

Evaporation of the chloroform extracts yielded a small quantity of residue which on recrystallization from acetone and chloroform (5:1 by volume) by the addition of ether yielded 0.050 g. of triphenylsulfonium bromide, m.p. 284–285°. The melting point was unchanged on admixture with an authentic sample of triphenylsulfonium bromide.

Triphenylsulfonium Hydroxide.—One gram (1.00 g.) of triphenylsulfonium bromide was dissolved in 100 ml. of water and treated with a gram equivalent of moist silver oxide. The solution was stirred for 3 days at room temperature in the dark. The mixture was filtered and the filtrate was observed to be strongly basic to litmus. Evaporation of the aqueous solution yielded a strongly basic oil which could not be induced to crystallize. On standing at room temperature the material lost its basicity and yielded a brown amorphous gum from which nothing could be identified.

Diphenyl-*p*-tolylsulfonium Bromide.—Diphenyl-*p*-tolylsulfonium bromide was prepared in the same manner as described above for the preparation of triphenylsulfonium bromide by the Grignard reaction. The Grignard reagent prepared from 77.8 g. of *p*-tolyl bromide and 7.74 g. of magnesium was refluxed with 10 g. of diphenyl sulfoxide at 70° for 24 hours. Hydrolysis of the reaction mixture with dilute aqueous hydrobromic acid yielded 6.01 g. (34.1% yield) of the sulfonium bromide, m.p. 214.5–217°. Pure material was obtained on further recrystallization from acetone and chloroform (5:1 by volume) by the addition of ether. Pure material melted at 224–225°.

Anal. Calcd. for $C_{18}H_{17}SBr$: C, 63.87; H, 4.79. Found: C, 64.29; H, 5.03.

The compound was readily soluble in chloroform, water, ethanol and pyridine but insoluble in acetone, benzene and ether. The compound gave a blue precipitate with the cobaltous ammonium thiocyanate complex.³

Diphenyl-*m*-tolylsulfonium Bromide.—Diphenyl-*m*-tolylsulfonium bromide was prepared by a procedure similar to the one described above for the preparation of triphenyl-

sulfonium bromide. The Grignard reagent was prepared from 77.8 g. of *m*-tolyl bromide and 7.74 g. of magnesium and treated with 10.0 g. of diphenyl sulfoxide at 70° for 48 hours. The yield of the sulfonium bromide after one recrystallization from acetone and chloroform (5:1 by volume) by the addition of ether was 4.12 g. (23.4% yield), m.p. 209–223°. Pure material was obtained on further recrystallizations from the same solvent system.

Anal. Calcd. for $C_{18}H_{17}SBr$: C, 63.87; H, 4.79. Found: C, 63.99; H, 5.09.

The compound was soluble in water, chloroform, ethanol and pyridine but insoluble in ether, benzene or acetone. It gave a blue precipitate with the cobaltous ammonium thiocyanate complex.³

Diphenyl-2,4-xylylsulfonium Bromide.—The procedure was similar to the one employed in the preparation of triphenylsulfonium bromide given above. The Grignard reagent was prepared from 44.0 g. of 2,5-dimethylbromobenzene and 6.10 g. of magnesium and treated with 7.20 g. of diphenyl sulfoxide for 75 hours at 70°. The crude material, 1.60 g. (12.1% yield), m.p. 225–230°, was recrystallized from acetone and chloroform (5:1 by volume) by the addition of ether to yield pure material, m.p. 239–239.5° dec.

Anal. Calcd. for $C_{20}H_{19}SBr$: C, 64.69; H, 5.16. Found: C, 64.44; H, 5.35.

The compound was soluble in water, chloroform, ethanol and pyridine but insoluble in acetone, benzene or ether. The substance gave a blue precipitate with the cobaltous ammonium thiocyanate complex in aqueous solution.³

Absorption Spectra.—Measurements were made in 95% ethanol solution with a Beckman spectrophotometer, model DU. Since the data for triphenylsulfonium bromide and triphenylsulfonium nitrate were practically identical within experimental error only one curve for these two substances is shown.

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

N-(β -Aminoethyl)-morpholine as a Reagent for the Characterization of Esters

BY R. W. BOST AND LEO V. MULLEN, JR.

The suitability of N-(β -aminoethyl)-morpholine as a reagent for esters was investigated. It was found to be an excellent reagent for esters of aromatic acids and aliphatic dicarboxylic acids.

The structure of N-(β -aminoethyl)-morpholine suggested that it might be an excellent reagent for the characterization of esters. It possesses an amino group located at a favorable position to give added basicity to the morpholine molecule. The compound also contains a tertiary nitrogen atom which should enable the molecule to undergo quaternization with ease, thus affording a second derivative of the ester in doubtful cases, or where the N-(β -aminoethyl)-morpholide is an oil. In addition, N-(β -aminoethyl)-morpholine is inexpensive, stable, and a good solvent (b.p. 202°) for esters.

In this work thirty nine esters representing the aliphatic and aromatic monocarboxylic acids and the aliphatic dicarboxylic acids were studied. It was found to be an excellent reagent for the characterization of aromatic esters and aliphatic dicarboxylic esters, giving rise to good yields of pure, crystalline, stable derivatives whose melting point spread was wide enough to insure complete identification. Although the melting point spread of the derivatives of the aliphatic monocarboxylic esters was not as great as desired, with the exception of ethyl caprate, pelargonate, and caprylate, identi-

fication is afforded by the reagent. Where the N-(β -aminoethyl)-morpholide was an oil, it was converted to the quaternary salt with methyl iodide. All melting points are corrected. The N-(β -aminoethyl)-morpholine used in this work was obtained from the Carbide and Carbon Chemicals Corporation, Charleston, W. Va. It was redistilled and the portion boiling at 202° was used.

Experimental

Preparation of N-(β -Aminoethyl)-morpholides. (A) From Aliphatic Esters.—To 0.02 mole of N-(β -aminoethyl)-morpholine was added 0.02 mole of ester and the reaction refluxed 3 hours. Upon cooling (ice-bath) the resulting solution, the N-(β -aminoethyl)-morpholide precipitated. Precipitation is facilitated by addition of 5 ml. of ligroin to the cold reaction mixture of those aliphatic esters containing less than eleven carbon atoms. The derivatives of esters containing more than eleven carbon atoms were easily recrystallized from ethanol, while those of eleven or fewer carbon atoms were best purified from hot ligroin.

The derivatives of low boiling esters of formic, acetic, and propionic acids were best prepared by refluxing the reagent and ester with 5 ml. of ethylene glycol for 3 hours, followed by removal of the glycol under reduced pressure.

(B) From Aromatic Esters.—To 0.02 mole of reagent was added 0.02 mole of ester and refluxed 2 hours. Upon cooling the resulting solution (ice-bath), the product precipitated. Addition of 5 ml. of ether to cold mixture aids

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
<i>n</i> -Butyl formate	Oil
Ethyl acetate	95.2	C ₈ H ₁₆ O ₂ N ₂	16.28	16.21
<i>iso</i> -Propenyl acetate	95.2	C ₈ H ₁₆ O ₂ N ₂	16.28	16.32
Benzyl acetate	95.2	C ₈ H ₁₆ O ₂ N ₂	16.28	16.26
Ethyl phenylacetate	88.9	C ₁₄ H ₂₀ O ₂ N ₂	11.29	11.31
Ethyl propionate	85	C ₉ H ₁₈ O ₂ N ₂	15.05	15.17
Ethyl butyrate	Oil
Ethyl valerate	Oil
Ethyl enanthate	Oil
Ethyl caprylate	59	C ₁₄ H ₂₈ O ₂ N ₂	10.93	10.97
Ethyl pelargonate	61.3	C ₁₅ H ₃₀ O ₂ N ₂	10.37	10.39
Ethyl caprate	60.1	C ₁₆ H ₃₂ O ₂ N ₂	9.85	9.93
Ethyl undecylate	55.5	C ₁₇ H ₃₄ O ₂ N ₂	9.39	9.52
Ethyl laurate	68.5	C ₁₈ H ₃₆ O ₂ N ₂	8.97	8.91
Ethyl myristate	76	C ₂₀ H ₄₀ O ₂ N ₂	8.23	8.14
Ethyl palmitate	81	C ₂₂ H ₄₄ O ₂ N ₂	7.60	7.60
Methyl stearate	85	C ₂₄ H ₄₈ O ₂ N ₂	7.07	7.05
Ethyl benzoate	123.4	C ₁₃ H ₁₈ O ₂ N ₂	11.96	11.90

Ethyl <i>o</i> -benzoyl-benzoate	150.2	C ₂₀ H ₂₂ O ₄ N ₂	8.28	8.28
Ethyl cinnamate	121.9	C ₁₅ H ₂₀ O ₂ N ₂	10.77	10.85
Ethyl anisate	130.6	C ₁₄ H ₂₀ O ₃ N ₂	10.60	10.47
Methyl salicylate	Oil
Ethyl <i>p</i> -hydroxybenzoate	184	C ₁₃ H ₁₈ O ₃ N ₂	11.20	11.06
Ethyl anthranilate	126	C ₁₃ H ₁₉ O ₃ N ₂	16.86	17.04
Ethyl <i>p</i> -aminobenzoate	155.6	C ₁₃ H ₁₉ O ₂ N ₃	16.86	16.74
<i>n</i> -Butyl phthalate	124	C ₂₀ H ₃₀ O ₄ N ₂	14.36	14.26
Ethyl <i>o</i> -nitrobenzoate	Oil
Ethyl <i>m</i> -nitrobenzoate	131.9	C ₁₃ H ₁₇ O ₄ N ₃	15.05	14.91
Ethyl <i>p</i> -nitrobenzoate	186.3	C ₁₃ H ₁₇ O ₄ N 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 ₄ N ₄	17.83	17.94
Ethyl malonate	120.5	C ₁₅ H ₂₈ O ₄ N ₄	17.07	17.18
Ethyl succinate	174	C ₁₆ H ₃₀ O ₄ N ₄	16.37	16.20
Ethyl glutarate	152.7	C ₁₇ H ₃₂ O ₄ N ₄	15.73	15.69
Ethyl adipate	165	C ₁₈ H ₃₄ O ₄ N ₄	15.13	14.99
Ethyl pimelate	137.9	C ₁₉ H ₃₆ O ₄ N ₄	14.58	14.72
Ethyl suberate	157.2	C ₂₀ H ₃₈ O ₄ N ₄	14.07	13.92
Ethyl azelate	141.3	C ₂₁ H ₄₀ O ₄ N ₄	13.59	13.68
Ethyl sebacate	146	C ₂₂ H ₄₂ O ₄ N 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 ₈ H ₁₇ O ₂ N ₂ I	9.33	9.40
Ethyl benzoate	182	C ₁₄ H ₂₁ O ₂ N ₂ I	7.44	7.37
Ethyl butyrate	216 dec.	C ₁₂ H ₂₅ O ₂ N ₂ I	7.86	7.69
Ethyl valerate	217.5 dec.	C ₁₃ H ₂₇ O ₂ N ₂ I	7.56	7.57
Ethyl enanthate	218.5 dec.	C ₁₄ H ₂₉ O ₂ N ₂ I	7.29	7.13

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[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. STARNES¹ AND E. L. WOOD²

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, halo ketones 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

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