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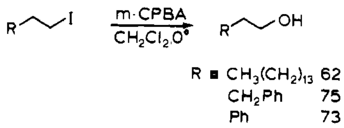
Received February 27, 1978

Hypervalent Organoiodine Chemistry.[1] Syn Elimination of Alkyl Iodoso Compounds

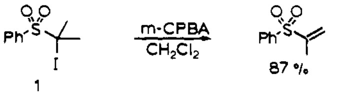
Sir:

We report here evidence that the oxidation of alkyl iodides in nonpolar media gives an oxidized iodine intermediate (the iodoso compound) which can lead to olefins by a syn elimination process. It is known that amine oxides,[2] sulfoxides,[3] and selenoxides[4] undergo thermal pericyclic eliminations of hydroxylamine, sulfenic acid (RSOH), and selenenic acid (RSeOH), respectively, to form olefins. Alkyl iodide oxides (iodoso compounds), although unknown as stable compounds,[5] should also be capable of a similar syn elimination of hypoiodous acid (IOH).

Alkyl iodides are inert to a number of oxidizing agents such as ozone, periodate, and hydrogen peroxide which serve to convert sulfides and selenides to their oxides. However, treatment with *m*-chloroperbenzoic acid (*m*-CPBA, 1.5 equiv) in dichloromethane or carbon tetrachloride leads to oxidation of the iodide. Primary alkyl iodides are converted to the corresponding alcohols in good yields; only trace amounts of *m*-chlorobenzoate esters are formed. Labeled 2-phenyl-1-iodoethane-*1,1-d*$_2$ leads to partially scrambled products (35% of 2-phenylethanol-*2,2-d*$_2$). This observation, together with the formation of complex mixtures of alcohols and benzoates from neophyl, cyclohexylmethyl and 2-dodecyl iodides, suggests that carbonium ion intermediates are involved.



The oxidation of alkyl iodides bearing strongly electron-attracting substituents such as carbomethoxy and sulfonyl at the α carbon proceeds differently than those reported above. For example, 2-phenylsulfonyl-2-iodopropane (**1**)[6] and ethyl 2-iododecanoate (**2**)[6] are converted in a high yield reaction to



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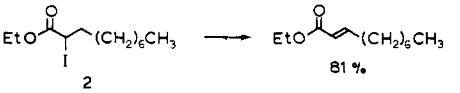

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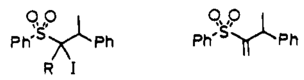
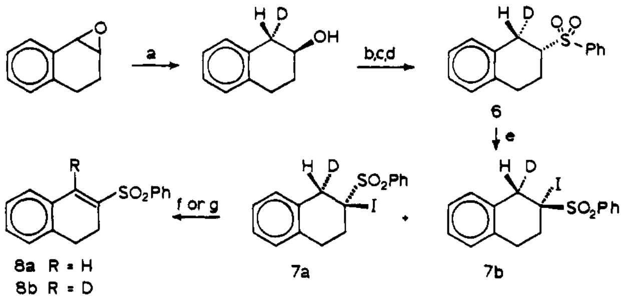
the unsaturated compounds. Approximately 2 equiv of peracid are required for complete oxidation since at least one of the products (I_2) is oxidized under these conditions.

The study of the stereochemistry of this elimination reaction was initially attempted with the easily available compounds **3** and **4**. The results were ambiguous, however, since exclusive elimination toward the methyl group to give **5** was observed on oxidation of **3**, while **4** gave none of the expected vinyl sulfone product. A suitable system was the tetralin **6**, prepared as shown in Scheme I. Although base-catalyzed isotopic exchange of protons α to sulfones frequently occurs with retention of configuration,[9] the metalation–iodination steps (e in Scheme I) consistently led to a 1:1 mixture of **7a** and **7b.** An 87:13 ratio of **7a** to **7b** was obtained by partial dehydroiodination of the 1:1 mixture with 0.7 equiv of 1,5-diazabicyclo[5.4.0]undec-5-ene (DBU). The configurational assignment for **7** was made on the basis of the following considerations: (1) a positive isotope effect for the presumed anti elimination (E_2),[10] (2) the presence of a four-bond long-range (W) coupling for the proton assigned as trans to the sulfonyl substituent,[11] and (3) the observation of a larger Eu(fod)$_3$ shift for the proton cis to the sulfonyl.[11b]



3 R = CH_3
4 R = H
5

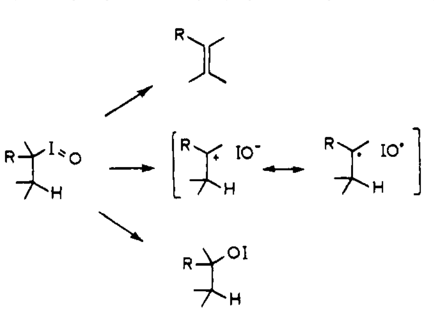
Scheme I[a]



[a] Step a: $LiAlD_4$, $AlCl_3$, Et_2O (85%, ref 7). Step b: CH_3SO_2Cl, NEt_3 (96%). Step c: PhSH, *t*-BuOK, *t*-BuOH (61%). Step d: H_2O_2, *o*-$NO_2C_6H_4SeO_2H$, CH_2Cl_2 (81%, ref 8). Step e: LiN-*i*-Pr_2, THF, −78 °C; I_2, THF, −78 °C (84%). Step f: *m*-$ClC_6H_4CO_2H$ (2.0 equiv), CH_2Cl_2, 25 °C (67%). Step g: EtOH, EtOK (88%).

Treatment of the 87:13 mixture of **7a** and **7b** with *m*-CPBA gave vinyl sulfone **8** which was 89 ± 2% d_1 (**8b**) by ^{1}H NMR analysis. Base-catalyzed elimination (EtOH, EtOK) yielded vinyl sulfone which was 21% d_1.[12] The *oxidative elimination, therefore, proceeds with syn stereochemistry.*

We propose an iodoso compound as an intermediate along the reaction pathway. For most primary iodides, the iodoso compound rearranges to the hypoiodite, which is (oxidatively?) converted to the alcohol under the reaction conditions. This



rearrangement may occur by either a 1,2-alkyl shift or via a radical or ion pair. If the carbonium ion is secondary and/or prone to Wagner-Meerwein rearrangements, more complex product mixtures are obtained.[13] When carbonium ion formation is suppressed by electron-withdrawing substituents (R = CO_2CH_3, SO_2Ph), a pericyclic syn elimination to the olefin predominates.

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Ogata and Aoki[14] have previously observed the formation of acetoxy-, vicinal diacetoxy-, and iodoacetoxyalkanes upon oxidation of iodoalkanes with peroxyacetic acid in acetic acid. These results are consistent with the solvolysis or elimination of an intermediate iodoso compound followed by further reaction of any olefin formed with peracid or acyl hypoiodite. Under these conditions primary iodides gave acetoxy compounds, whereas alcohols were isolated in the present work. More recently, Beeley and Sutherland have proposed an elimination of hypoiodous acid to account for olefin formation during the Baeyer-Villiger oxidation of an iodonorbornanone.[15]

Acknowledgment. We thank the Dow Chemical Co., the National Science Foundation, and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work.

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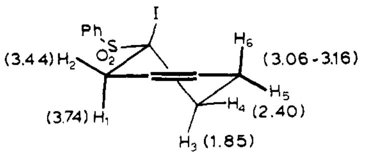

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(12) Complete oxidative or base elimination of the 1:1 mixture of diastereomers **7** produced **8a** and **8b** in a 48:52 (52 ± 5% d_1, *m*-CPBA in CH_2Cl_2) or 47:53 (53 ± 3% d_1, EtOK in EtOH) ratio.
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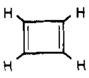
Cyclobutadiene Is Not Square

Sir:

The most crucial current issue of cyclobutadiene chemistry concerns the ground-state geometry of the parent compound **1**.[1] The full characterization of simple crystalline derivatives (**2** and **3**), in which the electronic state of the system is only slightly perturbed, has led to the unambiguous demonstrations (a) that the ground states of **2**[2] and **3**[3] are singlet and (b) that their cyclobutadiene rings are not square, but rectangular. These results contrast to those for **1**. While repeated failures to observe ESR signals (ascribable to a triplet state) strongly indicate a singlet ground state for **1**,[2a] an IR spectral analysis has concluded that **1** detained in an argon matrix possesses a square geometry.[4] However, this conclusion is, in essence, based on the assignment of an absorption at 1240 cm^{-1} to a C—C stretching vibration.[5] Although some theoretical treatments have proposed a square triplet (ST) (excited) state[4a,6] or an "effectively" square singlet (SS) ground state[7] for the matrix-isolated species, more recent calculations conclude that the ST lies above the SS in the energy surface of the system and a rectangular singlet (RS) represents the ground state of **1**.[8,9] Earlier we emphasized the necessity of further IR studies on both **1** and its perdeuterio derivative **4**.[1a,5a] The spectral evidence presented herein now disproves the previous conclusion that the ring is square and is only consistent with a geometry less symmetrical than D_{4h}, very likely rectangular, for **1**.



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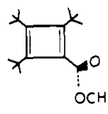

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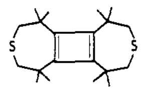

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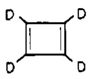

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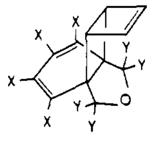
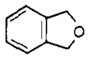


5a X = H Y = H
5b X = D Y = H
5c X = H Y = D
5d X = D Y = D



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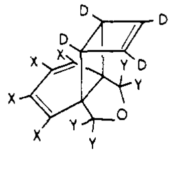
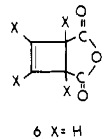
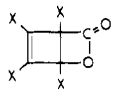


9a X = H Y = H
9b X = D Y = H
9c X = H Y = D
9d X = D Y = D



6 X = H
10 X = D



7 X = H
11 X = D

Of the known photoprecursors (**5a**,[10] **6**,[1b,5b] and **7**[4]) of **1**, irradiation (medium-pressure mercury lamp, Vycor filter) of **5a** in an argon matrix (7K, guest-host ratio 1:100-500) proceeds most efficiently to provide the highest concentration of **1**, but the concurrent generation of phthalan **8** masks several regions of the infrared spectrum. However, deuterium incorporation in **5a** as indicated in **5b–d** shifts the IR absorptions of **8**, and use of all these precursors has permitted the careful inspection of the vibrational modes of **1** in the entire region from 4000 to 400 cm^{-1}. Thus IR spectra of the photolysates of **5a** and **5d** recorded with a Nicolet 7199 FT-IR interferometer (resolution 0.5 cm^{-1}, 100-500 scans averaged) clearly showed that, in addition to the two reported bands at 1240 and 572 cm^{-1}, there were observed, for the first time, two weak absorptions at 1523 and 723 cm^{-1} (below 1700 cm^{-1}), which had escaped previous detection. The appearance of these bands from other precursors **6** and **7** was subsequently confirmed. The deuterio series including **9a–d**, **10**, and **11** behaved correspondingly to the protio series, exhibiting, after irradiation, absorptions which increased in intensity upon irradiation of *all* of the precursors (**5a,d**, **6**, **7**, and **9a,b**, **10**, and **11**) employed and decreased upon warming to 35 K.[11] Figures 1-3 show the

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