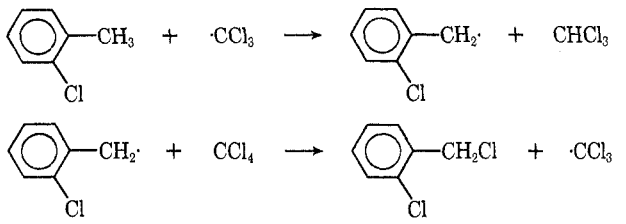
exchange, α,2-dichlorotoluene (7.5%) and α,2-dichloro-1,4-dimethylbenzene (10%), respectively. These latter compounds must arise by a secondary process which is depicted below.



Irradiation of 4-iodoaniline in carbon tetrachloride gave only traces of the corresponding chloro compound; the nature of the dark, insoluble material which was formed was not investigated further.

We suggest that this photochemical conversion of aromatic iodo into aromatic chloro compounds may prove to be of synthetic value because of the mild reaction conditions employed and the effectiveness of the halogen exchange.

Experimental Section

Photochemical Reactor.—A Rayonet photochemical reactor (The Southern New England Ultraviolet Co.) equipped with 16 3000-Å lamps was used. The reactions were carried out in a 30 × 5 cm quartz tube at room temperature (the temperature rose slowly during the time of reaction to 45°).

Gas Chromatography.—An Aerograph A90-P3 instrument with a 30 ft × 3/8 in. column with 30% QF-1 on 45–60 Chrom W was employed.

General Procedure.—The iodo compound (1 g) was dissolved in 500 ml of carbon tetrachloride and the solution irradiated for 5 hr. The violet solution was then evaporated *in vacuo*, the residue dissolved in ether (100 ml), and the ether solution extracted once with 20 ml of a 5% sodium bisulfite solution. The ether layer was dried over anhydrous sodium sulfate and evaporated. The chloro compounds were isolated by crystallization from hexane (in the case of solids), or their presence and purity quantitatively determined by gas chromatography (in the case of liquids). The crude acids (see Table I) obtained after evaporation of the ether solution were methylated with diazomethane prior to gas chromatography.

Syntheses of Some Haloalkyl Methyl Ethers[1a]

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The absence of reports of the preparation of several simple haloalkyl methyl ethers probably stems, in part, from tendencies toward elimination and/or participation inherent in the ethers and/or in intermediates in the syntheses of these ethers. We report here syntheses of several haloalkyl methyl ethers, which were needed in our studies of halogen participation.[2] In the case of the preparations of four of the ethers, our results are reported because they differ significantly from those reported in the literature.

In our work, various attempts to prepare 2-chloro-1-propyl methyl ether by methylating 2-chloro-1-propanol failed, presumably because the nucleophilicity of the alcohol is decreased by the inductive effect of the chlorine. A yield of 53% was finally obtained from the reaction of 1-methoxy-2-propanol with thionyl chloride. The reported[3] 13% yield of 2-bromo-1-propyl methyl ether from the reaction of 1-methoxy-2-propanol with phosphorous tribromide was reproducible. Modifying the procedure by distilling the product directly as it is formed, under vacuum, improved this yield to 58%. 2-Iodo-1-propyl methyl ether was prepared (86% yield, with 14% recovery of starting material) from 2-bromo-1-propyl methyl ether and sodium iodide in refluxing acetone. Attempted preparation of the compound from the reaction of 2-tosyloxy-1-propyl methyl ether with sodium iodide in acetone unaccountably failed.

A 35% yield of 3-chloro-1-butyl methyl ether from 3-chloro-1-butanol was obtained *via* reaction of the benzenesulfonate of the alcohol with sodium methoxide in methanol. Only 4% 3-bromo-1-butyl methyl ether was formed from 1,3-dibromobutane and methanolic sodium methoxide. (A 35% yield of 3-bromo-1-butyl methyl ether from the reaction of propene with bromomethyl methyl ether has been reported.)[4]

4-Chloro-1-pentyl methyl ether was prepared without difficulty in 76% yield from 4-chloro-1-bromopentane and sodium methoxide in methanol. The analogous reaction of dibromopentane was twice[5,6] reported to proceed with about 50% yield of 4-bromo-1-pentyl methyl ether. In our hands the reaction was less successful. Five variations of conditions were tried, some more than once. In all cases a mixture of isomers, 4-bromo-1-pentyl and 5-bromo-2-pentyl methyl ethers, was obtained. Yields of this mixture ranged from 3 to 28%. The proportion of 4-bromo-1-pentyl methyl ether in the mixture also depended upon conditions, ranging from about 50 to 92%. Pure 4-bromo-1-pentyl methyl ether was obtained from the mixture by selective reaction of 5-bromo-2-pentyl methyl ether with sodium iodide in acetone.

The halogenation of 5-methoxy-1-pentene led to a mixture of dihalopentyl methyl ethers (Scheme I), which could not be separated by preparative gas chromatography because of decomposition during the runs. High-speed spinning-band distillation using a Teflon band was employed in the separation of 1,5-dichloro-2-pentyl methyl ether from its isomer, 4,5-dichloro-1-pentyl methyl ether. This procedure failed in the case of the bromine analogs because they both decomposed upon heating. Since 4,5-dibromo-1-pentyl methyl ether decomposed more slowly than the isomer, it was possible to isolate this *vic*-dibromide. The distribution of products in the two halogenations seems to indicate that participation is more important in the chlorination than in the bromination (Scheme II). The results obtained in these halogenations are similar to those reported[7] for the iodination of 4-penten-1-ol in

(1) (a) We gratefully acknowledge partial support of the research and partial support of the purchase of a Varian HA-100D nmr spectrometer by the National Science Foundation through Grants GP-6638 and GP-8510, respectively; (b) NDEA Fellow, 1966–1969.

(2) P. E. Peterson and F. J. Slama, *J. Amer. Chem. Soc.*, **90**, 6516 (1968).

(3) R. L. Jacobs and R. D. Schuetz, *J. Org. Chem.*, **26**, 3472 (1961).

(4) S. Mamedov and M. R. Kulibekov, *Zh. Obshch. Khim.*, **27**, 1499 (1957); *Chem. Abstr.*, **52**, 3750a (1958).

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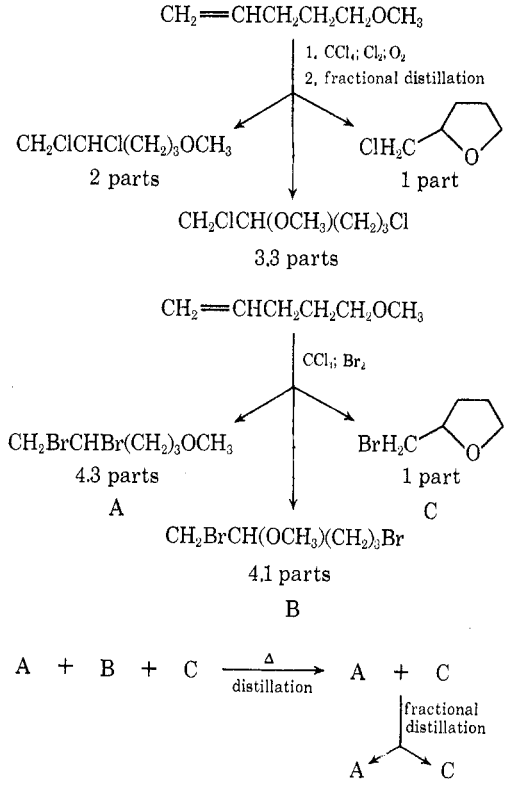
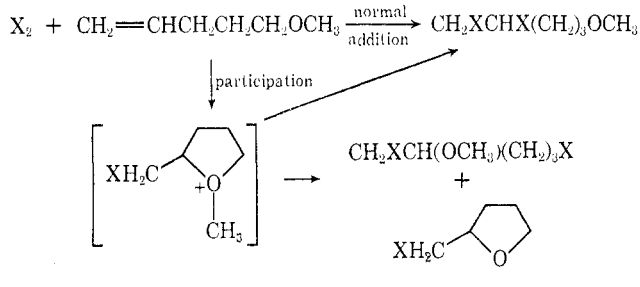
SCHEME I

SYNTHESES OF DIHALOPENTYL METHYL ETHERS



SCHEME II



aqueous acetone to produce some 2-iodomethyltetrahydrofuran. The preparation of 4,5-dibromo-1-pentyl methyl ether in 80% yield by the method of Scheme I has been reported,[8] with no mention of isomeric products. Identification of the isomers by their nmr spectra, taken in two solvents, was unequivocal.

Experimental Section

Distillations and Analyses.—Distillations were performed on platinum spinning-band columns, except as noted. Analyses were performed by Scandinavian Microanalytical Laboratories, Herlev, Denmark.

2-Chloro-1-propyl Methyl Ether.—Thionyl chloride (71.4 g, 0.60 mol) was added dropwise to 1-methoxy-2-propanol (54 g, 0.60 mol) and pyridine (50.4 g, 0.60 mol) in an ice-cooled flask. The flask was then heated to 120° for 1 hr. Distillation afforded 29.5 g (53%) of 2-chloro-1-propyl methyl ether: bp 98° (1 atm); nmr (CCl_4) δ 1.46 (d, 3, CCH_3), 3.32 (s, 3, OCH_3), 3.2–3.6 (m, 2, CH_2), and 3.8–4.1 (m, 1, CH).

Anal. Calcd for C_4H_9OCl: C, 44.25; H, 8.36. Found: C, 44.45; H, 8.51.

2-Bromo-1-propyl Methyl Ether.—Phosphorus tribromide (136 g, 0.5 mol) was added slowly to prechilled 1-methoxy-2-propanol (90.0 g, 1.0 mol) and kept at −10° until the initial exothermic process was completed. The flask was placed on a distilling column in a 100° bath. The distillate, collected immediately at a pressure of 62 Torr, was washed with 10% sodium bicarbonate and with saturated sodium chloride. Redistillation afforded 92 g (58%) of 2-bromo-1-propyl methyl ether: bp 62° (79 Torr); nmr (CCl_4) δ 3.3 (s, 3, CH_3O), 1.64 (d, 3, CH_3C), 3.4–3.7 (m, 2, CH_2), and 4.0–4.5 (m, 1, CH).

2-Iodo-1-propyl Methyl Ether.—Sodium iodide (40 g, 0.276 mol), reagent grade acetone (60 ml), and 2-bromo-1-propyl methyl ether (20.0 g, 0.122 mol) were refluxed for 48 hr. Solids were precipitated with ether. Distillation afforded 14% of the starting bromide and 21.1 g (86%) of 2-iodo-1-propyl methyl ether: bp 67° (54 Torr); nmr (CCl_4) δ 1.84 (d, 3, CH_3C), 3.2–3.7 (multiplet and singlet, 5, CH_2 and CH_3O), and 3.9–4.6 (m, 1, CH).

Anal. Calcd for C_4H_9OI: C, 23.91; H, 4.52. Found: C, 24.05; H, 4.54.

3-Chloro-1-butyl Methyl Ether.—Pyridine (100 ml, 1.25 mol), benzenesulfonyl chloride (49.2 g, 0.28 mol) and 3-chloro-1-butanol (21.6 g, 0.20 mol, prepared by lithium aluminum hydride reduction of 3-chlorobutyric acid) were mixed for 2 hr at −5 to −10°, and then poured into 320 ml of prechilled 6 *N* hydrochloric acid. The mixture was extracted with chloroform and dried with magnesium sulfate. Chloroform was removed in a rotary evaporator. Methanol (100 ml) containing 0.17 mol of sodium methoxide was added dropwise and refluxed for 10 min. Filtration and distillation afforded 8.62 g (35% from the alcohol) of 3-chloro-1-butyl methyl ether: bp 65° (95 Torr); ir (CCl_4) 1105 cm^{-1} (ether); nmr (CF_3COOH) δ 1.56 (d, 3, CH_3C), 3.60 (s, 3, CH_3O), 1.8–2.5 (m, 2, $CHClCH_2$), and 3.61–4.5 (m, 3, CH_2OCH_3 and CHCl).

4-Chloro-1-pentyl Methyl Ether.—4-Chloro-1-bromopentane (0.107 mol) (prepared from 2-methyl-tetrahydrofuran *via* reaction with acetyl chloride to form 4-chloro-1-pentyl acetate,[9] which was subjected to acidic methanolysis, followed by reaction of the resulting 4-chloro-1-pentanol with phosphorus tribromide) was added to methanol (50 ml) which contained sodium methoxide (0.107 mol), refluxed 1 hr, and distilled, to afford 3.04 g of starting material (4-chloro-1-bromopentane) and 10.11 g (76%) of 4-chloro-1-pentyl methyl ether: bp 65° (32 Torr); ir 1113 cm^{-1} (ether); nmr (CCl_4) δ 1.48 (d, 3, CH_3C), 3.24 (s, 3, CH_3O), 3.25–3.4 (m, 2, CH_2OCH_3), 3.8–4.2 (m, 1, CHCl), and 1.6–1.9 (m, 4, $CH_2CH_2CH_2O$).

Anal. Calcd for $C_6H_{13}OCl$: C, 52.74; H, 9.59. Found: C, 52.75; H, 9.55.

Mixture of 4-Bromo-1-pentyl and 5-Bromo-2-pentyl Methyl Ethers.—1,4-Dibromopentane (230 g, 1.0 mol) was allowed to react for 4 days at room temperature with sodium iodide (150 g, 1.0 ml) in dry acetone (450 ml). After filtration, the acetone was removed by distillation. Methanol (220 ml) was added. Sodium methoxide (0.33 mol) in methanol (220 ml) was added dropwise to the refluxing solution over 1.5 hr. Distillation afforded 20.03 g (28%) of a mixture of 4-bromo-1-pentyl and 5-bromo-2-pentyl methyl ethers bp [69–70° (22 Torr)].

Isolation of 4-Bromo-1-pentyl Methyl Ether.—A mixture (9 g, 0.05 mol) containing about 50% 4-bromo-1-pentyl methyl ether and 50% 5-bromo-2-pentyl methyl ether was dissolved in dry acetone and added to a flask containing sodium iodide (4.5 g, 0.03 mol) in acetone. After 12 hr at room temperature, filtration and distillation afforded several cuts, one of which was pure 4-bromo-1-pentyl methyl ether (1.89 g): bp 71° (22 Torr); nmr (CCl_4) δ 1.5–2.2 (7, including a doublet at 1.68), 3.1–3.5 (5, including a singlet at 3.25), and 3.8–4.4 (m, 1, CH_3CHBrC); ir 1105 cm^{-1} (ether). The ether was separable from its isomer, 5-bromo-2-pentyl methyl ether, by gas chromatography on a 150-ft DC-550 capillary column, and was shown to be 99.8 ± 0.2% isomerically pure. The highest boiling fraction (4.86 g) was impure 5-iodo-2-pentyl methyl ether: bp 78–81° (13 Torr); nmr (CCl_4) δ 1.3–2.2 (m, 4, $CH_2CH_2CH_2I$), 1.19 (d, 3, CH_3), 3.0–3.6 (6, including a singlet at 3.23).

4,5-Dichloro-1-pentyl and 1,5-Dichloro-2-pentyl Methyl Ethers.—Chlorine (17.1 g, 10.9 ml, 0.24 mol) was evaporated into a stream of oxygen and led into ice-cold carbon tetrachloride (100 ml) containing 4-methoxy-1-pentene (25.0 g, 0.25 mol). A high-speed Teflon spinning-band column was used to separate the isomers. The resulting fractions contained 17.6 g (43%) of

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(9) S. Searles, Jr., K. Pollart, and F. Block, *J. Amer. Chem. Soc.*, **79**, 952 (1957).

1,5-dichloro-2-pentyl methyl ether, 10.6 g (26%) of 4,5-dichloro-1-pentyl methyl ether, and 3.7 g (13%) of 2-chloromethyltetrahydrofuran: bp 75–77° (28 Torr) [lit.[10] 55–56° (20 Torr)]. The isomeric ethers were separable analytically on a DC-550 gas chromatographic column and were identified by their spectra.

1,5-Dichloro-2-pentyl methyl ether: bp 103° (19 Torr); nmr (CCl_4) δ 3.38 (s, 3, CH_3O), 3.2–3.6 (m, 5, $ClCH_2CH$ and $ClCH_2$), and 1.5–2.1 (m, 4, $CH_2CH_2CH_2Cl$).

Anal. Calcd for $C_6H_{12}OCl_2$: C, 42.14; H, 7.04. Found: C, 42.14; H, 7.04.

4,5-Dichloro-1-pentyl methyl ether: bp 95–100° (19 Torr); nmr (CCl_4) δ 3.27 (s, 3, CH_3O), 3.36 (t, 2, OCH_2), 1.4–2.6 (m, 4, $CH_2CH_2CH_2O$), 3.4–3.9 (m, 2, $ClCH_2$), and 3.8–4.2 (m, 1, CH).

Anal. Calcd for $C_6H_{12}OCl_2$: C, 42.14; H, 7.04. Found: C, 42.33; H, 7.05.

That 2-chloromethyltetrahydrofuran was not arising from the dichloro compounds during distillation was evidenced by its sharp disappearance from distillation fractions early in the distillation.

4,5-Dibromo-1-pentyl Methyl Ether.—5-Methoxy-1-pentene (20.0 g, 0.20 mol) and bromine (30 g, 0.187 mol) were allowed to react in carbon tetrachloride (100 ml) in subdued light. Because of the pyrolytic instability of 1,5-dibromo-2-pentyl methyl ether, the only compounds isolated in pure form by slow distillation were 2-bromomethyltetrahydrofuran, bp 60–61° (14 Torr) [lit.[10] bp 63.5–64° (17 Torr)], and 4,5-dibromo-1-pentyl methyl ether: bp 105° (7 Torr) [lit.[8,9] bp for "$CH_2BrCHBr(CH_2)_3OCH_3$," 100° (8 Torr)]; nmr (CCl_4) δ 3.9–4.3 (m, 1, CH), 3.4–3.9 (m, 2, $BrCH_2$), 3.36 (t, 2, CH_2O), 3.27 (s, 3, CH_3O), and 1.2–2.4 (m, 4, $CH_2CH_2CH_2O$).

Registry No.—2-Chloro-1-propyl methyl ether, 5390-71-6; 2-bromo-1-propyl methyl ether, 22461-48-9; 2-iodo-1-propyl methyl ether, 22461-49-0; 3-chloro-1-butyl methyl ether, 3565-66-0; 4-chloro-1-pentyl methyl ether, 22461-51-4; 4-bromo-1-pentyl methyl ether, 4457-68-5; 5-bromo-2-pentyl methyl ether, 3706-57-8; 1,5-dichloro-2-pentyl methyl ether, 22434-10-2; 4,5-dichloro-1-pentyl methyl ether, 22461-54-7.

(10) G. Eglinton, E. R. H. Jones, and M. C. Whiting, *J. Chem. Soc.*, 2873 (1952).

Stereoselective Addition of Bromine to 2-Buten-2-yl Tosylates. Formolysis of *erythro*-2,3-Dibromo-2-butyl Tosylate[1a]

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It is widely recognized that the electrophilic addition of bromine to olefins proceeds *via* an intermediate bromonium ion, or its equivalent, to give *trans* adducts. This cyclic intermediate was first postulated by Roberts and Kimball[2] and later observed in the nmr studies of Olah and Bollinger.[3] Olefins which can form highly stabilized cations are less prone to form bridged cations, and they may give mixtures of stereoisomeric products.[4]

Of particular interest to this study is the stereochemistry of the addition of bromine to olefins containing an sp^2-hybridized bond to an atom other than hydrogen or carbon. Lemieux has demonstrated that bromination of dihydropyran and related compounds occurs *via* a stabilized oxonium ion, and that this reaction yields significant amounts of the *cis*- as well as the *trans*-dibromide.[5] Stevens has shown that bromine-82 adds to 1-bromocyclohexene with *trans* stereospecificity.[6]

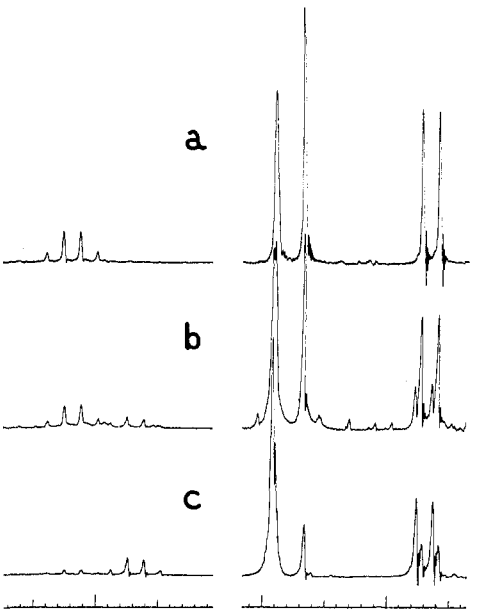

Figure 1.—Nmr spectrum (CCl_4): (a) crystallized *erythro*-2,3-dibromo-2-butyl tosylate; (b) mixture of *erythro* and *threo* diastereosmers from the addition of bromine to *trans*-2-buten-2-yl tosylate; (c) mixture of diastereosmers from the addition of bromine to the *cis* isomer.

In the present study, the stereochemistry of the addition of bromine in carbon tetrachloride to 2-buten-2-yl tosylates was determined.[7] The nmr spectra (Figure 1) of the products of the addition to the *cis* and *trans* isomers, indicate some stereoselectivity in the addition to the double bond (Scheme I). The lack of complete stereospecificity can be interpreted in terms of stabilized oxonium ions **2** and **3** which may be formed directly or from **1** and **4** in competition with attack of bromide ion. The stereochemical assignment is based on the assumption of a preponderance of *trans* addition. The products of the addition of bromine to 1-cyclohexen-1-yl tosylate proved to be so unstable that they could not be identified.

The α,β-dibromo tosylates are of some interest as solvolytic substrates which may undergo solvolysis with α- or β-bromine assistance or with both. Accordingly, the crystalline **6** was dissolved in formic acid containing sodium formate and was found to have undergone rapid formolysis to give 3-bromo-2-butanone (eq 1).

$$6 \xrightarrow[HCOONa]{HCOOH} CH_3CHBrC(=O)CH_3 \qquad (1)$$

Information concerning the role of β-bromine in solvolyses was available from an unpublished study of

(1) (a) We acknowledge partial support of the purchase of a Varian HA-100D nmr spectrometer through National Science Foundation Grant GP-8510. (b) NSF Graduate Trainee, 1966–1969.

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(4) (a) R. C. Fahey and H. J. Schneider, *ibid.*, **90**, 4429 (1968); (b) J. H. Rolston and K. Yates, *ibid.*, **91**, 1469 (1969); (c) J. H. Rolston and K. Yates, *ibid.*, **91**, 1477 (1969).

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