nol molecule starts to depart, and the central carbon–oxygen bond begins to acquire more sp^2 character.[8] As a result of this $sp^3 \rightarrow sp^2$ change,[9] bonds will spread out and there will be a relief from the eclipsing strain mentioned above.[10] The magnitude of such relief will depend on its original value in the ground state and is, of course, much greater for ester III than for ester I. In summary, this represents a higher initial energy and a lower energy difference, ΔE_a, between the ground and transition states of ester III than of ester I. Figure 1 illustrates this concept. The reported $\Delta S^\ddagger$ values, assuming constant contributions from the solvent, are also in accordance with the diagram given. $\Delta S^\ddagger$ changes from −38.5 to −21.9 eu in going from ester III to ester I. This means that the transition state of ester III is more ordered in relation to its ground state than in the case of ester I.

The increasing values of ΔE_a (or $\Delta H^\ddagger$) in going from ester III to ester I mean that in the former the transition state is reached earlier, and consequently is less sensitive to temperature variation. This conclusion can also be reached by a consideration of the much greater steric crowding present in the former ester's transitions state (vide supra).

Registry No.—I, 51231-09-5; II, 51231-03-9; III, 51231-12-0; mercuric chloride, 7487-94-7.

References and Notes

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(2) Fellow of the Fundação de Amparo à Pesquisa do Estado de São Paulo.

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(8) The degree of rupture of the central carbon and the phenol oxygen atoms does not change the basic idea given above. It does, however, change $\Delta F^\ddagger$ and hence the magnitude of steric acceleration.

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(10) There will also be an angle strain on passing from the 109° of the sp^3 state to the 120° of the sp^2 state. Such strain will work against the sp^3-sp^2 change. Since such changes take place easily in the cyclopentane series, angular strain can be of minor importance as compared to conformational strain.

Reactions of Dichlorine Heptoxide and of Hypohalites with Alkyl Iodides[1]

Kurt Baum* and Charles D. Beard

Fluorochem, Inc., Azusa, California 91702

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Stable aromatic polyvalent iodine compounds[2] are obtained from iodides with oxidizing reagents such as chlorine,[2] peracetic acid,[3] or dinitrogen pentoxide.[4] However, for aliphatic iodides, stable halogen adducts have been reported only with electron-withdrawing substituents such as fluorine[5,6,7] or sulfone.[8,9] Methyl iodide dichloride decomposes at −30° to give methyl chloride,[10] and similar reactions of alkyl iodides with peracetic acid[11] and with chlorine[12] have been studied kinetically at higher temperatures. The preparation of trifluoromethyl perchlorate from trifluoromethyl iodide and chlorine perchlorate has recently been reported.[13] The present work deals with reactions of alkyl iodides with dichlorine heptoxide and with hypohalites.

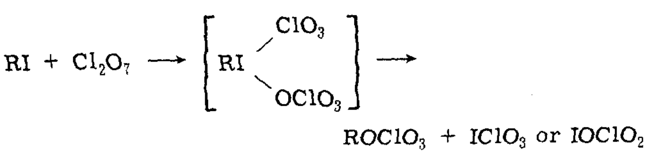
Ethyl iodide reacted rapidly at 0° with dichlorine heptoxide in carbon tetrachloride to give a white precipitate identified as iodine pentoxide. The composition of the soluble products was determined by NMR using a quantitative internal standard, and for a given reactant mixture the reproducibility of yields was 5–10%. With equimolar amounts of the reagents, or with an excess of dichlorine heptoxide, the products soluble in carbon tetrachloride were ethyl perchlorate (63% yield based on ethyl iodide), ethyl acetate (22%), and small amounts of diethyl ether (0–3%). With a 2:1 molar ratio of ethyl iodide to dichlorine heptoxide, the ethyl iodide was consumed completely to give ethyl perchlorate (33%), ethyl acetate (13%), and diethyl ether (21%). When a higher ratio of ethyl iodide to dichlorine heptoxide was used the additional ethyl iodide remained unreacted, and the same product mixture was obtained.

Since the above yields are all based on ethyl iodide consumed, almost the same total quantity of perchlorate is produced from 2 mol of ethyl iodide as from 1 mol. If the products of the experiment using 1 mol of ethyl iodide per mole of Cl_2O_7 are subtracted from the products of the 2-mol experiment, the second mole is seen to yield about 40% diethyl ether, 3% ethyl perchlorate, and 4% ethyl acetate. These results suggest that the equimolar reaction gives a by-product, not detectable by NMR, that converts additional ethyl iodide to ether.

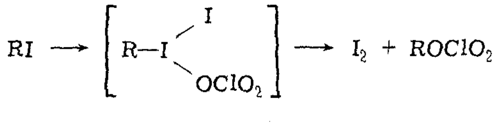
In the reaction of methyl iodide with dichlorine heptoxide similar products were obtained with the exception of the ester, presumably because of the greater oxidation resistance of the methyl group. Equimolar amounts of the reagents gave methyl perchlorate (45%) and dimethyl ether (12%), whereas a 2:1 ratio of methyl iodide to dichlorine heptoxide gave methyl perchlorate (24%) and dimethyl ether (26%). Thus, the first mole of methyl iodide gives predominantly perchlorate, and the second, ether.

In the above experiments the entire amount of ethyl iodide was added rapidly to the dichlorine heptoxide solution. To assess the stability of the implicated ether-forming intermediate, a series of experiments was carried out in which equimolar amounts of ethyl iodide and dichlorine heptoxide were reacted, the solutions were filtered, and after varying time intervals, a second mole of ethyl iodide was added. When this time interval was 15 min, 85% of the second mole was consumed; when the interval was 1 hr, 50% was consumed; and when it was 3 hr none of the added ethyl iodide was consumed.

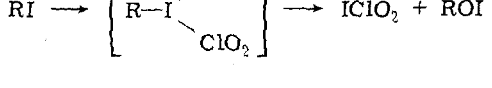
Thus, the initial reaction of ethyl iodide with dichlorine heptoxide gives a compound, not visible by NMR, that reacts further with ethyl iodide at a rate slower than the initial reaction to give ether. Simple stoichiometry for the reaction of molar amounts of ethyl iodide and dichlorine heptoxide to form ethyl perchlorate would give perchloryl iodide or its isomer. Several paths can be envisioned for the reaction of inorganic intermediates of this type with ethyl iodide. Displacement of iodine, possibly via a trivalent intermediate, could take place as follows. Reaction of these or



$$RI + Cl_2O_7 \longrightarrow \left[RI \begin{matrix} ClO_3 \\ OClO_3 \end{matrix} \right] \longrightarrow ROClO_3 + IClO_3 \text{ or } IOClO_2$$

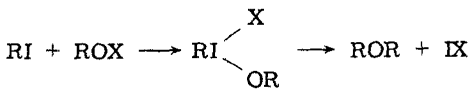


$$RI \longrightarrow \left[R\text{—}I \begin{matrix} I \\ OClO_2 \end{matrix} \right] \longrightarrow I_2 + ROClO_2$$



$$RI \longrightarrow \left[R\text{—}I \begin{matrix} OI \\ ClO_2 \end{matrix} \right] \longrightarrow IClO_2 + ROI$$

other ROX type intermediates with ethyl iodide could give ether. To shed light on the mechanism of ether formation, reactions of alkyl iodides with hypochlorites were studied.



$$RI + ROX \longrightarrow RI\begin{matrix}X\\OR\end{matrix} \longrightarrow ROR + IX$$

Chlorine oxide, Cl_2O, and I_2O_5 could be formed from $IClO_3$ by a self-oxidation reaction, with transfer of oxygens from chlorine to iodine. The reaction of chlorine oxide with 2 mol of ethyl iodide in carbon tetrachloride at 0° was found to give ethyl chloride (40% yield), diethyl ether (20%), and ethyl acetate (8%). Since chloride was not detected in the dichlorine heptoxide reaction, chlorine oxide cannot be the reactive intermediate.

Ethyl hypochlorite was also treated with alkyl iodides at 0° in carbon tetrachloride. Equimolar amounts of ethyl hypochlorite and methyl iodide gave a quantitative yield of ethyl hypoiodite and methyl chloride. The latter was easily removed under vacuum to provide a convenient source of hypoiodite solution. Similarly, ethyl hypochlorite and ethyl iodide gave ethyl hypoiodite and ethyl chloride. The structure of ethyl hypoiodite was established by independent synthesis. Ethyl hypochlorite and iodine gave the same material contaminated with iodine chloride. This method has been reported for the synthesis of *tert*-butyl hypoiodite from *tert*-butyl hypochlorite.[14,15] Ethyl hypoiodite was found to react with ethyl iodide to give diethyl ether and ethyl acetate. This result is significant with respect to the dichlorine heptoxide reaction since a hypoiodite is a possible intermediate. Other types of R–OX intermediates cannot be ruled out, however.

$$C_2H_5OCl + C_2H_5I \longrightarrow C_2H_5OI + C_2H_5Cl$$

$$C_2H_5OCl + CH_3I \longrightarrow C_2H_5OI + CH_3Cl$$

$$C_2H_5OCl + I_2 \longrightarrow C_2H_5OI + ICl$$

Experimental Section

NMR spectra were recorded with a Varian T-60 spectrometer and ir spectra were recorded with a Perkin-Elmer 700 spectrometer. A Varian 920 chromatograph with a 5 ft × 0.25 in. column of 12% QF-1 on Chromosorb W was used for GLC determinations.

Dichlorine heptoxide was utilized as a 0.3 *M* reagent in carbon tetrachloride, prepared by the previously described method.[16] Alkyl perchlorates are sensitive explosives if not diluted with solvent, and previously noted precautions should be observed.[16]

Reaction of Ethyl Iodide with Dichlorine Heptoxide. Ethyl iodide (0.0936 g, 0.6 mmol) was added dropwise with stirring to 2 ml of 0.3 *M* dichlorine heptoxide in carbon tetrachloride at 0°. A granular solid, identified by elemental analysis as iodine pentoxide, and a purple solution were formed immediately. The solution was filtered. Analysis by NMR integration, using added chlorobenzene as a quantitative internal standard, showed 0.378 mmol of ethyl perchlorate (63%) and 0.066 mmol (22%) of ethyl acetate. A similar experiment using 0.187 g (1.2 mmol) of ethyl iodide and 2 ml of 0.3 *M* dichlorine heptoxide solution gave 0.40 mmol (33% based on ethyl iodide) of ethyl perchlorate, 0.078 mmol (13%) of ethyl acetate, and 0.126 mmol (21%) of diethyl ether. The identity of the components was confirmed by ir and GLC comparison with authentic samples.

Reaction of Methyl Iodide with Dichlorine Heptoxide. The reaction of 0.3 mmol of methyl iodide with 1 ml of 0.3 *M* dichlorine heptoxide reagent by the above procedure gave methyl perchlorate (45%) and dimethyl ether (12%). Similarly, 0.6 mmol of methyl iodide gave methyl perchlorate (24%) and dimethyl ether (26%).

Reaction of Ethyl Iodide with Chlorine Oxide. Ethyl iodide (0.0936 g, 0.6 mmol) was added to 1 ml of a 0.3 *M* solution of Cl_2O in carbon tetrachloride[17] with stirring at 0°. NMR analysis of the solution showed 0.24 mmol (40%) of ethyl chloride, 0.06 mmol (20%) of diethyl ether, and 0.024 mmol (8%) of ethyl acetate.

Reaction of Ethyl Hypochlorite with Alkyl Iodides. Methyl iodide (0.0852 g, 0.6 mmol) was added with stirring at 0° to a solution of 0.6 mmol of ethyl hypochlorite[18] in 2 ml of carbon tetrachloride. The NMR spectrum of the resulting colorless solution showed a quantitative yield of methyl chloride and of ethyl hypoiodite. The methyl chloride was removed under vacuum to give a solution of ethyl hypoiodite for spectral characterization: NMR (CCl_4) δ 4.37 (q, 2 H, J = 6.5 Hz, CH_2) and 1.32 ppm (t, 3 H, J = 6.5 Hz, CH_3); ir (CCl_4) 2970 (m), 1480 (m), 1450 (w), 1270 (m), 1240 (m), 1010 (s), and 870 cm^{-1}. The identical compound, contaminated by iodine chloride, was obtained by adding an equimolar amount of iodine to the ethyl hypochlorite solution, a procedure reported for the preparation of *tert*-butyl hypoiodite from *tert*-butyl hypochlorite.[14]

By the above procedure, the reaction of ethyl iodide with an equimolar amount of ethyl hypochlorite gave a quantitative yield of ethyl chloride and ethyl hypoiodite.

Reaction of Ethyl Hypoiodite with Ethyl Iodide. An equimolar amount of ethyl iodide was added at 0° to a solution of ethyl hypoiodite prepared as above. Reaction took place over a period of 1 hr, giving a purple solution. NMR analysis showed ethyl acetate (12%) and diethyl ether (41%).

Registry No.—Ethyl iodide, 75-03-6; dichlorine heptoxide, 10294-48-1; methyl iodide, 74-88-4; chlorine oxide, 7791-21-1; ethyl hypochlorite, 624-85-1; ethyl hypoiodite, 55661-06-8.

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Restricted Rotation in Hindered Aryl Methyl Sulfoxides as Detected by Low-Temperature Proton Magnetic Resonance

Gerald W. Buchanan,* Cesar Reyes-Zamora, and Cecilia Cheung

Department of Chemistry, Carleton University,
Ottawa, Ontario, Canada K1S 5B6

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The degree of conjugation between an aromatic ring and the methylsulfinyl group has been the object of considerable attention in the recent literature. Katritsky et al.[1] on the basis of infrared spectral intensities have suggested that the MeSO group is a net resonance donor except when para to a strong electron-donating function. Results of a recent ^{13}C NMR examination,[2] however, do not support this concept. Also, rather little is known regarding the preferred conformations of methyl phenyl sulfoxides, although X-ray[3] and dipole moment[4] studies on the corresponding sulfones indicate a preference for the conformation in which the methyl group is orthogonal to the plane of the benzene ring.