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Thiocarbamates and Related Compounds. X.[1] A New Reaction of Thiocyanates

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Thiocyanates react with alcohols and olefins in the presence of sulfuric acid to yield N-substituted thiocarbamates.

In earlier papers of this series[3a–e] we have reported that in many cases a prolonged treatment of thiocyanates with concentrated sulfuric acid at 0 to 5° leads to thiocarbamates (eq. 1). Schmidt and Kollek[4] have used this method to prepare several *n*-alkylthiocarbamates containing an odd number of carbon atoms, beginning with C_{13}.

We have now found that thiocyanates react with alcohols and olefins in the presence of sulfuric acid to give products which, upon hydrolysis, yield N-substituted thiocarbamates (eq. 2).

$$\text{R—SCN} \xrightarrow[(\text{H}_2\text{SO}_4)]{\text{H}_2\text{O}} \text{R—SCONH}_2 \qquad (1)$$

$$\text{R—SCN} \xrightarrow[(\text{H}_2\text{SO}_4)]{\text{R'OH}} \text{R—SCONH—R'} \qquad (2)$$

Under the same conditions the thiocarbamates do not react with alcohols or olefins. Similarly, it has been found[5] that amides do not undergo acid-catalyzed reactions with alcohols or aldehydes. We were able to carry out reaction 2 with the following secondary and tertiary alcohols and olefins which are stable in presence of sulfuric acid: isopropyl alcohol (Tables I and V), *sec*-butyl alcohol (Table II), *t*-butyl alcohol and isobutylene (Table II), cyclohexanol and cyclohexene (Tables III and V), and camphene (Tables IV and V). Simple primary alcohols (methanol, ethanol, etc.) did not react with thiocyanates even after considerably prolonged treatment with sulfuric acid or fuming sulfuric acid. N-Methylol arylamides reacted with the thiocyanates according to equation 3 (Table VI).

$$\text{R—SCN} \xrightarrow[(\text{H}_2\text{SO}_4)]{\text{Ar—CONHCH}_2\text{OH}} \text{R—SCONHCH}_2\text{NHCO—Ar} \qquad (3)$$

It was found that reactions 2 and 3 are applicable to all thiocyanates which yield unsubstituted thiocarbamates as in equation 1.[3a–e]

Primary alkyl thiocyanates reacted with alcohols and olefins to give N-substituted thiocarbamates in good yields in most cases (*cf.* Table III, no. 9–18); 1,4-dithiocyanatebutane and 1,5-dithiocyanatepentane yielded the expected N,N'-substituted bis-thiocarbamates (*cf.* Table V, no. 30–33).

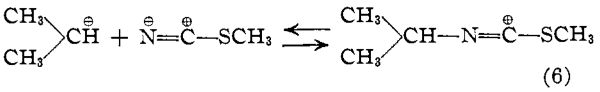
In some cases aryl thiocyanates could be converted to the corresponding N-substituted thiocarbamates in yields higher than those observed for the alkyl thiocyanates. Benzyl thiocyanate and some *ortho*-substituted phenyl thiocyanates (*e.g.*, 2-methyl-4-amino- and 2-nitrophenyl thiocyanate) did not react with alcohols and olefins.[3b,d]

The constitution of the N-substituted thiocarbamates was confirmed by syntheses from S-substituted monothiochlorocarbonates and primary amines (equation 4), and by their behavior in the presence of alkali. All of the N-substituted thiocarbamates and N,N'-disubstituted bis-thiocarbamates described in paper IX of this series[1] gave no depression of mixed melting points with compounds synthesized by the method reported in this paper. The S-alkyl esters of N-*t*-butylmonothiocarbamic acid were easily hydrolyzed by aqueous sodium hydroxide to give *t*-butylamine (equation 5). Upon treatment of thiolesters of N-cyclohexylmonothiocarbamic acid with sodium hydroxide, N,N'-dicyclohexylurea was formed instead of the expected cyclohexylamine.

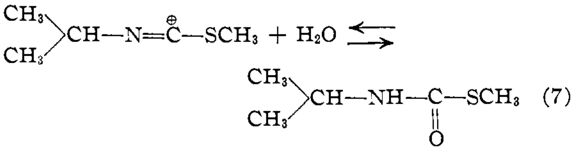
$$\text{R—SCOCl} \xrightarrow[-\text{HCl}]{+\text{R'NH}_2} \text{R—SCONH—R'} \qquad (4)$$

$$\text{R—SCONHC(CH}_3)_3 \xrightarrow[\text{OH}^-]{+\text{H}_2\text{O}} \text{R—SH} + \text{H}_2\text{NC(CH}_3)_3 + \text{CO}_2 \qquad (5)$$

The formation of N-substituted thiocarbamates from alcohols (olefins) and thiocyanate may be formulated as follows (example: isopropyl alcohol–methyl thiocyanate).


(6)

$$(\text{CH}_3)_2\overset{\ominus}{\text{C}}\text{H} + \overset{\ominus}{\text{N}}\text{=}\overset{\oplus}{\text{C}}\text{—SCH}_3 \rightleftarrows (\text{CH}_3)_2\text{CH—N=}\overset{\oplus}{\text{C}}\text{—SCH}_3 \qquad (6)$$


(7)

$$(\text{CH}_3)_2\text{CH—N=}\overset{\oplus}{\text{C}}\text{—SCH}_3 + \text{H}_2\text{O} \rightleftarrows (\text{CH}_3)_2\text{CH—NH—}\underset{\underset{\text{O}}{\|}}{\text{C}}\text{—SCH}_3 \qquad (7)$$

In the presence of sulfuric acid, isopropyl alcohol resp., propylene yield "crypto-carbonium ions" which in turn react with a polar mesomeric form of methyl thiocyanate (equation 6). Subsequent hydrolysis leads to the formation of the thiol ester of N-isopropylmonothiocarbamic acid. Triphenylcarbinol and 1,1-diphenylethanol yield stable carbonium ions in concentrated sulfuric acid (*i*-factor = 4[6]) (equations 9 and 10), but do not react with thiocyanates to give N-substituted thiocarbamates. The postulated reversibility of the reaction of thiocyanates with alcohols and olefins as expressed by equations 6 and 7 is made plausible by the observation that upon addition of 4-chlorophenyl

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[1] Paper IX of series, *Monatsh.*, **84**, 1238 (1953); paper VIII of series, *ibid.*, **84**, 518 (1953).

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[3] (a) I. R. Riemschneider, *Mitt. physiolog.-chem. Inst.*, **R30**, Feb., 1949; (b) III, with F. Wojahn and G. Orlick, THIS JOURNAL, **73**, 5905 (1951); (c) IV, *Chim. e Ind.* (*Milano*), **34**, 353 (1952); (d) VII, *Monatsh.*, **84**, 313 (1953); (e) XI, with O. Lorenz, *Z. Naturforschg.*, **10B**, 787 (1955).

[4] K. Schmidt and P. Kollek-Bös, THIS JOURNAL, **75**, 6067 (1953).

[5] E. E. Magat, *ibid.*, **73**, 1028 (1951); J. J. Ritter and P. P. Minieri, *ibid.*, **70**, 4045 (1948).

[6] A. Hantzsch, *Ber.*, **54**, 2573 (1921); L. P. Hammett and A. J. Deyrup, THIS JOURNAL, **55**, 1900 (1933); V. Gold, V. Hawes and F. L. Tye, *J. Chem. Soc.*, 2167 (1952).

thiocyanate to a solution of S-phenyl N-cyclohexylmonothiocarbamate in sulfuric and glacial acetic acid small amounts of S-4-chlorophenyl N-cyclohexylmonothiocarbamate may be isolated after several hours (equation 8).

$$C_8H_5—SCONH—C_8H_{11} + p\text{-}Cl—C_6H_4—SCN \rightleftarrows p\text{-}Cl—C_6H_4—SCONH—C_8H_{11} + C_6H_5—SCN \quad (8)$$

TABLE I

THIOL ESTERS OF N-ISOPROPYLMONOTHIOCARBAMIC ACID, R–SCONHCH(CH_3)$_2$, PREPARED FROM ISOPROPYL ALCOHOL AND THIOCYANATES, R–SCN

No.	R	Yield,[b] %	Solvent[c]	M.p., °C.	Formula	Nitrogen, % Calcd.	Nitrogen, % Found
1[a]	CH_3	18	H	75	$C_5H_{11}ONS$	10.5	10.4
2[a]	C_2H_5	25	H	60	$C_6H_{13}ONS$	9.5	9.5
3[a]	p-$CH_3C_6H_4$	49	H:B[d]	96–97	$C_{11}H_{15}ONS$	6.7	6.5

TABLE II

THIOL ESTERS OF N-ALKYL MONOTHIOCARBAMIC ACID, R–SCONHR′, PREPARED FROM *sec*- AND *t*-BUTYL ALCOHOL[e] AND THIOCYANATES, R–SCN

No.	R	R′	Yield,[b] %	Solvent[c]	M.p., °C.	Formula	Nitrogen, % Calcd.	Nitrogen, % Found
4[a]	CH_3	$C(CH_3)_3$	25	H	88	$C_6H_{13}ONS$	9.5	9.3
5[a]	C_2H_5	$C(CH_3)_3$	13	H	48	$C_7H_{15}ONS$	8.7	8.8
6[a]	n-C_9H_{19}	C_2H_5-CH-CH_3	98	H	46	$C_{14}H_{29}ONS$	5.4	5.8
7[a]	C_6H_5	$C(CH_3)_3$	40	H	115	$C_{11}H_{15}ONS$	6.7	6.5
8[f]	p-$CH_3C_6H_4$	$C(CH_3)_3$	6	H	117	$C_{12}H_{17}ONS$	6.3	6.3

TABLE III

THIOL ESTERS OF N-CYCLOHEXYLMONOTHIOCARBAMIC ACID, R–SCONHC$_6$H$_{11}$, FROM CYCLOHEXANOL AND THIOCYANATES, R–SCN

No.	R	Yield,[b] %	Solvent[c]	M.p., °C.	Formula	Nitrogen, % Calcd.	Nitrogen, % Found
9[g]	CH_3	45	H	113	$C_8H_{15}ONS$	8.1	7.7
10[g]	C_2H_5	60	H	67	$C_9H_{17}ONS$	7.5	7.6
11[g]	n-C_3H_7	67	H	45	$C_{10}H_{19}ONS$	7.0	7.2
12[g]	n-C_4H_9	66	H	68	$C_{11}H_{21}ONS$	6.5	6.7
13[g]	n-C_5H_{11}	80	H	39	$C_{12}H_{23}ONS$	6.1	6.6
14[h]	n-C_6H_{13}	41	H	36	$C_{13}H_{25}ONS$	5.8	5.9
15[g]	n-C_7H_{15}	88	H	57	$C_{14}H_{27}ONS$	5.5	5.7
16[g]	n-C_8H_{17}	87	H	43	$C_{15}H_{29}ONS$	5.2	5.8
17[g]	n-C_9H_{19}	88	H	66	$C_{16}H_{31}ONS$	4.9	5.2
18[g]	n-$C_{10}H_{21}$	90	H	59	$C_{17}H_{33}ONS$	4.7	4.3
19[a]	C_6H_5	80	H:B[d]	114	$C_{13}H_{17}ONS$	6.0	6.0
20[a]	p-$CH_3C_6H_4$	90	H:B[i]	125	$C_{14}H_{19}ONS$	5.7	6.4
21[a]	p-ClC_6H_4	98	H:B[i]	137	$C_{13}H_{16}ONSCl$	5.2	5.3

TABLE IV

THIOL ESTERS OF N-ISOBORNYLMONOTHIOCARBAMIC ACID, R–SCONHC$_{11}$H$_{17}$, FROM CAMPHENE[k] AND THIOCYANATES, R–SCN

No.	R	Yield,[b] %	Solvent	M.p., °C.	Formula	Nitrogen, % Calcd.	Nitrogen, % Found
22[l]	CH_3	34	H	80	$C_{12}H_{21}ONS$	6.2	6.3
23[l]	C_2H_5	19	H	91	$C_{13}H_{23}ONS$	5.8	6.3
24[l]	n-C_4H_9	66	H	36	$C_{15}H_{27}ONS$	5.2	5.7
25[l]	n-C_5H_{11}	54	H	36–37	$C_{16}H_{29}ONS$	4.9	5.2
26[l]	C_5H_9[m]	76	H	111	$C_{16}H_{27}ONS$	5.0	5.3
27[l]	C_6H_5	85	H	90	$C_{17}H_{23}ONS$	4.9	4.7
28[l]	p-$CH_3C_8H_4$	48	H	75	$C_{18}H_{25}ONS$	4.7	5.2
29[l]	p-ClC_6H_4	51	H	103	$C_{17}H_{22}ONSCl$	4.3	4.8

TABLE V

DITHIOLESTERS OF BIS-N-ALKYL DITHIOCARBAMIC ACID, R′–HNOCS–R–SCONH–R′, FROM ALCOHOLS OR OLEFINS AND 1,4-DITHIOCYANATOBUTANE, 1,5-DITHIOCYANATOPENTANE, OR *p*-DITHIOCYANATOBENZENE (NCS–R–SCN)

No.	R	R′	Yield,[b] %	Solvent[c]	M.p., °C.	Formula	Nitrogen, % Calcd.	Nitrogen, % Found
30[a]	–$(CH_2)_4$–	$CH(CH_3)_2$	48	A	166	$C_{12}H_{24}O_2N_2S_2$	9.6	9.3
31[g]	–$(CH_2)_4$–	C_6H_{11}	87	A	174	$C_{18}H_{32}O_2N_2S_2$	7.5	7.3
32[l]	–$(CH_2)_4$–	$C_{11}H_{17}$	60	H	64	$C_{26}H_{44}O_2N_2S_2$	5.8	5.4
33[g]	–$(CH_2)_5$–	C_6H_{11}	88	A	138	$C_{19}H_{34}O_2N_2S_2$	7.3	7.0
34[a]	–C_6H_4–	$CH(CH_3)_2$	90	A	203–204	$C_{14}H_{20}O_2N_2S_2$	8.9	8.8
35[l]	–C_6H_4–	$C_{11}H_{17}$	64	H:B[i]	173	$C_{28}H_{40}O_2N_2S_2$	5.6	6.1

TABLE VI

THIOL ESTERS OF N-METHYLENEBENZAMIDO-MONOTHIOCARBAMIC ACID, $R{-}SCONHCH_2NHCOC_6H_5$, FROM N-METHYLOLBENZAMIDE AND THIOCYANATES, R–SCN

No.	R	Yield,[b] %	Solvent[c]	M.p., °C.	Formula	Nitrogen, % Calcd.	Nitrogen, % Found
36[a]	n-C_4H_9	22	A	161	$C_{13}H_{18}O_2N_2S$	10.5	10.4
37[a]	C_5H_9[m]	25	A	169	$C_{14}H_{18}O_2N_2S$	10.1	9.8
38[a]	n-C_7H_{15}	50	A	150–151	$C_{16}H_{24}O_2N_2S$	9.1	8.9
39[a]	n-$C_{10}H_{21}$	46	A	143	$C_{19}H_{30}O_2N_2S$	8.0	7.7

EXPLANATIONS OF TABLES I–VI

[a] The reaction was carried out in concentrated sulfuric acid at 0°; reaction time 4 to 6 hours. [b] Crude product. [c] A = ethanol, B = benzene, H = hexane. [d] 1:1. [e] The use of isobutylene instead of *t*-butyl alcohol requires very dilute sulfuric acid (*e.g.*, 6 parts of glacial acetic acid for 1 part of sulfuric acid). Despite the extension of reaction time to 12 hours, the yields were low. See Experimental part. [f] Prepared by treating 4.5 g. of *p*-tolyl thiocyanate (b.p. 116° (10 mm.)) with 5.5 g. of isobutylene in 15 ml. of glacial acetic acid and 2.5 ml. of concentrated sulfuric acid below 10°; reaction time 24 hours; *cf.* also footnote *e*. [g] The reaction was carried out in a mixture of 1 part glacial acetic acid and 4 parts of concentrated sulfuric acid at 0°; reaction time 20–24 hours. See Experimental part. [h] Conditions the same as in footnote g, but reaction time 5 hours. [i] 1:2. [k] Camphene undergoes a rearrangement in acid medium to give thiol esters of N-isobornylmonothiocarbamic acid. [l] The reaction was carried out in a mixture of equal parts of glacial acetic and sulfuric acids at 0°; reaction time 24 hours. Extension of reaction time to 48 hours resulted only in a small increase of the yield, *e.g.*, from 66 to 76% for the ester listed under no. 24. [m] Cyclopentyl.

Experimental Part[7]

Synthesis of N-Substituted Thiol Esters of Monothiocarbamic Acid from Alcohols or Olefins and Thiocyanates. General.—The reaction of thiocyanates with the alcohols and olefins listed in Tables I–VI was accomplished by treatment with concentrated sulfuric acid or sulfuric acid diluted with glacial acetic (or formic acid) for several hours and subsequent hydrolysis by ice-water. In concentrated sulfuric acid the reaction was completed in 4–6 hours in most cases. The addition of glacial acetic or formic acid necessitated an extension of the treatment up to 24 hours. The concentration of sulfuric acid necessary to give a successful reaction (equation 2) varies with the nature of the alcohol. See Table I–VI, footnotes *a*, *g*, *l*.

The reactions have to be carried out between 0–10°, since at higher temperatures the thiocyanates decompose to S,S′-esters of dithiocarbonic acid, sulfides or disulfides.[3d] The side-process of thiocarbamate formation (equation 1), observed in some cases, was suppressed by the addition of excess alcohol. The formation of N-substituted thiocarbamates takes place faster than the formation of unsubstituted thiocarbamates (equation 1), *cf.* note XI.[3e]

S-Methyl N-Isopropylmonothiocarbamate.—To a solution of 1.8 g. (0.03 mole) of isopropyl alcohol in 25 ml. of concentrated sulfuric acid, 2.2 g. (0.03 mole) of methyl thiocyanate (b.p. 130–132°) was slowly added at −5°. The solution became slightly warmer and exhibited a weak yellow coloration. The reaction vessel was kept stoppered at 0–5° for 6 hours and then the contents slowly poured on to 300 g. of finely crushed ice. Colorless crystals were separated by filtration, dried and recrystallized from hexane several times; *cf.* Table I, no. 1.

The same procedure was used to synthesize the thiol esters of N-isopropylmonothiocarbamic acid listed in Table I (no. 2 and 3), and Table V (no. 30 and 34).

S-Phenyl N-*t*-Butylmonothiocarbamate. (a) **From Phenyl Thiocyanate and *t*-Butyl Alcohol.**—To a mixture of concentrated sulfuric acid and 1.85 g. (0.025 mole) of *t*-butyl alcohol was added dropwise with stirring 3.4 g. (0.025 mole) of phenyl thiocyanate (105° (14 mm.)). The stirring was continued for 5 hours with cooling on an ice-bath. The reaction mixture was stirred into 250 ml. of ice-water and yellow crystals separated. After drying, the solid was recrystallized several times from hexane following treatment with activated charcoal; *cf.* Table II, no. 7.

(b) **From Phenyl Thiocyanate and Isobutylene.**—To a mixture of 30 ml. of glacial acetic acid and 5 ml. of 95% sulfuric acid, 7.0 g. (0.051 mole) of phenyl thiocyanate was added dropwise at 0°. At the same time a slow stream of isobutylene was passed through the reaction mixture at a temperature below 10°; during 40 minutes the reaction mixture absorbed 6.0 g. (0.107 mole) of isobutylene. After standing for 24 hours at 10°, the contents of the reaction vessel were poured into 250 ml. of ice-water, and a yellow oil separated. Since the latter could not be caused to crystallize, the product was extracted with ether. The ethereal solution was dried and the ether distilled off. The residue was freed from unreacted phenyl thiocyanate in vacuum; 5.5 g. of phenyl thiocyanate distilled at 1.5 mm. between 71 and 73°. The residue remaining after the distillation was recrystallized from hexane; yield 0.7 g. of N-*t*-butyl ester; *cf.* Table II, no. 7 and footnote *e*.

S-*n*-Butyl N-Cyclohexylmonothiocarbamate.—Cyclohexanol (2.5 g., 0.025 mole) [or cyclohexene (2.05 g., 0.025 mole)] was dissolved in a mixture of 20 ml. of concentrated sulfuric acid and 5 ml. of glacial acetic acid; 2.9 g. (0.025 mole) of *n*-butyl thiocyanate (b.p. 185–187°) was added slowly at −5°. This mixture was kept at 3–5° for 24 hours and subsequently stirred into 200 g. of finely crushed ice. Colorless crystals separated which were filtered off, dried and recrystallized several times from hexane; *cf.* Table III, no. 12.

The use of cyclohexene instead of cyclohexanol led to higher yields of crude products. However, cyclohexanol was preferred since it yielded purer products.

Yield and concentration of sulfuric acid: In experiments with 20 ml. of H_2SO_4 and 0, 10 and 20 ml. instead of 5 ml. of glacial acetic acid, the yield of S-*n*-butyl N-cyclohexylmonothiocarbamate was 85, 45 and 4%, respectively. The reaction mixtures resulting from the last two experiments yielded some unreacted *n*-butyl thiocyanate.

Yield and reaction time: After 6, 12, 18, 24 and 48 hours, respectively, 2.9 g. (0.025 mole) of *n*-butyl thiocyanate and 2.5 g. (0.025 mole) of cyclohexanol in 20 ml. of concentrated sulfuric acid and 5 ml. of glacial acetic acid gave under the above conditions the following yields of S-*n*-butyl N-cyclohexylmonothiocarbamate: 50, 68, 72, 74 and 75%.

Reaction rate and concentration of sulfuric acid: 2.9 g. (0.025 mole) of *n*-butyl thiocyanate and 2.5 g. (0.025 mole) of cyclohexanol were treated with 10 ml. of 95% sulfuric acid and 0, 2.5 and 5 ml. of glacial acetic acid for 5 hours at 0–5°. The respective yields of S-*n*-butyl N-cyclohexylmonothiocarbamate corresponded to 83, 60 and 30%. Unreacted *n*-butyl thiocyanate was recovered from the reaction mixture resulting from the latter experiment.

S-*n*-Butyl-N-methylenebenzamidothiocarbamate.—N-Methylolbenzamide (3.0 g., 0.022 mole, m.p. 100–104°) was added in portions, and 2.5 g. (0.022 mole) of 2-butyl thiocyanate (b.p. 185–187°) added dropwise, to 20 ml. of concentrated sulfuric acid with stirring at −5°. After 5 hours the homogeneous solution was stirred into 200 g. of finely crushed ice. The separation of colorless crystals was observed. The product was filtered off, dried and repeatedly recrystallized from ethyl alcohol; *cf.* Table VI, no. 36.

Alkaline Degradation of N-Substituted Monothiocarbamic Acid Thiol Esters. S-Phenyl N-*t*-Butylmonothiocarbamate.—S-Phenyl N-*t*-butylmonothiocarbamate (1.0 g., 0.0048 mole, m.p. 115°) was treated with 75 ml. of 5% NaOH and refluxed for one hour. Approximately 50 ml. of the reaction mixture was distilled into 20 ml. of 2 *N* HCl. The residual solution was diluted with twice its volume of ethyl alcohol and an excess of a lead acetate solution was added. Upon neutralization of the solution with acetic acid, large amounts of lead mercaptide separated. The solution containing HCl was evaporated to dryness on a

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(7) All melting points are uncorrected.

water-bath. The residue consisted of 0.4 g. (77% yield) of *t*-butylamine hydrochloride, which was identified by its benzoyl derivative (m.p. 134–135°[8]) prepared by the Schotten–Baumann method.

S-*n*-Butyl N-Cyclohexylmonothiocarbamate.—S-Butyl N-cyclohexylmonothiocarbamate (5.4 g., 0.025 mole, m.p. 68°) was treated with 30 ml. of 20% aqueous NaOH and heated under reflux. The N-substituted thiocarbamate was observed to melt. This was followed by a very rapid separation of crystalline N,N′-dicyclohexylurea. After 30 minutes the heating was interrupted and the separated crystals filtered off. The yield of dry crystals was 2.4 g. (86%). The crude product was recrystallized from alcohol, m.p. 233°.[9] Yellow lead mercaptide could be isolated from the aqueous filtrate.

Attempted Reaction of Triphenylcarbinol and 1,1-Diphenylethanol with Thiocyanates.—Triphenylcarbinol dissolved in concentrated sulfuric acid with red coloration, and diphenylethanol with orange coloration, with the formation of triphenylcarbonium and diphenylmethylcarbonium ions, respectively (equations 9 and 10[6])

$$(C_6H_5)_3COH + 2H_2SO_4 \longrightarrow (C_6H_5)_3C^+ + H_3O^+ + 2HSO_4^- \quad (9)$$

$$(C_6H_5)_2COHCH_3 + 2H_2SO_4 \longrightarrow (C_6H_5)_2C^+CH_3 + H_3O^+ + 2HSO_4^- \quad (10)$$

These carbonium ions did not combine with thiocyanates either under the conditions described above for other alcohols, nor when a large excess of thiocyanate (20 ml. of butyl thiocyanate with 0.6 g. of 1,1-diphenylethanol) was used, followed immediately by hydrolysis. Whenever the sulfuric acid was strongly diluted with glacial acetic acid (5 parts glacial acetic acid, 1 part sulfuric acid), no ionization of the carbinols took place and 1,1,3,3-tetraphenylbutene-1 (m.p. 114°) was formed from 1,1-diphenylethanol (reaction time 24 hours).

Anal. Calcd. for $C_{28}H_{24}$: C, 93.3; H, 6.7. Found: C, 93.9; H, 6.6.

In the presence of a large excess of thiocyanate, and following immediate hydrolysis, 1,1-diphenylethanol yielded 1,1,3,3-tetraphenylcyclobutane (m.p. 141°).

Anal. Calcd. for $C_{28}H_{24}$: C, 93.3; H, 6.7. Found: C, 93.4; H, 6.8.

Triphenylmethylcarbinol (1.3 g., m.p. 163°) (or 1.2 g. of 1,1-diphenylethanol of m.p. 88°) was shaken with 10 ml. of carbon tetrachloride and 20 ml. of concentrated sulfuric acid. The CCl_4 was separated from the colored layer and the latter treated dropwise with 0.58 g. of *n*-butyl thiocyanate at −5°. Solid triphenylmethylcarbinol dissolved in sulfuric acid slowly. After stirring for several hours the reaction mixture was poured into water and 1.2 g. (1.0 g.) of unchanged carbinol separated.

Preparation of Thiocyanates.—All of the alkyl mono- and dithiocyanates (with the exception of methyl and ethyl thiocyanate) were prepared from 1 mole of alkyl halide (or alkyl dihalide) and 1.5 moles (or 3 moles) of potassium thiocyanate in boiling alcohol in yields of 79–90%. To get very pure samples, the compounds were subjected to repeated fractional distillation. Boiling points are given in Table I of paper VII of this series.[3d]

The following method for the preparation of phenyl thiocyanate was arrived at: 124 g. of freshly distilled aniline (1.3 moles) was dissolved in a warm mixture of 400 g. of concentrated sulfuric acid and 800 ml. of water. The solution of the aniline salt was stirred under cooling by ice–salt mixture until the temperature fell to +2°, and then was diazotized with 96 g. of sodium nitrite. To the diazonium salt solution, a concentrated aqueous potassium thiocyanate solution, and then a thin paste of cuprous thiocyanate were added. (The latter was prepared by powdering 320 g. of $CuSO_4$, dissolving it in 2 liters of hot water, and adding 600 g. of $FeSO_4$, followed, with cooling, by an aqueous solution of 140 g. of potassium thiocyanate. The mixture was filtered by suction, and the colorless residue made into a paste with water.) The temperature fell from −2 to −8°. Whenever the catalyst was added at higher temperatures, a spontaneous decomposition of the diazonium salt took place at +10°, accompanied by generation of heat. The decomposition could be stopped by adding small pieces of ice. Stirring was continued for 4 hours (during which time the reaction mixture was allowed to reach room temperature) until the evolution of nitrogen, which had already begun at low temperatures, was almost completed. Alternately, the reaction mixture could be kept in a refrigerator overnight. The resulting paste, which appeared slimy when the decomposition was incomplete, was subjected to steam distillation. In working with larger amounts it was profitable to filter part of the liquid free from phenyl thiocyanate. After 5 hours the greater part of the oil (about 90 g.), which was at first colorless, was distilled over. The oil was separated and dried over $CaCl_2$. Aniline (15 g.) was added,[10] the mixture heated to 80–90° and after cooling and scratching with a glass rod, diphenylthiourea separated. After suction filtration, the filtrate was washed twice with 100-ml. portions of 2 *N* HCl and sodium bicarbonate and, finally, with water, and dried over calcium chloride. The phenyl thiocyanate was distilled under the vacuum of an oil-pump. After a small low boiling fraction was collected, at 71–73° (1.5 mm.), colorless product distilled over. It was important to prevent the temperature of the oil-bath from rising above 125°, since above this temperature diphenylthiourea began to distil. Other boiling points: 94–97° (9 mm.), 104–106° (14 mm.); yield about 70 g. (39%). Phenyl thiocyanate is a colorless liquid which becomes intensely yellow upon standing.

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[8] Campbell, *et al.*, THIS JOURNAL, **68**, 140 (1946).

[9] P. Skita and A. Rolfes, *Ber.*, **53**, 1248 (1920).

[10] To separate the phenyl isothiocyanate formed.