1072. *Thiocyanogen, Thiocyanates, and Isothiocyanates. Part II.*[1] *Reactions of Cyanogen Bromide with Arylalkyl Sulphides and with Triphenylmethyl Esters of Thiolcarboxylic Acids.*

By R. G. R. Bacon and J. Köchling.

In a cyanogen bromide melt, the reaction $R_2S + BrCN \rightarrow RSCN + RBr$ was succeeded by slight isomerisation, $R{\cdot}SCN \rightarrow R{\cdot}NCS$, when R was benzyl, and by complete isomerisation when R was diphenylmethyl or triphenylmethyl. The cyanide R•CN was also a major product from bistriphenylmethyl sulphide, mainly owing to a secondary reaction between triphenylmethyl bromide and cyanogen bromide. The corresponding product from bisdiphenylmethyl sulphide was mainly the isonitrile, R•NC, isolated as *N*-diphenylmethylformamide. Preparation of the requisite arylalkyl sulphides from the halides and various metal sulphides was investigated. Similar treatment of the esters $Ph_3C{\cdot}S{\cdot}COPh$ and $Ph_3C{\cdot}S{\cdot}COMe$ with cyanogen bromide resulted in an equal amount of fission on each side of the sulphur atom, giving triphenylmethyl isothiocyanate, the aryl isothiocyanate, and other products.

von Braun and his co-workers[2] prepared thiocyanates by the fission of sulphides with cyanogen bromide, $RSR' + BrCN \rightarrow R{\cdot}SCN + R'Br$ (R,R′ = alkyl or arylalkyl); they were particularly concerned with the relative ease of displacement of the groups R and R′. This

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[1] Part I, R. G. R. Bacon and R. S. Irwin, *J.*, 1961, 2447.

[2] J. von Braun and P. Engelbertz, *Ber.*, 1923, **56**, 1573; J. von Braun, 1926, **59**, 1202; J. von Braun, *Annalen*, 1931, **490**, 189.

reaction is now classified as a nucleophilic substitution[3] involving an intermediate sulphonium ion. Within the general case,

$$\mathrm{RSR'+X{\cdot}Hal \longrightarrow RR'\overset{+}{S}X+Hal^- \longrightarrow RSX+R'Hal,}$$

there are examples in which X may be not only CN, but also an alkyl[4] or acyl group,[5] or another halogen atom.[6] We applied the reaction to three symmetrical sulphides, R_2S, in which R was $PhCH_2$, Ph_2CH, and Ph_3C, *i.e.*, a primary, secondary, or tertiary arylalkyl group, respectively. We have also extended the reaction to triphenylmethyl esters of thiolcarboxylic acids, $R{\cdot}CO{\cdot}S{\cdot}CPh_3$, but we have not ascertained whether it has general applicability to thiolcarboxylates.

When the preparation of a secondary or tertiary arylalkyl thiocyanate is attempted by reactions involving thiocyanate ions or radicals, the resulting product may be partly or exclusively the corresponding isothiocyanate,[1,7] a result which may or may not be due to subsequent isomerisation of an initially formed thiocyanate. The production of an isothiocyanate from reaction of a sulphide with cyanogen bromide would necessarily require the secondary isomerisation step.

We looked for improved methods in preparing the requisite bisarylalkyl sulphides. The conventional process, treatment of halides with an alcoholic solution of hydrated sodium sulphide, gives very poor yields in the diaryl- or triaryl-methyl series, owing to the strong competition of solvolysis. As an alternative, solutions of diphenylmethyl bromide, usually in boiling carbon tetrachloride, were tested against suspensions of metal sulphides other than those of the alkali elements. Bisdiphenylmethyl sulphide was thus obtained in 80—90% yield with mercuric or silver sulphide, but was not produced by other sulphides examined:

$$\mathrm{Ph_2CHBr+HgS \longrightarrow Ph_2CH{\cdot}S^-+HgBr^+}$$

$$\mathrm{Ph_2CH{\cdot}S^-+Ph_2CHBr \longrightarrow (Ph_2CH)_2S+Br^-}$$

This method gave a poor yield of sulphide with benzyl bromide and none with triphenylmethyl bromide; various fractions which resulted were not further examined.

Diphenylmethyl bromide and copper(I) sulphide gave tetraphenylethane (20—30%), whilst copper(II) sulphide gave a similar yield of bisdiphenylmethyl disulphide. The former reaction is a reductive coupling by Cu^+, a result which is better known for interaction of diarylmethyl halides and metals; it may be formulated:

$$\mathrm{Ph_2CHBr+Cu^+ \longrightarrow Ph_2CH{\cdot}+Cu^{2+}+Br^-}$$

$$\mathrm{2Ph_2CH{\cdot} \longrightarrow Ph_2CH{\cdot}CHPh_2}$$

or,

$$\mathrm{Ph_2CH{\cdot}+Cu^+ \longrightarrow Ph_2CH^-+Cu^{2+}}$$

$$\mathrm{Ph_2CH^-+Ph_2CHBr \longrightarrow Ph_2CH{\cdot}CHPh_2+Br^-}$$

The reaction leading to the disulphide may be regarded as an oxidation by Cu^{2+} of an intermediate thiol anion:

$$\mathrm{Ph_2CHBr+Cu^{2+}+S^{2-} \longrightarrow Ph_2CH{\cdot}S^-+Cu^{2+}+Br^- \longrightarrow Ph_2CH{\cdot}S{\cdot}+Cu^++Br^-}$$

$$\mathrm{2Ph_2CH{\cdot}S{\cdot} \longrightarrow (Ph_2CH{\cdot}S)_2}$$

Thiols are known[8] to be readily oxidised to disulphides by copper(II) sulphide at ordinary temperatures. In some cases, treatment of diphenylmethyl bromide with suspensions of

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[3] D. S. Tarbell and D. P. Harnish, *Chem. Rev.*, 1951, **49**, 1; cf. J. L. Gleave, E. D. Hughes, and C. K. Ingold, *J.*, 1935, 236, 240.

[4] P. G. Stevens, *J. Amer. Chem. Soc.*, 1945, **67**, 407.

[5] E. L. Gustus and P. G. Stevens, *J. Amer. Chem. Soc.*, 1933, **55**, 378.

[6] S. W. Lee and G. Dougherty, *J. Org. Chem.*, 1940, **5**, 81; R. H. Baker, R. M. Dodson, and B. Riegel, *J. Amer. Chem. Soc.*, 1946, **68**, 2636.

[7] (*a*) A. Iliceto, A. Fava, and U. Mazzucato, *Tetrahedron Letters*, 1960, No. 11, 27; (*b*) A. Iliceto, A. Fava, U. Mazzucato, and P. Radici, *Gazzetta*, 1960, **90**, 919; (*c*) A. Iliceto, A. Fava, U. Mazzucato, and D. Rossetto, *J. Amer. Chem. Soc.*, 1961, **83**, 2729.

[8] K. H. Slagle and E. E. Reid, *Ind. Eng. Chem.*, 1932, **24**, 448.

metal sulphides caused partial conversion into diphenylmethyl ether, presumably owing to the adventitious presence of water or metal oxides.

The fission of dibenzyl sulphide by cyanogen bromide was effected in boiling methyl cyanide solution, or more rapidly in the absence of solvent by using a refluxing melt of an excess of cyanogen bromide; benzyl thiocyanate and benzyl bromide were thus obtained in yields of 70—90%. Benzyl isothiocyanate was also isolated, to the extent of ~ 15% from reaction in molten cyanogen bromide, and in much smaller yield from reaction in methyl cyanide. This result was unexpected, since reported data do not suggest that benzyl thiocyanate should isomerise at moderate temperatures. Dibenzyl disulphide, also isolated from some experiments, proved to be a secondary product, produced by fission of the thiocyanate on extended contact with chromatographic alumina.

Bisdiphenylmethyl sulphide readily underwent fission in a refluxing melt of cyanogen bromide but not with the reagent in methyl cyanide solution. The isolated sulphur-containing moiety was exclusively the isothiocyanate (80%). Cyanogen bromide was thus a favourable medium for the isomerisation, $Ph_2CH{\cdot}SCN \rightarrow Ph_2CH{\cdot}NCS$, which Fava and his co-workers[7] found to occur readily in methyl cyanide and other polar solvents. Less than half of the diphenylmethyl bromide expected from the reaction could be accounted for as the alcohol and ether, into which the bromide is converted on silica in a chromatographic column. A further 25% was accounted for by the cyanide-exchange reaction, which is discussed below, and which produced diphenylmethyl isocyanide and cyanide in an approximately 3:1 ratio:

$$Ph_2CHBr + CNBr \longrightarrow Ph_2CH{\cdot}NC(\text{or } Ph_2CH{\cdot}CN) + Br_2$$

The isocyanide was not isolated, but was detected as its hydrolysis product, *N*-diphenylmethylformamide, presumably formed on the chromatographic column.

Fission of bistriphenylmethyl sulphide by a refluxing melt of cyanogen bromide afforded triphenylmethyl isothiocyanate, typically in about 80% yield, accompanied by triphenylmethyl cyanide in almost 100% yield. Correspondingly, there was only about 8% of the expected triphenylmethyl bromide, which was isolated as the alcohol, into which it is quantitatively converted on chromatographic columns of alumina or silica. Triphenylmethyl thiocyanate is unknown, and it was recently shown[1,9] that the compound thus named in the older literature is the isothiocyanate. Its production from cyanogen bromide is clearly due to isomerisation of initially formed thiocyanate.

The appearance of triphenylmethyl cyanide proved to be mainly due to a reaction between the bromide and cyanogen bromide, $Ph_3CBr + BrCN \rightarrow Ph_3C{\cdot}CN + Br_2$, and to a minor extent to a similar, but slower, decomposition of the isothiocyanate, $Ph_3C{\cdot}NCS + BrCN \rightarrow Ph_3C{\cdot}CN + BrSCN$. The bromine which should result from the first reaction was detected. The thiocyanogen bromide postulated as a product of the second reaction would have instantly decomposed to bromine and polythiocyanogen.[10] In the case of diphenylmethyl bromide, fusion with cyanogen bromide yielded exclusively the isocyanide, again detected as the derived formamide. The exchange of bromine for cyanide on these arylalkyl groups may well be accompanied by bromine–bromine exchange, $RBr + Br^*CN \rightarrow RBr^* + BrCN$, which would require isotopic labelling for detection. There is evidence that cyanogen bromide undergoes heterolysis both as Br^+CN^- and as Br^-CN^+; *e.g.*, it usually donates electropositive bromine to a carbanion in a Grignard reagent,[11] but donates electropositive cyanide to an aromatic nucleus in substitutions under Friedel–Crafts conditions.[12] A further problem arising from our observations concerns what factors determine donation of the CN group in the cyano- or isocyano-form; this we intend to study.

Fission of the triphenylmethyl esters of thiolcarboxylic acids, $Ph_3C{\cdot}S{\cdot}COPh$ and

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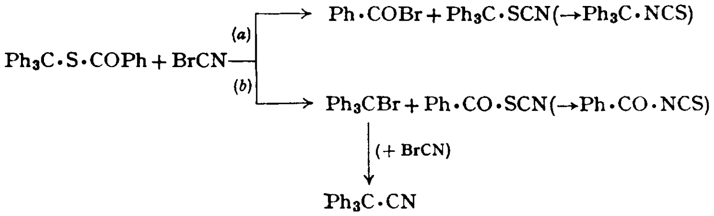
[9] A. Iliceto, A. Fava, and U. Mazzucato, *J. Org. Chem.*, 1960, **25**, 1445.
[10] F. Seel and E. Müller, *Chem. Ber.*, 1955, **88**, 1747.
[11] M. S. Kharasch and O. Reinmuth, "Grignard Reactions of Nonmetallic Substances," Prentice-Hall, Inc., New York, 1954, pp. 787—788.
[12] P. Karrer and E. Zeller, *Helv. Chim. Acta*, 1919, **2**, 482; 1920, **3**, 261.

$Ph_3C{\cdot}S{\cdot}COMe$, also occurred readily in a melt of cyanogen bromide. This type of reaction appears not to have been previously reported. The products, separable by chromatography on silica, were due to fission on either side of the sulphur atom, as postulated in the following reaction scheme for the thiolbenzoate:



The isolated triphenylmethyl isothiocyanate (0·50 mol.) was clearly the result of isomerisation of the thiocyanate initially formed by process (*a*). The isolated benzoyl isothiocyanate[13] was likewise the result of isomerisation of benzoyl thiocyanate, initially formed by process (*b*); the acyl derivatives are known only in the isothiocyanato-form. The triphenylmethyl compounds produced by process (*b*) consisted partly of the bromide (0·14 mol.), but mainly of the cyanide (0·33 mol.) resulting from the secondary reaction. The triphenylmethyl bromide and benzoyl bromide were quantitatively hydrolysed to the corresponding alcohol and acid on silica columns during isolation, and some of the benzoyl isothiocyanate was similarly converted into benzamide. The relative amounts of the products showed that fission had occurred to an approximately equal extent at the S–COPh and $S–CPh_3$ bonds.

The fission of triphenylmethyl thiolacetate occurred similarly to that of the thiolbenzoate, the isolated triphenylmethyl derivatives being by route (*a*) the isothiocyanate (0·48 mol.), and by route (*b*) the cyanide (0·46 mol.) or the alcohol (0·08 mol.) which is derived from the bromide. These proportions again indicate approximately equal ease of fission on either side of the sulphur atom. The production of acetyl isothiocyanate and acetic acid was indicated by the spectral characteristics of chromatographic fractions.

EXPERIMENTAL

Melting points were determined on a Kofler hot-stage apparatus. Solvents were purified by standard procedures. Chromatographic silica gel was always dehydrated for 12 hr. at 150° under water-pump vacuum, and stored in a desiccator over phosphorus pentoxide. Chromatographic alumina (Peter Spence, Type H) was normally shaken with 5% of 10% aqueous acetic acid before use. The identity of all chromatographic fractions was checked by infrared spectroscopy. Silver sulphide was prepared[14] by precipitation; other metal sulphides were laboratory-grade reagents. Light petroleum had b. p. 40—60°.

Reaction of Arylalkyl Halides with Metal Sulphides.—(a) *Benzyl halides*. Benzyl chloride with a refluxing aqueous ethanolic solution of sodium sulphide nonahydrate[15] (15 hr.) yielded dibenzyl sulphide (78%), m. p. 49°. A suspension of red mercuric sulphide (0·02 mole) was vigorously stirred (12 hr.) in a refluxing solution of benzyl bromide (0·02 mole) in carbon tetrachloride (50 ml.). Filtration and fractional distillation of the filtrate yielded unchanged benzyl bromide (40%); recrystallisation of the residue from aqueous ethanol afforded dibenzyl sulphide (18%), m. p. and mixed m. p. 47—50°. Colourless crystals (1·5 g.) of a substance, m. p. 133—136°, were extracted with hot acetone from the mercury salts. A similar preparation with silver sulphide yielded dibenzyl sulphide (17%) and a small crystalline fraction, m. p. 115—116°.

(b) *Diphenylmethyl bromide*. The bromide[16] (0·2 mole) was preferably prepared by the method of Iliceto *et al.*,[7b] and treated with sodium sulphide nonahydrate (0·15 mole) in refluxing

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[13] A. E. Dixon and J. Taylor, *J.*, 1908, **93**, 684.

[14] G. Brauer, "Handbuch der Präparativen Anorganischen Chemie," Enke Verlag, Stuttgart, 1954, p. 773.

[15] R. L. Shriner, H. C. Struck, and W. J. Jorison, *J. Amer. Chem. Soc.*, 1930, **52**, 2060.

[16] Cf. J. F. Norris, R. Thomas, and B. M. Brown, *Ber.*, 1910, **43**, 2940; N. P. Buu-Hoï, *Annalen*, 1944, **556**, 1.

aqueous ethanol (50 ml.) for 3 hr. Distillation of the product removed diphenylmethyl ethyl ether (67%), and left some bisdiphenylmethyl sulphide mixed with benzhydrol. A similar reaction in acetone, and recrystallisation of the product from light petroleum, successively yielded benzhydrol (50%) and bisdiphenylmethyl sulphide (22%), m. p. and mixed m. p. 64—67°. A solution of the bromide (0·005—0·025 mole) in carbon tetrachloride (50—250 ml.), containing a suspension of an equimolar quantity of red mercuric sulphide, was stirred at reflux temperature for 12 hr., filtered, and evaporated, and the residue chromatographed with light petroleum on a column of alumina (70 g. per g.). This yielded pure bisdiphenylmethyl sulphide (88—98%), m. p. 66—67° (lit.,[17] 66—67°), identical with the product obtained (28% overall yield) in four stages from benzophenone[18] (Found: C, 85·0; H, 6·0; S, 8·5. Calc. for $C_{26}H_{22}S$: C, 85·2; H, 6·0; S, 8·7%). Alternatively, the preparation was carried out with mercuric sulphide in refluxing benzene or acetone, or with silver sulphide (80% yield) in carbon tetrachloride.

In carbon tetrachloride under similar conditions, none of the desired sulphide was obtained with calcium, zinc, cadmium, or lead sulphides; unchanged bromide was converted, on columns of alumina neutralised as described above, into benzhydrol (78—83%), m. p. 68—69°, eluted by benzene, which was preceded, in the case of the product from lead sulphide, by bisdiphenylmethyl ether (22%), m. p. 110—112°, eluted by light petroleum. The product from a similar reaction with copper(I) sulphide gave the alcohol (52%), the ether (21%), and also 1,1,2,2-tetraphenylethane (28%), m. p. 213°. With copper(II) sulphide as reagent, the product furnished the alcohol (73%) and bisdiphenylmethyl disulphide (21%), m. p. 150—153°, eluted by light petroleum (Found: C, 78·1; H, 5·3; S, 16·2. Calc. for $C_{26}H_{22}S_2$: C, 78·4; H, 5·5; S, 16·1%).

(c) *Triphenylmethyl halides.* Triphenylmethyl chloride and sodium sulphide nonahydrate in ethanol[19] furnished the sulphide in yields of only 8—12%. By using t-butyl alcohol as solvent and subjecting the sodium sulphide (5 mol.) to preliminary dehydration over phosphorus pentoxide, the yield was raised to 32—40%; the product melted with decomposition[19] at 170—180° (Found: C, 87·3; H, 6·0; S, 6·0. Calc. for $C_{38}H_{30}S$: C, 88·0; H, 5·8; S, 6·2%). A suspension of red mercuric sulphide (9 mmoles) in a refluxing solution of triphenylmethyl bromide (3 mmoles) in carbon tetrachloride (50 ml.) was stirred for 12 hr., filtered, and evaporated. Chromatography of the residual oil on silica afforded bistriphenylmethyl peroxide ($\sim$30%), eluted by 3:7 benzene–light petroleum, and triphenylmethanol (58%), eluted by benzene. A similar preparation under nitrogen afforded triphenylmethanol and several unidentified oily fractions.

Fission Reactions with Cyanogen Bromide.—The cyanogen bromide,[20] m. p. $\sim$50°, b. p. 60—62°, was stored in a refrigerator. Except for some preparations carried out in solvent, the procedure for the fission reaction was to mix the sulphide with a large excess (10—20 mol.) of cyanogen bromide and to maintain the mixture for 1 hr. as a briskly refluxing melt, which was stirred in an oil-bath kept at 85—90°. Cyanogen bromide which solidified in the condenser was periodically returned to the flask. After cooling, the product was extracted with ether, which sometimes left a small amount of cyanuric bromide. Solvent and excess of cyanogen bromide were removed under reduced pressure and the residue chromatographed on silica gel or alumina (50 g. per g.).

(a) *Dibenzyl sulphide.* Treatment of the sulphide (4·6 mmoles) with molten cyanogen bromide (10 mol.), followed by chromatography on silica gel, yielded benzyl bromide (73%), and benzyl isothiocyanate (15 %), eluted by 1:9 benzene–light petroleum, and benzyl thiocyanate (82%), m. p. 41—42° (from light petroleum). Similar treatment of the sulphide (0·12 mole) with an equimolar amount of cyanogen bromide yielded benzyl bromide, separated by distillation, and benzyl thiocyanate (85% on recrystallisation). Cyanogen bromide (5 mol.) was added to a 0·2M-solution of the sulphide in methyl cyanide and the mixture refluxed for 1—3 hr. Chromatography furnished benzyl thiocyanate in yields of up to 80%, together with small amounts (<4%) of the isothiocyanate. If chromatography was carried out on alumina (neutralised as described above), some thiocyanate was converted into dibenzyl disulphide, the extent of conversion varying with the time of contact. Treatment of the sulphide with cyanogen bromide in refluxing ether or carbon tetrachloride, or in methyl cyanide at 20°, did not cause reaction.

(b) *Bisdiphenylmethyl sulphide.* Treatment of the sulphide (3 mmoles) with molten cyanogen bromide (15 mol.) yielded a viscous oil, which, when chromatographed on silica gel, afforded

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[17] H. Dannenberg and Aziz-ur Rahman, *Chem. Ber.*, 1956, **89**, 1625.

[18] *Org. Synth.*, Coll. Vol. III, 351; H. Staudinger and J. Siegwart, *Ber.*, 1916, **49**, 1918; A. Schönberg, O. Schütz, and S. Nickel, *Ber.*, 1928, **61**, 2175.

[19] D. Vorländer and E. Mittag, *Ber*, 1919, **52**, 413.

[20] *Org. Synth.*, Coll. Vol. II, 150.

diphenylmethyl isothiocyanate (80%), m. p. 56—58°, eluted by 1:4 benzene–light petroleum. Increase in the polarity of the eluant, and recrystallisation of fractions, successively afforded: diphenylmethyl ether (19%), m. p. 111°; diphenylmethyl cyanide (6%), m. p. and mixed m. p. 73—74°; benzhydrol (14%), m. p. 67—68°; a substance (~3%), m. p. 278—280°, containing N, O, and probably two $CHPh_2$ groups; and *N*-diphenylmethylformamide (16%), eluted by 1:1 benzene–ether, m. p. and mixed m. p. 135° (from ether) (lit.,[21] 132—134°) (Found: C, 79·6; H, 6·35; N, 6·8. Calc. for $C_{14}H_{13}NO$: C, 79·6; H, 6·2; N, 6·6%). The amide was identical in its infrared spectrum with an authentic sample, which was prepared (70%), m. p. 135° (from ether), by adding diphenylmethylamine to excess of 90% formic acid, evaporating, and heating the resulting salt for 1 hr. at 200—220°. For comparison, diphenylmethyl bromide was converted into diphenylmethyl thiocyanate,[7b] m. p. 35—36°, which was isomerised to the isothiocyanate during 2 hr. in refluxing methyl cyanide solution.[7] Treatment of diphenylmethyl bromide (0·01 mole) with a suspension of silver thiocyanate (0·01 mole) in dry acetone (50 ml.) afforded a product which contained some thiocyanate, but which yielded diphenylmethyl isothiocyanate (80%) by chromatography on silica gel. The isothiocyanate, m. p. 58—60° (from light petroleum) (lit.,[17] 59—60°), showed a strong and broad infrared absorption band with peaks at 2080 and 2160 cm.$^{-1}$, whilst the thiocyanate showed a strong and sharp single peak at 2150 cm.$^{-1}$. No reaction was observed between bisdiphenylmethyl sulphide (3 mmoles) and cyanogen bromide (15 mmoles) during 3 hr. in refluxing methyl cyanide.

(c) *Bistriphenylmethyl sulphide.* Treatment of the sulphide (2 mmoles) with molten cyanogen bromide (24 mol.), followed by chromatography on silica gel, successively yielded triphenylmethyl isothiocyanate (65—80%), m. p. and mixed m. p. 135—138°, eluted by 3:7 benzene–light petroleum, triphenylmethyl cyanide (97%), m. p. and mixed m. p. 126—128°, eluted by 2:3 benzene–light petroleum, and an oil, eluted by 1:1 benzene–ether, from which triphenylmethanol (3—15%), m. p. 158—163°, was extracted by light petroleum. The isothiocyanate was identical in its infrared spectrum with samples prepared in other ways,[1, 9] and the cyanide was identical with an authentic sample.[22]

(d) *Diphenylmethyl bromide.* Treatment of the bromide (4 mmoles) with molten cyanogen bromide (12 mol.), followed by chromatography on silica gel, successively afforded diphenylmethyl ether (39%), benzhydrol (22%), and *N*-diphenylmethylformamide (29%), m. p. and mixed m. p. 135°, eluted by ether.

(e) *Triphenylmethyl bromide.* Treatment of the bromide (3 mmoles) with molten cyanogen bromide (16 mol.), followed by chromatography on silica gel, afforded triphenylmethane (2%), m. p. 85—90°, eluted by 3:7 benzene–light petroleum, triphenylmethyl cyanide (78%), m. p. and mixed m. p. 127°, eluted by 1:1 benzene–light petroleum, and an oil, giving triphenylmethanol (8%), m. p. and mixed m. p. 164—165° (from light petroleum). The ether removed by distillation from the extract of the crude reaction product was yellow, gave a precipitate of silver bromide with ethanolic silver nitrate, and converted styrene into its dibromide, m. p. and mixed m. p. 72—74°.

(f) *Triphenylmethyl isothiocyanate.* Reaction was carried out as described in (e). Chromatography of the product on silica gel afforded triphenylmethyl cyanide (12%) and unchanged triphenylmethyl isothiocyanate.

(g) *Triphenylmethyl thiolbenzoate.* The thiolbenzoate[23] was decomposed in molten cyanogen bromide (18 mol.). Chromatography of the resulting viscous oil successively yielded: triphenylmethyl isothiocyanate (49%), m. p. and mixed m. p. 136—138°, eluted by 1:4 benzene–light petroleum; benzoyl isothiocyanate (~0·3 g.) as a pungent oil, eluted by 3:7 benzene–light petroleum and readily hydrolysed to benzamide, m. p. 125—128°; triphenylmethyl cyanide (33%), m. p. and mixed m. p. 124—127°, eluted by 1:1 benzene–light petroleum; triphenylmethanol (14%), m. p. and mixed m. p. 158—163°, eluted by benzene; and benzoic acid (38%), eluted by 1:3 ether–benzene. The infrared spectrum of the benzoyl isothiocyanate was identical with that of an authentic sample.[13]

(h) *Triphenylmethyl thiolacetate.* The ester (71%), m. p. 138—140°, was prepared in the same way as the thiolbenzoate and was similarly decomposed by cyanogen bromide. When chromatographed on silica gel, the resulting oil successively yielded: triphenylmethyl isothiocyanate (48%), m. p. 134—138°, eluted by 1:4 benzene–light petroleum; a lachrymatory liquid (~0·2 g.), which

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[21] G. W. H. Cheeseman, *J.*, 1957, 115.

[22] E. Fischer and O. Fischer, *Annalen*, 1878, **194**, 242.

[23] E. Biilmann and N. V. Due, *Bull. Soc. chim. France*, 1924, **35**, 384.

was eluted by 1 : 1 benzene–petroleum ether, and which showed the infrared characteristics of an authentic sample of acetyl isothiocyanate;[24] triphenylmethyl cyanide (46%), m. p. 124—127°, eluted by 3 : 1 benzene–light petroleum; triphenylmethanol (8%), m. p. 155—165°, eluted by benzene; and a pungent liquid (0·3 g.), eluted by benzene–ether, and showing the infrared spectral characteristics of acetic acid.

Reactions Occurring on Chromatographic Columns.—The following observations refer, typically, to the behaviour of compounds (1 g.) on columns (30 × 2·5 cm.) of silica gel or alumina, the absorbents having been treated as previously described, and elution being carried out with the usual succession of solvents. On the dried silica gel, no change occurred during elution of benzyl or diphenylmethyl thiocyanate, or diphenylmethyl, triphenylmethyl, or benzoyl isothiocyanate, but diphenylmethyl bromide was hydrolysed to the alcohol and ether, and triphenylmethyl bromide to the alcohol. On the acid-treated alumina, no change occurred during elution of benzyl thiocyanate, or diphenylmethyl thiocyanate or isothiocyanate, but the halides were completely hydrolysed, and triphenylmethyl isothiocyanate was partially hydrolysed. If, however, the compounds were left on columns of the same alumina for long periods (*e.g.*, 40hr.) before elution, changes occurred in all cases. Typical percentage conversions were as follows: benzyl thiocyanate into dibenzyl disulphide (40%); diphenylmethyl thiocyanate into the isothiocyanate (24%), bisdiphenylmethyl disulphide (28%), benzhydrol (35%), and *NN'*-bisdiphenylmethylthiourea (8%), m. p. 216° (lit.,[17] 210—211°); diphenylmethyl isothiocyanate into the same thiourea (30%) and diphenylmethylamine (22%). In general, the extent of such reactions depended both on time of contact and on the scale of the operation.

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[24] J. Hawthorne, *J.*, 1906, 556.