, 1247.

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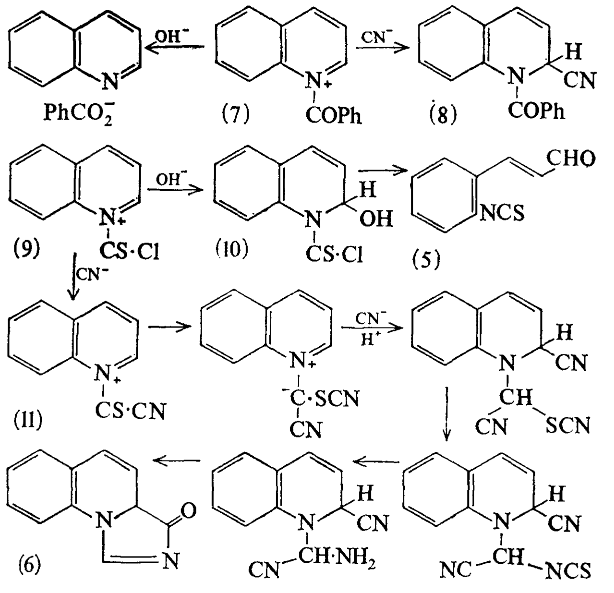
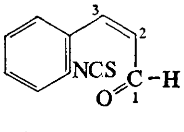
compound (5) established the formula $C_{10}H_7NOS$. The infrared spectrum shows a strong band at 1670 (conjugated CHO) and a broad strong band at 2075 (NCS) cm.$^{-1}$. Bands at 967 and 1000 cm.$^{-1}$ are attributed to the *trans* δ(CH) out-of-plane bending vibration and to the out-of-plane H deformation vibration of the *trans*-olefin respectively. The n.m.r. spectrum in deuteriochloroform shows the phenyl group as a multiplet centred at τ 2·6 (4H), H-1 as a doublet at 0·22 (J 7·5 c./sec.), H-2 as a quartet at 3·25 (J 16·0, 7·5 c./sec.), and H-3 as a doublet at 2·20 (J 16 c./sec.). The coupling constant agrees with the *trans*-isomer. Elemental analysis and mass spectrometry of compound (6) established the formula $C_{11}H_8N_2O$. The infrared spectrum shows a strong band at 1670 (CON$<$) cm.$^{-1}$. The mass-spectral data showed a parent ion *m/e* 184, fragment ions *m/e* 156 (M — CO)$^+$, 155 (M — CHO)$^+$, and a base peak 129 (156 — HCN)$^+$ or (155 — CN)$^+$. The n.m.r. spectrum of (6) in deuteriochloroform containing deuterium oxide shows the protons H-6—9 as a broad singlet at τ 2·71 (4H), H-1 as a singlet at 1·38, H-5 as a doublet at 3·22 (J_{45} 9·0 c./sec.), H-3a as a doublet at 3·78 (J_{3a4} ~7 c./sec.), and H-4 as a doublet of doublets at 4·05.

Some explanation of the above reactions has been put forward by Dr. P. N. Edwards of our department from the principle of hard and soft acids and bases.[8] In the normal Reissert quaternary intermediate (7), the soft base CN^- would attack the fairly hard C-2 centre because this is a softer centre than the benzoyl carbonyl group (only N^+ attached as against N^+ and O), and give the Reissert compound (8), whereas hard base OH^- attacks the carbonyl group to re-form quinoline and sodium benzoate. A different situation exists, however, in quaternary compound (9) obtained from quinoline and thiophosgene. Here we have a relatively soft centre at the thiocarbonyl group to that at C-2. Consequently, hard OH^- attack now takes place at C-2 giving rise to the dihydroquinoline (10) which after ring-fission and isomerisation yields the aldehyde (5). Soft CN^- attacks the thiocarbonyl centre, and the steps in the conversion of the thiocarbonyl cyanide (11) into 3-oxoimidazo[1,5-*a*]quinoline (6) can be visualised to take place as set out schematically.

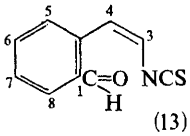


Increase in OH^- concentration should raise the yield of the aldehyde (5). This indeed was found to be so. Thus, reaction of quinoline with thiophosgene and dilute sodium hydroxide in methylene dichloride–water gave the *trans*-aldehyde (5) in 36% yield. Substitution of sodium hydroxide by barium carbonate gave the *cis*-isomer (12) as an oil. The n.m.r. spectrum of the *cis*-isomer (12) in carbon tetrachloride showed the phenyl group as singlet centred at τ 2·65 (4H), H-1 as a doublet at 0·13 (J_{12} 7·5 c./sec.), H-2 as four lines (J_{23} 12 c./sec.), and H-3 as two lines at 2·35. The coupling constant agrees with the *cis*-isomer. After standing overnight, 30% conversion had occurred into the *trans*-isomer. A later spectrum (3 days) showed complete isomerisation to the *trans*-isomer.

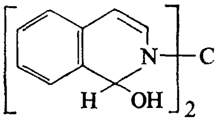


(12)

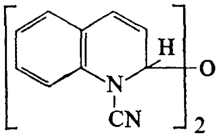
The action of thiophosgene on isoquinoline in the presence of dilute alkali was then investigated. Two products, (13) and (16), were obtained. The n.m.r. spectrum in deuteriochloroform of the isothiocyanate (13), an oil, shows the phenyl group as a multiplet centred at τ 2·0—2·7, H-3 as a doublet at 2·9 (J_4 8·5 c./sec.), H-4 as a doublet at 3·65 (J_3 8·5 c./sec.) (the coupling constant agrees with the *cis*-isomer), and H-1 as a singlet at —0·17. In contradistinction with the *trans*-aldehyde (5), no band in the 960 cm.$^{-1}$ region due to the CH out-of-plane deformation vibration of a *trans*-olefin was present in the infrared spectrum; it did, however, show a broad strong band at 2075 (NCS) and at 1695 (CHO) cm.$^{-1}$. The second compound, a pentacyclic derivative (16), was probably formed by dehydration of the dihydrothioamide (14). Shimidzu[9] obtained a similar type of 'ether' compound (15) from the reaction of cyanogen bromide on quinoline.



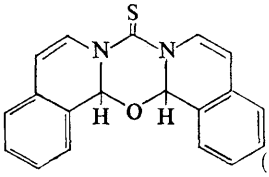
(13)



(14)



(15)



(16)

Finally we turned our attention to the reaction of thiophosgene and alkali upon the pyridine nucleus. Very

[8] R. G. Pearson, *Chem. in Britain*, 1967, **3**, 103.

[9] T. Shimidzu, *J. Pharm. Soc. Japan*, 1926, No. 529, 243.

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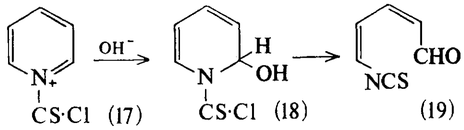
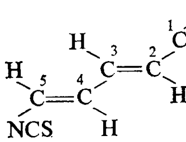
low yields (less than 5%) of a product C_6H_5NOS, crystallising as plates, m.p. 84·5—85·5°, identified possibly as the *trans,trans*-isomer of 1-formyl-4-isothiocyanatobuta-1,3-diene (20) were obtained with 2N-sodium hydroxide.

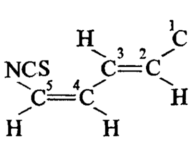


(17) (18) (19)



(20)

The yield was later raised to 18% by the use of barium carbonate. The reaction pathway requires addition of OH^- to (17) which can then undergo ring-scission to the diene (19) and isomerisation to the diene isomer (20). The i.r. spectrum showed $\nu_{max.}$ 2096s (NCS), 1667s (conj. polyene CHO), 980 (*trans*-HC⁚CH), 1610s, and 1580 cm.$^{-1}$ (C⁚C vibrations in a diene). The n.m.r. spectrum of the diene (20) showed the formyl proton of C-1 as a sharp doublet centred at τ 0·43 (1H) (*J* 7·5 c./sec.) due to coupling with H-2 which appeared as a 4-line pattern between 3·56 and 3·88 (1H) (*J* 15, 8 c./sec.); H-3 appeared as a multiplet centred approx. at 3·0, and H-4 and H-5 were centred at 3·41



(21)

In a repeat reaction of thiophosgene and barium carbonate upon pyridine and immediate work-up of the reaction mixture, an isomeric compound was obtained as needles, m.p. 55°, identified possibly as the *trans,cis*-isomer of 1-formyl-4-isothiocyanatobuta-1,3-diene (21). The i.r. spectrum showed $\nu_{max.}$ 2065br,s (NCS), 1665s (conj. polyene CHO), 980 (*trans*-CH⁚CH), 1608s, and 1565 cm.$^{-1}$ (C⁚C vibrations in a diene). The n.m.r. of this isomer (21) showed H-1 as a sharp doublet centred at τ 0·32 (1H) (*J* 8 c./sec.); H-3 appeared as a 4-line pattern centred at 2·58 (J_{34} 10·5, J_{32} 15·5 c./sec.) indicative of a *trans*-configuration, and H-2, -4, and -5 appeared as a multiplet at 3·6—4·0.

A closer examination of the synthesis, isomerisation, and properties of the diene will be reported later.

EXPERIMENTAL

Nuclear magnetic resonance spectra were obtained on a Varian A-60 spectrometer. Mass spectra were determined in an A.E.I. MS9 spectrometer.

2-*Cyano*-1-*ethoxythiocarbonyl*-1,2-*dihydroquinoline*.— Ethoxythiocarbonyl chloride (12·45 g.) [3] in methylene dichloride (40 ml.) was added dropwise during ½ hr. to a rapidly stirred mixture of quinoline (6·4 5 g.) in methylene dichloride (70 ml.) and potassium cyanide (9·75 g.) in water (70 ml.) at 0—5°. After a further 8 hr. the methylene dichloride layer was collected and washed with water, dilute hydrochloric acid, water, dilute sodium hydroxide, and water, then dried (Na_2SO_4) and concentrated, to yield an oil (11·2 g.) which solidified on standing. Crystallisation from cyclohexane gave the *dihydroquinoline* as prisms, m.p. 97—98° (Found: C, 63·9; H, 5·0; N, 11·3; S, 13·1. $C_{13}H_{12}N_2OS$ requires C, 63·9; H, 4·9; N, 11·5; S, 13·1%), τ ($CDCl_3$) 2·35—2·85 (4H multiplet, aromatic protons and proton at C-2), 3·3 (1H doublet, *J* 9 c./sec., proton at C-4), 3·95 (1H 4-line pattern, *J* 9 and 6 c./sec., proton at C-3), 5·4 (2H multiplet due to hindered rotation, CH_3-CH_2), 8·66 (3H triplet, *J* 7 c./sec., CH_3-CH_2).

2-*Cyano*-1-*phenoxythiocarbonyl*-1,2-*dihydroquinoline*.— Phenoxythiocarbonyl chloride [4] (8·8 g.) in methylene dichloride (40 ml.) was added dropwise during 15 min. to a rapidly stirred mixture of quinoline (12·9 g.) in methylene dichloride (70 ml.) and potassium cyanide (8·15 g.) in water (70 ml.) at 0—5°. After a further 8 hr., more methylene dichloride (100 ml.) was added to the mixture and the methylene dichloride layer was collected and washed with water, dilute hydrochloric acid, water, dilute sodium hydroxide, and water, then dried (Na_2SO_4) and concentrated, to yield the product (17·5 g.). Crystallisation from toluene (carbon) gave the *dihydroquinoline* as needles, m.p. 185—186° (Found: C, 69·85; H, 4·25; N, 9·5; S, 10·9. $C_{17}H_{12}N_2OS$ requires C, 69·8; H, 4·1; N, 9·6; S, 10·95%), τ ($CDCl_3$) 2·08—3·0 (10H multiplet, aromatic protons and proton at C-2), 3·15 (1H doublet, *J* 9 c./sec., proton at C-4), 3·85 (1H 4-line pattern, *J* 9 and 6 c./sec., proton at C-3).

1-*Cyano*-2-*ethoxythiocarbonyl*-1,2-*dihydroisoquinoline*.— Obtained as for the dihydroquinoline derivative by reaction for 17 hr. of a mixture of ethoxythiocarbonyl chloride (12·45 g.) in methylene dichloride (40 ml.), isoquinoline (6·45 g.) in methylene dichloride (70 ml.), and potassium cyanide (9·75 g.) in water (70 ml.). The resulting dark brown solid (11·3 g.) after two recrystallisations from ethanol gave the *product* (1 spot t.l.c.) as prisms, m.p. 109—110° (Found: C, 64·0; H, 5·0; N, 11·2; S, 13·0. $C_{13}H_{12}N_2OS$ requires C, 63·9; H, 4·9; N, 11·5; S, 13·1%), τ ($CDCl_3$) 2·55—2·95 (6H multiplet, aromatic protons and protons at C-1 and C-3), 3·9 (1H doublet, *J* 8 c./sec., proton at C-4), 5·35 (2H quartet, *J* 7 c./sec., CH_3-CH_2), 8·57 (3H triplet, *J* 7 c./sec., CH_3-CH_2).

1-*Cyano*-2-*phenoxythiocarbonyl*-1,2-*dihydroisoquinoline*.— Obtained as for the dihydroquinoline derivative by reaction for 10 hr. of a mixture of phenoxythiocarbonyl chloride (10·0 g.) in methylene dichloride (60 ml.), isoquinoline (15·0 g.) in methylene dichloride (80 ml.), and potassium cyanide (9·5 g.) in water (80 ml.). The resulting oil (22·8 g.) was triturated with benzene (30 ml.), and the product (6·9 g.), m.p. 150—152°, collected. Recrystallisation from benzene gave the *dihydroisoquinoline* (4·7 g.) as plates, m.p. 164° (Found: C, 69·8; H, 4·2; N, 9·6; S, 11·0. $C_{17}H_{12}N_2OS$ requires C, 69·8; H, 4·1; N, 9·6; S, 10·95%), τ ($CDCl_3$) 2·2—3·0 (11H multiplet, aromatic protons and protons at C-1 and C-3), 3·8 (1H doublet, *J* 8 c./sec., proton at C-4).

2-*Cyano*-1-*ethoxycarbonyl*-1,2-*dihydroquinoline*.—Prepared as described for the corresponding ethoxythiocarbonyl compound from ethyl chloroformate (10·85 g.) in methylene dichloride (40 ml.) quinoline (6·45 g.) in methylene dichloride (70 ml.), and potassium cyanide (9·45 g.) in water (70 ml.), this *compound* (8·2 g.) crystallised from light petroleum (b.p. 40—60°) as prisms, m.p. 64—66° (Found: C, 68·3; H, 5·4; N, 12·1. $C_{13}H_{12}N_2O_2$ requires C, 68·4; H, 5·25;

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N, 12·3%), τ ($CDCl_3$) 2·2—3·0 (4H multiplet, aromatic protons), 3·3 (1H doublet, J_{34} 9 c./sec., proton at C-4), 3·85 (1H doublet, J_{23} 6 c./sec., proton at C-2), 4·1 (1H 4-line pattern, proton at C-3), 5·7 (2H quartet, J 7 c./sec., CH_3–CH_2), 8·7 (3H triplet, J 7 c./sec., CH_3–CH_2).

1-*Cyano*-2-*ethoxycarbonyl*-1,2-*dihydroisoquinoline*.— Similarly, ethyl chloroformate (10·85 g.) in methylene dichloride (40 ml.), isoquinoline (6·45 g.) in methylene dichloride (70 ml.), and potassium cyanide (9·75 g.) in water (70 ml.) gave the *dihydroisoquinoline* (12·1 g.), which crystallised from cyclohexane as prisms, m.p. 84—85° (Found: C, 68·5; H, 5·3; N, 12·3. $C_{13}H_{12}N_2O_2$ requires C, 68·4; H, 5·25; N, 12·3%), τ ($CDCl_3$) 2·55—3·0 (4H multiplet, aromatic protons), 3·1 (1H doublet, J 8 c./sec., proton at C-3), 3·65 (1H singlet, proton at C-1), 4·0 (1H doublet, J 8 c./sec., proton at C-4), 5·78 (2H quartet, J 7 c./sec., CH_3–CH_2), 8·68 (3H triplet, J 7 c./sec., CH_3–CH_2).

Reaction of Quinoline with Thiophosgene and Potassium Cyanide.—Thiophosgene (2·3 ml.) in methylene dichloride (20 ml.) was added dropwise during 30 min. to a well agitated mixture of quinoline (7·74 g.) in methylene dichloride (60 ml.) and potassium cyanide (4·89 g.) in water (25 ml.) at 5—10°. The mixture was stirred for a further 8 hr. and allowed to stand for 2 days. Methylene dichloride (100 ml.) and water (50 ml.) were added to the reaction mixture, and the whole was filtered through a thin layer of Hyflo Supercel. The methylene dichloride layer was collected and washed with water, 2N-hydrochloric acid, water, 2N-sodium hydroxide, and water, then dried (Na_2SO_4) and concentrated, to yield a black gum (2·7 g.). Preparative thin-layer chromatography (0·2425 g.) on Kieselgel 254, using benzene–ethyl acetate (70 : 30) for development, gave one main and one subsidiary fluorescing bands, and at least five minor coloured bands which were not further investigated. The faster-running band gave o-*isothiocyanato*-trans-*cinnamaldehyde* (0·0222 g., 4·3% yield on thiophosgene) as pale yellow needles, m.p. 78·5° (from cyclohexane) (Found: C, 63·3; H, 3·8; N, 7·0; S, 16·9. $C_{10}H_7NOS$ requires C, 63·5; H, 3·7; N, 7·4; S, 16·9%). The 2,4-*dinitrophenylhydrazone* crystallised from dimethylformamide as maroon needles, m.p. 270° (decomp.) (Found: C, 52·1; H, 3·4; N, 18·8. $C_{16}H_{11}N_5O_4S$ requires C, 52·05; H, 3·0; N, 18·95%). The slower-running band gave 3-*oxoimidazo*[1,5-a]*quinoline* (0·1087 g., 22% yield on thiophosgene) as needles, m.p. 143—144° (from propan-2-ol) (Found: C, 71·3; H, 4·4; N, 15·7. $C_{11}H_8N_2O$ requires C, 71·75; H, 4·35; N, 15·2%).

o-*Isothiocyanato*-trans-*cinnamaldehyde*.— Thiophosgene (31 ml.) in methylene dichloride (100 ml.) was added dropwise and simultaneously with 2N-sodium hydroxide (200 ml.) during 30 min. to a well agitated mixture of quinoline (52 g.) in methylene dichloride (200 ml.) and 2N-sodium hydroxide (200 ml.) below 10°. After agitation for a further 1 hr. the mixture was filtered through a pad of Hyflo Supercel and washed with methylene dichloride (100 ml.) and water (100 ml.). The combined filtrates were collected, and the organic phase was separated and washed with water, 2N-hydrochloric acid, and water, then dried (Na_2SO_4–Hydrite) and the methylene dichloride removed. The residue (43·4 g.) was extracted with hot ether (6 × 150 ml.) and the extract evaporated to about 250 ml. The aldehyde (24·1 g.), m.p. 77—78°, which separated crystallised from cyclohexane as needles, m.p. 78°. A further amount (3·3 g.) was obtained from the ether mother-liquors. It was identical (infrared) with the aldehyde obtained above.

o-*Isothiocyanate*-cis-*cinnamaldehyde*.—Thiophosgene (7·5 ml.) in methylene dichloride (30 ml.) was added dropwise during 5 min. to a rapidly stirred suspension of barium carbonate (20 g.) in water (120 ml.) and quinoline (12·9 g.) in methylene dichloride (80 ml.) at 0°. After 1 hr. the mixture was filtered and worked up in the usual way, to yield the *cis*-isomer as an oil (14·9 g.). On standing overnight the compound isomerised to a solid identical with the *trans*-aldehyde described above.

Reaction of Isoquinoline with Thiophosgene and Sodium Hydroxide.—Thiophosgene (1·55 ml.) in methylene dichloride (5 ml.) and 2N-sodium hydroxide (10 ml.) were added dropwise and simultaneously during 15 min. to a well agitated mixture of isoquinoline (2·6 g.) in methylene dichloride (10 ml.) and 2N-sodium hydroxide (10 ml.) at 5—10°. The mixture was agitated for a further 90 min. The methylene dichloride phase was collected and washed with water, 2N-hydrochloric acid, and water, then dried and concentrated, to yield an oil (3 g.) which set to a semi-solid on standing. The reaction mixture was slurried with light petroleum (b.p. 60—80°) and the solid (1·25 g.) collected, m.p. 119—120°. Recrystallisation from benzene–cyclohexane gave 15b,16a-*dihydro*-8H-*di-isoquinolino*[1,2-b : 2′,1′-e]-[1,3,5]*oxadiazine*-8-*thione* as needles, m.p. 129° (Found: C, 72·0; H, 4·2; N, 8·1; S, 9·9. $C_{19}H_{14}N_2OS$ requires C, 71·75; H, 4·4; N, 8·8; S, 10·05%). Evaporation of the light petroleum filtrates (above) gave an oil (1·6 g.). The oil was dissolved in dry ether and filtered from a little insoluble material. Excess of reagent was removed under diminished pressure to yield cis-o-*isothiocyanatovinylbenzaldehyde* as a pale yellow oil (Found: C, 63·7; H, 4·1; N, 7·2. $C_{10}H_7NOS$ requires C, 63·5; H, 3·7; N, 7·4%), $\nu_{max.}$ (film) 2070s,br (NCS), 1695 (α,β-unsat. CO), and 716 cm.$^{-1}$ (*cis* CH out-of-plane deformation).

Reaction of Pyridine with Thiophosgene and Barium Carbonate.—(*a*) Thiophosgene (15·3 ml.) in methylene dichloride (60 ml.) was added dropwise during 10 min. to a vigorously stirred suspension of barium carbonate (40 g.) in water (200 ml.) and pyridine (15·8 ml.) in methylene dichloride (140 ml.) at 0°. The mixture was stirred for a further 15 min. and the whole was filtered through a thin layer of Hyflo Supercel and washed with methylene dichloride (300 ml.) and water (500 ml.). The methylene dichloride layer was washed with water, 2N-hydrochloric acid, and water (with sufficient sodium hydrogen carbonate to remove excess acidity), then dried (Na_2SO_4) overnight at 5° and concentrated (during 1½ hr. from a bath at 20°), to yield a brown crude product (2·4 g.), m.p. 71—73°. Recrystallisation from cyclohexane gave 1-*formyl*-4-*isothiocyanato*-*buta*-1,3-*diene*, possibly as the *trans,trans*-isomer, as plates, m.p. 84·5—85·5° (Found: C, 51·75; H, 3·75; N, 9·8. C_6H_5NOS requires C, 51·8; H, 3·6; N, 10·05%).

(*b*) In a repeat experiment using the same quantities, immediate work-up of the methylene dichloride extract gave a crude product (2·07 g.). Repeated extraction with light petroleum (b.p. 40—60°), evaporation, and recrystallisation of the residue (1·23 g.) from cyclohexane gave 1-formyl-4-isothiocyanatobuta-1,3-diene, possibly as the *trans,cis*-isomer, as needles, m.p. 52—55° (Found: C, 51·8; H, 3·5; N, 10·0%).

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