

1073. *Thiocyanogen, Thiocyanates, and Isothiocyanates. Part III.*¹
Substitution Reactions of Triphenylmethyl Isothiocyanate with Acids and Salts.

By R. G. R. BACON, J. KÖCHLING, and T. A. ROBINSON.

The reported substitutions are of the type $\text{Ph}_3\text{C}\cdot\text{NCS} \rightarrow \text{Ph}_3\text{CX}$ and probably involve the ion Ph_3C^+ as an intermediate. In strong acids, the isothiocyanate undergoes protonation and ionic dissociation, and gives the alcohol on addition of water; its dissociation is complete in concentrated sulphuric acid. Triphenylmethanol or its carboxylic esters are obtained from solutions in some carboxylic acids, but formic acid eventually causes complete reduction to triphenylmethane, whilst trifluoroacetic acid gives some triphenylmethylamine; thiocarboxylic acids give good yields of their triphenylmethyl esters. Observations on the reversibility of hydrolysis and alcoholysis of triphenylmethyl isothiocyanate are reported. The appropriate alkali-metal salts in organic solvents effect the substitutions, $\text{Ph}_3\text{C}\cdot\text{NCS} + \text{MX} \rightarrow \text{Ph}_3\text{CX}$ ($\text{X} = \text{OH}, \text{OMe}, \text{CN}, \text{N}_3, \text{S}\cdot\text{COR}$); the iodide, thus obtained, undergoes homolysis. The ready substitution reactions of triphenylmethyl isothiocyanate with solutions of silver nitrate, silver perchlorate, silver salts of carboxylic acids, and ferric chloride exemplify the assistance afforded by a transition-metal ion, but much more drastic conditions are needed for reaction with silver cyanide or mercuric cyanide.

MOBILITY of the substituent group in organic thiocyanates is known chiefly with respect to the isomerisation reaction, for which there is evidence² of ionisation as the intermediate step:

¹ Part II, R. G. R. Bacon and J. Köchling, preceding Paper.

² A. Iliceto, A. Fava, U. Mazzucato, and O. Rossetto, *J. Amer. Chem. Soc.*, 1961, **83**, 2729.

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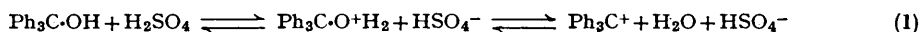
$R\cdot SCN \rightleftharpoons R^+SCN^- \rightleftharpoons R\cdot NCS$. We have previously referred^{3,4} to other kinds of mobility, predictable from the pseudohalide character of the group, which have occasionally been observed with secondary and tertiary thiocyanates and isothiocyanates, namely, substitution by nucleophiles, *e.g.*, $R\cdot SCN + X^- \rightarrow RX + SCN^-$, and elimination to give olefins, *e.g.*, $\searrow CH\cdot C(SCN)\zeta \rightarrow \searrow C:\zeta + HNCS$. Other reactions, such as $RS\cdot CN + X^- \rightarrow RS^- + XCN$, and $RN:C:S + HX \rightarrow RNH\cdot CS\cdot X$, often intervene.

Nucleophilic substitution is the basis, however, of two known diagnostic tests for labile thiocyanates: production of a deep-red colour with methanolic ferric chloride,⁵ and of a precipitate with ethanolic silver nitrate.^{6,7} When we examined quantitatively the response of some thiocyanates and isothiocyanates to these tests, the following order of reactivity was observed: $Ph_3C\cdot NCS > Ar\cdot CMe_2\cdot NCS > CHR:CH\cdot CHR'\cdot NCS > Ph\cdot CHMe\cdot SCN$ (or $\cdot NCS$) $> ArCH_2\cdot SCN > CHR(SCN)\cdot CHR'\cdot SCN > Ar\cdot SCN$ (Ar = phenyl, substituted phenyl, naphthyl; R, R' = alkyl). With the exception of the aryl thiocyanates, for which reaction was negligible, conversions of 50–100% readily occurred with all the compounds at 50–70°. Thus, considerable mobility was exhibited both by thiocyanato- and isothiocyanato-groups, particularly on secondary and tertiary carbon atoms carrying aryl or α -olefinic substituents. These are centres at which the isomerisation, $R\cdot SCN \rightarrow R\cdot NCS$ also occurs easily.³

The relative response to nucleophiles of members of isomeric pairs, $R\cdot SCN$ and $R\cdot NCS$, needs to be assessed. In the example shown in the series above (R = CHMePh), percentage conversions for the thiocyanate were not more than twice as great as for the isothiocyanate under similar conditions. On the other hand, it has been claimed⁶ that *t*-butyl thiocyanate is so much more reactive than the isothiocyanate towards silver nitrate that mixtures of the two isomers may thus be analysed.

The present Paper is exclusively concerned with triphenylmethyl isothiocyanate, the most reactive of the compounds tested. As recent publications have shown,^{1,3,8} the isomeric thiocyanate is unknown, being too labile to be isolable under any preparative conditions yet tried. We found, in accordance with the isothiocyanato-structure, that reduction by lithium aluminium hydride yielded *N*-methyltriphenylmethylamine. It is known to react both additively and substitutively with amines;⁸ rates of reaction with aniline⁹ and with water or sodium azide in aqueous acetone¹⁰ have been recorded; it undergoes solvolysis with ethanol;^{11–13} it forms thiolcarboxylic esters with the corresponding acids.¹³ The present Paper concerns its reactions with various acids and nucleophilic anions, the latter being assisted in some cases by transition-metal cations.

Triphenylmethyl chloride or bromide dissociates in certain solvents, such as nitromethane or sulphur dioxide, to give yellow solutions containing the ion Ph_3C^+ . The isothiocyanate is colourless in such solvents, but gives deep-yellow solutions in concentrated sulphuric acid and some other strong acids. This protonation and dissociation of the isothiocyanate is represented in equation (2) analogously to the known protonation and dissociation of triphenylmethanol,¹⁴ which is represented in equation (1).



Solutions of the alcohol or isothiocyanate in concentrated sulphuric acid show the same absorption spectra, each with two maxima of similar intensity at 405 and 430 μ , due to the

³ R. G. R. Bacon and R. S. Irwin, *J.*, 1961, 2447.

⁴ R. G. R. Bacon, R. G. Guy, and R. S. Irwin, *J.*, 1961, 2436.

⁵ J. L. Wood and L. F. Fieser, *J. Amer. Chem. Soc.*, 1941, **63**, 2323.

⁶ M. S. Kharasch, E. M. May, and F. R. Mayo, *J. Amer. Chem. Soc.*, 1937, **59**, 1580.

⁷ R. G. R. Bacon and R. G. Guy, *J.*, 1961, 2428.

⁸ A. Iliceto, A. Fava, and U. Mazzucato, *J. Org. Chem.*, 1960, **25**, 1445.

⁹ C. G. Swain and D. C. Dittmer, *J. Amer. Chem. Soc.*, 1955, **77**, 3924.

¹⁰ C. G. Swain, C. B. Scott, and K. H. Lohmann, *J. Amer. Chem. Soc.*, 1953, **75**, 136.

¹¹ S. Bodfors and S. Ahrland, *Acta Chem. Scand.*, 1951, **5**, 227.

¹² A. Hantzsch and A. Burawoy, *Ber.*, 1930, **63**, 1181.

¹³ H. L. Wheeler and T. B. Johnson, *Amer. Chem. J.*, 1901, **28**, 345.

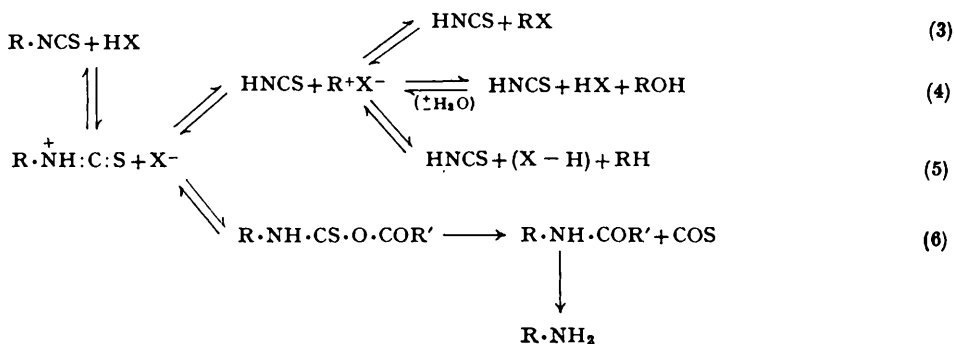
¹⁴ R. J. Gillespie and J. A. Leisten, *Quart. Rev.*, 1954, **8**, 40.

triphenylmethyl carbonium ion. Cryoscopic studies have shown^{14, 15} that the dissociation (1) is complete in dilute solutions of the alcohol in sulphuric acid, and such solutions have accordingly been used¹⁶ as reference standards in spectrophotometric determinations of triphenylmethyl carbonium ions in other media. Such comparison, made with reference to the absorption maximum at 430 m μ , showed that the dissociation of the isothiocyanate represented in (2) was likewise complete at the concentrations examined ($0.5\text{--}3.0 \times 10^{-5}$ mole/l.).

A solution of the isothiocyanate in concentrated sulphuric acid gave a quantitative yield of the alcohol when added to water:



In other strong mineral acids the isothiocyanate also dissociated to give yellow or brown solutions or suspensions. High yields of the alcohol resulted when solutions in warm 70% nitric or perchloric acid were added to water. Reaction of the isothiocyanate with carboxylic or thiocarboxylic acids took a varying course, as shown in the annexed scheme ($\text{R} = \text{CPh}_3$; $\text{X} = \text{R}'\cdot\text{CO}\cdot\text{O}$ or $\text{R}'\cdot\text{CO}\cdot\text{S}$):



In acetic acid, triphenylmethyl isothiocyanate gave colourless solutions, from which it was recovered unchanged after short periods at the boiling point, even when water was present. A yellow colour appeared when the isothiocyanate was mixed with formic, trichloroacetic, trifluoroacetic, or thiolacetic acid, and yellow or brown solutions resulted at, *e.g.* 80°; monochloroacetic acid gave a yellow colour after being melted. Ester formation, in accordance with equation (3), occurred in high yield with thiolacetic or thiolbenzoic acids; this behaviour is different from that reported for these acids with other isothiocyanates,¹⁷ which give amides through an initial addition process analogous to that shown in equation (6) for a carboxylic acid. Ester formation (3) was also indicated by the infrared spectral characteristics of products obtained by heating triphenylmethyl isothiocyanate with monochloro-, trichloro-, or trifluoro-acetic acid, but pure esters were not isolated. The intervention of hydrolysis, through the presence of water, in accordance with equation (4), was clearly shown for solutions in trifluoroacetic acid, and was indicated spectroscopically in the case of the chloro-acids.

Reduction, in accordance with equation (5), occurred rapidly and quantitatively in formic acid at $\sim 100^\circ$. This reaction, which may be regarded as the transfer of a hydride ion from a formate ion or formic acid molecule to a triphenylmethyl carbonium ion, is an example ($\text{X} = \text{NCS}$) of the more general process represented by the overall equation, $\text{Ph}_3\text{CX} + \text{H}\cdot\text{CO}_2\text{H} \rightarrow \text{Ph}_3\text{CH} + \text{HX} + \text{CO}_2$, which we have discussed elsewhere.¹⁸ Production

¹⁵ A. Hantzsch, *Z. phys. Chem.*, 1908, **61**, 257; L. P. Hammett and A. J. Deyrup, *J. Amer. Chem. Soc.*, 1933, **55**, 1900.

¹⁶ A. Bentley, A. G. Evans, and J. Halpern, *Trans. Faraday Soc.*, 1951, **47**, 711, and later papers by Evans *et al.*

¹⁷ H. L. Wheeler and H. F. Merriam, *J. Amer. Chem. Soc.*, 1901, **23**, 283.

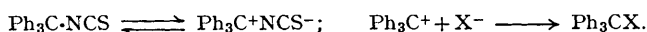
¹⁸ R. G. R. Bacon and J. Köchling, following Paper.

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of amides, through unstable addition compounds, as shown in equation (6), is known for some other isothiocyanates.¹⁹ This evidently occurred with triphenylmethyl isothiocyanate in trifluoroacetic acid, but hydrolysis, presumably due to adventitious water, led to the isolation of the amine salt, $\text{Ph}_3\text{C}\cdot\text{NH}_3^+\text{CF}_3\cdot\text{CO}_2^-$. *N*-Triphenylmethylfluoroacetamide, a new compound, was prepared from the amine and trifluoroacetic anhydride.

Uncatalysed hydrolysis of triphenylmethyl isothiocyanate, previously reported as occurring in aqueous acetone,¹⁰ was carried out in hot aqueous methyl cyanide, and its reversibility was shown by preparation of the isothiocyanate from triphenylmethanol and excess of thiocyanic acid in methyl cyanide. A mixture of triphenylmethyl isothiocyanate and water was stable over long periods at 100°, but the isothiocyanate, added in a hydrocarbon solvent, was hydrolysed during column chromatography on alumina, and also on silica if the latter had not been well dehydrated. Reversible alcoholysis occurred readily. The fall in intensity of the N:C:S infrared absorption peak of samples isolated from the reaction mixture indicated that > 50% of the ether $\text{Ph}_3\text{C}\cdot\text{OR}$ was present at equilibrium in boiling 0.06M-methanolic or -ethanolic isothiocyanate solutions. The ether was obtained quantitatively by carrying out the reaction in the presence of an excess of pyridine to combine with the acid. Conversely, the isothiocyanate was prepared in almost quantitative yield by treating the triphenylmethyl ether with a large excess of thiocyanic acid in ethereal solution.

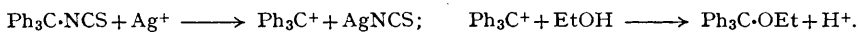
Triphenylmethyl isothiocyanate (then regarded as the thiocyanate) was used in kinetic studies of nucleophilic substitution,¹⁰ which mainly concerned triphenylmethyl halides. It was concluded that these reactions showed "exceptionally clear evidence for a carbonium-ion intermediate," *i.e.*,



As examples of such reactions, we report preparations of other triphenylmethyl derivatives, usually in 80—95% yield from the isothiocyanate, with the following reagents: potassium hydroxide, potassium cyanide, or sodium azide in methyl cyanide; sodium methoxide in methanol; potassium thioacetate or thiolbenzoate in ethanol. Lithium or potassium bromide did not react with triphenylmethyl isothiocyanate, *i.e.*, there was no indication that the reverse reaction is significant in preparation of the isothiocyanate from triphenylmethyl bromide and thiocyanate ion. Reaction between sodium iodide and triphenylmethyl isothiocyanate in boiling acetone solution resulted in copious formation of iodine; this was due to homolysis of the $\text{Ph}_3\text{C}\text{--I}$ bond,²⁰ since a high yield of bstriphenylmethyl peroxide resulted when this preparation of the iodide was attempted in a stream of oxygen. Failure to obtain the peroxide when boiling acetone solutions of triphenylmethyl isothiocyanate were treated with oxygen in the absence of iodide ion shows that the $\text{Ph}_3\text{C}\text{--NCS}$ bond does not undergo homolysis under the conditions used. The isothiocyanate was also stable in ultraviolet light.

Several substitutions of triphenylmethyl isothiocyanate were carried out with salts of silver, mercury, or iron. Reactions of this type may be assisted by the cation, and are more complicated mechanistically than substitutions with alkali-metal salts.²¹

The reaction with excess of ethanolic silver nitrate resulted in rapid and quantitative production of triphenylmethyl ethyl ether at ordinary temperatures:



The precipitate was not silver thiocyanate but was a previously described²² double salt, $\text{AgNCS}\cdot 2\text{AgNO}_3$, from which the silver nitrate could be extracted by methyl cyanide. This

¹⁹ F. Krafft and H. Karstens, *Ber.*, 1892, **25**, 452; P. Kay, *Ber.*, 1893, **26**, 2848.

²⁰ M. Gomberg, *Chem. Rev.*, 1924, **1**, 91.

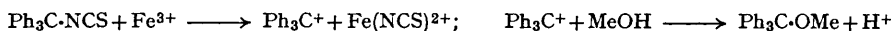
²¹ G. S. Hammond, M. F. Hawthorne, J. H. Waters, and B. M. Graybill, *J. Amer. Chem. Soc.*, 1960, **82**, 704.

²² K. Hellwig, *Z. anorg. Chem.*, 1900, **25**, 157.

feature of the reaction needs to be allowed for if ethanolic silver nitrate is used for quantitative analysis of an organic thiocyanate or isothiocyanate. When the reaction of triphenylmethyl isothiocyanate with silver nitrate was conducted in methyl cyanide, silver thiocyanate was precipitated quantitatively, and addition of water to the solution converted the readily hydrolysed triphenylmethyl nitrate²³ into triphenylmethanol. Reaction between silver perchlorate and triphenylmethyl isothiocyanate in benzene solution also resulted in quantitative precipitation of silver thiocyanate. A solution of triphenylmethyl perchlorate was thus obtained in an analogous manner to its earlier preparation from triphenylmethyl chloride,²⁴ and the solution was likewise used as an electrophilic reagent to convert phenol into its *p*-triphenylmethyl derivative.²⁵

A recommended method of preparation for triphenylmethyl esters of carboxylic acids is to heat a solution of triphenylmethyl bromide or chloride in a hydrocarbon with a suspension of the silver salt of the acid.^{10, 26} We have analogously converted triphenylmethyl isothiocyanate into the formate, acetate, trifluoroacetate, and benzoate, obtaining yields of 80–100% in benzene at room temperatures. The assistance of the silver ion in these reactions is indicated by the failure of ammonium acetate or benzoate to react in benzene with the isothiocyanate; in the case of triphenylmethyl halides, reaction may be carried out in benzene with the ammonium, or alkali-metal salts, as well as with the silver salts of carboxylic acids.^{26, 27} Triphenylmethyl formate, a new compound, is the subject of a separate communication.¹⁸ Samples of triphenylmethyl trifluoroacetate were extremely susceptible to hydrolysis and showed the infrared absorption characteristics which have been reported for this ester.²⁸

Carbonium-ion formation from triphenylmethyl halides is aided by mercuric chloride²⁹ as well as by silver salts. Attempts to replace the NCS group in triphenylmethyl isothiocyanate by the cyano-group from silver cyanide or mercuric cyanide were unsuccessful in various organic solvents. High yields were obtained when either salt was fused with the isothiocyanate at 160–180°; similar conditions were recommended³⁰ for conversions of triphenylmethyl halides into the cyanide. Comparison with the ready reaction of the isothiocyanate with potassium cyanide (see above) shows hindrance by the heavy metal in these instances, presumably because it is strongly bound to the cyanide ion. On the other hand, the ready formation of the red ferric thiocyanate complex, when triphenylmethyl isothiocyanate was treated with methanolic ferric chloride (p. 5601), provides an example of Fe³⁺-assisted solvolysis:



The ether was thus obtained almost quantitatively, whereas reaction of the isothiocyanate with methanol in the absence of ferric chloride gave the lower yields of ether (~60%) characteristic of this equilibrium system. Catalysis by ferric ion was also applied to conversion of triphenylmethyl isothiocyanate into its azide:



EXPERIMENTAL

Melting points were determined on a Kofler hot-stage apparatus.

Solvents.—Acetone was dried over calcium sulphate and redistilled. Methyl cyanide was refluxed over phosphorus pentoxide, distilled, and stored over molecular sieve type 5A (Linde

²³ S. J. Cristol and J. E. Leffler, *J. Amer. Chem. Soc.*, 1954, **76**, 4468; R. T. Merrow and R. H. Boschan, *J. Amer. Chem. Soc.*, 1954, **76**, 4622; G. W. H. Cheeseman, *Chem. and Ind.*, 1954, 281.

²⁴ M. Gomberg and L. H. Cone, *Annalen*, 1909, **370**, 142.

²⁵ H. Burton and G. W. H. Cheeseman, *J.*, 1953, 832.

²⁶ K. D. Berlin, L. H. Gower, J. W. White, D. E. Gibbs, and G. P. Sturm, *J. Org. Chem.*, 1962, **27**, 3595.

²⁷ C. S. Schoepfle, *J. Amer. Chem. Soc.*, 1925, **47**, 1469.

²⁸ D. W. A. Sharp and N. Sheppard, *J.*, 1957, 674.

²⁹ J. W. Bayles, A. G. Evans, and J. R. Jones, *J.*, 1955, 206, and later papers.

³⁰ W. M. Budde and S. J. Potempa, *J. Amer. Chem. Soc.*, 1952, **74**, 258; G. Lock and V. Rieger, *Chem. Ber.*, 1953, **86**, 74.

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Air Products Co.). Benzene, toluene, light petroleum (b. p. 40–60°), and ether were redistilled and stored over sodium. Ethanol was removed from chloroform by passage through a column of alumina.

Comparison of the Reactivity of Organic Thiocyanates and Isothiocyanates.—(a) Samples of the compounds (0.1 mmole) with 1 ml. of 10% ferric chloride solution (10 mol.) in 1:1 methanol-dioxan were heated in stoppered tubes for a standard time in a constant-temperature bath. The solutions were diluted to 100 ml. and the concentration of ferric thiocyanate was determined by spectroscopic comparison, at the frequency of maximum absorbance (600 $m\mu$), against standard solutions of ferric thiocyanate.

(b) Samples of the compounds (0.1 mmole) with 3.4 ml. of 5% ethanolic silver nitrate (10 mol.) were heated for a standard time in a constant-temperature bath. The precipitated double salt, $\text{AgSCN}\cdot 2\text{AgNO}_3$ (see below), was centrifuged, washed with ethanol, dried, and weighed.

Triphenylmethyl Isothiocyanate.—A 0.2M-solution of pure triphenylmethyl bromide in acetone was stirred for 3 hr. with a suspension of silver thiocyanate (0.1 mol.), the silver bromide was removed, the filtrate evaporated, and the pure isothiocyanate (90%) obtained by recrystallisation from light petroleum. Alternatively, a rapid exothermic reaction in acetone between pure triphenylmethyl chloride or bromide and an excess of ammonium or potassium thiocyanate gave the isothiocyanate, isolated (88%) by precipitation with water and recrystallisation. The isothiocyanate was also prepared (95%), in refluxing methyl cyanide, from triphenylmethanol and thiocyanic acid (obtained in the solvent from a suspension of silver thiocyanate and a stream of hydrogen sulphide).

The isothiocyanate, m. p. 138–140° (from acetone or light petroleum), showed in its infrared absorption spectrum a strong broad band with maxima at 2046 and 2100 cm^{-1} . A solution of the isothiocyanate (0.01 mole) and lithium aluminium hydride (0.011 mole) in ether was refluxed for 1 hr., decomposed, and the ethereal solution of the product was treated with dilute hydrochloric acid. The precipitated hydrochloride of *N*-methyltriphenylmethylamine was obtained (65%), m. p. 221° (from ethanol) (lit.,³¹ 216°) (Found: C, 77.1; H, 6.4; Cl, 11.7; N, 4.8. Calc. for $\text{C}_{20}\text{H}_{19}\text{N}\cdot\text{HCl}$: C, 77.5; H, 6.5; Cl, 11.5; N, 4.5%).

Reactions of Triphenylmethyl Isothiocyanate with Acids.—Stirred suspensions of the isothiocyanate (0.7 mmole) in the acid (10 ml.) were observed for 15 min. at 20°, and then for 15 min. at 80°. After cooling, the mixture was added to ice and water, extracted with methylene chloride, and the solution evaporated.

(a) Concentrated (98%) sulphuric acid yielded a deep-orange solution at 20°, not further deepening in colour when heated. Spectrophotometric examination of 10^{-5} M-solutions in concentrated sulphuric acid, in the range 360–470 $m\mu$, gave absorption curves identical with those given by triphenylmethanol under the same conditions. Plots of optical density against concentration at 430 $m\mu$, in the range 0.5 – 3.0×10^{-5} M, fell on the same straight line for both substances. The product, isolated after addition of a sulphuric acid solution of the isothiocyanate to water, was fairly pure triphenylmethanol (98%), m. p. 158–162°.

Similar treatment of the isothiocyanate in 70% nitric acid or 72% perchloric acid gave yellow suspensions at 20°, brown solutions at 80°, and somewhat impure triphenylmethanol on dilution. Concentrated hydrochloric acid or orthophosphoric acid gave only yellow suspensions, from which the isothiocyanate was recovered unchanged.

(b) Formic acid gave a yellow suspension at 20°; the colour deepened at 80°, but complete solution did not occur, and the isolated product was essentially unchanged isothiocyanate. At 100°, fading began in about 15 min., an almost colourless solution resulted in 75 min., and triphenylmethane (98%), m. p. and mixed m. p. 91–94°, was isolated (Found: C, 93.4; H, 6.6. Calc. for $\text{C}_{19}\text{H}_{16}$: C, 93.4; H, 6.6%).

(c) The isothiocyanate gave colourless solutions in acetic acid at 80°, or at the b. p. (1 hr.), or in boiling 4:1 acetic acid-water (1 hr.), and it was in all cases recovered unchanged. With monochloroacetic acid, the isothiocyanate formed a colourless solid mixture at 20° and an orange solution when kept at 80° (30 min.), but was recovered essentially unchanged; at 150° (30 min.) it yielded, after isolation, a brown oil, which could not be crystallised from benzene-light petroleum, and appeared, from its infrared spectrum, to contain the chloroacetic ester mixed with unchanged isothiocyanate. When employed similarly, trichloroacetic acid gave a yellow solid at 20°, an orange solution at 80°, and a brown solution at 150°; the former solution yielded a pale yellow solid, apparently containing triphenylmethanol and its trichloroacetic

³¹ I. Vosburgh, *J. Amer. Chem. Soc.*, 1916, **38**, 2081.

ester, together with unchanged isothiocyanate, whilst the latter solution yielded a gum, in which only ester absorption bands could be spectroscopically detected.

(d) In thiolacetic acid at 20°, the isothiocyanate gave a pale yellow solution, unchanged in colour on heating. After 30 min. at 80°, the solid product, isolated by addition to water, contained no unchanged isothiocyanate and was nearly pure triphenylmethyl thiolacetate. Recrystallisation from light petroleum gave the ester (86%), m. p. and mixed m. p. 143—146° (lit.,^{32a} 139—141°;^{32b} 147—147.5°). A solution of the isothiocyanate (5 mmoles) and thiolbenzoic acid (10 mmoles) in toluene (20 ml.) was refluxed for 2 hr. and the solvent evaporated under reduced pressure. Triphenylmethyl thiolbenzoate was obtained from the residue as colourless needles (61%), m. p. and mixed m. p. 189—191° (from ethanol) (lit.,³³ 188°).

(e) Suspensions of the isothiocyanate (2 mmoles) in trifluoroacetic acid (10 ml.) were yellow at 20°, and on heating gave orange solutions, which were examined after 30 min. under reflux. Addition of ice and water to the hot solution, followed by extraction with methylene chloride, yielded only triphenylmethanol (99%), m. p. and mixed m. p. 158—162°. If the solution in trifluoroacetic acid was cooled and then added to ice and water, and extracted, it yielded a mixture, m. p. 110—140°, containing triphenylmethanol and an unidentified fraction, m. p. 130—133°, showing a carbonyl peak at 1700 cm.⁻¹ in the infrared spectrum. If the solution in trifluoroacetic acid was evaporated under reduced pressure, it yielded an oil, from which light petroleum precipitated *triphenylmethylamine trifluoroacetate* (32%), m. p. 184—192° with partial sublimation from 150° (from 1:5 ether—light petroleum) (Found: C, 67.1; H, 5.0; N, 3.8. C₂₁H₁₈F₃NO₂ requires C, 67.5; H, 4.9; N, 3.8%). The salt decomposed when shaken with cold water for 15 min.; triphenylmethylamine was then isolated (80%), m. p. and mixed m. p. 103—106°, by extraction with methylene chloride. The salt was also prepared (82%), m. p. 186—194°, by treating triphenylmethylamine with trifluoroacetic acid in light petroleum.

For comparison, *N-triphenylmethyltrifluoroacetamide* was prepared by a procedure described³⁴ for trifluoroacetylation: triphenylmethylamine was treated in ether, below 0°, with trifluoroacetic anhydride (1.5 mol.), the mixture boiled for 15 min., and evaporated, yielding the amide (84%), m. p. 164—167° with sublimation from 160° (from light petroleum) (Found: C, 71.2; H, 4.5; N, 4.2. C₂₁H₁₆F₃NO requires C, 71.0; H, 4.5; N, 3.9%). The amide was not changed if a solution in trifluoroacetic acid was refluxed and evaporated under reduced pressure.

Solvolysis of Triphenylmethyl Isothiocyanate.—(a) The isothiocyanate was unchanged when stored, mixed with water, for several weeks, or when heated with water, in refluxing benzene or carbon tetrachloride solution, for several hours. A solution of the isothiocyanate in refluxing 5:1 methyl cyanide—water gave a mixture of unchanged isothiocyanate and triphenylmethanol.

(b) The following are typical observations illustrating the behaviour of triphenylmethyl isothiocyanate (0.2 g.) on columns of adsorbents (35 × 1.5 cm.), but the results could vary with times of elution and other factors. With an untreated sample of silica gel as adsorbent, 1:1 benzene—light petroleum eluted unchanged isothiocyanate (80%), and 1:1 benzene—ether eluted triphenylmethanol (19%). With the same adsorbent, previously dried by heating at 100° *in vacuo* and cooling in a desiccator over phosphorus pentoxide, only unchanged isothiocyanate was recovered. With alumina (Peter Spence, Type H) as adsorbent, only triphenylmethanol (100%) was obtained. With the same adsorbent, previously shaken with 10% of 10% aqueous acetic acid, some unchanged isothiocyanate (20%) was recovered, followed by triphenylmethanol (80%).

(c) The solvolysis of triphenylmethyl isothiocyanate in boiling methanol or ethanol was followed by diluting aliquots with water, isolating the product with methylene chloride, and obtaining its infrared absorption spectrum under standard conditions. The ratio of the optical density of the methoxyl band at 1080 cm.⁻¹ to that of the isothiocyanate band at 2050 cm.⁻¹ was used to ascertain the degree of conversion, with the aid of a calibration graph for mixtures of known composition. In boiling 0.06M-methanolic isothiocyanate, a level value of ~ 60% methyl ether was reached in 10 hr.; the corresponding figure for boiling 0.06M-ethanolic isothiocyanate was ~ 50%. Data obtained in the presence of an excess of potassium iodide or hydrochloric acid suggested that these reagents accelerated the reaction and increased the yield of the ether. In the presence of an excess of pyridine (10 mol.), quantitative conversion into the

³² (a) D. Vorländer and E. Mittag, *Ber.*, 1913, **46**, 3450; (b) B. K. Morse and D. S. Tarbell, *J. Amer. Chem. Soc.*, 1952, **74**, 416.

³³ E. Billmann and N. V. Due, *Bull. Soc. chim. France*, 1924, **35**, 384.

³⁴ F. Weygand and R. Geiger, *Chem. Ber.*, 1956, **89**, 647.

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ether occurred in 3 hr. in boiling 0.06M-solutions of the isothiocyanate. To effect the reverse reaction, triphenylmethyl methyl ether (3 mmoles) was dissolved in an ethereal solution (70 ml.) containing a large excess (150 mmoles) of thiocyanic acid extracted from aqueous thiocyanic acid.³⁵ After refluxing for 3 hr., and shaking with aqueous sodium hydrogen carbonate, the solution was evaporated, and the product chromatographed to yield triphenylmethyl isothiocyanate (89%), m. p. 137°.

Reactions of Triphenylmethyl Isothiocyanate with Alkali-metal Salts.—Unless it is stated otherwise, the reactions were carried out with vigorous stirring, at the b. p., in the solvent (25–50 ml.), between triphenylmethyl isothiocyanate (1.00 g., 3 mmoles) and an excess of the salt (3–5 mol.); the product was precipitated by addition of water and was purified by recrystallisation or chromatography. A suspension of potassium hydroxide in methyl cyanide (2 hr.) yielded triphenylmethanol (92%), m. p. 162–164°. Sodium methoxide in methanol (2 hr.) yielded triphenylmethyl methyl ether (95%), m. p. 81–83°. A suspension of potassium cyanide in methyl cyanide (3 hr.) yielded triphenylmethyl cyanide (83%), m. p. and mixed m. p. 128–130° (from ether). If 5:1 methyl cyanide–water or acetone–water was used as solvent (12 hr.) at 20°, the resulting triphenylmethyl cyanide (~70%) was accompanied by some triphenylmethanol. A suspension of sodium azide in methyl cyanide (3 hr.) gave triphenylmethyl azide (79%), m. p. 65° (from ethanol) (lit.,³⁶ 64°) (Found: C, 80.15; H, 5.3; N, 15.0. Calc. for C₁₅H₁₅N₃: C, 80.0; H, 5.3; N, 14.7%); no reaction occurred under these conditions at 20°. Potassium thiolacetate in ethanol (1 hr.) gave an oil, which, after ether extraction and recrystallisation from ethanol, yielded triphenylmethyl thiolacetate (50%), m. p. and mixed m. p. (with a sample from triphenylmethyl chloride) 138–140°. Potassium thiolbenzoate in ethanol gave a solid product, which furnished pure triphenylmethyl thiolbenzoate (70%), m. p. and mixed m. p. 189°.

A solution of the isothiocyanate (4 mmoles) and sodium iodide (5 mol.) in acetone (50 ml.) gave a deep-purple solution when refluxed (3 hr.) in acetone under nitrogen. If air was admitted, a white precipitate of bistrisphenylmethyl peroxide appeared. Conducting the reaction in a stream of air resulted in a 75% yield of the peroxide, m. p. 187–188° (Found: C, 87.7; H, 5.65. Calc. for C₃₈H₃₀O₂: C, 88.0; H, 5.8%). When the isothiocyanate was similarly treated with air, but with iodide absent, it was recovered quantitatively. The isothiocyanate was also unchanged by ultraviolet irradiation in toluene solution. A solution of the isothiocyanate (3 mmoles) and lithium bromide (10 mol.) in acetone (25 ml.) was refluxed (24 hr.) and the product chromatographed. Recovered isothiocyanate (67%) was followed by oils, but no triphenylmethanol (into which triphenylmethyl bromide would have been converted) was detected; a similar result was obtained with a suspension of potassium bromide.

Reaction of Triphenylmethyl Isothiocyanate with Heavy-metal Salts.—(a) A solution of the isothiocyanate (1 mmole) in methyl cyanide reacted immediately when mixed with a solution of silver nitrate (1 mol.) in methyl cyanide. The precipitated silver thiocyanate, which was isolated (100%) after shaking for 3 hr., melted above 250° and showed a characteristic infrared absorption spectrum. When added to water, the filtrate, containing triphenylmethyl nitrate, gave an acidic solution, from which methylene chloride extracted triphenylmethanol (98%), m. p. and mixed m. p. 161–163°. A solution of the isothiocyanate (3 mmoles) in ethanol also reacted immediately with silver nitrate (10 mol.) in 3:1 ethanol–water, but the precipitate, isolated after shaking for 6 hr., was the double salt,²² AgSCN, 2AgNO₃ (91%), m. p. 158–162°, with an infrared absorption spectrum characteristic of the nitrate and isothiocyanate ions. The filtrate yielded triphenylmethyl ethyl ether, accompanied by a varying and minor amount of triphenylmethanol. When shaken at room temperature with methyl cyanide, the double salt was quantitatively separated into insoluble silver thiocyanate and soluble silver nitrate.

(b) A solution of triphenylmethyl isothiocyanate in benzene gave an immediate precipitate of silver thiocyanate (99%) when mixed with an excess of silver perchlorate in benzene. The resulting solution of triphenylmethyl perchlorate was also prepared in benzene–nitromethane and was mixed with an excess of phenol in nitromethane. After 7 days at room temperature, the solution was evaporated and chromatographed on alumina, when *p*-hydroxyphenyltriphenylmethane was obtained (50%), m. p. 279–284° (lit.,²⁵ 277–284°).

(c) A solution of the isothiocyanate (6.6 mmoles) in benzene (25 ml.) was shaken for 15 hr. with an excess (30 mmoles) of dried silver acetate. Filtration, removal of the solvent, and recrystallisation from light petroleum yielded triphenylmethyl acetate (80%), m. p. and mixed

³⁵ W. Gluud, K. Keller, and W. Klempt, *Ber.*, 1926, **59**, 1384.

³⁶ C. L. Arcus and R. J. Mesley, *J.*, 1953, 178.

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m. p. 84—86° (lit.,³⁷ 84°). No reaction was observed when dried ammonium acetate was used under similar conditions; triphenylmethyl bromide yielded the acetate (95%) with either the silver or the ammonium salt. The isothiocyanate was treated similarly with dried silver benzoate and the resulting solution mixed with light petroleum, which precipitated triphenylmethyl benzoate (90%), m. p. and mixed m. p. 168—170° (lit.,³⁸ 168—169°).

(d) Silver trifluoroacetate, m. p. 250—255°, was prepared (90%) by adding excess of silver oxide to an aqueous solution of trifluoroacetic acid at 50—60°, recrystallising from benzene, and drying *in vacuo* at 100°. Formation of a *complex* (98%) between this salt and 2,4,6-trimethylpyridine was incidentally observed (Found: C, 46.9; H, 4.75; N, 5.8. $C_2AgF_3O_2 \cdot 2C_8H_{11}N$ requires C, 46.7; H, 4.8; N, 6.1%). On mixing solutions of triphenylmethyl isothiocyanate (1.5 mmoles) and silver trifluoroacetate (1.5 mmoles) in thoroughly dried ether, silver thiocyanate (96%) was at once precipitated, and evaporation of the solution yielded colourless crystals of triphenylmethyl trifluoroacetate (98%), m. p. 110—112° (decomp.) Found: C, 70.5; H, 4.55. Calc. for $C_{21}H_{15}F_3O_2$: C, 70.8; H, 4.2%). All operations were conducted in a glove-box, since this ester was extremely prone to hydrolysis, and was converted into triphenylmethanol when recrystallisation was attempted in the laboratory. The infrared absorption spectrum of the ester was identical with that published.²⁸ It was similarly obtained quantitatively from triphenylmethyl bromide.

(e) Shaking triphenylmethyl isothiocyanate (1 mmole) and anhydrous ferric chloride (1.5 mmoles) in methanol (30 ml.) for 12 hr. produced a blood-red solution which was diluted with water, and the product extracted with methylene chloride. Chromatography on neutralised alumina yielded a little unchanged isothiocyanate (3%), eluted with 1:9 benzene–light petroleum, and triphenylmethyl methyl ether (93%), m. p. and mixed m. p. 83—84°, eluted with 1:1 benzene–light petroleum. An experiment performed under similar conditions without ferric chloride yielded 37% of the unchanged isothiocyanate and 58% of the methyl ether. Triphenylmethyl isothiocyanate (3 mmoles), sodium azide (10 mmoles), and anhydrous ferric chloride (1.5 mmoles, added as a 5% solution in ether) were shaken for 15 hr. in chloroform. The product, m. p. 50—60°, yielded triphenylmethyl azide (50%), m. p. and mixed m. p. 64—66° (from ethanol). No reaction occurred under these conditions if the ferric chloride was omitted.

(f) Triphenylmethyl isothiocyanate (3 mmoles) was unaffected by mercuric or silver cyanide (10 mmoles) in refluxing benzene, acetone, methyl cyanide, or diethylene glycol dimethyl ether. Shaking the isothiocyanate in 5:1 acetone–water with mercuric cyanide for 15 hr. at 20° gave a quantitative yield of triphenylmethanol. The isothiocyanate (3 mmoles) was fused with mercuric or silver cyanide (10 mmoles) at 160—180° and the mixture stirred for 2 hr. Chromatography on silica afforded a little unchanged isothiocyanate (7%), eluted by 1:4 benzene–light petroleum, and triphenylmethyl cyanide (86%), eluted by benzene.

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³⁷ C. G. Swain, T. E. C. Knee, and A. MacLachlan, *J. Amer. Chem. Soc.*, 1960, **82**, 6101.

³⁸ G. S. Hammond and J. T. Rudesill, *J. Amer. Chem. Soc.*, 1950, **72**, 2769.