Hypoiodite Reaction: Mechanism of the Reaction of Mercury(II) Oxide–Iodine with Olefins

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Evidence is presented that the reaction of mercury(II) oxide–iodine with olefins in aprotic solvents proceeds through ' iodine oxide.' From a study of the products, which include rearranged carbonyl compounds, vinyl iodides, and 2,2′-di-iodo-ethers, and from an investigation of the reactions of epoxides and iodohydrins with mercury(II) oxide–iodine, it is concluded that ' iodine oxide ' addition occurs by a regiospecific ionic mechanism initiated by attack on the double bond by positive iodine.

THE use of mercury(II) oxide–iodine [1-5] as a positive iodine source is well established. We have previously reported its reaction with olefins [6] to give rearranged carbonyl compounds, vinyl iodides, and 2,2′-di-iodo-ethers, which we rationalised on the basis of an electrophilic addition reaction of iodine oxide (I_2O). Electrophilic addition of iodine to olefins has also been shown to occur with other iodine derivatives (INO_2, INO_3, INCO, IN_3, and IOMe) [7,8] as well as in the Woodward–Prevost

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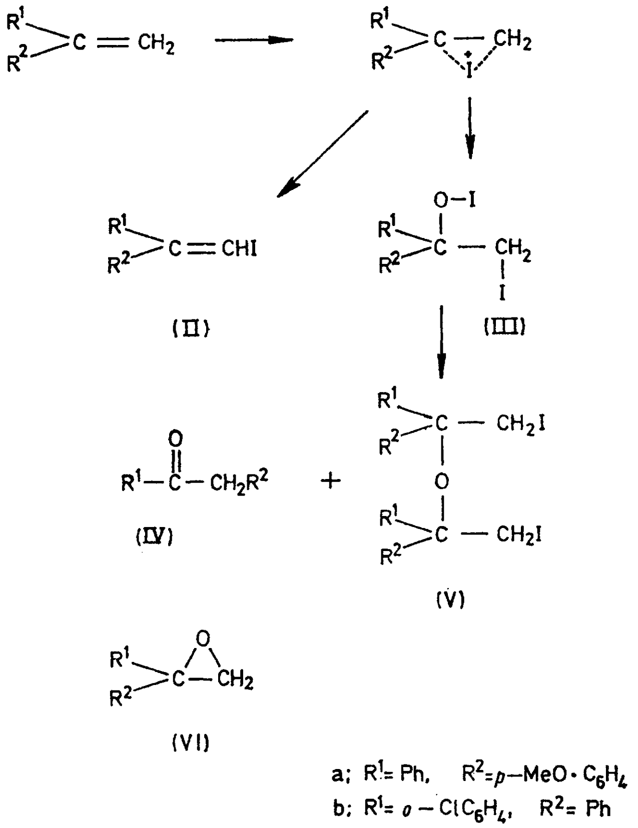
and related reactions.[9] This paper presents evidence that the reaction of mercury(II) oxide–iodine with olefins proceeds by an ionic mechanism and that ' iodine oxide ' is an intermediate.

The existence of iodine oxide as a reactive intermediate has been suggested,[10,11] but there is no direct evidence for this although derivatives have been prepared.[12] The stability and reactivity of the mercury(II) oxide–iodine reagent have been investigated and the best conditions for its utilisation in diol cleavage have been formulated.[11] In view of the established intermediacy of mercury complexes [13] in reactions which involve mercury(II) salts, mercury(II) oxide and iodine were mixed in chloroform, the mixture was filtered, and the reactivity of the filtrate, tested with 1,2-diphenylethane-1,2-diol, was compared with its mercury content. The experiment showed that the filtered solution was more active than would be expected of a mercury complex which would have to contain two positive iodine atoms. From a solubility study it was shown that at least half the mercury present could be accounted for by the solubility of mercury(II) oxide in chloroform. Furthermore no marked shift of the olefinic proton resonances of styrene in carbon tetrachloride was observed when it was treated with either mercury(II) oxide or mercury(II) iodide for 6 h. In view of these results we suggest that the reactive species is iodine oxide.

The products obtained from the reaction of olefins with mercury(II) oxide–iodine have been explained on the basis of regiospecific electrophilic addition of iodine oxide [6] with subsequent reaction to form iodoalkenes (II) of di-iodo-ethers (V), or rearrangement to ketones (IV). In order to establish that the rearranged products were obtained by a pinacol-type rearrangement from the adduct (III), the relative migratory aptitudes of the 1,1-diphenylethylenes (Ia and b) were investigated. The reactions of these olefins gave the rearranged ketones (IVa) and (IVb) as 100 and 90% of the total rearranged products isolated, respectively. These results indicate relative migratory aptitudes in qualitative agreement with those found for pinacols [14] and different from the values determined [15] for 1,2-shifts to a radical centre. Furthermore if the reaction of I_2O is initiated by the hypoiodite radical ($\dot{O}I$), phenylacetophenone (IV; $R^1 = R^2 = Ph$) could only have arisen from 1,1-diphenylethylene (I; $R^1 = R^2 = Ph$) *via* an epoxide intermediate (VI; $R^1 = R^2 = Ph$). Since, however, benzophenone was the major product from the reaction of mercury(II) oxide–iodine with 1,1-diphenylethylene oxide (VI; $R^1 = R^2 = Ph$) and was produced in low yield (6%) in the reaction of mercury(II) oxide–iodine with 1,1-diphenylethylene, the rearranged products must be formed from the iodo-hypoiodite adduct (III; $R^1 = R^2 = Ph$).



Yields of rearrangement products (IV) from olefins and iodohydrins

Olefin	Yield of (IV)[6] %	Iodohydrin	Yield of (IV) %
Cyclohexene	3·0	2-Iodocyclohexanol	3·7
Octadec-1-ene	39·0	1-Iodo-octadecan-2-ol	20·0
Pent-1-ene	3·6	1-Iodopentan-2-ol	19·0
Styrene	8·6	2-Iodo-1-phenylethanol	75·0
1,1-Diphenylethylene	45·0	2-Iodo-1,1-diphenyl-2-ethanol	2·0

Further evidence that the rearranged products were derived from iodo-hypoiodites was obtained from a study of the reaction of iodohydrins with mercury(II) oxide–iodine. Since alcohols rapidly form hypoiodites with an excess of this reagent,[3] the formation of the same rearranged products from iodohydrins and from the corresponding alkenes (see Table) further supports the

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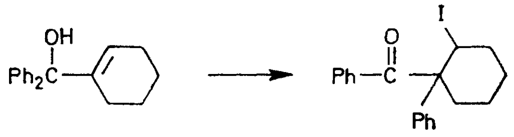
regiospecific, ionic addition pathway. As expected, enhanced yields of rearranged products were obtained from the iodohydrins. In addition the rearrangement product phenylacetophenone (IV; $R^1 = R^2 = Ph$) was obtained by the reaction of 2-iodo-1,1-diphenylethanol with t-butyl hypochlorite–iodine. Thus, in this case at least, the presence of mercury species was not necessary for heterolysis of the C–I bond in the rearrangement process. It is conceivable that the rearrangement occurs by a concerted mechanism which is facilitated by the polarity of the O–I bond.

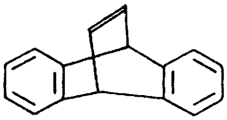
In view of a report of the rearrangements of allyl alcohols[16] with positive halogenating agents, the reaction of cyclohex-1-enyl(diphenyl)methanol (VII) with mercury(II) oxide–iodine was investigated. The product, 2-iodo-1-phenylcyclohexyl phenyl ketone (VIII), is in accord with the rearrangement rationalised in terms of an ionic addition of positive halogen to the olefin, followed by a 1,2-shift of the phenyl group with subsequent loss of a proton.



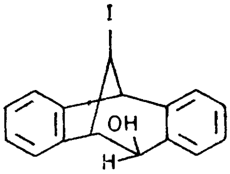
(VII) (VIII)

Reactions which can proceed by either a free radical or an ionic mechanism can be forced to go predominantly by one pathway if reaction conditions favouring that pathway are chosen.[17] Although no information is available on the properties of the hypoiodite radical $(\mathrm{I\dot{O}})$ it would be expected to be more electrophilic than the iodine atom on the basis of the electronegativities of oxygen and iodine. Further it has been established that peroxy-radicals, which would be expected to be less electronegative than the hypoiodite radical, abstract hydrogen atoms from the α-methylene group of the 'alcohol' part of an ester in preference to hydrogen atoms α to the carbonyl group.[18] Hence, if iodine oxide added to the double bond *via* a free radical mechanism, it would be expected that the reaction would be initiated by the hypoiodite radical to form the most stable intermediate radical, which would be trapped by the iodine present in the reaction mixture to produce 2-iodo-2,2-diphenylethyl hypoiodite. Treatment of 1,1-diphenylethylene with mercury(II) oxide–iodine gave products in essentially the same relative yields when the reaction was carried out either by irradiation in dry carbon tetrachloride in a nitrogen atmosphere or by shaking in the dark in the absence of nitrogen. This result is not unexpected since iodine is a radical trap and its presence, in excess, in the reaction solution would inhibit any radical reactions by trapping the hypoiodite radical before it was able to react with the alkene.

Addition reactions of 9,10-dihydro-9,10-ethenoanthracene (IX) have been reported,[8,19,20] and whereas only one example of rearrangement in a free radical reaction has been described,[21] electrophilic ionic addition results in rearrangement of the bicyclo[2.2.2] system to the [3.2.1] system. The major product from the reaction of compound (IX) with mercury(II) oxide–iodine was 10,11-dihydro-*syn*-12-iodo-5,10-methano-5*H*-dibenzo[*a*,*d*]-cyclohepten-*exo*-11-ol (X), in keeping with electrophilic addition of iodine oxide with subsequent hydrolysis of the hypoiodite to the alcohol during work-up.



(IX)



(X)

Evidence for *trans*-addition of iodine oxide to cholest-2-ene was obtained by examination of the n.m.r. spectrum of the resulting bis(iodocholestanyl) ether. Even although the structure has not been fully elucidated it is clear that the di-iodo-ether is formed by *trans*-addition since both the low-field n.m.r. signals have half-band widths of 6 Hz, in keeping with those reported[22] for the *trans*-adducts of unsaturated steroids. However, the n.m.r. spectrum of bis-2-iodocyclohexyl ether, obtained from the reaction of cyclohexene with mercury(II) oxide–iodine, was inconclusive. The half-band widths of the low-field protons were 15 and 25 Hz. This is most likely due to conformational mobility of this product.

Further evidence for nucleophilic attack by oxygen on the intermediate iodonium ion was the isolation of 2-ethoxy-2,2-diphenylethyl iodide when 1,1-diphenylethylene in chloroform was treated with mercury(II) oxide–iodine in the presence of ethanol.

In view of the possibility of the iodo-hypoiodite undergoing elimination of iodine to form epoxides which could subsequently react with the positive iodinating species, we investigated the reaction of epoxides with mercury(II) oxide–iodine. Cyclohexene oxide, styrene oxide, and 1,1-diphenylethylene oxide underwent, respectively 51, 32, and 40% cleavage of the C–C bond, producing the corresponding aldehyde or ketone. No cleavage products were found in the corresponding olefin reactions. 1-Chloro-2,3-epoxypropane and pent-1- and 2-ene oxides were essentially unreactive and

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stilbene oxide produced diphenylacetaldehyde in almost quantitative yield. The cleavage reaction probably occurs by iodination at oxygen followed by ring opening with hypoiodite to generate the dihypoiodite, which has been postulated as the intermediate in the cleavage of vicinal diols by mercury(II) oxide–iodine.[3] The rearranged products can be accounted for either by rearrangement of a carbocation intermediate or by a synchronous process. Hence epoxides are not intermediates in the reaction of alkenes with mercury(II) oxide–iodine.

The reason for the low yield of products,[6] especially with straight-chain and cyclic olefins, was also investigated. In order to test whether this was due to di-iodoalkane formation,[23] cyclohexene and pent-2-ene were shaken in the dark with an excess of iodine in carbon tetrachloride. N.m.r. spectra recorded at regular intervals showed a loss in intensity of the =CH resonances and the appearance of new resonances in the iodomethylene region. Equilibrium was established between cyclohexene and pent-2-ene and their respective di-iodoalkanes after about 1·5 h, when the solutions contained 20 and 50% of the olefins, respectively. The di-iodoalkanes were unstable oils which decomposed under normal work-up conditions to starting olefin and iodine.

A similar experiment with 1,1-diphenylethylene showed no measurable loss of olefin after 24 h. This establishes that 2-iodo-1,1-diphenylethene is not produced by addition of iodine and subsequent elimination of hydrogen iodide when 1,1-diphenylethylene is treated with mercury(II) oxide–iodine.

EXPERIMENTAL

M.p.s were determined with a Kofler-hot-stage apparatus. N.m.r. spectra were recorded with a Perkin-Elmer R12A spectrometer (Me_4Si as internal standard). G.l.c. analyses were carried out on a Perkin-Elmer F7 Fractometer and on a Packard Becker 420 gas chromatograph. The light petroleum used had b.p. 40—60°. Column A consisted of 1% Silicone DOW 11 on Chromport XXX (60—70 mesh), column B 10% Carbowax on Chromport XXX (60—70 mesh, and column C 15% Apiezon L on Chromosorb P (80—100 mesh).

Reaction of Olefins with Mercury(II) *Oxide–Iodine.—General procedure.* The olefin (5 mmol) in dry carbon tetrachloride (150 ml) was shaken in the dark with yellow mercury(II) oxide (5 mmol) and iodine (20 mmol) for 22 h. The solution was filtered, washed successively with an excess of 10% sodium thiosulphate solution and water, dried, and concentrated. The products were separated by column and/or preparative t.l.c. on silica gel.

(i) 1-*p*-Methoxyphenyl-1-phenylethylene gave 2-*p*-methoxyphenylacetophenone (0·09 mmol), m.p. 95—96·5° [24] (from ethanol), $\nu_{max.}$ 1695 and 1250 cm^{-1}; δ ($CDCl_3$) 3·73 (3H, s), 4·19 (2H, s), and 6·7—8·2 (9H, m) (Found: C, 79·9; H, 6·3. $C_{15}H_{14}O_2$ requires C, 79·7; H, 6·2%); 2-*p*-methoxyphenyl-2-phenylvinyl iodide (0·1 mmol), m.p. 95—96° (from light petroleum), M^+ 320, δ ($CDCl_3$) 3·78 (3H, s) and 6·7—7·4 (10H, m); and starting material (3·6 mmol).

(ii) 1-*o*-Chlorophenyl-1-phenylethylene gave 2-o-*chlorophenyl-2-phenylvinyl iodide* (2 mmol) as an oil, δ (CCl_4) 7·05 (1H, s) and 7·07—7·5 (9H, m) (Found: C, 48·7; H, 2·8. $C_{14}H_{10}ClI$ requires C, 48·7; H, 2·9%), and a mixture of the isomers *o*-chloro-2-phenylacetophenone and 2-*o*-chlorophenylacetophenone (2·31 mmol), shown by g.l.c. (column C; 280°; t_R 360 and 390 s, respectively) to be in the ratio 10 : 1 by comparison with authentic specimens.

(iii) (*a*) 1,1-Diphenylethylene gave 2,2-diphenylvinyl iodide (1·45 mmol) and phenylacetophenone (2·2 mmol).

(*b*) 1,1-Diphenylethylene, treated as described in the general procedure except that the solution was irradiated with a 150 W tungsten source in a dry nitrogen atmosphere, gave 2,2-diphenylvinyl iodide (1·45 mmol) and acetophenone (2·5 mmol).

(*c*) 1,1-Diphenylethylene, treated as in the general procedure except that ethanol (40 mmol) was added to the solvent, gave 2-*ethoxy*-2,2-*diphenylethyl iodide* (1·5 mmol), m.p. 74—75° (from ethanol), δ ($CDCl_3$) 1·2 (3H, t), 3·2 (2H, q), 4·07 (2H, s), and 7·3 (10H, m) (Found: C, 54·6; H, 5·0. $C_{16}H_{17}IO$ requires C, 54·6; H, 5·4%); and phenylacetophenone (0·52 mmol), m.p. 59—60°.[25]

2-Ethoxy-2,2-diphenylethyl iodide was reduced with lithium aluminium hydride to give 1,1-diphenylethane, δ (CCl_4) 1·6 (3H, d), 4·1 (1H, q), and 7·15 (10H, s); and bis-1-phenylethyl ether, δ (CCl_4) 1·2 (3H, t), 1·8 (3H, s), 3·2 (2H, q), and 7·2 (10H, m).

(iv) 9,10-Dihydro-9,10-ethenoanthracene gave 10,11-dihydro-*syn*-12-iodo-5,10-methano-5*H*-dibenzo[*a,d*]cyclohepten-*exo*-11-ol (1·2 mmol), m.p. 138—139°,[26] δ (CCl_4) 2·8 (1H, s), 3·46 (1H, d), 3·96 (1H, d), 4·5 (1H, s), 4·76 (1H, t), and 7·3 (9H, m) (Found: C, 55·0; H, 3·9. Calc. for $C_{16}H_{13}IO$: C, 55·1; H, 3·7%).

(v) Cyclohex-1-enyl(diphenyl)methanol gave 2-*iodo*-1-*phenylcyclohexylphenyl ketone* (0·82 mmol), m.p. 146—148° (from ethanol), δ ($CDCl_3$) 1·4—2·0 (4H, m), 2·00—2·80 (4H, m), 5·35 (1H, m), and 7·2—7·6 (10H, m) (Found: C, 58·5; H, 4·8. $C_{19}H_{19}IO$ requires C, 58·4; H, 4·9%).

(vi) Cholest-2-ene gave a bisiodocholestanyl ether, m.p. 253—254·5°, *m/e* 756 ($M^+ - I_2$), δ ($CDCl_3$) 0·5—2·0 (m), 3·85 (m, $W_{\frac{1}{2}}$ 6 Hz), and 4·55 (m, $W_{\frac{1}{2}}$ 6 Hz) (Found: C, 64·3; H, 9·2. Calc. for $C_{54}H_{92}I_2O$: C, 64·1; H, 9·1%).

Reactions of Epoxides with Mercury(II) *Oxide–Iodine.—General procedure.* The epoxide was treated with 1 mol. equiv. of the reagent and the mixture was set aside in the dark for 2—3 days, washed ($Na_2S_2O_3$), and dried (Na_2SO_4). The amount of starting material was determined by g.l.c. analysis. The mixture was then treated with an excess of aqueous acidic 2,4-dinitrophenylhydrazine reagent and separated by chromatography on silica gel.

(i) Cyclohexene oxide (3·04 g, 31 mmol) after 2 days was 6% unchanged (column A; 30°) and yielded cyclopentanecarbaldehyde 2,4-dinitrophenylhydrazone (0·13 g), m.p. 156—160° [27] (from ethanol), and adipaldehyde bis-2,4-dinitrophenylhydrazone (0·47 g), m.p. 243·5—246·5° (decomp.) (Found: C, 45·7; H, 4·4. Calc. for $C_{18}H_{18}N_8O_8$: C, 46·0; H, 3·8%).

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(ii) Styrene oxide (1·1 g, 10 mmol) after 1 day afforded benzaldehyde (12%) and formaldehyde (32% in the $Na_2S_2O_3$ washings) (column A; 50°) and was completely consumed.

(iii) Stilbene oxide (1·96 g, 10 mmol) after 2 days afforded diphenylacetaldehyde (90%) but no benzaldehyde; no starting material remained (column A; 55°).

(iv) Pent-2-ene oxide (1 g, 12 mmol) after 2 days was >95% unchanged (column A; 30°).

(v) Pent-1-ene oxide (0·5 g, 6 mmol) after 3 days was 75% unchanged (column B; 70°); no 2,4-dinitrophenylhydrazone derivatives were observed.

(vi) 1-Chloro-2,3-epoxypropane (4·62 g, 50 mmol) was unchanged after 3 days.

(vii) 1,1-Diphenylethylene oxide (0·343 g, 1·75 mmol) after 1 day afforded benzophenone (40%) (column A; 180°).

Reaction of Iodohydrins with Mercury(II) *Oxide–Iodine.—General procedure.* The iodohydrin in dry carbon tetrachloride (to give a 0·05M-solution) was treated with mercury(II) oxide (1 mol. equiv.) and iodine (4 mol. equiv.) and shaken in the dark for 22 h. The solution was worked up as before and divided into two. One portion was shaken with aqueous acidic 2,4-dinitrophenylhydrazine to give a mixture which was separated by chromatography on silica gel. Attempts to isolate products from the other portion were less successful and are not reported.

(i) 2-Iodocyclohexanol (1·75 g, 7·75 mmol) gave cyclopentanecarbaldehyde 2,4-dinitrophenylhydrazone (0·08 g), m.p. 157—160°,[27] and starting material (0·84 g).

(ii) 1-Iodo-octadecan-2-ol (4·5 g, 11·4 mmol) gave octadecanal 2,4-dinitrophenylhydrazone (1·04 g), m.p. 100°.[28]

(iii) 1-Iodopentan-2-ol (3·41 g, 16 mmol) gave pentanal 2,4-dinitrophenylhydrazone (0·8 g), m.p. 105—107°.[25]

(iv) 2-Iodo-1-phenylethanol (2·9 g, 11·7 mmol) gave phenylacetaldehyde 2,4-dinitrophenylhydrazone (2·64 g), m.p. 121°.[29]

(v) 2-Iodo-1,1-diphenylethanol (0·46 g, 1·42 mmol) gave phenylacetophenone 2,4-dinitrophenylhydrazone (0·44 g), m.p. 203—206°.[25]

Reaction of 2-*Iodo*-1,1-*diphenylethanol with t-Butyl Hypochlorite–Iodine.*—The iodohydrin (1·0 g, 3 mmol) in carbon tetrachloride was treated with iodine (1·55 g, 6·1 mmol), and t-butyl hypochlorite (0·33 g, 3 mmol) was added in two portions in the dark during 5·5 h. The solution gave an oily mixture of starting material and phenylacetophenone (1·8 : 1 by n.m.r.). A portion of the oil in methanol on treatment with 2,4-dinitrophenylhydrazine reagent gave phenylacetophenone 2,4-dinitrophenylhydrazone, m.p. 200—201°.[30]

Reaction of Alkenes with Iodine.—General procedure. The alkene (30 mmol) in dry carbon tetrachloride was shaken with iodine (30 mmol) at ambient temperature in a coated vessel. Samples were analysed by n.m.r. spectroscopy.

(i) With cyclohexene the =CH signal at δ 5·6 decreased and a signal at δ 5·0, attributed to CH_2I, appeared and increased. After 1·5 h the mixture contained 20% of the original amount of cyclohexene. The constitution of the mixture was unaltered after a further 2 h.

(ii) With pent-2-ene the =CH signal at δ 5·4 decreased and a signal at δ 4·6 (m), attributed to CH_2I, appeared. After 1·5 h the mixture contained 50% of the original amount of cyclopentene. The constitution of the mixture was unaltered after a further 0·5 h.

(iii) The n.m.r. spectrum of 1,1-diphenylethylene was unchanged after 24 h.

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