[Contribution from the Department of Chemistry, Haverford College]

3,5-DINITROBENZOATES AND THEIR 1-NAPHTHYLAMINE ADDITION COMPOUNDS. II. PREPARATION FROM ALKYL HALIDES[1]

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The formation of 3,5-dinitrobenzoates from alkyl halides by reaction with silver 3,5-dinitrobenzoate was first suggested by Mulliken (1). The halide was reacted with the silver salt in 95% ethanol, the solvent evaporated, and the derivative extracted from the metallic salts with ether. The reaction gave good yields for primary and secondary iodides and for benzyl chloride. It failed for other chlorides and tertiary iodides and gave poor yields with bromides. Tseng and Chu (2) suggested benzene as solvent and reported obtaining a derivative from diphenylmethyl chloride. Furter (3) identified alkyl groups linked to oxygen and nitrogen by conversion to the alkyl iodide with hydriodic acid followed by heating of the iodide with silver 3,5-dinitrobenzoate in ether in a sealed tube.

Since iodide ion accelerates the reaction of alkyl chlorides and bromides with several reagents (4–6) due to the intermediate formation of the alkyl iodide, a method was developed for conversion of chlorides and bromides to the alkyl iodides, the latter being treated with silver 3,5-dinitrobenzoate without prior isolation from the reaction mixture. Conant, Kirner, and Hussey (7) used sodium iodide in acetone for the halide conversion. Methyl ethyl ketone was found preferable as a solvent because of its higher refluxing temperature. Sodium iodide is still sufficiently soluble in this solvent while sodium bromide and chloride, formed in the reaction, are almost insoluble and are filtered off before the silver salt is added. Rice and Pettit (6) suggested dimethylformamide as a suitable solvent for alkyl halide reactions, but in spite of its higher refluxing temperature it gave lower yields than did methyl ethyl ketone.

The following alkyl halides were characterized as 3,5-dinitrobenzoates or their 1-naphthylamine addition compounds (8): *Chlorides: n*-butyl, *n*-hexyl, *n*-heptyl, *n*-decyl, *n*-dodecyl, isoamyl, benzyl; *bromides:* ethyl, *n*-propyl, *n*-butyl, *n*-amyl, *n*-hexyl, *n*-octyl, *n*-decyl, isopropyl, isobutyl, isoamyl; *iodides:* (no halide exchange reaction) methyl, ethyl, *n*-amyl, *n*-heptyl, isopropyl, isobutyl.

sec-Butyl iodide gave a very low yield of the 1-naphthylamine addition compound, while isobutyl chloride, secondary butyl chloride, and cyclohexyl chloride gave no yield. Most secondary and tertiary halides decomposed yielding 3,5-dinitrobenzoic acid instead of the derivative. Since these react more rapidly than primary halides by S_N1 reactions, they were treated directly with silver 3,5-dinitrobenzoate without solvent at room temperature. Tertiary chlorides, bromides,

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and iodides, and *sec*-butyl and isopropyl iodide reacted rapidly, giving good yields after one minute. *sec*-Butyl and *sec*-octyl bromide gave small yields after 30 minutes. *sec*-Butyl chloride and cyclohexyl chloride failed to yield a derivative.

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EXPERIMENTAL

Silver 3,5-dinitrobenzoate. This salt was prepared by the method of Furter (3), and was powdered and stored in a dark bottle.

General method for preparing derivatives. Iodides. A mixture of 1 ml. of alkyl iodide, 2 g. of silver 3,5-dinitrobenzoate, 10 ml. of methyl ethyl ketone, and 10 ml. of ethanol was refluxed for one half-hour. The solvent was distilled off and the derivative was extracted with three 10-ml. portions of ether. The ether was distilled and the alkyl 3,5-dinitrobenzoate was recrystallized from ethanol. Yields in g. of recrystallized alkyl 3,5-dinitrobenzoate were: Methyl 0.36, ethyl 0.44, *n*-amyl 0.49, *n*-heptyl 0.54, isopropyl 0.20, isobutyl 0.25, *sec*-butyl very low yield of addition compound; benzyl chloride treated by this procedure gave 0.35 g.

Chlorides and bromides. To 1 ml. of the alkyl chloride or bromide was added 10 ml. of a sodium iodide solution in methyl ethyl ketone (10 g./100 ml.) and the mixture was refluxed for one hour. The precipitate of sodium chloride or bromide was filtered, and 10 ml. of ethanol and 2 g. of silver 3,5-dinitrobenzoate were added to the filtrate. This reaction mixture was refluxed for one hour and the dinitrobenzoate was extracted as before. Yields in g., *Chlorides:* *n*-propyl 0.08, *n*-butyl 0.10, *n*-hexyl 0.15, *n*-heptyl 0.16, *n*-decyl 0.18, *n*-dodecyl 0.15, isoamyl 0.08, benzyl 0.20, isobutyl (refluxed four hours with sodium iodide) 0.01, *sec*-butyl no derivative after four hours refluxing; *Bromides:* ethyl 0.26, *n*-propyl 0.51, *n*-butyl 0.51, *n*-amyl 0.55, *n*-hexyl 0.60, *n*-octyl 0.63, *n*-decyl 0.59, isopropyl 0.09, isobutyl 0.21, isoamyl 0.60.

Direct reaction with the silver salt. Secondary and tertiary halides. If an alkyl halide treated by the above procedures gave no yield or if it formed 3,5-dinitrobenzoic acid (m.p. 202°, giving red coloration with dilute base) it was tested with a 2% ethanolic silver nitrate solution (1 drop of alkyl halide to 2 ml. of solution). An immediate precipitate at room temperature indicates a tertiary halide or a secondary iodide (9). To 1 ml. of the halide was added one gram of silver 3,5-dinitrobenzoate and the mixture was shaken for one minute. The derivative was extracted with three 10-ml. portions of ether and the ether extract was washed with a 1 *M* NaOH solution until the wash solution no longer turned red. To increase the yield, 1-naphthylamine (0.05–0.1 g.) was added to the ether solution, the ether was evaporated, and the 1-naphthylamine addition compound of the alkyl 3,5-dinitrobenzoate was recrystallized from ethanol or ligroin. Yields of 3,5-dinitrobenzoate: *tert*-amyl chloride 0.03 g., *tert*-butyl bromide 0.03 g. Yields of 1-naphthylamine addition compounds: *tert*-butyl chloride 0.06, *tert*-amyl chloride 0.22, *tert*-butyl bromide 0.08, *sec*-butyl iodide 0.15, *tert*-butyl iodide 0.06.

If silver nitrate did not form an immediate precipitate with the alkyl halide at room temperature, the same procedure was followed except that the mixture was allowed to stand for 30 minutes instead of being shaken for one minute. Yields: *sec*-butyl bromide 0.02 g., *sec*-octyl bromide 0.03 g.

SUMMARY

A method for preparing 3,5-dinitrobenzoates from alkyl chlorides, bromides, and iodides is described.

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