

## Photoinduced Reactions. Part 116.<sup>1</sup> The Reaction of Epoxides with Oxygen-transfer Reagents

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A C—C bond cleavage of the epoxide ring to give the corresponding ketone has been achieved by various oxygen-transfer agents such as ozone, ozone or pyridine *N*-oxide with irradiation, and *m*-chloroperbenzoic acid. The reaction with ozone is interpreted in terms of a perepoxide intermediate.

ALTHOUGH epoxidation of olefins with various oxidants<sup>2</sup> is well established, there have been few studies of the behaviour of epoxides toward these same oxidants. Of particular interest in this connection is the C—C bond cleavage in the epoxide ring to give the corresponding ketone.<sup>3</sup> Recently, the intermediate formation of a perepoxide (formally an adduct between an epoxide and an oxygen atom) has been proposed for the reaction of certain alkenes with singlet oxygen, although it is still open to discussion.<sup>4</sup> These synthetic and mechanistic problems led us to treat the simple epoxides (1a)—(1f) with several oxidizing agents which are known to transfer one oxygen atom to the substrate as an overall process, *i.e.* ozone,<sup>5</sup> ozone<sup>6</sup> or pyridine *N*-oxide<sup>7</sup> with irradiation, *m*-chloroperbenzoic acid (MCPBA),<sup>8</sup> diethyl persulphoxide,<sup>9</sup> and carbonyl oxide.<sup>10</sup>

The epoxides (1a)—(1e) gave the corresponding ketones (2a)—(2e) (Scheme 1) with all these oxygen-transfer agents, except for carbonyl oxide (see the Table). The reaction with ozone (Expts. 1—13) was usually complicated and most of the products, other than the ketones (2a)—(2e), were inseparable by chromatographic methods. The photochemical oxidation with pyridine *N*-oxide (Expts. 14 and 16—18) afforded the ketones (2a)—(2d) in reasonable yields (>50%), where the concentration of the *N*-oxide had been adjusted so that it absorbed as much of the incident light as possible. Since direct irradiation of the oxide (1a) is known to yield (2a),<sup>3f</sup> a controlled photolysis of tetraphenylethylene oxide (1a) was carried out (Expt. 15). It was found that the yield of benzophenone (2a) was much higher in the presence of the *N*-oxide (Expt. 14, 71%) than in the

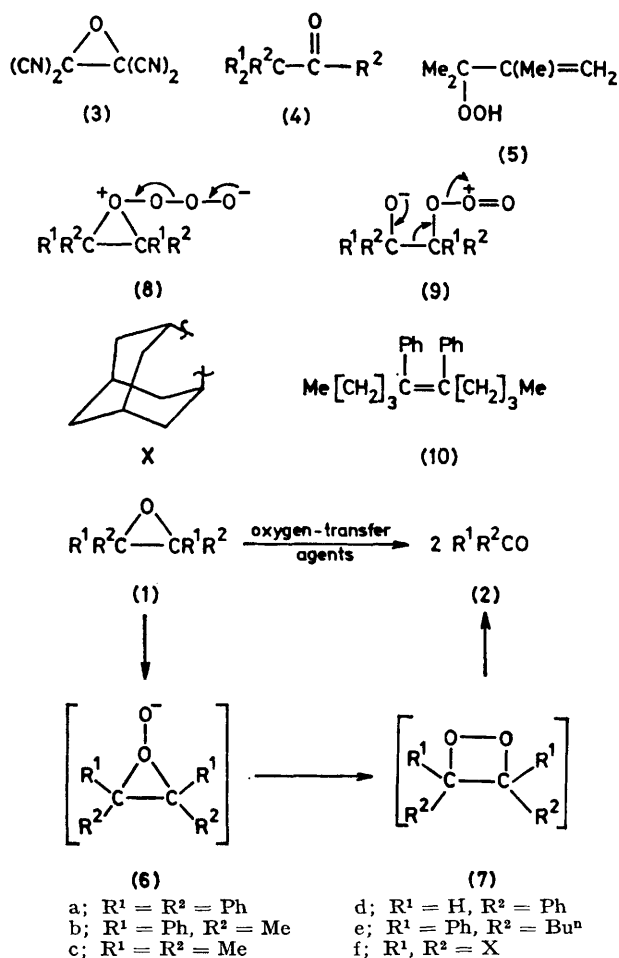
Products from the reactions of epoxides and oxygen-transfer agents

| Expt. | Method of oxidation                              |                  |                  |                                                   | Epoxide<br>(M × 10 <sup>2</sup> ) | Identified<br>products<br>(%) <sup>a</sup> | Conversion<br>of<br>epoxide<br>(%) |
|-------|--------------------------------------------------|------------------|------------------|---------------------------------------------------|-----------------------------------|--------------------------------------------|------------------------------------|
|       | Oxidant                                          | T/°C             | t/h              | Solvent                                           |                                   |                                            |                                    |
| 1     | O <sub>3</sub>                                   | −78              | 2                | CH <sub>2</sub> Cl <sub>2</sub>                   | (1a) (1.15)                       | (2a) (40)                                  | 5                                  |
| 2     |                                                  | −25              | 3                | CH <sub>2</sub> Cl <sub>2</sub>                   | (1a) (1.05)                       | (2a) (17)                                  | 54                                 |
| 3     |                                                  | −25              | 10               | CH <sub>2</sub> Cl <sub>2</sub> —AcOEt<br>(1 : 1) | (1a) (1.75)                       | (2a) (7)                                   | 76                                 |
| 4     |                                                  | −25              | 10               | CH <sub>2</sub> Cl <sub>2</sub> —AcOEt<br>(1 : 1) | (1a) (1.75) <sup>b</sup>          | (2a) (10),<br>(3) (17)                     | 70                                 |
| 5     |                                                  | 0                | 1                | CFCl <sub>3</sub> CF <sub>2</sub> Cl              | (1b) (1.45)                       | (2b) (31)                                  | 13                                 |
| 6     |                                                  | 0                | 4                | None                                              | (1c) (neat)                       | (2c) (50)                                  | 4                                  |
| 7     |                                                  | −25              | 4                | CH <sub>2</sub> Cl <sub>2</sub>                   | (1d) (4.77)                       | (2d) (8)                                   | 61                                 |
| 8     |                                                  | 0                | 1                | CCl <sub>4</sub>                                  | (1e) (1.62)                       | (2e) (trace)                               | 70                                 |
| 9     |                                                  | −78              | 0.5              | CH <sub>2</sub> Cl <sub>2</sub>                   | (1f) (0.68)                       | None                                       | 100                                |
| 10    | O <sub>3</sub> —hν                               | −78 <sup>c</sup> | 1.5 <sup>f</sup> | CH <sub>2</sub> Cl <sub>2</sub>                   | (1a) (1.74)                       | (2a) (12)                                  | 66                                 |
| 11    |                                                  | −78 <sup>c</sup> | 1.5 <sup>f</sup> | CFCl <sub>3</sub>                                 | (1a) (0.298)                      | (2a) (37)                                  | 19                                 |
| 12    |                                                  | −78 <sup>d</sup> | 0.5 <sup>f</sup> | CH <sub>2</sub> Cl <sub>2</sub>                   | (1a) (1.03)                       | (2a) (10),<br>(4a) (90)                    | 51                                 |
| 13    |                                                  | −78 <sup>e</sup> | 6 <sup>f</sup>   | CFCl <sub>3</sub>                                 | (1e) (0.617)                      | (2e) (trace)                               | 50                                 |
| 14    | PyrNO—hν                                         | RT <sup>d</sup>  | 1                | CH <sub>2</sub> Cl <sub>2</sub>                   | (1a) (0.287)                      | (2a) (71)                                  | 31                                 |
| 15    |                                                  | RT <sup>d</sup>  | 1                | CH <sub>2</sub> Cl <sub>2</sub>                   | (1a) (0.287) <sup>g</sup>         | (2a) (20)                                  | 91                                 |
| 16    |                                                  | RT <sup>d</sup>  | 2                | CH <sub>2</sub> Cl <sub>2</sub>                   | (1b) (0.313)                      | (2b) (64)                                  | 11                                 |
| 17    |                                                  | RT <sup>d</sup>  | 72               | CH <sub>2</sub> Cl <sub>2</sub>                   | (1c) (5.0)                        | (2c) (54)                                  | 12                                 |
| 18    |                                                  | RT <sup>d</sup>  | 4                | CH <sub>2</sub> Cl <sub>2</sub>                   | (1d) (1.09)                       | (2d) (50),<br>(4d) (50)                    | 10                                 |
| 19    | MCPBA                                            | RT               | 48               | CH <sub>2</sub> Cl <sub>2</sub>                   | (1a) (1.84)                       | (2a) (33),<br>(4a) (67)                    | 18                                 |
| 20    |                                                  | RT               | 50               | CH <sub>2</sub> Cl <sub>2</sub>                   | (1b) (2.9)                        | (2b) (10),<br>(4b) (85)                    | 9                                  |
| 21    | Et <sub>2</sub> S <sup>+</sup> —O—O <sup>−</sup> | RT <sup>e</sup>  | 9                | CH <sub>2</sub> Cl <sub>2</sub> —MeOH<br>(2 : 1)  | (1a) (1.58)                       | (2a) (trace)                               | 2                                  |
| 22    | Me <sub>2</sub> C=O <sup>+</sup> —O <sup>−</sup> | −78              | 1.5              | CH <sub>2</sub> Cl <sub>2</sub>                   | (1a) (1.94)                       | No reaction                                | 0                                  |

<sup>a</sup> Yields are based on the amount of converted epoxide. <sup>b</sup> Ozonation was conducted in the presence of tetracyanoethylene (0.0602M). <sup>c</sup> A tungsten-bromine lamp (Pyrex) was used as the light source. <sup>d</sup> A 10-W low-pressure mercury lamp (Vycor) was used as the light source. <sup>e</sup> A 400-W high-pressure mercury lamp through a 10% sodium nitrile solution (400 nm) was used as the light source. <sup>f</sup> Total time of irradiation (see Experimental section). <sup>g</sup> In the absence of pyridine *N*-oxide.

absence of it (Expt. 15, 20%). It should be mentioned that in the oxidation of tetramethylethylene oxide (1c) (Expts. 6 and 17) the hydroperoxide (5), which is a known product from 2,3-dimethylbut-2-ene and singlet oxygen, was not produced. 2,3-Dibutyl-2,3-diphenylethylene oxide (1e) was prepared in order to investigate the formation of Norrish type-II products,<sup>11</sup> but the yield of valerophenone (2e) was very low and there was no trace of acetophenone, one of the Norrish type-II products likely from compound (2e) (Expt. 8 and 13).

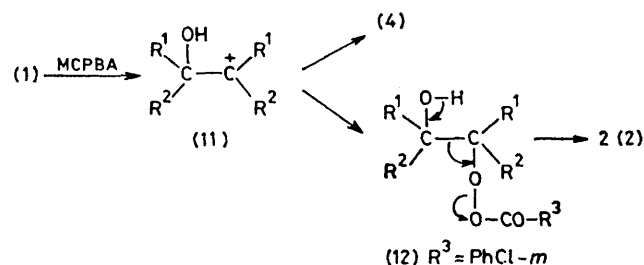
Apart from the oxidation with MCPBA, where the formation of the products appears to be rationalized by acid-catalysed ring-opening as illustrated in Scheme 2,<sup>12</sup> the results of the oxidation with other reagents, *i.e.* ozone, pyridine *N*-oxide, and diethyl persulphoxide, may be best explained in terms of the peroxide (6) and dioxetan (7) intermediates (Scheme 1).



SCHEME 1

Ozone usually functions as an electrophile or a 1,3-dipole, only rarely acting as a nucleophile.<sup>13</sup> The present ozonolysis reaction can be interpreted as an electrophilic ozone attack on the oxygen atom of the epoxide ring affording compound (8), followed by the elimination of an oxygen molecule to give the intermediate (6). An

attack of ozone on the ring carbon to form the zwitterion (9) seems unlikely, since ozone is acting as a nucleophile in this reaction mode and the epoxide (1a) is known to be stable to common nucleophiles.<sup>14</sup> The fact that adamantylideneadamantane oxide (1f), which should be highly protected from nucleophilic attack on the epoxide ring carbon, decomposed readily upon ozonolysis (Table, Expt. 9) also supports the hypothesis that ozone is acting as an electrophile in this reaction. Furthermore, tetracyanoethylene oxide (3) was produced from the reaction of ozone and the oxide (1a) in the presence of tetracyanoethylene (Table, Expt. 4). This fact supports the presence of the peroxidic intermediates (6), since tetracyanoethylene was stable to ozone under the same conditions.<sup>10</sup> However, extensive attempts to trap the intermediate (6) by methanol<sup>15</sup> or pinacolone<sup>16</sup> and to detect the electronically excited ketones by the use of 2-methylbut-2-ene<sup>17</sup> or 9,10-dibromoanthracene<sup>18</sup> as probes for the excited species, which are expected to be formed from the decomposition of the intermediate (7), were unsuccessful.

SCHEME 2 R<sup>1</sup> and R<sup>2</sup> as in Scheme 1

It should be noted that in the case of the pyridine *N*-oxide-*hν* system (Table) the yield of the ketones (2a)–(2d) was >50%, suggesting that the oxygen atom of the *N*-oxide is utilized in the transformation. We assume that this reaction also proceeds *via* the intermediate (6) and (7) as in the case of ozonolysis.

The reaction of olefins with oxygen produces both the epoxides and an oxygen atom as the final products<sup>19</sup> and the epoxides are presumably stable to an oxygen atom, although the slow reaction of unsubstituted ethylene oxide with an oxygen atom has been investigated in the gas phase.<sup>20</sup> Our results show that simple epoxides are reactive to some oxygen-transfer reagents.

#### EXPERIMENTAL

N.m.r. and i.r. spectra were taken on Varian T-60 and JASCO IRA-1 spectrometers, respectively. G.l.c. analyses were carried out with a Shimadzu GC-3BT apparatus (20% Carbowax 20 M on Celite 545 and 20% Silicone DC 550 on Celite 545 columns). T.l.c. was performed on Merck Kieselgel 60 PF<sub>254</sub>.

**Materials.**—Tetraphenylethylene oxide (1a),<sup>21</sup> 2,3-dimethyl-2,3-diphenylethylene oxide (1b),<sup>21</sup> tetramethylethylene oxide (1c),<sup>22</sup> and adamantylideneadamantane oxide (1f)<sup>23</sup> were prepared according to the literature methods. *trans*-Stilbene oxide (1d) was commercially available. 2,3-Dibutyl-2,3-diphenylethylene oxide (1e) was prepared

by the *m*-chloroperbenzoic acid (MCPBA) oxidation of 5,6-diphenyldec-5-ene (10) which was prepared by the reductive coupling of valerophenone (2e).<sup>24</sup> The olefin (10) was purified by column chromatography (silica gel—light petroleum), followed by distillation under reduced pressure to give an oil, b.p. 98–100 °C (bath temp)/0.2 mmHg;  $\delta$  (CDCl<sub>3</sub>) 0.6–1.6 (14 H, m), 2.35–2.8 (4 H, br t), and 6.98 (10 H, s);  $\nu_{\text{max}}$  (neat) 1 600, 1 495, 1 470, 1 460, 1 445, 1 070, 770, and 695 cm<sup>-1</sup>; *m/e* 292 (*M*<sup>+</sup>) (Found: C, 90.1; H, 9.7. C<sub>22</sub>H<sub>28</sub> requires C, 90.35; H, 9.65%). The epoxide (1e) was purified by column chromatography (silica gel—light petroleum), followed by distillation under reduced pressure to give an oil which solidified with time at room temperature, b.p. 96–98 °C (bath temp)/0.05 mmHg;  $\delta$  (CDCl<sub>3</sub>) 0.65–2.5 (18 H, m) and 7.07 (10 H, s);  $\nu_{\text{max}}$  (neat) 1 605, 1 500, 1 470, 1 450, 1 380, 1 115, 765, and 695 cm<sup>-1</sup> (Found: C, 85.71; H, 9.40. C<sub>22</sub>H<sub>28</sub>O requires C, 85.66; H, 9.15%).

**Oxidation Procedure.**—Ozone was generated by passing dry oxygen through a Nippon Ozone Co. Ozonator, Type 0-3-2 (O<sub>3</sub>, 1.5 g h<sup>-1</sup>). Other specific conditions are described in the Table.

(a) O<sub>3</sub>. Ozone was bubbled through a solution of the epoxide (ca. 100 ml).

(b) O<sub>3</sub>-*h* $\nu$ . Ozone was bubbled through a solution of the epoxide (ca. 100 ml) at -78 °C for a few minutes. When the solution became blue, as a result of the dissolved ozone, it was irradiated until it became light blue. The process was repeated several times.

In both (a) and (b), excess of ozone was removed by passage of nitrogen after completion of the reaction; the reaction mixture was then treated with an excess of dimethyl sulphide, at the same temperature as the ozonolysis, for 1 h and then slowly warmed to room temperature.

(c) Pyridine *N*-oxide-*h* $\nu$ . A mixture of pyridine *N*-oxide (15 equiv.) and the epoxide (1 equiv.) in methylene chloride solution (200 ml) was irradiated with passage of nitrogen at room temperature.

(d) MCPBA. A mixture of MCPBA (2 equiv.) and the epoxide (1 equiv.) in methylene chloride solution was treated at room temperature.

(e) Diethyl persulphoxide. Diethyl sulphide (3 equiv.) was photo-oxygenated using Rose Bengal as sensitizer in the presence of compound (1a). With no diethyl sulphide present, compound (1a) was completely stable under these conditions.

(f) Carbonyl oxide. A mixture of 2,3-dimethylbut-2-ene (130 equiv.) and compound (1a) (1 equiv.) in methylene chloride solution (ca. 15 ml) was ozonized at -78 °C.

**Isolation and Characterization of Products.**—Except in the case of the oxide (1c) the reaction mixture was evaporated under reduced pressure to remove the solvent. Benzophenone (2a) and the pinacolones (4a), (4b), and (4d) were isolated by preparative t.l.c. and their yields are listed in the Table. These products were identified by comparison with authentic samples (n.m.r. and i.r.). The yields of acetophenone (2b) and benzaldehyde (2d) were estimated from the n.m.r. spectra of the residue after evaporation. Both the compounds were separated by preparative t.l.c. and identified by comparison with authentic samples (n.m.r. and i.r.). The isolation yields were almost the same as those from n.m.r. spectroscopy. Because of its low solubility, tetracyanoethylene oxide (3) could be isolated from the residue after evaporation by washing it with ethanol. An i.r. spectrum of the material thus collected (17% yield) was indistinguishable from that of an authentic

sample. The yield of valerophenone (2e) was small and it was characterized only by g.l.c. Adamantan-2-one (2f) was undetected in the reaction mixture by t.l.c.

In the oxidation of the oxide (1a) with O<sub>3</sub>, O<sub>3</sub>-*h* $\nu$ , and pyridine *N*-oxide-*h* $\nu$ , attempts to isolate other epoxide-derived products by preparative t.l.c. on both silica gel and alumina were unsuccessful, the solid products having lower *R*<sub>F</sub> values than compound (2a), being inseparable. The reaction mixtures from compound (1c) were directly analysed by n.m.r. and g.l.c. In Expt. 6, a solution containing a substantial amount of acetone was separated by fractional distillation of the reaction mixture and its identity was confirmed by g.l.c. and n.m.r.

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