hydrolyze.[5] When subjected to the treatment just described they were recovered practically unchanged. The following method gave the best results.

Ten grams of the thiourea, with an exactly equivalent amount of sodium hydroxide, were added to 100 cc. of alcohol and the mixture was refluxed for eight to ten hours. The alcohol was removed by steam and the oil and water remaining were allowed to stand for several days. The crystallized thiourea was filtered off and recrystallized from dilute alcohol. Acidification of the filtrate brought down unchanged starting compound and benzoic acid. The yields were less than 45%.

In the table are listed the new benzoylthioureas prepared. Unless otherwise stated the compounds were hydrolyzed and the products identified by melting points and analyses. To illustrate: α-benzoyl-β-(*o*-chlorophenyl)-thiourea, I, yielded on hydrolysis *o*-chlorophenylthiourea. A few of the monosubstituted thioureas prepared in this way were:

2,5-Dichlorophenylthiourea, m. p. 192–193°.[6] *Anal.* Calcd. for $C_7H_6Cl_2N_2S$: N, 12.68. Found: N, 12.53.

3,4-Dichlorophenylthiourea, m. p. 203–204°.[7] *Anal.* Calcd. for $C_7H_6Cl_2N_2S$: N, 12.68. Found: N, 12.57.

2,6-Dibromo-4-methylphenylthiourea, m. p. 221–222°. *Anal.* Calcd. for $C_8H_8Br_2N_2S$: N, 8.65. Found: N, 8.58.

2,4,6-Tribromophenylthiourea, m. p. 217°. *Anal.* Calcd. for $C_7H_5Br_3N_2S$: N, 7.28. Found: N, 7.26.

***p*-Thioureidobenzoic acid,**[8] m. p. 255°. *Anal.* Calcd. for $C_8H_8N_2O_2S$: N, 14.29. Found: N, 14.24.

Summary

A method of preparing certain mono- and α,α-disubstituted thioureas by the hydrolysis of the corresponding benzoyl derivatives has been described.

A number of new derivatives of benzoyl isothiocyanate are reported. Since these compounds are readily prepared from the amines they will prove useful in their identification.

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[5] Dixon, *J. Chem. Soc.*, **67**, 1044 (1895); **85**, 811 (1904).

[6] *Cf.* Capps and Dehn, THIS JOURNAL, **54**, 4304 (1932).

[7] *Cf.* Dyson, George and Hunter, *J. Chem. Soc.*, **129**, 3042 (1926).

[8] Listed in the Centrallblatt Formel Register for 1927 but *cf.* Dyson, George and Hunter, *ibid.*, **130**, 442 (1927).

LAWRENCE, KANSAS RECEIVED APRIL 9, 1934

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF MCGILL UNIVERSITY]

Tetrachlorophthalimide as a Reagent in Qualitative Organic Analysis

BY C. F. H. ALLEN AND R. V. V. NICHOLLS

Potassium tetrachlorophthalimide has been found to be a suitable reagent to use in the identification of a wide variety of halogen compounds. It is superior to the 3-nitrophthalimide[1] because it is less expensive, and gives higher melting derivatives. It is not limited to the identification of alkyl halides, as are the procedures that make use of the Grignard reagent.[2] The new reagent reacted readily with the alkyl halides, the straight-chain α-halogen esters, the high-boiling chloroformates, the halohydrins, halo ketones, and halo ethers which were studied. With halogen derivatives that boil below 140° the reaction had to be carried out in a sealed tube. The reagent did not combine with α-bromo derivatives of ethyl isobutyrate and isovalerate. With the low-boiling chloroformates, no reaction occurred at the boiling point and explosions resulted when sealed tubes were used. Ethyl β-chloropropionate gave no derivative.

Anomalous results were obtained with three halogen derivatives. γ-Chlorobutyrophenone gave benzoylcyclopropane, on treatment with the reagent. Ethyl bromomalonate lost one carbethoxy group and gave the same derivative that was obtained from ethyl chloroacetate. Bromotricarbomethoxymethane lost all three carbomethoxy groups, and gave the N-methylimide, m. p. 210–211°.

Experimental

Tetrachlorophthalimide.—A finely ground, intimate mixture of 30 g. of tetrachlorophthalic anhydride[3] and 11 g. of U. S. P. ammonium carbonate in a 400-cc. Pyrex beaker, covered by a piece of cardboard or a watch glass with a hole through which passes a heavy glass stirring rod, is slowly heated with occasional stirring until the mass becomes molten. After cooling, the solid is pulverized and recrystallized from 150 cc. of nitrobenzene, washing with ether to remove the excess solvent. The imide thus prepared weighs 27 g. (91% yield) and melts at 336–337°.

Anal. Calcd. for $C_8HO_2NCl_4$: N, 4.9; Cl, 49.8. Found: N, 5.1, 5.1; Cl, 49.7.

Potassium Derivative.—A solution of 1.6 g. of potassium hydroxide in 20 cc. of dry methyl alcohol is added to a solution of 8 g. of the imide in 200 cc. of boiling dioxane (dried by refluxing over sodium). After cooling rapidly,

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[1] Sah and Ma, *Ber.*, **65**, 1630 (1932).

[2] Marvel, Gauerke and Hill, THIS JOURNAL, **47**, 3009 (1925); Hill, *ibid.*, **50**, 167 (1928); Gilman and Furry, *ibid.*, **50**, 1214 (1928); Schwartz and Johnson, *ibid.*, **53**, 1063 (1931).

[3] The necessary tetrachlorophthalic anhydride was supplied by the National Aniline and Chemical Co., and is gratefully acknowledged.

TABLE I

N-SUBSTITUTED TETRACHLOROPHTHALIMIDES

Substituent	M. p., °C.	Formula	Crystal form	Chlorine, % Calcd.	Chlorine, % Found
CH_3	210–211	$C_9H_3O_2NCl_4$	Needles[d]	47.5	47.3
C_2H_5	192–193	$C_{10}H_5O_2NCl_4$	Plates[d]	45.4	
n-C_4H_9	153–154	$C_{12}H_9O_2NCl_4$	Plates[b]	41.6	41.6
n-C_5H_{11}	145–146	$C_{13}H_{11}O_2NCl_4$	Needles[d]	40.0	40.3
i-C_5H_{11}	170–171	$C_{13}H_{11}O_2NCl_4$	Leaflets[b]	40.0	40.2
n-C_6H_{13}	150–151	$C_{14}H_{13}O_2NCl_4$	Leaflets[b]	38.5	38.8
n-C_7H_{15}	145–146	$C_{15}H_{15}O_2NCl_4$	Leaflets[b]	37.1	36.8
n-$C_{16}H_{33}$	129–130	$C_{24}H_{33}O_2NCl_4$	Leaflets[d]	27.9	27.7
—$COOC_4H_9$-n	151–152	$C_{13}H_9O_4NCl_4$	Leaflets[a]	37.0	36.6
—$CH_2COOC_2H_5$	180–181	$C_{12}H_7O_4NCl_4$	Needles[d]	38.3	38.2
—$CH_2COOC_4H_9$-n	116–117	$C_{14}H_{11}O_4NCl_4$	Needles[d]	35.6	35.9
—$CH(CH_3)COOCH_3$	165–166	$C_{12}H_7O_4NCl_4$	Plates[b]	38.3	38.2
—$CH(CH_3)COOC_2H_5$	159–160	$C_{13}H_9O_4NCl_4$	Rods[e]	36.9	36.6
—$CH(C_2H_5)COOC_2H_5$	116–117	$C_{14}H_{11}O_4NCl_4$	Rods[e]	35.6	35.4
—$CH(n\text{-}C_3H_7)COOC_2H_5$	113–114	$C_{15}H_{13}O_4NCl_4$	Plates[a]	34.4	34.4
—$CH(n\text{-}C_4H_9)COOC_2H_5$	122–123	$C_{16}H_{15}O_4NCl_4$	Plates[a]	33.3	33.6
—$CH_2CH_2OCOCH_3$	168–169	$C_{12}H_7O_4NCl_4$	Plates[d]	38.3	38.1
—CH_2CH_2OH	208–209	$C_{10}H_5O_3NCl_4$	Prisms[c]	43.2	43.0
—$CH_2CH_2OC_6H_5$	155–156	$C_{16}H_9O_3NCl_4$	Rods[c]	35.1	35.0
—$CH_2CH_2CH_2OH$	165–166	$C_{11}H_7O_3NCl_4$	Prisms[c]	41.4	41.1
—$CH_2CH_2CH_2Br$	164–165	$C_{11}H_6O_2NCl_4Br$	Prisms[e]	54.7	54.4[f] 54.7[g]
—$CH_2CH_2CH_2CN$	194–195	$C_{12}H_6O_2N_2Cl_4$	Leaflets[c]	40.4	40.8
—$CH_2COC_6H_5$	258–259	$C_{16}H_7O_3NCl_4$	Plates[d]	35.2	35.3
—$CH_2CH_2COC_6H_5$	205–206	$C_{17}H_9O_3NCl_4$	Leaflets[d]	34.1	33.7

[a] From methyl alcohol. [b] From ethyl alcohol. [c] From acetone. [d] From chloroform, poured into two volumes of methyl alcohol. [e] From dioxane, poured into two volumes of methyl alcohol, and water added. [f] Derivative prepared from trimethylene dibromide. [g] Same, from chlorobromide.

the precipitated salt is filtered by suction and dried in a vacuum desiccator. The salt probably contains some inorganic base, since the analyses for potassium do not always check in different preparations, and vary with the method of drying, but it is suitable for forming derivatives as described below. It is a slightly yellowish powder.

The sodium derivative was prepared in an analogous manner, or, less conveniently, in liquid ammonia, but is less reactive.

Anal. Calcd. for $C_8O_2NCl_4Na$: Na, 7.5. Found: lot A, Na, 8.0; lot B, Na, 7.5; lot C, Na, 7.8.

Preparation of Derivatives.—(A) From halogen compounds with boiling points above 140°. A mixture of 5 g. of the halide (if a liquid, 5 cc., dried over calcium chloride) and 2 g. of the potassium salt, in a small flask under a reflux condenser bearing a calcium chloride tube, was heated in an oil-bath at 200° for ten hours. The mixture was then extracted with three 5-cc. portions of boiling chloroform, filtered, and the filtrate evaporated to dryness. For recrystallization (decolorizing by animal charcoal if deeply colored) alcohol, acetone, dioxane or chloroform were used as indicated. If the boiling point of the halogen compound is above 170°, the minimum amount that can be identified is 1.5 g.; with all others, 5 g. is necessary. (B) If the boiling point is below 140°, the same quantities were heated in a sealed tube for six hours at 200°; the remainder of the procedure was carried on as in A.

The reagent gave gums with epichlorhydrin and bromostyrene.

The 2,4-dinitrophenylhydrazone of γ-chlorobutyrophenone, when prepared in the usual manner,[4] crystallized in vermilion prisms from benzene; m. p. 167°.

Anal. Calcd. for $C_{16}H_{15}O_4N_4Cl$: N, 15.5; Cl, 9.8; mol. wt., 362. Found: Cl, 10.2; mol. wt., 362.

Summary

An improved method for preparing tetrachlorophthalimide is described.

The potassium derivative of the latter reacts with many halogen compounds to give substituted tetrachlorophthalimides which are useful for purposes of identification.

MONTREAL, CANADA RECEIVED APRIL 11, 1934

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[4] Experimental work by Dr. Raymond Boyer in this Laboratory, 1932.