methyl ether of phenoldiphenein is formed by treatment of the latter with methyl iodide and potassium hydroxide and by the reaction of diphenic anhydride with anisole in the presence of anhydrous aluminum chloride. The presence of two acidic hydrogen atoms in phenoldiphenein is shown by analysis of the potassium salt. These transformations indicate that the structure of phenoldiphenein is similar to that of phenolphthalein and that the sodium salt of phenoldiphenein contains a quinoid ring. The groups in this salt give it a light yellow instead of a red color.

When dimethyl phthalate and diethyl phthalate are heated with acetic anhydride, each ester remains unchanged. Under similar conditions the monomethyl and mono-ethyl esters of phthalic acid yield phthalic anhydride. Phthalamic acid is converted into phthalimide and phthalic anhydride by treatment with acetic anhydride, and phthalamide gives *o*-cyanobenzamide and phthalimide.

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PREPARATION OF SOLID DERIVATIVES FOR THE IDENTIFICATION OF ETHERS

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Ethers are usually described as inert compounds; the carbon–oxygen bond is firmly held, and drastic treatments, such as heating with hydriodic acid or anhydrous aluminum chloride, are generally employed to split ethers. These methods are not suitable for the preparation of solid derivatives for the identification of small amounts of ethers. Recently it was shown that ethyl 3,5-dinitrobenzoate is formed by the treatment of the dinitrobenzoyl chloride with pure, dry ethyl ether in the presence of anhydrous zinc chloride.[2] This paper describes the preparation of crystalline 3,5-dinitrobenzoates from small amounts of representative, simple aliphatic ethers. Procedures for the conversion of typical aromatic ethers into crystalline bromo derivatives are also discussed.

Discussion of Experiments

All the temperatures given are uncorrected.

Purification of Ethers.—The aliphatic ethers were purified by the method described in a previous paper.[3] Experiments with samples of

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[1] Some of the experimental results described in this and a previous paper are taken from a thesis submitted to the Faculty of the Massachusetts Institute of Technology by G. C. Toone in partial fulfilment of the requirements for the degree of Master of Science. The bromo derivatives of the aromatic ethers were prepared by O. L. Baril.

[2] Underwood and Wakeman, THIS JOURNAL, 52, 387 (1930).

[3] Underwood and Toone, *ibid.*, 52, 391 (1930).

all the aliphatic ethers, except isobutyl and *n*-hexyl, obtained from the Eastman Kodak Company gave results similar to those obtained with the purified compounds.

Reactions of Simple Aliphatic Ethers with 3,5-Dinitrobenzoyl Chloride

General Procedure.—One cubic centimeter of each ether was added to a mixture of 0.1–0.15 g. of finely powdered, anhydrous zinc chloride and 0.5 g. of 3,5-dinitrobenzoyl chloride in a dry 7.6-cm. test-tube. A small reflux water condenser, constructed from two pieces of glass tubing, was attached immediately, and the mixture was refluxed *gently* by heating in an oil-bath for about one hour. The product was then poured into a small beaker. The test-tube was rinsed with 10 cc. of 1.5 *N* sodium carbonate solution and this was added to the reaction mixture. The contents of the beaker were stirred and heated in a water-bath, maintained at 90–100°, for about one minute. The mixture was allowed to stand at room temperature for five minutes, and then filtered by suction. The precipitate was washed on the filter with 5 cc. of 1.5 *N* sodium carbonate solution and with two 5-cc. portions of water, and then drained thoroughly. The solid was transferred to a 15-cm. test-tube and extracted with 10 cc. of carbon tetrachloride, kept at its boiling point by heating over a free flame, for about three minutes. The hot mixture was filtered immediately and the filtrate was evaporated to dryness by a current of air. The residue was crystallized from 2–3 cc. of carbon tetrachloride. Crystallization was facilitated by cooling the solution in ice. The crystals were dried in the air. The yield of alkyl 3,5-dinitrobenzoate was 0.1–0.15 g.

The ethers investigated and the melting points of the 3,5-dinitrobenzoates obtained are as follows: ethyl, 92–93°; *n*-propyl, 73.5–74°; isopropyl, 120–121°; *n*-butyl, 62–63°; isobutyl, 84.5–85.5°; *n*-amyl, 42–43°; iso-amyl, 60–61°; *n*-hexyl, 54.5–55.5°. In some experiments it was necessary to evaporate the carbon tetrachloride solutions of the products from *n*-amyl, iso-amyl and *n*-hexyl ethers almost to dryness in order to isolate the esters, and subsequently to recrystallize the latter from about 2 cc. of ethyl alcohol. Carbon tetrachloride was used instead of alcohol in our experiments in order to avoid reactions of unchanged dinitrobenzoyl chloride with the alcohol.

Several investigators have given different melting points for alkyl dinitrobenzoates.[4] Each melting point, except that of the *n*-amyl ester which is listed as 44.4–44.6° by Tseng,[4] obtained by us agrees with one previously reported. We found that we could raise the melting point of *n*-amyl

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[4] Malone and Reid, THIS JOURNAL, **51**, 3426 (1929); Reichstein, *Helv. Chim. Acta*, **9**, 802 (1926); Majima, Nagaoka and Yamada, *Ber.*, **55**, 215 (1922); Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons, Inc., New York City, 1904, Vol. I, pp. 168–172; Research on derivatives of alcohols carried out at the Massachusetts Institute of Technology by Tseng under the direction of Professor Mulliken.

3,5-dinitrobenzoate by preparing a relatively large amount of the ester and recrystallizing it several times from ethyl alcohol. The melting points given above are those usually obtained under the conditions we used. We checked the identity of our products by mixed melting points with samples of alkyl dinitrobenzoates prepared from pure alcohols.

Reactions of Aromatic Ethers

Anisole, Phenetole and *p*-Nitrobenzoyl Chloride.—It has been noted that diphenyl ether and anisole behave like aromatic hydrocarbons when heated with acetyl and benzoyl chlorides in the presence of anhydrous zinc chloride; ketones are formed by the introduction of an acetyl or benzoyl group into the aromatic nucleus.[2] The reactions of these (and other aromatic) ethers with 3,5-dinitrobenzoyl chloride gave products which had undesirable properties.

4′-Nitro-4-methoxybenzophenone and 4′-nitro-4-ethoxybenzophenone were readily prepared from anisole and phenetole. A mixture of 1 cc. of each ether, 0.8 g. of pure *p*-nitrobenzoyl chloride, 1 cc. of dry carbon disulfide and 0.1 g. of granular, anhydrous aluminum chloride was placed in a dry 7.6-cm. test-tube, and warmed gently over a free flame to start the reaction. After the evolution of hydrogen chloride had subsided, a small water condenser, constructed from two pieces of glass tubing, was attached to the tube and the mixture was refluxed *gently* for half an hour by heating in an oil-bath. The contents of the tube were rinsed into a small beaker with 15 cc. of water and allowed to cool. The mixture was next extracted, in a separatory funnel, with a 15-cc. and a 5-cc. portion of ether. The combined ether layers were shaken with 15 cc. of 10% sodium hydroxide solution, and then dried with 1 g. of anhydrous sodium sulfate for half an hour. The dry ether solution was decanted and the solvent was allowed to evaporate under a hood. The solid residue was crystallized two or three times from 5 cc. of alcohol. Our 4′-nitro-4-methoxybenzophenone melted at 120.5–121°, and the 4′-nitro-4-ethoxybenzophenone melted at 110.5–111°. These compounds are listed in Beilstein; the melting point of the ethoxy derivative is given as 112°. We found no references to the preparation of these substances from small amounts of the ethers. It is believed that our products are the most satisfactory solid derivatives now available for anisole and phenetole.

Attempts to prepare *p*-nitrobenzoyl derivatives of naphthyl, benzyl and other aromatic ethers gave oils which would not crystallize. Consequently, it was decided to investigate another reaction for ethers containing aromatic groups.

Bromination of Aromatic Ethers.—Procedures for the preparation of crystalline bromo derivatives from representative aromatic ethers were devised; details are given in Table I.

The bromo derivatives of *o*-cresylmethyl, benzyl, α-naphthylmethyl and β-naphthylmethyl ethers are new compounds. The other products are listed in Beilstein, but we found no references to the preparation of these compounds from small amounts of the ethers. In most cases it was necessary to modify considerably the preparative methods given in the literature; the rate of addition of bromine and temperature control are particularly important.

Brominations of anisole and phenetole gave oils which would not solidify.

Anal. Monobromo-*o*-cresyl methyl ether. Calcd. for C_8H_9OBr: Br, 39.76. Found: Br, 39.38, 39.41. Dibromobenzyl ether. Calcd. for $C_{14}H_{12}OBr_2$: Br, 44.90. Found: Br, 44.76, 44.79. Monobromo-α-naphthyl methyl ether. Calcd. for $C_{11}H_9OBr$: Br, 33.73. Found: Br, 33.69, 33.65. Monobromo-β-naphthyl methyl ether. Calcd. for $C_{11}H_9OBr$: Br. 33.73. Found: 33.68, 33.67.

TABLE I
EXPERIMENTAL RESULTS

No.	Ether			Bromine			Solid formed in
		G.	Solvent	G.	Solvent	Added in minutes	
1	*o*-Cresyl methyl	0.31	2 cc. alc.	0.42	....	5, drop by drop	10 minutes
2	Guaiacol	.31	3 cc. alc.	1.5	3 cc. alc.	8. Note *a*	Note *a*
3	Veratrole	.35	5 cc. alc.	0.84	3 cc. alc.	5	Note *b*
4	Resorcinol dimethyl	.35	3 cc. alc.	.88	....	5	At once
5	Hydroquinone dimethyl	.35	1 cc. gl. HAc	.84	1 cc. gl. HAc	5	At once
6	Anethole	.37	4 cc. abs. ether	.84	3 cc. abs. ether	8, drop by drop[e]	Note *e*
7	Safrole	.41	3 cc. alc.	2.0	....	8. Note *f*	At once[g]
8	Isosafrole	.41	2 cc. CS_2	2.03	....	15, drop by drop	24 hours
9	Eugenol methyl	.45	5 cc. dry ether	.8	....	10. Note *h*	Note *h*
10	Isoeugenol methyl	.45	5 cc. dry ether	.4	....	8. Note *h*	Note *h*
11	Diphenyl	.43	2 cc. alc.	.8	....	10, drop by drop	Overnight
12	Benzyl	.5	1 cc. alc.	.8	....	5	Overnight
13	α-Naphthyl methyl	.4	3 cc. $CHCl_3$	.42	....	8, drop by drop[i]	Overnight
14	β-Naphthyl methyl	.4	2 cc. gl. HAc	.42	....	3	5 minutes
15	α-Naphthyl ethyl	.43	3 cc. $CHCl_3$	.42	....	5	Overnight[j]
16	β-Naphthyl ethyl	.43	1 cc. gl. HAc	.42	....	3. Note *k*	10 minutes

TABLE I (*Concluded*)

No.		Products			
	Derivative	Crystallized from	Form	G.	M. p., °C.
1	Monobromo	8 cc. alc.	Plates	0.46	63–64
2	Tribromo	3 cc. alc.	Needles	.7	115.5–116
3	Dibromo	2 cc. alc.	Prisms	.25	92–92.9
4	Dibromo	8 cc. alc., twice[c]	Needles	.55	140–141
5	Dibromo	15 cc. gl. HAc[d]	Needles	.69	142
6	Monobromo dibromide	18 cc. pet. ether[e]	Needles	.68	107.6–108
7	Tribromo dibromide	7 cc. benzene	Needles	1.14	169–170
8	Monobromo dibromide	5 cc. pet. ether[g]	Needles	0.55	109
9	Monobromo dibromide	8 cc. abs. alc. at 60°[h]	Needles	.88	77.5–78
10	Dibromide	8 cc. dry ether	Plates	.61	101–101.5
11	Dibromo	6 cc. alc.	Leaflets	.94	54–55
12	Dibromo	10 cc. alc.	Plates	.47	107–108
13	Monobromo	8 cc. alc.	Needles	.6	46
14	Monobromo	18 cc. pet. ether	Plates	.63	62–63
15	4-Bromo	10 cc. alc.	Prisms	.55	47.8
16	1-Bromo	15 cc. pet. ether	Plates	.48	66.1

[a] The mixture of guaiacol and bromine was heated for twenty minutes on a water-bath. After the alcohol had been removed by distillation, 1 cc. of glacial acetic acid was added; crystallization occurred at once.

[b] The reaction mixture obtained from veratrole was diluted with 40 cc. of water, stirred, allowed to stand for two hours and filtered.

[c] Before crystallization, dibromoresorcinol dimethyl ether was washed with 1 cc. of alcohol.

[d] The dibromo derivative of hydroquinone dimethyl ether was washed with 3 cc. of 80% acetic acid before crystallization.

[e] The ether solution of anethole was cooled in ice during the addition of bromine; the crystals formed when the solvent evaporated were ground with 1 cc. of cold alcohol in a mortar before crystallization.

[f] The mixture of safrole and bromine was heated for fifteen minutes on a water-bath.

[g] Before crystallization, the impure monobromo-isosafrole dibromide was ground in a mortar with 3 cc. of cold alcohol.

[h] During the addition of bromine the ether solutions of eugenol methyl ether and of isoeugenol methyl ether were cooled in ice. Subsequently the reaction mixtures were allowed to stand for half an hour at room temperature, and then cooled in a bath of ice and concd. hydrochloric acid. Crystallization was induced by scratching the wall of the container with a sharp glass rod. Monobromo-eugenol methyl ether dibromide was washed with 3 cc. of cold alcohol before crystallization.

[i] The chloroform solution of α-naphthyl methyl ether was cooled in ice during the addition of bromine and for fifteen minutes longer; subsequently it was allowed to stand overnight at room temperature.

[j] In some experiments with α-naphthyl ethyl ether the bromo derivative crystallized only when allowed to stand for a long time.

[k] The reaction mixture obtained from β-naphthyl ethyl ether was cooled for ten minutes after the addition of bromine.

Oxidation of Cresyl Ethers.—Brominations of *p*-cresyl methyl, *p*-cresyl ethyl and *o*-cresyl ethyl ethers gave oils which would not solidify. Details of a procedure for the oxidation of these compounds to anisic, *p*-ethoxybenzoic and *o*-ethoxybenzoic acids are given below. A mixture of 0.5 g. of the ether, 2.5 g. of concd. sulfuric acid, 37 cc. of water and 1.75 g. of powdered potassium dichromate was heated at its boiling point in a flask connected with a reflux water condenser. The periods of heating were four, three and two hours, respectively. The mixture was cooled to room temperature, diluted with 50 cc. of water, transferred to a separatory funnel and extracted with 30, 10 and 10-cc. portions of ether. The combined ether layers were shaken with 25 cc. of 10% sodium carbonate solution. The sodium carbonate extract was acidified with 20 cc. of 6 *N* hydrochloric acid. The precipitated anisic and *p*-ethoxybenzoic acids were collected on a filter, washed with 5 cc. of water and crystallized from 50 cc. of hot water and from 10 cc. of alcohol, respectively. *o*-Ethoxybenzoic acid was precipitated as an oil; this was extracted with two 25-cc. portions of ether. The ether solution was dried with 2 g. of anhydrous sodium sulfate for an hour, decanted and allowed to stand until the solvent evaporated. About 0.1 g. of an oil which melted at 19–19.5° was thus obtained. The yields of anisic and *p*-ethoxybenzoic acids were 0.2 and 0.3 g.; the products melted at 183.9 and 195.2–195.5°, respectively.

Summary

Small amounts of ethyl, *n*-propyl, isopropyl, *n*-butyl, isobutyl, *n*-amyl, iso-amyl and *n*-hexyl ethers are converted into the corresponding 3,5-dinitrobenzoates by treatment with 3,5-dinitrobenzoyl chloride in the presence of anhydrous zinc chloride. The reactions of *p*-nitrobenzoyl chloride with small quantities of anisole and phenetole give 4′-nitro-4-methoxybenzophenone and 4′-nitro-4-ethoxybenzophenone. Crystalline bromo derivatives can be readily prepared from small amounts of *o*-cresyl methyl, resorcinol dimethyl, hydroquinone dimethyl, eugenol methyl, isoeugenol methyl, diphenyl, benzyl, α-naphthyl methyl, β-naphthyl methyl, α-naphthyl ethyl and β-naphthyl ethyl ethers, guaiacol, veratrole, anethole, safrole and isosafrole. The oxidation of *p*-cresyl methyl, *p*-cresyl ethyl and *o*-cresyl ethyl ethers on a small scale gives anisic, *p*-ethoxybenzoic and *o*-ethoxybenzoic acids.

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