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Sulphur dioxide has been found to promote a novel liquid-phase oxidation of 1,3-butadiene in acetic anhydride with oxygen gas and catalytic amounts of concentrated protic acids (*e.g.* hydrobromic acid). 1,2-Diacetoxy-3-butene and 1,4-diacetoxy-2-butene together with small amounts of 1-hydroxy-2-acetoxy-3-butene and 1-hydroxy-4-acetoxy-2-butene are formed in the reaction.

According to Woodward and Hoffmann (1), the concerted 1,4-cycloaddition of sulphur dioxide to conjugated dienes is thermally allowed as a linear cheletropic reaction, with the required disrotatory process having been observed (2). It is also known that thermal five-membered ring fragmentation of these adducts occurs *via* a concerted process, and 1,4-*cis* elimination may be predicted on the basis of orbital symmetry arguments (3). These reactions have found application in the purification of dienes *via* the formation, separation and decomposition of cyclic sulfones (4). Sulphur dioxide, however, has never been previously considered as a promoter of oxidation in dienic systems.

In this regard, based on similar interactions between selenium dioxide and conjugated dienes, a convenient route leading to the formation of 1,3-butadiene diacetoxy-derivatives has been recently reported by Javaid, *et al.*, (5). Selenium dioxide differs greatly from sulphur dioxide with regard to its oxidizing potential; only in certain cases has the latter been shown to act as an oxidizing agent (6). We have now further found that relative to selenium dioxide oxidation and to other known oxidative procedures, the diacetoxylation of 1,3-butadiene carried out in acetic anhydride and in the presence of sulphur dioxide and molecular oxygen, is distinctively different.

The yield of the diacetoxy derivatives is affected by molecular oxygen; this effect is reminiscent of a liquid-phase catalytic process reported by Bryant, *et al.*, (7) in which benzyl esters are produced from methylbenzene derivatives in carboxylic acids and in the presence of a homogeneous palladium (II) acetate-stannous acetate catalyst with air as the ultimate oxidant. Oxidations by palladium (II) acetate are of recent discovery (8) and owe their importance to the ready reoxidation of palladium metal, allowing for full catalytic synthesis even on an industrial scale. By contrast, while molecular oxygen is the ultimate oxidant in these reactions, sulphur dioxide does not appear to have been reduced.

Small amounts of 2,5-dihydrothiophene 1,1-dioxide

have been identified among our reaction products while even reported diacetoxylation of 1,3-butadiene with selenium dioxide (5), small amounts of organoselenium compounds in a reduced state have been isolated. The formation of 2,5-dihydrothiophene 1,1-dioxide cannot be solely based on the greater tendency (relative to selenium dioxide) of sulphur dioxide to undergo cycloaddition with dienes, since detectable amounts of sulphur trioxide have been found in our reaction media. Therefore, it seems reasonable to assume that sulphur dioxide, while promoting the diacetoxylation of 1,3-butadiene, may be concurrently autoxidized to sulphur trioxide. This finding is not entirely unexpected. In the base catalyzed oxidation of organic sulfides with molecular oxygen to give carboxylic and sulphonic acids, as reported by Wallace, *et al.*, (9), the observed rapid decrease in oxidation rate has been attributed to the comsumption of base by acidic oxidized products which form in the initial steps of the reaction.

The effect of added alkali acetates or concentrated protic acids on the oxidation was also studied. With added sodium acetate, the yield of the diacetoxy derivatives did not change significantly. In this case, the 1,2- and 1,4-diacetoxylation of the conjugated diene probably does not involve an electrophilic attack of the metal salt onto the diene, as reported by Uemura, *et al.*, (10) in typical diacetoxylations performed with thallium (III) and lead (IV) acetates. Rather, the acetate ions seem to facilitate competitive autoxidation of sulphur dioxide, and at the end of the reaction an increased amount of sulphur trioxide is found. It is known that many compounds capable of forming anions interfere with autoxidation (see, *e.g.*, the reported superiority of hexamethylphosphoramide over other solvents (11)). In this case, however, the formation of sulphur trioxide is better explained assuming the formation (see Scheme) of a highly unstable, deprotonated, mixed anhydride of peracetic acid with sulphurous acid (F), which may lose sulphur dioxide or be oxidized to sulphur trioxide. This assumption is consistent with the reported behaviour of other mixed anhydrides

(e.g., mixed sulphuric carboxylic anhydrides) as far as ease of formation (12) and thermal stability (13) are concerned. Further, while studying the oxidation of the inner cyclic anhydride of an unstable α-sulphinocarboxylic acid (14) with peracids, we found that free sulphur trioxide was formed (15). Thus, our assumption concerning the existence of the intermediate F in the reaction mechanism seems plausible.

With added catalytic amounts of concentrated protic acids, the yield of the diacetoxy derivatives increased significantly. Assuming that the diacetoxylation of 1,3-butadiene proceeds via the formation of 2,5-dihydrothiophene 1,1-dioxide, it may be postulated that protic acids catalyze the thermal fragmentation of the 1,3-butadiene sulphur dioxide adduct. While with other cyclic sulfur dioxide adducts (14), the opening of the cyclic compounds proceeds via either a concerted process or via a two-step ionic mechanism involving the formation of a zwitterion, in this case the thermal fragmentation of our intermediate must proceed through an acid catalyzed, unconcerted process, requiring a great amount of C-S bond dissociation before an appreciable amount of overlap is developed within the forming conjugated system. Autoxidation at the resultant carbanion probably involves the formation of radicals from the anion by electron transfer (16) to oxygen (Equations 1 and 2). The resultant radicals
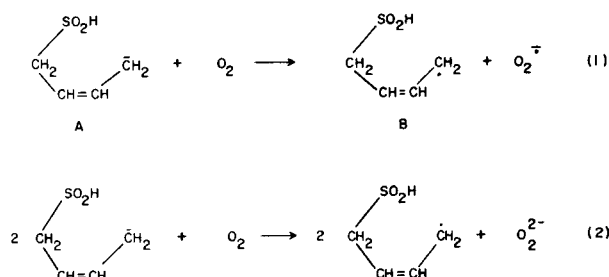
can then react with oxygen by a free radical chain reaction to form unstable peroxide ions (Equations 3 and 4).
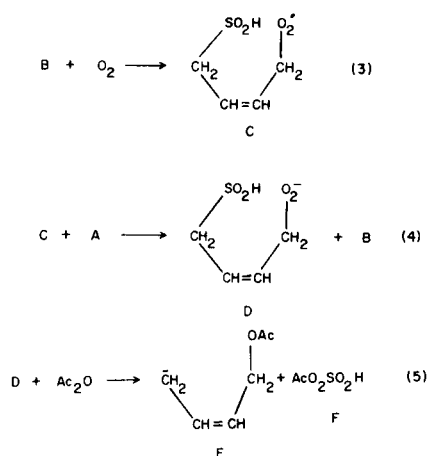
Acetolysis of the unstable peroxide ion (Equation 5) would then generate the highly unstable mixed anhydride of peracetic acid with sulphurous acid (F), which may react as has already been indicated.

This proposed reaction mechanism seems to be the most reasonable based on our experimental work. In further support of it, we have found that by diacetoxylating 1,3-butadiene in acetic anhydride with sulphur dioxide and oxygen and in the presence of free radical scavengers (e.g., aromatic amines and hydroquinone), the yields of both diacetoxy compounds decrease greatly.

EXPERIMENTAL

Infrared spectra were recorded on a Perkin-Elmer 457 instrument and nmr spectra were determined on a Varian HA 100 spectrometer using tetramethylsilane as an internal reference. Qualitative and quantitative gas chromatographic analyses were conducted on P. E. G. 20M and S. E. 30 columns fitted on a Carlo Erba model GT 200 gas chromatograph, using helium as carrier gas.

All the experimental runs were carried out in pressure equipment in a barricaded area; the progress of the reaction was followed by measurements of changes in pressure.

General Procedure.

In a typical run, a solution of hydrobromic acid (0.5 ml., 48%) in acetic anhydride (150 ml.) was placed in a mechanically stirred stainless steel autoclave (475 ml.) which was subsequently closed and slowly cooled to -40° while deaerating under vacuum. After injecting the required liquefied amounts of sulphur dioxide (35 mmoles) and 1,3-butadiene (150 mmoles), the autoclave was brought to room temperature and pressurized with oxygen (24.0 atmospheres) and nitrogen (165.0 atmospheres) while stirring. On reaching (60 minutes) the reaction temperature (100°), a periodic repressuring with nitrogen was necessary to maintain the pressure for the designated (17) period of time (30 minutes). After that time, the autoclave was rapidly (30 minutes) cooled to room temperature and unreacted 1,3-butadiene was carefully recovered and estimated with maleic anhydride using a standard method (18). Relative to absorbed 1,3-butadiene (84 mmoles), a 56% conversion was found.

The reaction mixture was quenched with water and immediately extracted with dichloromethane. In the aqueous phase, free sulphate ions were determined (2 mmoles: after neutralization with sodium hydroxide and evaporation, by the Eschka method (19) 12 mmoles of sulphate ions were found.)

The organic layer was evaporated under vacuum; the residue was diluted with dichloromethane and washed with aqueous sodium hydroxide to completely remove acetic anhydride. After drying the resulting organic solution over anhydrous sodium sulphate, the solvent was removed under vacuum leaving a residue which was extracted with diethyl ether. From the diethyl ether insoluble residue, 2,5-dihydrothiophene 1,1-dioxide (2 mmoles) was separated by crystallization with ethanol and its identity confirmed through an independent synthesis (20). The ethereal extract was evaporated to dryness and the residue was fractionated by vacuum distillation. The fraction boiling at 60-65° (3 mm) gave 1,2-diacetoxy-3-butene (16 mmoles) and 1-hydroxy-2-acetoxy-3-butene (2 mmoles). A second fraction (b.p. 80° at 3 mm) was a mixture of 1,4-diacetoxy-2-butene (22 mmoles) and 1-hydroxy-4-acetoxy-2-butene (3 mmoles). Thus, in mmoles % relative to absorbed 1,3-butadiene, the yield of acetoxy derivatives was 51%.

Identification of the acetoxy derivatives has been preliminarly performed through an exhaustive acetylation with acetic anhydride in pyridine under reflux conditions for five hours to the corresponding diacetates, by comparison with independently prepared samples (10). All the products have been further identified by preparative gc performed with known sample mixtures (5).

Blank experiments showed that the reaction conditions used did not cause the interconversion of 1,2- and 1,4-diacetoxy compounds.

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