precipitation. The derivatives were purified from hot absolute ethanol. In preparing the derivatives of nitro esters heat should be applied slowly.

From Esters of Dibasic Acids.—To 0.04 mole of the reagent was added 0.02 mole of ester and refluxed 1 hour. When the resulting solution was cooled (ice-bath), the derivative precipitated and was purified from hot absolute ethanol.

Preparation of the Quaternary Salts.—To 0.05 g. of the N-(β-aminoethyl)-morpholide dissolved in the minimum amount of anhydrous methanol was added 1 ml. of methyl iodide and the mixture gently refluxed for 2 hours. The quaternary salt was precipitated by the dropwise addition of ethyl ether to the chilled reaction mixture and purified from anhydrous methanol.

TABLE I

DATA ON N-(β-AMINOETHYL)-MORPHOLIDES

Ester	M.p., °C. (cor.)	Formula	N Analyses, % Calcd.	Found
n-Butyl formate	Oil	....	...	...
Ethyl acetate	95.2	$C_8H_{16}O_2N_2$	16.28	16.21
iso-Propenyl acetate	95.2	$C_8N_{16}O_2N_2$	16.28	16.32
Benzyl acetate	95.2	$C_8H_{16}O_2N_2$	16.28	16.26
Ethyl phenylacetate	88.9	$C_{14}H_{20}O_2N_2$	11.29	11.31
Ethyl propionate	85	$C_9H_{18}O_2N_2$	15.05	15.17
Ethyl butyrate	Oil	....	...	...
Ethyl valerate	Oil	....	...	...
Ethyl enanthate	Oil	....	...	...
Ethyl caprylate	59	$C_{14}H_{28}O_2N_2$	10.93	10.97
Ethyl pelargonate	61.3	$C_{15}H_{30}O_2N_2$	10.37	10.39
Ethyl caprate	60.1	$C_{16}H_{32}O_2N_2$	9.85	9.93
Ethyl undecylate	55.5	$C_{17}H_{34}O_2N_2$	9.39	9.52
Ethyl laurate	68.5	$C_{18}H_{36}O_2N_2$	8.97	8.91
Ethyl myristate	76	$C_{20}H_{40}O_2N_2$	8.23	8.14
Ethyl palmitate	81	$C_{22}H_{44}O_2N_2$	7.60	7.60
Methyl stearate	85	$C_{24}H_{48}O_2N_2$	7.07	7.05
Ethyl benzoate	123.4	$C_{13}H_{18}O_2N_2$	11.96	11.90
Ethyl *o*-benzoylbenzoate	150.2	$C_{20}H_{22}O_3N_2$	8.28	8.28
Ethyl cinnamate	121.9	$C_{15}H_{20}O_2N_2$	10.77	10.85
Ethyl anisate	130.6	$C_{14}H_{20}O_3N_2$	10.60	10.47
Methyl salicylate	Oil	....	...	...
Ethyl *p*-hydroxybenzoate	184	$C_{13}H_{18}O_3N_2$	11.20	11.06
Ethyl anthranilate	126	$C_{13}H_{19}O_2N_3$	16.86	17.04
Ethyl *p*-aminobenzoate	155.6	$C_{13}H_{19}O_2N_3$	16.86	16.74
n-Butyl phthalate	124	$C_{20}H_{30}O_4N_4$	14.36	14.26
Ethyl *o*-nitrobenzoate	Oil	....	...	...
Ethyl *m*-nitrobenzoate	131.9	$C_{13}H_{17}O_4N_3$	15.05	14.91
Ethyl *p*-nitrobenzoate	186.3	$C_{13}H_{17}O_4N_3$	15.05	15.02
Ethyl 3,5-dinitrobenzoate	189.5	$C_{20}H_{18}O_{11}N_6$	16.20	16.08
Ethyl oxalate	170	$C_{14}H_{26}O_4N_4$	17.83	17.94
Ethyl malonate	120.5	$C_{15}H_{28}O_4N_4$	17.07	17.18
Ethyl succinate	174	$C_{16}H_{30}O_4N_4$	16.37	16.20
Ethyl glutarate	152.7	$C_{17}H_{32}O_4N_4$	15.73	15.69
Ethyl adipate	165	$C_{18}H_{34}O_4N_4$	15.13	14.99
Ethyl pimelate	137.9	$C_{19}H_{36}O_4N_4$	14.58	14.72
Ethyl suberate	157.2	$C_{20}H_{38}O_4N_4$	14.07	13.92
Ethyl azelate	141.3	$C_{21}H_{40}O_4N_4$	13.59	13.68
Ethyl sebacate	146	$C_{22}H_{42}O_4N_4$	13.14	13.08

TABLE II

METHIODIDES OF N-(β-AMINOETHYL)-MORPHOLIDES

N-(β-Aminoethyl)-morpholide of ester	M.p., °C. (cor.)	Formula	N Analyses, % Calcd.	Found
Methyl formate	134	$C_8H_{17}O_2N_2I$	9.33	9.40
Ethyl benzoate	182	$C_{14}H_{21}O_2N_2I$	7.44	7.37
Ethyl butyrate	216 dec.	$C_{12}H_{25}O_2N_2I$	7.86	7.69
Ethyl valerate	217.5 dec.	$C_{13}H_{27}O_2N_2I$	7.56	7.57
Ethyl enanthate	218.5 dec.	$C_{14}H_{29}O_2N_2I$	7.29	7.13

CHAPEL HILL, N. C. RECEIVED NOVEMBER 6, 1950

[CONTRIBUTION FROM THE VENABLE CHEMICAL LABORATORY OF THE UNIVERSITY OF NORTH CAROLINA]

2,4-Dinitrothiophenol as a Reagent for the Characterization of Organic Halogen Compounds

BY R. W. BOST, P. K. STARNES[1] AND E. L. WOOD[2]

2,4-Dinitrothiophenol was studied with many diverse types of halogen compounds in order to determine its suitability as a reagent for their characterization. The alkyl 2,4-dinitrophenyl sulfides are easily formed, readily purified, are stable, possess excellent crystalline structure, and have sharp melting points. In addition, the sulfide may be converted to the corresponding sulfone thus affording a double check on the compound. 2,4-Dinitrothiophenol is an excellent reagent for the characterization of organic halogen compounds.

In previous work done in this laboratory[3,4] 2,4-dinitrochlorobenzene was shown to be an excellent reagent for mercaptans. It is readily apparent that sodium 2,4-dinitrothiophenolate will give the same derivative with ethyl bromide that 2,4-dinitrochlorobenzene gives with sodium ethyl mercaptide.

It seemed desirable therefore to study the reactivity of 2,5-dinitrothiophenol with various halogen compounds and determine its suitability for characterizing these substances. Approximately sixty different halogen compounds were studied. The primary and secondary alkyl iodides, bromides, and chlorides react with the reagent. In many cases it is unnecessary to heat the reactants. In addition to the alkyl halides, the reagent is useful for characterizing a wide variety of halogen compounds such as halohydrins, halonitriles, haloamides, haloesters, haloketones and haloethers. Vicinal and disjunctive halogen compounds react to give the desired derivatives. In general, aryl halides are inert under the conditions studied except in those cases where there is pronounced activation of the halogen atom. The tertiary and the alkylidene halides do not react with the reagent to give the desired product.

The oxidation of the alkyl 2,4-dinitrophenyl sulfide to the sulfone is easily accomplished except

---

(1) Standard Oil Co. of N. J., Elizabeth, N. J.

(2) Dept. of Chemistry, University of Tennessee, Knoxville, Tenn.

(3) R. W. Bost, J. O. Turner and R. D. Norton, THIS JOURNAL, 54, 1985 (1932).

(4) R. W. Bost, J. O. Turner and M. W. Conn, *ibid.*, 55, 4956 (1933).

TABLE I

DATA ON 2,4-DINITROPHENYL SULFIDES AND SULFONES

Halide used	Reaction conditions[a] Min.	Sulfides M.p., °C.	Sulfides Formula	Sulfides Analyses, S, % Calcd.	Sulfides Analyses, S, % Found	Sulfones M.p., °C.	Sulfones Formula	Sulfones Analyses, S, % Calcd.	Sulfones Analyses, S, % Found
Methyl iodide	5 (S)	128				185(189.5)			
Ethyl iodide	30 (S)	115				156(160)			
n-Propyl bromide	10 (H)	84				126(127.5)			
n-Butyl bromide	10 (H)	66				92			
Isobutyl bromide	24 hr. (S)	76				105			
s-Butyl bromide	24 hr. (S)	66	$C_{10}H_{12}O_4N_2S$	12.48	12.78	120	$C_{10}H_{12}O_6N_2S$	11.12	10.87
n-Amyl bromide	10 (H)	80				83			
n-Hexyl bromide	10 (H)	74				97			
n-Heptyl bromide	10 (H)	82				101			
n-Octyl bromide	10 (H)	78				98			
n-Nonyl bromide	15 (H)	86				92			
n-Decyl bromide	15 (H)	85				93			
n-Dodecyl bromide	20 (H)	89				101			
n-Tetradecyl bromide	20 (H)	94	$C_{20}H_{32}O_4N_2S$	8.09	7.84	104.5	$C_{20}H_{32}O_6N_2S$	7.48	7.16
n-Hexadecyl bromide	20 (H)	95				105			
Benzyl chloride	60 (S)	130				178(182.5)			
β-Phenylethyl bromide	15 (H)	89.5				133			
Ethylenebromohydrin	30 (H)	100							
Propylenebromohydrin	30 (H)	93	$C_9H_{10}O_5N_2S$	12.42	12.22				
Allyl bromide	Immed.	71							
Methyl chloroacetate	30 (S)	96				141.5	$C_9H_8O_8N_2S$	10.54	10.65
Ethylene dibromide	10 (H)	248(Di)[b]							
β-Chloropropionitrile	24 hr. (S)	121	$C_9H_7O_4N_3S$	12.66	12.68	152	$C_9H_7O_6N_3S$	11.24	11.32
sym-Dichloromethyl ether	Immed.	163(A)	$C_{14}H_{10}O_9N_4S_2$	14.49	14.63				
Phenacyl bromide	Immed.	171.5(Bz)	$C_{14}H_{10}O_5N_2S$	10.07	9.96	181	$C_{14}H_{10}O_7N_2S$	9.15	9.32
Chloromethyl ether	Immed.	Unstable							
Methylene iodide	60 (S)	207(Di)	$C_{13}H_8O_8N_4S_2$	15.55	15.30				
sym-Dichloroacetone	Immed.	195(Di)	$C_{15}H_{10}O_9N_4S_2$	14.11	13.82				
β-Bromopropionic acid	72 hr. (S+)[c]	157(Di)	$C_9H_8O_6N_2S$	11.77	11.74				
2-Bromoöctane		Oil							
n-Propyl chloride	30 (H)	84							
Isopropyl chloride	60 (H)	No reacn.							
n-Butyl chloride	30 (H)	66							
n-Amyl chloride	30 (H)	80							
Isoamyl chloride	30 (H)	80							
n-Hexyl chloride	30 (H)	74							
Chloroacetal	30 (H)	Oil							
Chloroacetonitrile	5 (H)	141(Bu)	$C_8H_5O_4N_3S$	13.40	13.33	142	$C_8H_5O_6N_3S$	11.82	11.50
Chloroacetamide	30 (H)	188(Bu)	$C_8H_7O_5N_3S$	12.47	12.47	187	$C_8H_7O_7N_3S$	11.09	10.88
o-Chlorobenzyl chloride	10 (S)	144(Bu)	$C_{13}H_9O_4N_2ClS$	9.87	10.02	211	$C_{13}H_9O_6N_2ClS$	8.96	8.70
γ-Chlorobutyronitrile	20 (H)	115	$C_{10}H_9O_4N_3S$	12.00	11.92	125	$C_{10}H_9O_6N_3S$	10.71	10.43
β-Phenoxy-*β*′-chloroethyl ether	30 (H)	94	$C_{16}H_{16}O_6N_2S$	8.80	8.85	86	$C_{16}H_{16}O_8N_2S$	8.09	8.06
2,4-Dinitrochlorobenzene	Immed.	195(Bu)	$C_{12}H_6O_8N_4S$	8.75	8.72				
Phenoxyethyl bromide	12 hr. (S)	145	$C_{14}H_{12}O_5N_2S$	10.01	10.46	124	$C_{14}H_{12}O_7N_2S$	9.10	8.94
γ-Phenoxypropyl bromide	40 (S)	105	$C_{15}H_{14}O_5N_2S$	9.59	9.42	137	$C_{15}H_{14}O_7N_2S$	8.75	8.61
δ-Phenoxybutyl bromide	12 hr. (S)	75	$C_{16}H_{16}O_5N_2S$	9.20	9.00	Oil			
β-Bromoethyl ether	12 hr. (S)	66	$C_{10}H_{12}O_5N_2S$	11.77	12.26	99	$C_{10}H_{12}O_7N_2S$	10.54	10.56
Isoamyl bromide	30 (S)	80	$C_{11}H_{14}O_4N_2S$	11.86	11.74	124	$C_{11}H_{14}O_6N_2S$	10.61	10.69
Isopropyl bromide	60 (S)	95				140			

[a] S = allowed to stand at room temperature; H = heated to 70° on steam-bath. [b] Recrystallization solvents: Bu = 1-butanol, Di = dioxane, Bz = benzene, A = acetone. [c] + = Dioxane was used as a reaction solvent.

in the case of the halohydrins, haloketones, haloethers, *β*-bromopropionic acid, methylene and ethylene halides where side reactions predominate.

In a few cases identical melting points were obtained; however, a mixed melting point showed a marked depression in all such cases.

Ethanol may be used as a reaction solvent; however, butyl carbitol gives a higher yield and a purer product and was used in all cases except where indicated in Table I.

The alkyl 2,4-dinitrophenyl sulfides and sulfones, in general, may be purified from ethanol. For sulfides melting above 120°, 1-butanol was found to be a superior solvent for purification.

Experimental

2,4-Dinitrothiophenol.—This reagent was synthesized by the method of Wilgerodt,[5] with slight modifications. Yields of 90 to 95% of a product melting at 130–131° were obtained. During the preparation and filtration the temperature was kept below 15°. Since the moist mercaptan is susceptible to oxidation, rapid filtration (avoiding prolonged aspiration) is advisable. The moist filter cake was then dried in a vacuum desiccator over phosphorus pentoxide. The dry mercaptan showed no change in melting point after several months.

Preparation of Alkyl 2,4-Dinitrophenyl Sulfides. (A) General Method Using Alkyl Bromides and Iodides.—To 5.0 g. (0.025 mole) of 2,4-dinitrothiophenol in 50 cc. of butyl carbitol was added 5 cc. of 28% potassium hydroxide. To the deep red solution was added the organic halogen compound. In many cases there was an immediate reaction, otherwise the mixture was heated to 70° (steam-bath). Usually from 10 to 30 minutes heating was sufficient. In some cases better results were obtained if the reaction mixture was allowed to stand at room temperature for the period indicated in Table I. After the reaction was complete, the cooled mixture was diluted with several volumes of ice-water, and the precipitated alkyl 2,4-dinitrophenyl sulfide recrystallized from a suitable solvent. Ethanol, 1-butanol, dioxane, benzene and acetone were used as solvents for recrystallization (see table).

(B) General Method Using Alkyl Chlorides.—Five grams (0.025 mole) of 2,4-dinitrothiophenol, 50 cc. of butyl

---

(5) Wilgerodt, *Ber.*, **17**, 352 (1884)

carbitol, 5 cc. of 28% potassium hydroxide, 3 g. of potassium iodide and 0.025 mole of the organic chlorine compound were added in the order given, shaking after each addition. The mixture was heated for the length of time indicated in the table. The alkyl 2,4-dinitrophenyl sulfide was isolated and purified as described in (A).

Alkyl 2,4-Dinitrophenyl Sulfones.—The alkyl 2,4-dinitrophenyl sulfides were converted to the corresponding sulfones by the permanganate method of Bost, Turner and Norton.[6]

---

[6] Bost, Turner and Norton, THIS JOURNAL, **54**, 1985 (1932).

CHAPEL HILL, N. C. RECEIVED NOVEMBER 4, 1950

[CONTRIBUTION FROM NAUGATUCK CHEMICAL DIVISION OF UNITED STATES RUBBER CO.]

The Preparation of 2-Vinylthiazoles

BY D. L. SCHOENE

A general method for the preparation of a series of polymerizable, new 2-vinylthiazoles has been developed. The procedure involves the condensation of α-chloroaldehydes and ketones with α-benzoxythiopropionamide to give the corresponding 2-(α-benzoxyethyl)-thiazoles which are pyrolyzed to yield the vinyl compounds. A 2-isopropenylthiazole was also prepared by an analogous synthesis.

In spite of the current interest in polymerizable vinyl compounds and the ease of synthesis of the thiazole ring, no record has been found of the preparation of 2-vinylthiazoles.[1]

A practical process for the synthesis of these compounds has now been developed. A series of 2-(α-benzoxyethyl)-thiazoles was prepared by the general method of Olin and Johnson[2] and these, or the corresponding alcohols,[3] on pyrolysis gave the desired 2-vinylthiazoles. Pyrolysis was accomplished at atmospheric pressure by dropping the liquid benzoates or alcohols through a vertical Pyrex tube filled with alumina and heated to 400–550°.[4] Yields of 75% were obtained in the better runs.

A synthesis of 2-isopropenyl-4-methylthiazole was also accomplished using similar reactions. In this case the condensation between α-benzoxy-α-methyl thiopropionamide and chloroacetone yielded directly 25% of the isopropenylthiazole together with 48% of the expected benzoxyisopropylthiazole, subsequent pyrolysis of which proceeded smoothly.

The unsaturated thiazoles were characterized by copolymerizing them with butadiene.[5] A homopolymer of 4-methyl-2-vinylthiazole was also prepared.

Experimental

2-(α-Benzoxyethyl)-thiazoles.—These compounds were prepared according to the general procedure of Olin and Johnson[2] by adding the appropriate chloroaldehyde or ketone to a benzene solution of α-benzoxythiopropionamide.[6] The reactions were exothermic and slow additions were required for the larger runs. After two hours of reflux, dilute sodium hydroxide was added to neutrality and the organic layer was distilled. Crude yields were nearly quantitative. Yields of distilled products and physical constants are given in Table I.

In the initial work with chloroacetal and chloroacetaldehyde monohydrate, 95% ethanol was used as the solvent in accordance with the procedure of the original investigators. Reaction appeared complete but the products were resinous and could not be distilled without decomposition. The substitution of benzene as the solvent reduced tar formation and was used throughout this work with satisfactory results. Since this work was completed, Erlenmeyer[1c] has reported an 86% yield using chloroacetaldehyde with absolute ethanol as the solvent. His product had a broad distillation range.

2-Vinylthiazoles.—(A) A 20-mm. o.d. Pyrex tube was packed to a depth of 20 cm. with 4–8 mesh activated alumina and supported vertically in an electrically heated furnace. The temperature was measured by a thermocouple held against the outer surface of the tube; the temperature in the reaction area undoubtedly was somewhat lower. A slow stream of nitrogen was passed through the tube while the liquid benzoates were added at the rate of 60–75 drops per minute. The pyrolysates were condensed in an ice-cooled receiver containing 1 g. of phenyl-β-naphthylamine. Initial pyrolysates were colorless but often darkened due to carbonization as the runs progressed. The products were dissolved in ether, extracted with alkali, dried over potassium carbonate and vacuum-distilled through a short packed column.

Tight packing of the pyrolysis tube was found to be responsible for most of the carbonization losses. When carbonization was severe, the purity of the distilled product, as well as yield, suffered. Essential data and yields, based on the amount of ester consumed, are given in Table II.

(B) Pyrolysis of 2-(α-benzoxyethyl)-4-methylthiazole and the parent alcohol were also accomplished by distilling from fused potassium bisulfate according to the procedure of Brooks.[7] Two grams of potassium bisulfate and 74 g. of the alcohol gave a 19% yield of the vinylthiazole, while 30 g. each of the benzoate and potassium bisulfate gave a 49% yield. A high proportion of non-distillable residue makes the method of less interest than the alumina process.

2-Isopropenyl-4-methylthiazole.—α-Benzoxy-α-methylthiopropionamide was obtained in 82% yield as a white crystalline solid on adding[6] hydrogen sulfide to the benzoate of acetone cyanohydrin, m.p. 41.5°; b.p. 105–111° (1 mm.) (lit.,[8] m.p. 35–36°, 36–37°). To a solution of 382 g. (1.7 moles) of this thioamide in benzene was added 160 g. (1.73 moles) of chloroacetone. After two hours of reflux the product was distilled, yielding 59 g. (25%) of 2-isopropenyl-4-methylthiazole, b.p. 41–45° (1 mm.), $n^{30}\mathrm{D}$ 1.5395, as well as 210 g. (48%) of the expected 2-(α-benzoxyisopropyl)-4-methylthiazole, b.p. 110–130° (1 mm.).

Anal. Calcd. for C_7H_9NS: S, 23.02. Found: S, 22.80.

A 200-g. portion of the ester was pyrolyzed at 500° yielding 46 g. (43%) of 2-isopropenyl-4-methylthiazole, b.p. 41–45° (1 mm.), $n^{25}\mathrm{D}$ 1.5345.

Anal. Calcd. for C_7H_9NS: S, 23.02. Found: S, 21.41.

The product formed by pyrolysis, although of the same boiling range, was less pure than that formed during the condensation.

---

[1] Regarding unsaturated thiazoles see: (a) E. R. Buchman and E. M. Richardson, THIS JOURNAL, **67**, 395 (1945); (b) G. B. Bachman and L. V. Heisey, *ibid.*, **71**, 1985 (1949); (c) H. Erlenmeyer, *et al.*, *Helv. Chim. Acta*, **31**, 1142 (1948).

[2] J. F. Olin and T. B. Johnson, THIS JOURNAL, **53**, 1473 (1931). See also reference (1c).

[3] Olin and Johnson[2] attempted without success the dehydration of 2-(α-hydroxyethyl)-4-phenylthiazole using phosphorus pentoxide in benzene.

[4] Recent work has indicated that reduced pressure will permit the use of lower temperatures with more satisfactory results.

[5] D. L. Schoene, U. S. Patent 2,515,318 (1950).

[6] J. F. Olin and T. B. Johnson, *Rec. trav. chim.*, **50**, 72 (1931).

[7] L. A. Brooks, THIS JOURNAL, **66**, 1295 (1944).

[8] Beilstein First Supplement to Fourth Edition, Vol. IX, p. 89.