STEREOCHEMICAL STUDIES OF EPOXIDE FORMATION FROM SINGLET OXYGEN REACTIONS[†]

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Summary

Photoepoxidation of two stereoisomers of di-*tert*-butyl-bis(bicyclo-[3.3.1]non-9-ylidene) was carried out by Rose Bengal and tetraphenylporphine sensitization in the presence of phenylmethyl sulphoxide and also by biacetyl sensitization. Three epoxides (*cis,trans*, *cis,cis* and *trans,trans*) were stereospecifically obtained. The results are discussed with respect to the detailed mechanism of each photoepoxidation.

1. Introduction

Considerable interest is focused on the photo-oxygenation of sterically hindered olefins such as adamantylideneadamantane 1 (Fig. 1) because singlet oxygenation of 1 gives the remarkably stable dioxetane and sometimes the epoxide as well [1 - 4]. In spite of the continuous interest in hindered olefins, no intrinsic stereochemical study of the photo-oxygenation has yet been carried out. The main subject of this paper is the photoepoxidation of two stereoisomers of di-*tert*-butyl-bis(bicyclo[3.3.1]non-9-ylidene) 2 (*anti*-2 and *syn*-2) (Fig. 1); comparisons are made with previous results for the formation of dioxetanes from these olefins [5].

2. Materials and methods

Reagent grade CH_2Cl_2, CCl_4 and CH_3COCH_3 were distilled before use. Rose Bengal (RB) (Tokyo Kasei), *meso*-tetraphenylporphine (TPP) (Strem Chemicals), biacetyl (Tokyo Kasei) and *m*-chloroperbenzoic acid (MCPBA) (Wako Pure Chemicals) were commercially available. Phenylmethyl sulphox-

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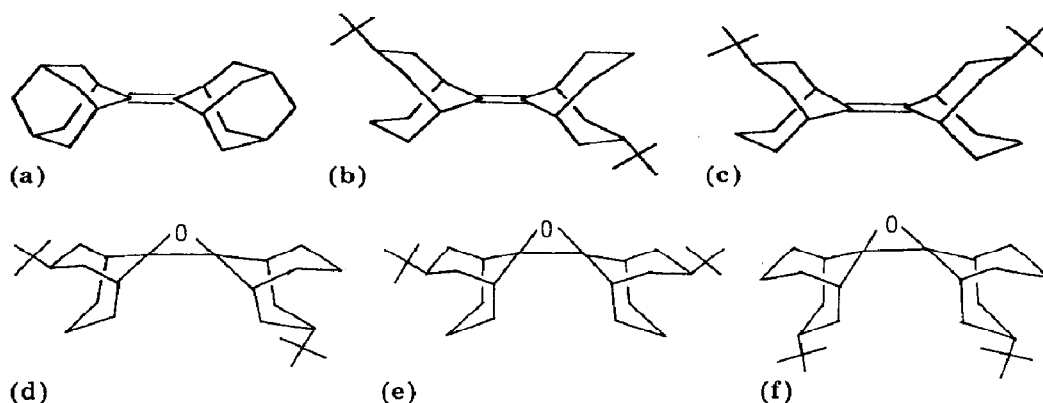
Fig. 1. Structural formulae for (a) **1**, (b) *anti*-**2**, (c) *syn*-**2** and (d) the *cis,trans*, (e) the *cis,cis* and (f) the *trans,trans* isomers of di-*tert*-butyl-bis(bicyclo[3.3.1]non-9-ylidene) epoxide **3**.

ide (PhSOMe) was prepared by photo-oxidation of the corresponding sulphide [6].

The physical properties of the *anti*-**2** and the *syn*-**2** olefins have been described previously [5] and more details of the synthetic procedure and the assignment of their stereochemistries are to be published elsewhere [7].

All the photo-oxygenations were carried out in water-cooled Pyrex test-tubes under irradiation using a 300 W halogen lamp (Ushio) and bubbling oxygen in the presence of a sensitizer. The conditions and results are given in Table 1. After irradiation the reaction mixture was subjected to silica gel column chromatography (25 mm × 250 mm) using CCl_4 as eluent. The *cis,trans*-**3** epoxide was obtained by elution with 100 - 320 ml of CCl_4. The *cis,cis*-**3** and *trans,trans*-**3** epoxides were eluted separately with 320 - 740 ml and 640 - 880 ml of CCl_4 respectively. These three stereoisomeric epoxides produced in the reaction were identified by means of ^1H nuclear magnetic resonance (NMR), ^{13}C NMR, mass spectra and elemental analyses.

The results for *cis,trans*-**3** are as follows: melting point, 224.5 - 225 °C; ^1H NMR δ (ppm) (tetramethylsilane (TMS); CCl_4), 0.90 (singlet (s); 18 H), 1.50 - 2.10 (multiplet (m); 26 H); ^{13}C NMR δ (ppm) (TMS; $CDCl_3$), 72.6 (s), 72.4 (s), 41.7 (doublet (d)), 41.6 (d), 33.0 (triplet (t)), 32.3 (d), 32.1 (t), 31.9 (d), 30.7 (t), 29.6 (t), 27.3 (quadruplet (q)), 27.2 (q), 21.6 (t), 21.4 (t) (two singlet peaks are hidden in the ranges 33.0 ± 0.01 ppm and 32.2 - 32.1 ppm); mass spectrum, m/e = 372 (M^+).

The results for *cis,cis*-**3** are as follows: melting point, 197.5 - 198.5 °C; ^1H NMR δ (ppm) (TMS; CCl_4), 0.90 (s; 18 H), 1.50 - 2.10 (m; 26 H); ^{13}C NMR δ (ppm) (TMS; $CDCl_3$), 72.1 (s), 41.4 (d), 33.0 (s), 32.4 (d), 31.5 (t), 30.9 (t), 27.4 (q), 21.1 (t); mass spectrum, m/e = 372 (M^+).

The results for *trans,trans*-**3** are as follows: melting point, 169 - 171 °C; ^1H NMR δ (ppm) (TMS; CCl_4), 0.90 (s; 18 H), 1.50 - 2.20 (m; 26 H); ^{13}C NMR δ (ppm) (TMS; $CDCl_3$), 73.0 (s), 41.7 (d), 33.2 (t), 32.6 (s), 31.9 (d), 29.2 (t), 27.5 (q), 21.5 (t); mass spectrum, m/e = 372 (M^+).

TABLE 1

Photoepoxidation of *anti*-2 and *syn*-2

System	Olefin	Time (h)	Yield (%) for the following epoxides[a]		
			Cis,trans-3	Cis,cis-3	Trans,trans-3
MCPBA[b]	Anti-2	1	91		
	Syn-2	1		75	23
RB, $h\nu$, O_2[c]	Anti-2	23	71		
	Syn-2	22		68	32
TPP, $h\nu$, O_2[d]	Anti-2	2	78		
+PhSOMe	Syn-2	2		73	27
$CH_3COCOCH_3$[e]	Anti-2	2	58		
$h\nu$, O_2	Syn-2	2		26	27

[a]Isolated yields.
[b]The olefin (about 0.20 mmol) in 5 ml of CH_2Cl_2 was treated with MCPBA (0.61 mmol).
[c]A CH_3COCH_3–CH_2Cl_2 (1:1) solution (20 ml) containing the olefin (about 0.20 mmol) and RB was irradiated.
[d]A CCl_4 solution (20 ml) containing the olefin (about 0.20 mmol), PhSOMe (0.40 mmol) and TPP was irradiated.
[e]A CH_2Cl_2 solution (20 ml) containing the olefin (about 0.20 mmol) and the α-diketone $CH_3COCOCH_3$ (about 0.20 mmol) was irradiated.

It is calculated that $C_{26}H_{44}O$ requires 83.80% C and 11.90% H; the results of analysis showed 83.51% C and 11.99% H for *cis,trans*-3, 83.66% C and 11.93% H for *cis,cis*-3 and 83.33% C and 11.72% H for *trans,trans*-3.

3. Results and discussion

A solution of 2 (0.20 mmol) in 20 ml of CH_3COCH_3–CH_2Cl_2 (1:1) containing RB as the sensitizer was photolysed with a 300 W halogen lamp under bubbling oxygen in a water-cooled Pyrex tube. The reaction took about 1 day to complete and bleaching of the dye occurred so quickly that several further additions of RB were required. The reaction mixture was separated by column chromatography. Photo-oxygenation of *anti*-2 gave a single epoxide *cis,trans*-3. In contrast, photo-oxygenation of *syn*-2 gave two epoxides, *cis,cis*-3 and *trans,trans*-3 (Table 1). No dioxetane was detected under the reaction conditions. MCPBA oxidation of *anti*-2 and *syn*-2 produced the corresponding epoxides as expected from the concerted mechanism.

The assignment of the stereoisomeric epoxides is based mainly on the epoxide ring carbon absorption in the ^{13}C NMR; 72.6 and 72.4 ppm for *cis,trans*-3, 72.1 ppm for *cis,cis*-3 and 73.0 ppm for *trans,trans*-3. The latter two isomers were tentatively distinguished on the assumption that the less hindered face of the olefin would be attacked more easily. Indeed, the yield of *cis,cis*-3 was greater than that of *trans,trans*-3. This working hypothesis is consistent with the previous results for dioxetane formation [5].

Clearly, the RB-sensitized photo-oxygenation of the *anti*-2 and *syn*-2 olefins gives rise to the formation of epoxides with retention of stereochemistry. The reaction most probably involves a concerted mechanism. This may suggest that these results confirm the deoxygenation of an intermediate perepoxide. However, the fact that hindered olefins are readily oxidized to epoxides with hydrogen peroxide as reported recently by Jefford *et al.* [3] and the considerable dye bleaching observed here may account for the concomitant formation of peroxidic species which result in the stereoscopic epoxidation. Recently Lamberts and Neckers [8] reported the syntheses of structurally modified RB derivatives, in which the lactonic form of RB was described as colourless. The lactonic modification of RB was suggested to account for the dye bleaching accompanied by the formation of hydrogen peroxide [2, 3]:
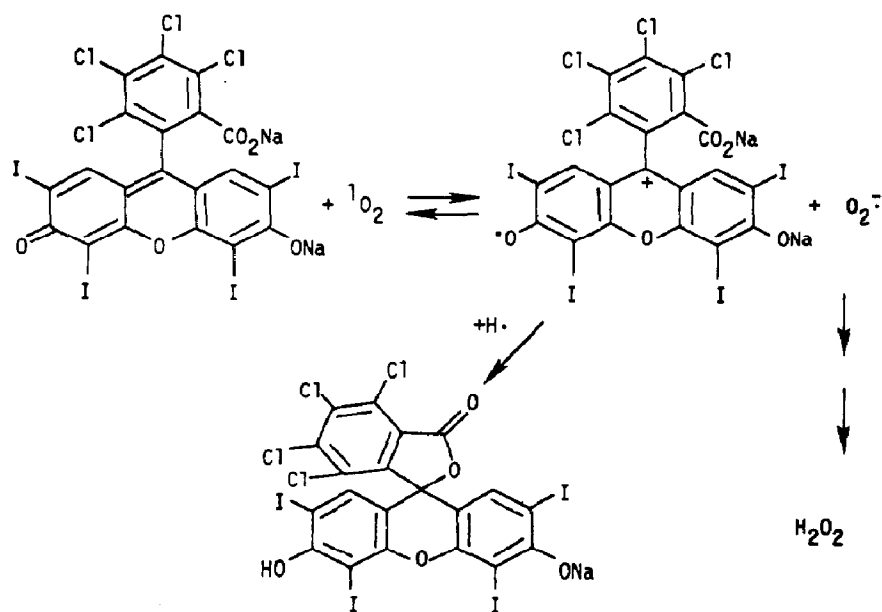
Meanwhile, the TPP-sensitized photo-oxygenation in the presence of PhSOMe (two equivalents) was carried out similarly in CCl_4. Almost complete inhibition of dioxetane formation by the sulphoxide was observed and the resulting epoxides retained their configurations (Table 1). The reaction was complete in a much shorter period than the RB-sensitized reaction. In this case, it seems more probable that the perepoxide is quantitatively trapped by the sulphoxide, as suggested by Schaap *et al.* [4]:
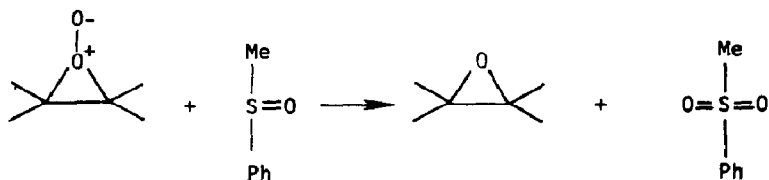
A second interesting problem is the α-diketone-sensitized photoepoxidation (Bartlett oxidation) which can offer important suggestions for the photoepoxidation mechanism. In this reaction, two mechanisms involving an α-diketone–olefin–oxygen termolecular complex [9 - 12] or a simple acyl-peroxy radical [13] have been suggested. However, the stereochemical results [9, 13] were consistent with either mechanism, both of which should lead to non-stereospecific epoxidation from the radical reaction [14, 15].

Biacetyl-photosensitized oxygenation of 2 in CH_2Cl_2 was carried out under conditions similar to those of the dye-sensitized experiment. Surprisingly, the photoepoxidation occurred stereospecifically (Table 1). Other radical epoxidations related to Bartlett oxidation were attempted, *i.e.* radical autoxidation with azo-iso-butyronitrile and amino-radical-catalyzed epoxidation with oxygen reported by Michejda and coworkers [16]. However, these two non-photochemical radical epoxidations did not occur. The hypothetical mechanism suggested by Bartlett, in which photoepoxidation is initiated by electron transfer to the α-diketone to produce the easily formed semidione and cation radical of the olefin [10, 12], could be excluded. In fact, for dioxetane, cation-radical-initiated oxygenation of either stereoisomeric olefin (*anti*-2 or *syn*-2) gave a mixture of all three dioxetanes [5]. Therefore, the peracid formed from the acylperoxy radical by hydrogen abstraction may be an actual oxidizing species even though the acylperoxy radical is suggested as the oxidizing species by Sawaki and Ogata [13]. The approach of a radical to the olefin can result in serious hindrance at the trimethylene bridges, whereas the concerted approach of the peracid would allow free access:
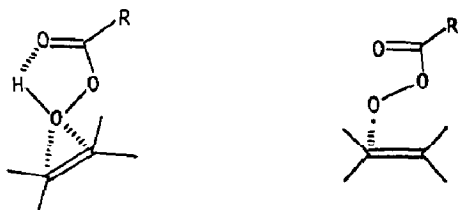
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