

THE PHOTOOXIDATION OF CYCLOHEPTATRIENES SENSITIZED BY  $\alpha$ -DICARBONYL COMPOUNDS: AN OCCURRENCE OF DIOXYGENATION REACTION

Akira MORI and Hitoshi TAKESHITA\*

Research Institute of Industrial Science, 86, Kyushu University, Hakozaki, Fukuoka 812

The photooxygenation of cycloheptatrienes, sensitized by  $\alpha$ -dicarbonyl compounds, produced (6+2) $\pi$ -, (4+2) $\pi$ - and (2+2) $\pi$ -cycloadducts with oxygen. Although the product distributions resembled closely to those of the genuine singlet-oxygen oxidation, it has suffered a quenching by 2,6-di-tert-butyl-p-cresol, indicating it to be a radical reaction.

A recent report by Bartlett,<sup>1)</sup> which described a new photochemical epoxydation of olefins in the presence of  $\alpha$ -diketones under aerated conditions, has prompted us to reinvestigate a quenching effect of oxygen on photoaddition reaction of methyl acetopyruvate to cycloheptatriene (tropolidene, 1),<sup>2)</sup> where we detected some unidentified products. We will herein describe the results of the Bartlett oxidation of 1 and its derivatives. Previously, the singlet oxygen ( $^1\text{O}_2$ ) oxidation of 1 was reported to give tropone (2)<sup>3,4,5)</sup> and (4+2) $\pi$ - and (6+2) $\pi$ -cycloadducts.<sup>4,5)</sup>

When a benzene solution of 1 and benzil was externally irradiated (a 400W high-pressure Hg lamp) under an oxygen atmosphere, a rapid consumption of 1 occurred to give an oxygenation mixture. The silica gel chromatography of the mixture afforded 2, 3, 4, 5 (benzaldehyde), and 6, together with the formerly isolated ene reaction product (7, R=Ph).<sup>6)</sup> The structures of 3 and 4 were confirmed by direct comparisons with authentic samples.<sup>5)</sup> The structure of 6, colorless crystals, mp 56-57°C, was clarified to be cis-3,4,6,7-diepoxy-cyclohept-1-ene.<sup>7)</sup>

The oxygenation of 1 with other diketones (biacetyl, methyl acetopyruvate, and camphorquinone) gave similar results to each other. Table 1 shows that, assuming both 4 and 6 to be secondary products from a (6+2) $\pi$ -adduct, the isolated yields of these products are parallel to those of genuine  $^1\text{O}_2$  oxidation products.<sup>5,8)</sup>

Table 1. The Isolated Yields (%) of Oxygenation Products under Various Conditions

Oxygenation Products				PhCH=O		
Sensitizers	( <u>2</u> )	( <u>3</u> )	( <u>4</u> )	( <u>5</u> )	( <u>6</u> )	( <u>7</u> )
Benzil	3	17	8	trace	21	2
Biacetyl	2	14	8	trace	13	2
Methyl acetopyruvate	trace	11	3	trace	6	2
Camphorquinone	trace	5	trace	3	18	—
Methylene blue <sup>5)</sup>	trace	8.4	23.4	trace	—	—

Thus, no monooxygenation product has been detected, and this surprising feature invited us to study on the other tropylidenes. When a benzene solution of 7-methoxytropolidene (8) and benzil was irradiated in a similar way to the above, a (4+2) $\pi$ -adduct, 9 (10%),<sup>5)</sup> was obtained together with 5 (less than 1%). Furthermore, 7,7'-bitropyl

(10) produced a cis-diepoxide, 11 (6%), colorless crystals, mp 144–145°C, a (4+2) $\pi$ -adduct, 12 (4%), colorless crystals, mp 174–175°C (dec), and another (4+2) $\pi$ -adduct from the valence-isomer of 10, 13 (8%), colorless crystals, mp 94–95°C. The formation of dioxygenation products therefore seems to be a general feature for tropylienes.

However,  $^1\text{O}_2$  is not responsible for the oxygenation; the reaction can be quenched by adding 2,6-di-*tert*-butyl-*p*-cresol. Consequently, the pathway, as has been shown by Bartlett,<sup>1)</sup> is certain to contain a radical intermediate, and the following chart will represent a possible mechanism:

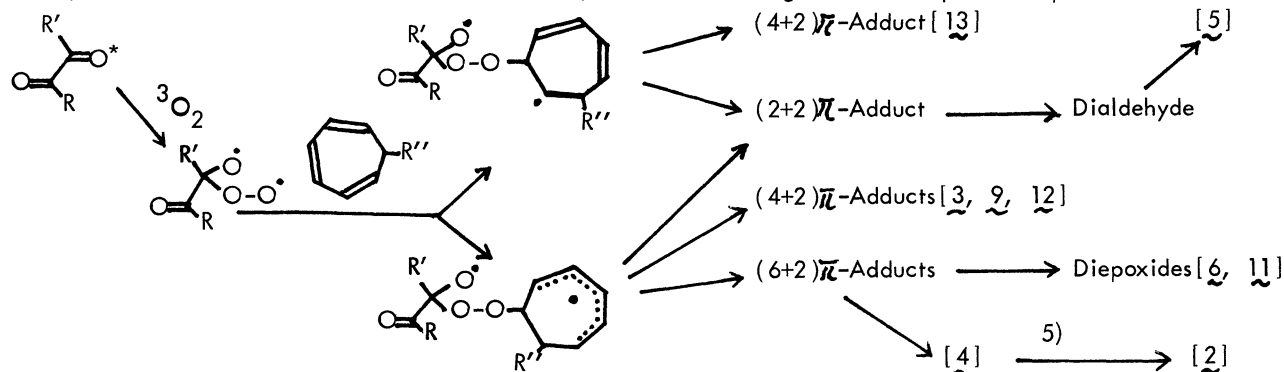


Table 2. The NMR Data of New Compounds		
	$^{13}\text{C}$ -NMR	H-NMR [measured in $\text{CDCl}_3$ and expressed with ppm from TMS, the internal standard]
<u>6</u>	32.3, 50.9, 54.4, 127.3.	1.1–1.4(1H, m), 2.6–2.9(1H, m), 3.2–3.5(4H, m), 5.86(2H, s).
<u>11</u>	42.6, 46.5, 49.9, 58.6, 123.1, 125.9, 127.5, 131.1.	1.6–1.9(2H, m), 3.15(2H, dd, 7, 4), 3.37(2H, d, 4), 5.38(2H, dd, 9, 4.5), 5.83(2H, s), 6.15(2H, dt, 9, 3), 6.68(2H, m).
<u>12</u>	10.8, 23.6, 40.1, 73.2, 125.0, 125.1, 127.6, 130.1.	0.85(1H, dt, 9.5, 3.5), 1.14(1H, dtt, 9.5, 5, 1.5), 1.50(2H, dd, 5.5, 3.5), 4.92(2H, m), 5.18(2H, dd, 9, 5), 6.14(2H, m), 6.28(2H, dd, 4.5, 3.5), 6.58(2H, m).
<u>13</u>	39.1, 47.1, 73.5, 78.8, 122.4, 122.7, 124.6, 125.1, 125.5, 128.9, 130.6, 131.2, 133.1, 135.2.	1.67(1H, dt, 8, 6.5), 3.22(1H, dddd, 8, 5, 3, 2), 4.64(1H, tdd, 7, 2.5, 1.5), 4.94(1H, m), 5.24(2H, m), 5.84(1H, dm, 10), 6.16(4H, m), 6.64, 6.75(1H, ddm, 8.5, 7).

#### References and Notes

- 1) N. Shimizu and P. D. Bartlett, *J. Am. Chem. Soc.*, **98**, 4198 (1976).
- 2) H. Takeshita, A. Mori, and S. Itô, *Bull. Chem. Soc. Jpn.*, **47**, 1767 (1974).
- 3) G. O. Schenck, *Angew. Chem.*, **69**, 579 (1957).
- 4) A. S. Kende and J. Y. -C. Chu, *Tetrahedron Lett.*, **1970**, 4837. They have characterized the products after the catalytic reduction. Genesis of 2 was interpreted in terms of a rearrangement of 7-hydroperoxytropyliene.
- 5) M. Yagihara, N. Fukazawa, T. Watanabe, Y. Kitahara, and T. Asao, Abstract Papers of 6th Symposium on the Chemistry of Non-Benzenoid Aromatic Compounds, p. 156 (Oct. 1973, Fukuoka). We thank Prof. Asao, Tohoku University, for disclosures of valuable data prior to publications.
- 6) H. Takeshita, A. Mori, N. Yamamoto, and T. Fujita, *Kyushu Daigaku Seisan Kagaku Kenkyusho Hokoku*, **66**, 9 (1977).
- 7) H. Prinzbach and C. Rücker (*Angew. Chem.*, **88**, 611 (1976)) have obtained 6 as a mixture with the trans-isomer.
- 8) Apparently, the  $\alpha$ -diketones behaved as a sensitizer; only a catalytic amount of benzil was required. However, other diketones revealed a considerable decomposition.

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