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Substitutive Chlorination of Naphthalene Esters

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Naphthalene esters are easily chlorinated by molecular chlorine in chlorinated organic solvents in the presence of small amounts of ferric chloride. This method is a convenient synthesis of highly chlorine-substituted naphthalene acids and esters which heretofore have been difficult to prepare.

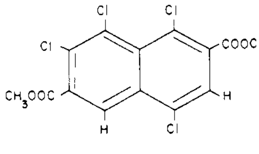
THE DIRECT CHLORINATION of aromatic acids, including naphthalenecarboxylic acids, is difficult. Naphthalene carboxylate esters are easily chlorinated by molecular chlorine in the presence of small amounts of ferric chloride, and this is the easiest method for synthesizing chlorinated naphthalenecarboxylic acids and their derivatives.

To substitute three or more chlorines on the rings of naphthalenecarboxylic acids requires rather drastic conditions. By using concentrated sulfuric acid as solvent, 1,8-naphthalic anhydride has been chlorinated in good yield to tetrachloro-1,8-naphthalic anhydride in the presence of ferric sulfate (*3*). On the other hand, alkylaromatic hydrocarbons readily undergo nuclear chlorination under much milder conditions. They are generally reacted with molecular chlorine in a chlorinated organic solvent, such as carbon tetrachloride, in the presence of various catalysts, such as metallic salts, pyridine, and iodine (*1, 5, 6, 7, 10, 11*). Under these latter conditions, naphthalenecarboxylic acids are not chlorinated, but the methyl esters undergo ready nuclear chlorination using similar conditions.

Compounds with ester groups on both rings, such as 2,6-dicarbomethoxynaphthalene, as well as compounds with an ester group on only one ring, such as α- and β-methyl naphthoates, can be chlorinated by this method. The ester is dissolved in a chlorinated organic solvent, such as carbon tetrachloride, tetrachloroethylene or 1,1,2,2-tetrachloroethane, containing ferric chloride and iron and the solution is treated with molecular chlorine. The extent of chlorine substitution depends on several factors, including solvent and time and temperature of reaction. It becomes increasingly difficult to substitute chlorines on the rings when a number of positions are occupied, though most difficulty is encountered in substituting the last available position. Low boiling solvents, such as carbon tetrachloride, have poor solubility properties for the esters and the extent of chlorine substitution is low. Tetrachloroethylene is a good solvent for the reaction, but is not inert to chlorine under the conditions used and long reaction times are necessary for extensive substitution. By using 1,1,2,2-tetrachloroethane as solvent, highly substituted materials can be obtained in a short reaction time with efficient use of chlorine. The product is worked up by steam distillation to remove solvent and the water insoluble product collected and purified by either distillation or crystallization from solution.

Unless complete substitution was achieved, mixtures of chlorinated products were obtained in most experiments. Starting material was not recovered in any experiments, so that crude yields were high. Results for typical experiments are given in Table I. The products were identified by infrared and nuclear magnetic resonance (NMR) spectroscopy and by elemental analyses.

No study was made of the position of the chlorines on chlorinated α- and β-methyl naphthoates. They are probably mixtures. NMR spectroscopy gave good evidence for the structure of the tetrachloro-2,6-dicarbomethoxynaphthalene. This material was the easily crystallized material from a gross reaction mixture. The remainder of the product was an oily material that could not be induced to crystallize. Since it had the same number of aromatic hydrogens (two) as the easily crystallized compound, it was assumed to be a mixture of isomeric tetrachloro-2,6-dicarbomethyoxynaphthalenes. The NMR spectrum of the crystallized tetrachloro compound showed that the ester groups were in similar environments and that the hydrogens were different and not coupled. There are nine possible tetrachloro isomers. Three were ruled out because they have equivalent hydrogens and five more were ruled out because the ester groups were in different environments, one being flanked by two chlorines and the other flanked by either one or no chlorines. Therefore, it was concluded that the material was 1,4,7,8-tetrachloro-2,6-dicarbomethoxynaphthalene (I). This compound has not been reported previously in the literature. It has been found to render flame retardant properties to reinforced plastics (*2*). Hexachloro-2,6-dicarbomethoxynaphthalene also has not been reported in the literature.



H TYPE	CHEMICAL SHIFT
-COOCH$_3$	4.02 ppm
AROMATIC	7.67 ppm 8.50 ppm

I

Under prolonged chlorination conditions, the naphthalene esters are degraded to chlorocarbon compounds. Octachloronaphthalene, 1,4-dihydronaphthalene (isolated as the quinone) and decachloroindan have been isolated from the

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Table I. Chlorination of Naphthalene Esters[a]

Naphthalene Ester	Solvent	Reaction Temp., ° C.	Reaction Time, Hours	Isolated Product Yield, %	Product(s)
α-Methyl naphthoate	Tetrachloroethylene	110	3.0	85	Trichloro-α-methyl naphthoate
α-Methyl naphthoate	Tetrachloroethylene	110	6.5	83	Mixture tetrachloro- and pentachloro-α-methyl naphthoates
α-Methyl naphthoate	Tetrachloroethylene	110	22.0	62	Mixture pentachloro- and hexachloro-α-methyl naphthoates
β-Methyl naphthoate	Carbon tetrachloride	67	20.0	87	Trichloro-β-methyl naphthoate
2,6-Dicarbomethoxynaphthalene	1,1,2,2-Tetrachloroethane	110	2.2	55	1,4,7,8,-Tetrachloro-2,6-dicarbomethoxynaphthalene
2,6-Dicarbomethoxynaphthalene	Tetrachloroethylene	110	22.0	44	Hexachloro-2,6-dicarbomethoxynaphthalene

[a] Chlorine flow rate was 1.68 moles Cl_2 per mole ester per hour.

reaction mixtures. Benzene derivatives have been observed to undergo degradation under chlorination reaction conditions. Dealkylation has been observed in the case of chlorinating 2,3,4,5,6-pentachloro-1-ethylbenzene in boiling carbon tetrachloride; the products were found to be hexachlorobenzene and ethyl chloride (*5*). Hexachlorobenzene has also been observed as a product when phthalic anhydride was chlorinated at 170° to 265° C. in the presence of ferric chloride (*4*). The naphthalene esters probably are first decarboxylated to octachloronaphthalene, and 1,4-dihydronaphthalene and decachloroindan are formed from octachloronaphthalene.

EXPERIMENTAL

NMR work was done with a Varian A-60 instrument using tetramethylsilane (TMS) as internal standard. A Perkin-Elmer Model 521 Grating Infrared Spectrophotometer was used for IR work. All melting points were determined on a Mel-Temp capillary melting point apparatus and are uncorrected. Elemental analyses were performed by Huffman Laboratories, Inc., Wheat Ridge, Colo., and by Galbraith Laboratories, Inc., Knoxville, Tenn.

General Chlorination Procedure. The ester, catalyst, and solvent were placed in a three-necked flask equipped with condenser, stirrer, thermometer, and gas inlet tube. The mixture was heated to desired temperature and chlorine passed through a $^3/_{32}$-in. flowmeter at a flow rate of 1.68 moles Cl_2 per mole ester per hour. After completion of the reaction, the mixture was steam distilled to remove solvent. The product was collected and purified by distillation or crystallization.

Chlorination of α-Methyl Naphthoate. α-Methyl naphthoate (25.0 grams) was chlorinated according to the general procedure in 250 ml. of tetrachloroethylene for 3 hours at 110° C. Powdered iron and ferric chloride (1.0 gram each) were used as catalysts. After removing solvent by steam distillation, the residue was distilled under 3 mm. pressure to give 32.9 grams of a yellow liquid boiling at 200–10° C. The NMR spectrum of this compound showed a ratio of 1.33:1 aromatic to methyl hydrogens. Infrared spectrum showed the presence of an ester group and elemental analysis confirmed the material to be trichloro-α-methyl naphthoate.

Anal. Calcd. for $C_{12}H_7Cl_3O_3$: C, 49.78; H, 2.44; Cl, 36.73. Found: C, 49.84; H, 2.95; Cl, 36.77.

α-Methyl naphthoate (25 grams) was chlorinated in tetrachloroethylene at 110° C. for 22 hours as described above. After removing solvent, the product (43 grams) was dissolved in chloroform and a solid (11.0 grams) precipitated by adding methanol. The solvent was stripped to give an oily residue weighing 32 grams. This latter material was distilled at 3 mm. pressure to give 21.9 grams of a yellow, viscous oil boiling at 205–220° C. NMR spectra of the solid and liquid indicated that both materials were mixtures of pentachloro and hexachloro-α-methyl naphthoates, with the hexachloro ester predominating as shown by elemental analyses.

The same mixture of products was obtained by chlorinating α-methyl naphthoate in 1,1,2,2-tetrachloroethane at 110° C. for 4.75 hours.

Chlorination of β-Methyl Naphthoate. β-Methyl naphthoate (10 grams) was chlorinated in 150 ml. of carbon tetrachloride at 67° C. for 20 hours in the presence of 1.0 gram each of powdered iron and ferric chloride. The reaction mixture was filtered to remove catalyst. The filtrate was washed with water, dried, and evaporated to give 13.3 grams of solid product. The solid was recrystallized from hexane to give trichloro β-methyl naphthoate melting at 148–149° C.

Anal. Calcd. for $C_{12}H_7Cl_3O_2$: C, 49.78; H, 2.44; Cl, 36.73. Found: C, 49.62; H, 2.37; Cl, 36.54.

Chlorination of β-methyl naphthoate in tetrachloroethylene at 110° C. for 6 hours gave an oily liquid which could be distilled, but would not crystallize. It had an average of five chlorines per molecule as shown by NMR and chlorine analysis.

Chlorination of 2,6-Dicarbomethoxynaphthalene. 2,6-Dicarbomethoxynaphthalene (24.4 grams) was chlorinated for 7 hours in 300 ml. of tetrachloroethylene at 110° C. according to the general procedure. The product (32.7 grams) recovered by filtration after steam distillation of the solvent was recrystallized several times from chloroform-methanol mixture to give 21.2 grams of solid melting at 140–141.5° C. The NMR spectrum of the compound showed it to be a tetrachloro-2,6-dicarbomethoxynaphthalene having a single chemical shift of 4.02 p.p.m. (TMS = 0.00 p.p.m.) for the carbomethoxy methyl hydrogens and two chemical shifts for aromatic hydrogens at 7.67 and 8.50 p.p.m. It was assigned the structure 1,4,7,8-tetrachloro-2,6-dicarbomethoxynaphthalene.

Anal. Calcd. for $C_{14}H_8Cl_4O_4$: C, 44.01; H, 2.11; Cl, 37.12. Found: C, 44.12; H, 2.27; Cl, 36.94.

The same product was obtained in a 2.25-hour reaction in 1,1,2,2-tetrachloroethane at 110° C.

In a 22-hour reaction under the conditions described above for the tetrachloroethylene experiment, hexachloro-2,6-dicarbomethoxynaphthalene was isolated and purified in 44% yield. It was a crystalline solid melting at 167.5–169° C. (recrystallized from hexane).

Anal. Calcd. for $C_{14}H_6Cl_6O_4$: C, 37.29; H, 1.34; Cl, 47.18. Found: C, 37.40; H, 160; Cl, 47.12.

Octachloronaphthalene. β-Methyl naphthoate (10 grams) was chlorinated in 250 ml. of tetrachloroethylene for 20 hours at 110° C. in the presence of 2.0 grams of ferric chloride and 1.0 gram of iron powder. After steam distillation to remove solvent, a brown solid (20.0 grams) was collected which on recrystallization from chloroform gave yellow needles (13.0 grams) melting at 196–198° C. It was identified as octachloronaphthalene by comparison of its IR spectrum with that reported in the literature (*8*).

Perchloro-1,4-dihydronaphthalene. α-Methyl naphthoate (10 grams) was chlorinated in 200 ml. of 1,1,2,2-tetrachloroethane at 110° C. for 6 hours in the presence of 1.0 gram each of ferric chloride and iron powder. After removing solvent by steam distillation, the solid product (21.0 grams) collected by filtration was dissolved in chloroform and precipitated with methanol to give 5.8 grams of a dark brown solid. After several recrystallizations from tetrachloroethylene a light yellow solid melting at 216–218° C. was obtained. The NMR spectrum of the material showed the absence of hydrogens. The IR spectrum showed carbonyl absorption typical of a quinone [IR in KBr: ν(cm.$^{-1}$)—1818(w), 1678(s), 1588(s), 1505(m), 1353(s), 1279(s), 1217(s), 1127(s), 944(m), 915(s), 895(m), 816(m), 730(s), 600(s)]. The material analyzed for hexachloro-1,4-naphthoquinone whose melting point has been reported as 216–217° C. (*12*).

Anal. Calcd. for $C_{10}Cl_6O_2$: C, 32.92; Cl, 58.31. Found: C, 32.96; Cl, 58.46. Hexachloro-1,4-naphthoquinone was presumably formed from perchloro-1,4-dihydronaphthalene by hydrolysis during the workup.

Decachloroindan. α-Methyl naphthoate (25 grams) was chlorinated in 250 ml. of 1,1,2,2-tetrachloroethane at 140° C. for 22 hours. The crude product was dissolved in chloroform and precipitated with methanol to give 18.6 grams of a solid which on recrystallization from hexane melted at 133–135° C. One reported melting point for decachloroindan is 136–137° C. (*9*). The infrared spectrum of this material was typical of a perhalogenated hydrocarbon without functional groups [IR in KBr: ν(cm.$^{-1}$)—1375(s), 1262(m), 1210(m), 1170(m), 985(m), 868(m), 800(m), 748(s), 637(s), 562(m)]. The elemental analysis agreed with the decachloroindan structure.

Anal. Calcd. for C_9Cl_{10}: C, 23.36; Cl, 76.64. Found: C, 23.43; Cl, 76.58.

Decachloroindan was the only product isolated when 2,6-dicarbomethoxynaphthalene was chlorinated in hexachlorobutadiene-1,3 at 160° C. for 8 hours.

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Halogenated Phthalimidoacetic Acids

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Twelve halogenated phthalimidoacetic acids have been prepared by condensation of glycine with halogenated phthalic acids or anhydrides at 170° to 185° C.

THE PHTHALOYLATION of an amino acid is conveniently achieved by condensation of the amino acid with the phthalic anhydride at 170° to 185° C. This reaction may be accomplished either by fusion of an equimolar mixture of the reactants (*1*) (Method A), or by reaction in a suitable solvent, such as nitrobenzene (*2, 3*) (Method B). The phthalic acid may be used instead of the anhydride (*2, 6*). Twelve halogenated phthalimidoacetic acids, nine of which had not previously been reported, have been prepared from glycine by these methods. The choice of halogenated phthalic acid or anhydride as the starting material was determined by which compound was more readily accessible. The experimental results for the method giving the best yield of each halogenated phthalimidoacetic acid are summarized in Table I.

Comparison of the ultraviolet absorption spectra of these compounds in alcoholic and in aqueous base solutions showed that basic conditions produced the hypsochromic and hypochromic effects characteristic of saponification of the imide ring (*2, 3*). Table II summarizes the spectral