Bull. Chem. Soc. Jpn., 71, 1397—1400 (1998) 1397

Tetrachlorocyclopentadienone *O*-Oxide, a Facile Oxygen-Atom-Transfer Reagent: The Disproportionation of Cycloalkyldioxyl Radicals

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(Received December 18, 1997)

Photolysis of tetrachlorodiazocyclopentadiene (**1**) in oxygen-saturated hydrocarbon solvents results in the transient formation of tetrachlorocyclopentadienone *O*-oxide (**3**). This rapidly decomposes, giving rise to products derived from oxidation of the hydrocarbons. Cyclopentane, cyclopentene, cycloheptane, cycloheptene, cycloheptatriene, and indene have been studied. Cycloheptatriene and indene gave only low yields of tractable products, but the others gave the corresponding ketones and secondary alcohols as the major products. Although yields varied considerably, the ketone and alcohol products were always obtained, within experimental error, in a 1 : 1 molar ratio. This observed product ratio supports the disproportionation of cycloalkyldioxyl radicals as a crucial step.

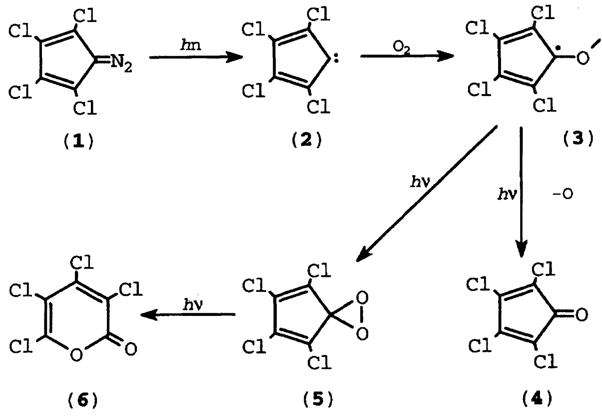
In earlier papers of this series,[1,2] we reported that tetrachlorocyclopentadienone *O*-oxide (**3**), generated in solution from the photolysis of tetrachlorodiazocyclopentadiene (**1**) in the presence of dioxygen, can oxidize hydrocarbons such as cyclohexane and cyclohexene in high yields and with some degree of selectivity. A free radical mechanism involving the disproportionation of cycloalkyldioxyl radicals was proposed for these oxidations.

Carbonyl oxides such as **3** have received considerable attention in recent years. Numerous oxidations involving these species have been studied.[3—18] Examples of carbonyl oxides have also been identified and characterized spectroscopically in low-temperature matrices, the first being the unchlorinated analogue of **3**, cyclopentadienone *O*-oxide;[19,20] and more recently Sander has reported the first NMR observation of a carbonyl oxide.[21] The low temperature work and theoretical studies of carbonyl oxides have been reviewed by Sander,[22] whilst Bunnelle has reviewed the preparation, properties and reactions of carbonyl oxides.[23] Sawaki et al. have recently reported that the introduction of potent electron-withdrawing groups (trifluoromethyl) results in a dramatic change in the reactivity of the resulting carbonyl oxide.[24] The formation of tetrachlorocyclopentadienone *O*-oxide (**3**) from carbene **2** and O_2, and its structure and photochemistry were first studied in Ar and N_2 matrices at 12 K.[25] The results suggested that it would be less likely to undergo photochemical rearrangement (to **6** via **5**), and more likely to decompose by O-atom expulsion, than previously studied carbonyl oxides (Scheme 1). Thus **3** was identified as a likely reagent for efficient oxygen-atom-transfer reactions in more normal conditions, such as ambient-temperature solutions. The results to data have borne this out: **3** has usually promoted oxidations in considerably higher yield than the carbonyl oxides studied earlier.[1,2]

We have now extended our studies of the oxidation of hydrocarbons by **3** to include cyclopentane, cyclopentene, cycloheptane, cycloheptene, cycloheptatriene, and indene. In this paper we report our findings.

Results

In a typical experiment, a solution of tetrachlorodiazocyclopentadiene (**1**) (ca. 5×10^{-2} M, $1\ \mathrm{M}=1\ \mathrm{mol\,dm^{-3}}$) in the hydrocarbon was placed in the 20-cm^3 Pyrex photolysis vessel described previously,[1,2] kept saturated with O_2 by continuous passage of a gentle stream of the gas, and irradiated with a medium-pressure Hg arc. In some experiments, additional portions of **1** were added at hourly intervals. After complete photolysis of **1**, the resulting solution was analyzed by gas chromatography (GC), using authentic samples of the



Scheme 1.

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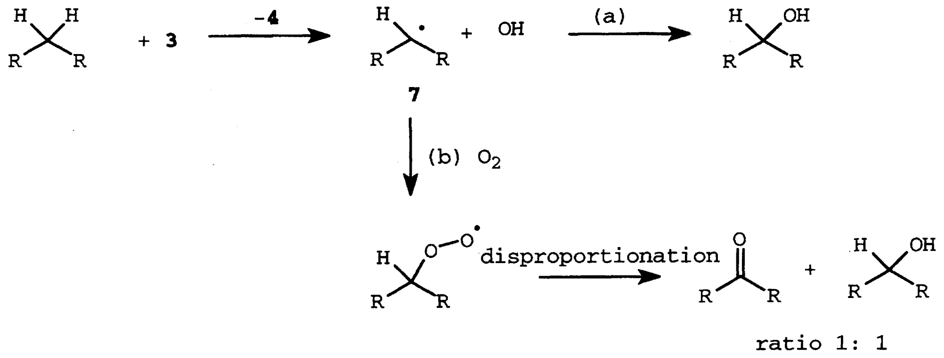


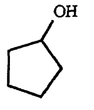
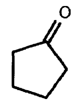
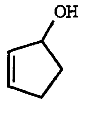
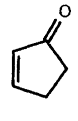
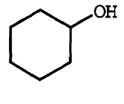
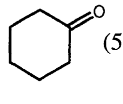
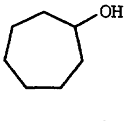
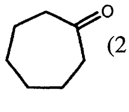
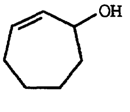
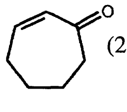
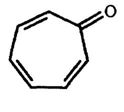
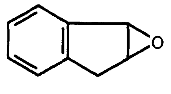
Scheme 2.

products for comparison.

The Table 1 gives the products and yields obtained from each of the hydrocarbons studied. Yields are based on the amount of **1** consumed. Since the hydrocarbons were also the reaction solvents, the percentage conversion of the hydrocarbons to products was in all cases low and was not determined.

In most cases, the products were secondary alcohols or ketones. Cycloheptatriene gave only a very low yield of tropone, and a marked increase in viscosity of the reaction mixture indicated that the major pathway produced polymers. Indene gave a complex mixture of products, only one component of which, the epoxide shown in the Table, was identified.

Table 1. Products Obtained from Hydrocarbons by Photolysis of **1** in the Presence of O_2

Hydrocarbon	Products (% yields)[a]			
Cyclopentane[b]		(13)		(14)
Cyclopentene[b]		(35)		(33)
Cyclohexane[c]		(50)		(50)
Cycloheptane[b]		(23)		(21)
Cycloheptene[b]		(27)		(26)
Cycloheptatriene[b]		(< 1)+polymer[e]		
Indene[b]		(10) + 13 others[d]		

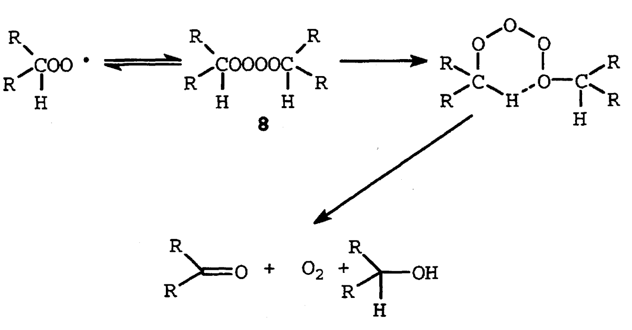
a) Yields based on quantity of **1** consumed. b) This work. c) Data from Ref. 1. d) Products not identified. e) Polymer formation indicated by a pronounced increase in viscosity.

Discussion

The results in Table 1 show a wide range of yields for the oxidations. The reactions show some selectivity. Firstly, there was apparently no secondary oxidation to produce diols, diones, etc. Secondary, in the cycloalkene series, oxidation only at the allylic position was observed. Nevertheless, from the standpoint of synthetic utility, photooxidations brought about by **1** and O_2 are not very promising. It is especially disappointing that the oxidations of cyclohepatriene and indene did not give useful amounts of tropone and indenone, respectively.

The most remarkable result is the equimolar formation, within experimental error, of the secondary alcohols and ketones in all cases except cycloheptatriene and indene. This parity in the yield of the two products occurs over a wide range of overall yield. Moreover, we have already shown that, in the conditions of our photooxidations with **1**, secondary alcohols are not oxidized to ketones.[1)] Therefore, unless an astonishing coincidence is admitted, it is clear that the predominant mechanism for these oxidations must produce one molecule of secondary alcohol for each molecule of ketone.

We have previously proposed the mechanism of Scheme 2 to account for the photooxidation of cyclohexane[1)] and cyclohexene,[2)] although in the case of cyclohexene the reaction yields suggested that the process was a chain reaction. The data of Table 1 provides the first clear indication that the



Scheme 3.

disproportionation of cycloalkyloxyl radicals is the predominant pathway, even when the yields of products are much lower than those obtained with cyclohexene. In addition, the data of Table 1 suggests that these reactions do not occur via a chain reaction, necessitating a revision of our previously postulated mechanism. As in our previous mechanism, only the disproportionation step can account for the equimolar production of alcohol and ketone.[26)]

An alternative mechanism, involving the dimerization of cycloalkyldioxyl radicals (Scheme 3), has been proposed for some related oxidations, based on kinetic studies.[27—29)] In this alternative mechanism, each pair of cycloalkyldioxyl radicals would give rise to just one ketone/alcohol product pair. The 150% yields of 2-cyclohexene-1-one and 2-cyclohexene-1-ol which we obtained from cyclohexene are inconsistent with this mechanism.[25)] There is no such inconsistency with the remainder of our results, none of which entail yields of $> 100\%$. Consequently, we believe that the equimolar ratio of alcohol : ketone arises via the dimerization of **7** to the corresponding dialkyl tetraoxide (**8**) (Scheme 3). Low-temperature kinetic electron spin resonance (ESR) studies of isopropyldioxyl radicals are also in accord with this mechanism.[27)]

Conclusions

The oxidations of cycloalkanes and cycloalkenes by the carbonyl oxide (**3**) has now been studied for a range of examples. In all but two cases (cycloheptatriene and indene), the major products are corresponding secondary alcohols and ketones. Remarkably, these two products are always produced in equimolar ratio, within experimental error.

The consistent equimolarity of alcohol and ketone products suggests that both are formed in the same step. A mechanism involving the disproportionation of cycloalkyldioxyl radicals has been proposed, which accounts for the equimolarity of the alcohol and ketone products. We conclude, therefore, that the predominant mechanism for these reactions is that shown in Scheme 3.

Overall, the results presented in Table 1 confirm that oxidation by **3** is a facile but selective process. We conclude, therefore, that the equimolar product ratio arises from the disproportionation of alkyldioxyl radicals (**7**). The exact source of **7** is currently under investigation. Nevertheless, the oxidations of hydrocarbons by photolysis of **1** in the presence of O_2 are still the most effective so far reported for this type of system.

Experimental

Materials and Equipment. Tetrachlorodiazocyclopentadiene (**1**) was prepared from hexachloropentadiene as described previously.[1)] All other materials were commercial samples.

Photooxidations were carried out in specially constructed Pyrex vessels. These had two concentric annular containers fused together, the inner acting as a cooling jacket, through which a stream of cold water was passed.[1,2)] A Philips HPK 125-W medium-pressure Hg arc lamp was positioned in the centre, so as to be surrounded by the reaction mixture, thus maximizing the photon flux through the sample. Reaction vessels were constructed in two sizes, of approximately 20 and 100 cm^3 capacity. In the work described in this paper, only the smaller size was used. Oxygen was passed through the sample by means of a capillary tube, which not only kept the solutions saturated with O_2 but also provided gentle agitation.

Procedures. In a typical experiment, tetrachlorodiazocyclopentadiene (**1**) (0.23 g, 1.0 mmol) was dissolved in 20 cm^3 of the hydrocarbon and the resulting solution was placed in one of the specially-constructed annular photochemical vessels. A steady stream of oxygen was bled through the solution for 10 min prior to commencement of the photolysis and was maintained for the duration of the reaction. The sample was then irradiated with a Philips HPK 125-W medium-pressure Hg arc lamp. At all times, the sample was cooled by passage of cold water through the outer annular cooling jacket of the reaction vessel. Irradiation was discontinued when the orange color of **1** dissipated. In some experiments, further portions of **1** were added and photolysis continued.

The resulting solutions were analyzed by GC on at least two different columns. Available columns were Carbowax, FFAP, E301 and OV-101. Products were identified by comparison of GC retention times with authentic samples. These identities were confirmed and the yields were determined by co-injecting each authentic material with a sample of the reaction mixture.

The following control experiments were carried out: (1) UV irradiation of O_2-saturated hydrocarbon solutions; (2) photolysis of **1** in deoxygenated hydrocarbon solutions; (3) bubbling of O_2 through a solution of **1** in the dark; (4) photolysis of **1** in oxygenated hydrocarbon solution in the presence of a singlet oxygen quencher (β-carotene or Rose Bengal). In none of these control experiments was the oxidation of the hydrocarbon observed. Oxidation of the hydrocarbons was only detected when **1**, UV irradiation and bubbling O_2 were present in the reaction mixture.

We thank the SERC (now the EPSRC) for supporting this work with an Earmarked Studentship (AM) and equipment grants (IRD).

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26) Our attention has drawn to an apparent deficiency in our original mechanism (see Refs. 1 and 2), suggesting that the probability of hydrogen transfer from a hydrocarbon to a alkyldioxyl radical is low due to the endothermic nature of the process (see Moad and Solomon, "The Chemistry of Free Radical Polymerisation," Pergamon, Oxford (1995), p. 79). We are currently conducting further studies to clarify the generation of the alkyldioxyl radicals in our system. However, the evidence presented herein strongly supports the generation and subsequent disproportionation of alkyldioxyl radicals yielding a 1 : 1 ratio of ketone : alcohol as a key step in this type of oxidation (and consequently brings our earlier mechanistic conclusions into question).

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