in portions with external cooling by cold water to maintain this temperature, and then cycloheptatriene (91% cycloheptatriene-7% toluene sample, generously supplied by the Shell Chemical Co.) added with swirling to the solution in an ice bath until the characteristic yellow color of trityl carbonium ion had vanished and precipitation of tropenium fluoroborate had commenced. Dry ether (600 ml.) was added to precipitate the remainder of the salt, and the white microcrystalline product filtered and washed with ether; yield of tropenium fluoroborate, 89% (23.5 g.), m.p. *ca.* 210° dec.,[19] $\lambda_{\max}^{96\%\ H_2SO_4}$ 273.5 mμ (ε 4320) (lit.[5a]: m.p. >210° dec., $\lambda_{\max}^{96\%\ H_2SO_4}$ 273.5 mμ (ε 4350)).

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[19] Tropenium fluoroborate also does not show a definite melting point; darkening begins at about 210° and continues to about 260–270° where the last trace of crystal faces disappears and only a crumbled darkened powder remains.

Triphenylmethyl Isothiocyanate

Antonio Iliceto, Antonino Fava,
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This report deals with the structure of the product (I) m.p. 138–138.5°, which is obtained in the reaction of triphenylmethyl (trityl) halides (chloride or bromide) with alkali thiocyanates[1–3] or thiocyanic acid.[4] This compound is also referred to in the recent literature[2,5] as trityl thiocyanate. Experimental evidence obtained by us shows that the compound is trityl isothiocyanate.

The infrared absorption spectrum of I shows a complex band with a maximum at 2046 cm.$^{-1}$ (chloroform). Position, intensity, and form of the band are characteristic of isothiocyanates, and not of thiocyanates which show a weaker (by a factor of 10) sharp absorption band around 2150 cm.$^{-1}$ (These two bands have been ascribed to the asymmetric stretching vibration of the isothiocyano- and thiocyano- groups respectively.)[6]

Elbs reports that I can be distilled at high temperature without undergoing any change.[1] Its high thermal stability has been confirmed in an experiment, in which I was heated at 150° for two hours and was recovered unaltered. If I were a thiocyanate, one would expect it to isomerize readily under these conditions. This prediction is based upon the consideration of the thermal isomerization rate of arylmethyl thiocyanates: While benzyl thiocyanate is known to isomerize with great difficulty (repeated distillation at 250°),[7] benzhydryl thiocyanate isomerizes at a measurable rate at 70° (half-time, sixty-six hours in methyl ethyl ketone) and its 4-methyl derivative isomerizes with greater ease (half-time four hours under the same conditions).[8] This and other ancillary evidence (solvent and salt effects) all showing that the isomerization reaction proceeds through an electron deficient transition state, point out that the isomerization is facilitated by increasing the ability of the organic substrate to support a positive charge. The inference therefore is that trityl thiocyanate would isomerize very rapidly. The fact that upon heating, I remains unaltered indicates that it already is an isothiocyanate.

Thioureas can be obtained by the reaction of I with amines. Thus, allylamine reacts with I yielding an adduct which has been proved to be 1-trityl-3-allylthiourea.

Assumption that I is a thiocyanate has led in the past to some misunderstanding about its reactivity toward amines. Such is the case of Swain and Dittmer concerning the 'aminolysis' of I.[5] These workers report that, while aniline rather rapidly reacts with I giving the quaternary ammonium thiocyanate, no reaction is observed with *n*-butylamine, even after months.[9] It has been presently established that *n*-butylamine reacts readily with I, both in the pure state and in cyclohexane solution, to give an adduct which, while not showing any reaction of thiocyanate ion, appears to be 1-trityl-3-*n*-butylthiourea.

The above evidence points out the isothiocyanate structure of I. It must be emphasized, however, that owing to its organic residue, I is an isothiocyanate of a particular nature. The peculiarities of its chemical behavior arise from the stability of the trityl carbonium ion and the consequent cleavage, contrary to most isothiocyanates, of the alkyl carbon-to-nitrogen bond, (1):[10]

$$(C_6H_5)_3C{-}NCS \rightleftarrows (C_6H_5)_3C^+NCS^- \rightleftarrows (C_6H_5)_3C^+ + NCS^- \quad (1)$$

Because of this, the reaction of I with a nucleophile may frequently lead to displacement of the thiocyanate ion. In such cases, the familiar reactions of isothiocyanates with nucleophiles (arising from

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[1] K. Elbs, *Ber.* **17**, 700 (1884).

[2] C. G. Swain, C. B. Scott, and R. H. Lohmann, *J. Am. Chem. Soc.*, **75**, 136 (1953).

[3] H. Bredereck and E. Reif, *Ber.*, **81**, 426 (1948).

[4] E. Bilmann and N. V. Due, *Bull. Soc. Chim.*, [4], **35**, 384 (1929).

[5] C. G. Swain and D. C. Dittmer, *J. Am. Chem. Soc.*, **77**, 3924 (1955).

[6] For a detailed discussion of the infrared spectra of I and similar isothiocyanates see: U. Mazzuccato, A. Foffani, A. Iliceto, and G. Svegliado; paper presented at the meeting of European Molecular Spectroscopists, Bologna (Italy) Sept. 7–12 (1959).

[7] H. Hennicke, *Ann.*, **344**, 24 (1906).

[8] A. Iliceto, A. Fava, and U. Mazzuccato, *Tetrahedron Letters*, No.11, 27 (1960).

[9] Swain and Dittmer's statement as to the unreactivity of I towards *n*-butylamine was based solely on the lack of formation of thiocyanate ions.[5]

[10] As expected, the cleavage occurs unimolecularly: This is shown by the solvolysis of I,[2] and by the kinetics of the isotopic exchange between I and labeled thiocyanate ions which is first order in I and zero order in SCN$^-$ (A. Iliceto, A. Fava, and S. Bresadola, to be published).

attack on the carbon atom of the $-N=C=S$ group) may be totally absent.

To put it generally, the outcome of the reaction of I with a nucleophile, N, will ultimately depend upon the competition between displacement, (2), and attack on the isothiocyanate carbon atom, (3):

$$(C_6H_5)_3C^+ + N \longrightarrow \text{products} \qquad (2)$$

$$(C_6H_5)_3C{-}N{=}C{=}S + N \longrightarrow \text{products.} \qquad (3)$$

Which course a particular reaction will take depends, in a given medium, on the nature of the nucleophile and, for a given nucleophile, on the reaction medium. (Displacement is expected to be favored in the more polar solvents and in the reaction with the weaker nucleophiles.)

This situation is well illustrated by the reaction of I with different amines in different media: In cyclohexane, *n*-butylamine gives the corresponding thiourea exclusively, while aniline, although reacting very slowly, gives displacement of thiocyanate ion. In the absence of solvent, the reaction pattern is not altered, except that the reaction with aniline appears to be considerably accelerated. These findings are consistent with the high nucleophilicity of *n*-butylamine compared with aniline, and the low ionizing power of the media. The high reactivity, towards displacement, of aniline in pure aniline, can probably be ascribed to electrophilic catalysis (due to the relatively high acidity of aniline). On the other hand, the reaction course with *n*-butylamine may be notably altered in a solvent of high ionizing power, such as acetonitrile: in this medium, besides the thiourea, a sizeable amount of ammonium thiocyanate is also formed. Thus the more polar solvent favors the displacement reaction which occurs by way of a rate determining ionization.

In the light of these observations it is not surprising that some aspects of the chemical behavior of I have deceived earlier workers.[11]

EXPERIMENTAL

Solvents and chemicals were commercial reagent grade. Trityl chloride was recrystallized before use,[12] m.p. 111–112°.

Infrared spectra. A Perkin-Elmer double beam Model 21 instrument with sodium chloride optics was used. The solvent was carbon tetrachloride.

Sulfur analysis in the adducts of I *with amines.* To the extent that amines react with I giving either displacement or addition to the carbon-nitrogen double bond, sulfur in the reaction product will either be as thiocyanate ion or thiourea. The adducts were analyzed for thiocyanate ion by exaustively extracting their benzene solution with dilute aqueous alkali and titrating the acidified aqueous extract with standard bromate,[13] using naphthoflavone as end point indicator. Thiourea-type sulfur was determined by weighing silver sulfide precipitated from the ethanolic solution of the adducts by means of ammoniacal silver nitrate.[11]

Triphenylmethyl isothiocyanate (I). To a solution of 2.78 g. (0.01 mole) of trityl chloride in 10 ml. of acetone was added a solution of 1.2 g. (0.012 mole) of potassium thiocyanate in 30 ml. of the same solvent. The mixture, after 4 hr. at room temperature was filtered, evaporated to 8 ml. *in vacuo* and cooled to 0° for a few hours. Two and one half grams of colorless crystals, m.p. 136–138°, separated. Additional product (0.2 g.) was recovered by diluting the mother liquor to 50 ml. with water, and recrystallizing the precipitate from acetone; total yield, 90%; m.p. 138–138.5° after recrystallization from acetone. The ultraviolet spectrum of I is characterized by an absorption band with maximum at 254 mμ; ϵ_{max} 2800.[15]

In an experiment, I was heated at 150° for 2 hr. After this treatment neither its melting point (also in mixture with untreated I) nor its infrared spectrum showed any change.

I reacts with allylamine (for reaction conditions see below, under "reaction of I with *n*-butylamine in cyclohexane") to give 1-trityl-3-allylthiourea, m.p. 177–177.5°. This has been compared and shown to be identical (mixed melting point and infrared spectrum) with a sample prepared from tritylamine and allyl thiocyanate.[3]

N-n-butyltritylamine was obtained from trityl chloride and *n*-butylamine (five-fold excess). After recrystallization from ethanol it melted at 52.5–53.5°.

Anal. Calcd. for $C_{23}H_{25}N$: C, 87.57; H, 7.99; N, 4.44. Found: C, 87.77; H, 7.91; N, 4.40.

N-n-butyltritylamine hydrochloride was obtained by bubbling dry hydrochloric acid into a benzene solution of the amine, m.p. 166–167°.

Anal. Calcd. for $C_{23}H_{26}NCl$: N, 3.98; Cl, 10.07. Found: N, 3.95; Cl, 10.21.

Reactions of I *with n-butylamine: 1-trityl-3-n-butylthiourea.* (a) *In cyclohexane.* The amine (0.146 g., 2.0 mmoles) was treated with I (0.301 g., 1.0 mmole) dissolved in cyclohexane (10 ml.). After filtration and washing with petroleum ether (b.p. 40–60°), an adduct was obtained, m.p. 132–134° (0.355 g., 95% yield).

(b) *Without solvent.* In 1 ml. of amine 0.301 g. (1.0 mmole) of I was dissolved and left at room temperature for 12 hr. Evaporation to dryness gave a quantitative yield of an adduct, m.p. 132.5–133.5°.

Both raw materials obtained under (a) and (b) above, were shown not to contain any appreciable amount of ionizable thiocyanate. Two recrystallizations from acetone gave 1-trityl-3-*n*-butylthiourea m.p. 134–134.5°.

Anal. Calcd. for $C_{24}H_{26}N_2S$: C, 76.95; H, 7.00; N, 7.48; S, 8.56. Found: C, 77.36; H, 7.13; N, 7.25; S, 8.44. Analysis of the thioureic sulfur gave 8.49%.

(c) *In acetonitrile.* A solution of 0.301 g. (1.0 mmole) and 0.146 g. (2.0 mmoles) of I in 4 ml. of acetonitrile was heated at 60° for 1 hr. Thereafter, aliquots of the solution were titrated for thiocyanic and thioureic sulfur giving 20% and 78% of the total sulfur respectively. The remaining solution was added to dilute aqueous alkali and benzene. The benzene layer was evaporated to dryness *in vacuo* and the residue extracted with cyclohexane. The solid residue consisted of pure 1-trityl-3-*n*-butylthiourea. From the cyclo-

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(11) H. L. Wheeler, *Am. Chem. Jour.*, **26**, 345 (1901).

(12) C. R. Hanser and B. E. Hudson, Jr., *Org. Syntheses*, Coll. Vol. III, 846 (1955).

(13) F. P. Treadwell and C. Mayr, *Zeit. anorg. Chem.*, **92**, 127 (1915).

(14) H. Salkowski, *Ber.*, **26**, 2498 (1893); *Houben-Weyl, Methoden der Organishen Chemie*, George Thieme, Stuttgart (1953) Band II, 599; G. Losco and C. A. Peri, *Chimica Industria*, **33**, 557 (1951).

(15) The ultraviolet spectrum of I could support the view that I is an isothiocyanate, as can be seen from the close similarity with the spectra of benzyl and benzhydryl isothiocyanates. Like I, the latter show an absorption maximum in the same region with approximately the same intensity. Benzyl and benzhydryl thiocyanates, on the other hand, show, in that region, absorption of lower intensity without any well defined maximum.

hexane solution N-n-butyltritylamine hydrochloride was precipitated by bubbling in dry hydrochloric acid. After washing with boiling acetone the melting point was 165–166°, undepressed on admixture with an authentic sample.

Reaction of I with aniline. (a) *In cyclohexane.* In 5 ml. of cyclohexane containing 0.093 g. (1.0 mmole) of aniline, 0.150 g. (0.5 mmole) of I was dissolved, sealed in a vial and heated at 80° for 5 hr. After this time the solution showed a slight cloudiness which disappeared on extraction with water. The water layer titrated for thiocyanate ion accounted for 2.8% of the total sulfur. No thioureic sulfur was detected in the cyclohexane layer. This, evaporated to dryness, left a residue which, crystallized form acetonitrile, yielded I, m.p. 136–137°. Accounting for the solubility of I in acetonitrile, 93% recovery of unchanged I was obtained.

(b) *Without solvent.* In 1 ml. of aniline 0.301 g. (1.0 mmole) of I was dissolved under gentle heating. After a few hours at room temperature, the excess aniline was removed *in vacuo*. From the residue taken up in ethanol, N-phenyltritylamine (85%) was crystallized, m.p. 149–150° (lit.,[16] m.p. 149–150°).

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(16) M. Gomberg, *Ber.*, **35**, 1829 (1902).

Reaction of Salts of Organophosphorus Acids with Isocyanates[1]

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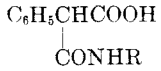
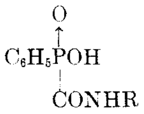
A general analogy in reactivity may be drawn between the α-hydrogen atom of a carboxylic acid and the P-hydrogen atom of a monobasic phosphinic acid, RP(O)H(OH). Reactions involving the carboxyl group and isocyanates are, of course, well known. In addition, Blicke and Zinnes[2] have shown that a carboxylic acid possessing an activated α-hydrogen, such as phenylacetic acid, forms an Ivanov reagent which can be condensed with phenyl isocyanate and the product hydrolyzed to yield N-phenyl phenylmalonamic acid (I). The base-catalyzed condensation involving the phosphorus-hydrogen group in dialkyl phosphonates with isocyanates to give dialkyl carbamoylphosphonates is also well established.[3]

We have found that the tertiary amine salts of phenylphosphinic acid and mandelic acid undergo condensation with isocyanates in the presence of excess amine. Reaction takes place at the P—H and α-O—H groups, respectively, to give salts of the corresponding carbamoyl derivatives (II and III). Tertiary amine half-salts of phosphonic acids condense at the weakly acidic O—H group with the formation of salts of the half-carbamoyl esters (IV), products analogous to those formed from mandelic acid. The acids themselves are readily formed from the salts by treatment with excess mineral acid. These products are obtained in excellent yield, and salt formation therefore appears to be a suitable method for preventing an undesired reaction between an acidic group and an isocyanate. In a single experiment, treatment of phenylphosphinic acid with excess isopropylmagnesium bromide, followed by reaction with phenyl isocyanate, gave a low yield of II after hydrolysis of the bromomagnesium salt. No further investigation of this reaction was carried out, but it is possible that a phosphorus-Ivanov reagent was formed as an intermediate prior to the addition of the isocyanate.



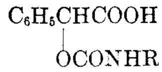
$$\begin{array}{l} C_6H_5CHCOOH \\ \quad | \\ \quad CONHR \end{array}$$

I



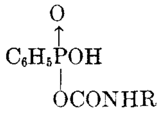
$$\begin{array}{l} \quad O \\ \quad \uparrow \\ C_6H_5POH \\ \quad | \\ \quad CONHR \end{array}$$

II



$$\begin{array}{l} C_6H_5CHCOOH \\ \quad | \\ \quad OCONHR \end{array}$$

III



$$\begin{array}{l} \quad O \\ \quad \uparrow \\ C_6H_5POH \\ \quad | \\ \quad OCONHR \end{array}$$

IV

Triethylamine appears to be the most useful salt-forming reagent in this reaction from the standpoint of ease of handling of the products; N-ethylmorpholine and diethylcyclohexylamine gave hygroscopic salts and no reaction involving the phosphorus compound was observed in the presence of pyridine or under Schotten-Baumann conditions. Anilinium and n-butylammonium salts gave only the urea derivatives. Benzene or other hydrocarbons in which the starting salts, prepared *in situ* by mixing equimolar amounts of acid and amine, are somewhat soluble are suitable solvents; an attempted reaction in acetone with phenylphosphinic acid was unsuccessful. Attempts to prepare the triethylamine salt of phenylphosphinic acid in carbon tetrachloride led to a vigorous reaction from which triethylamine hydrochloride precipitated. It is possible that the trichloromethyl derivative has been formed as appears to be the case with dialkyl phosphonates.[4]

EXPERIMENTAL[5]

Triethylammonium phenyl(phenylcarbamoyl)phosphinate. To a stirred two-phased mixture of 14.2 g. (0.1 mole) of

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(1) Based on a portion of the doctoral thesis submitted to the University of Maryland in June 1959 by Robert B. Fox; presented in part at the 130th meeting of the American Chemical Society at Atlantic City, N. J., September 1956, Abstracts p. 50–0.

(2) F. F. Blicke and H. Zinnes, *J. Am. Chem. Soc.*, **77**, 4849 (1955).

(3) (a) R. B. Fox and D. L. Venezky, *J. Am. Chem. Soc.*, **78**, 1661 (1956). (b) A. N. Pudovik and A. V. Kuznetsova, *Zhur. Obshcheĭ Khim.* **25**, 1369 (1955). (c) A. N. Pudovik, I. V. Konovalova, and R. E. Krivonosova, *Zhur. Obshcheĭ Khim.*, **26**, 3110 (1956). (d) E. C. Ladd and M. O. Harvey, Canadian Patent **509,034** (1955).

(4) F. R. Atherton and A. R. Todd, *J. Chem. Soc.*, 674 (1947).

(5) All melting points were taken in sealed capillary tubes and are corrected; those accompanied by decomposition gave a gas, but sintering did not take place.