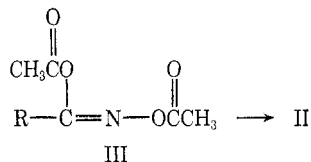


O); mass spectrum (*m/e*, rel intensity) 173, 1 (M^+), 57, 60 ($CH_3CH_2CO^+$), 43, 100 (CH_3CO^+), no other peaks above 2% relative intensity.

Treatment of Ib in the same manner yielded IIb, corresponding in properties to IIb prepared³ by Urbanski. A similar derivative was prepared in high yield from miserotoxin.²

The key to high yield preparation of II compounds (which can be considered as N-acyloxyimides or triacylhydroxylamines) is the use of steam-bath heat rather than reflux, as used by Urbanski.³ Thus, Urbanski isolated only IIb as the main product, no matter what R was present in I. Indeed, we found that, if the reaction mixture is heated to reflux, a self-sustaining exothermic reaction takes place which results in complete conversion of all II compounds into IIb. The II derivatives are excellent for mass spectral studies since the $RC=O^+$ fragment is readily formed and this provides a handle for interpretation.

The mechanism of this reaction is obviously complex and must involve several steps. The clearest step of the reaction is likely to be the last one, which is probably a 1,3-acyl migration from III. At the present



there is no way of choosing between several ways³ of arriving at III. However, elucidation of the mechanism may well have a bearing on a known rearrangement⁴ of cyclic nitro ketones.

Registry No.—IIa, 22427-07-2.

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Photochemical Synthesis of Aromatic Chloro Compounds from Aromatic Iodo Compounds¹

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The photodecomposition of aromatic iodo compounds has long been known, but only recently has this process been used for synthetic purposes. Thus, photolysis of aromatic iodides has led to syntheses of biphenyls, phenanthrenes, and organophosphorus and organoboron compounds, all in acceptable yields.³

Aromatic iodo compounds are now readily accessible from a wide variety of aromatic hydrocarbons through initial thallation with thallic trifluoroacetate followed by treatment with aqueous potassium iodide,⁴ and we

(1) We gratefully acknowledge partial financial support of this work by the Smith Kline and French Laboratories, Philadelphia, Pa.

(2) NRCC Postdoctoral Fellow, 1968-1970.

(3) For a review, see R. K. Sharma and N. Kharasch, *Angew. Chem.*, **80**, 69 (1968); *Angew. Chem. Intern. Ed. Engl.*, **7**, 36 (1968).

(4) A. McKillop, J. S. Fowler, M. J. Zelesko, J. D. Hunt, E. C. Taylor, and G. McGillivray, *Tetrahedron Lett.*, 2427 (1969).

were therefore interested in exploring further their potential as synthetic intermediates.

We have found that irradiation of dilute solutions of aromatic iodo compounds in carbon tetrachloride with 3000-Å light leads to formation of the corresponding chloro compounds. Replacement of an iodo substituent by chlorine using iodine monochloride as the chlorine donor is known to take place on irradiation with visible light,⁵ but the only reported use of carbon tetrachloride as a chlorine donor is in the formation of 4-chlorobiphenyl from 4-iodobiphenyl.⁶ Exchange of chlorine for iodine takes place cleanly without contamination by positional isomers. In most cases irradiation for 5 hr was sufficient to effect a 70-75% conversion into the chloro compound, although actual yields were higher because of recovery of unchanged starting material. Longer reaction times were avoided because of possible complications involving reactions with the iodine liberated in the course of the photolysis. Within a given period of time, percentage conversion of the aromatic iodide into the corresponding chloride was (compared with iodobenzene) greater for compounds with electron-donating substituents; the electron-withdrawing carboxyl group, for example, considerably slowed the reaction⁷ and substantial amounts of unreacted *o*-iodobenzoic acid could be recovered.

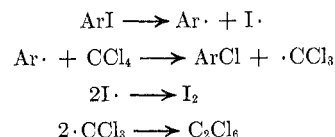
Representative results are summarized in Table I.

TABLE I
PHOTOLYSIS OF AROMATIC IODO COMPOUNDS IN
CARBON TETRACHLORIDE

Substrate	% yield of corresponding chloro compound ^a
Iodobenzene	76 ^b
2-Iodotoluene	60
2-Iodoanisole	78
4-Iodoanisole	96
2-Iodophenol	80
1,4-Dimethyl-2-iodobenzene	75
2-Iodophenylacetic acid	81
3-(4-Iodophenyl)butanoic acid	78
4-(4-Iodophenyl)butanoic acid	87
3-(4-Iodophenyl)propanoic acid	76
2-Iodobenzoic acid	51

^a Based on recovered starting material and determined by glpc. Identity of products was confirmed by melting point, spectral analysis, and/or chromatographic means. ^b Irradiated for 8 hr.

In accordance with the generally accepted mechanism for photodecomposition of iodo compounds, we suggest the following reaction scheme to account for our results.



Hexachloroethane could be isolated from the photolyses in yields up to 5%, in agreement with the above suggested reaction pathway.

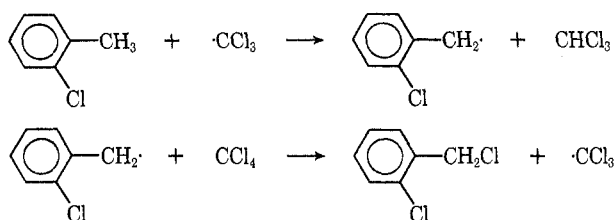
Irradiation of 2-iodotoluene and 1,4-dimethyl-2-iodobenzene gave, in addition to the product of halogen

(5) B. Milligan, R. L. Bradow, J. E. Rose, H. E. Hubbert, and A. Roe, *J. Amer. Chem. Soc.*, **84**, 158 (1962).

(6) N. Kharasch, R. K. Sharma, and M. Hussain, unpublished results; see ref 60 in ref 3.

(7) W. Wolf and N. Kharasch, *J. Org. Chem.*, **30**, 2493 (1965).

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 reported³ 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 reported⁷ for the iodination of 4-penten-1-ol in

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

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(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).