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Synthetic Photochemistry. XII.[1] The Sensitized Photooxidation Reaction of Some Spirocyclic Derivatives of Vinylcyclopropanes

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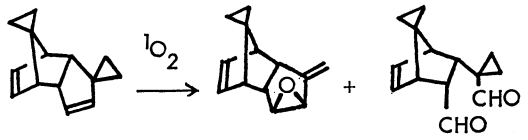
Synopsis. The dye-sensitized photooxidation of the Diels-Alder adducts prepared from 2-substituted tropones and spiro[2.4]hepta-4,6-diene was caried out. A marked difference in the reactivities was observed between the two structural types of adducts; 3,3-ethylene derivatives gave nor-epoxides, but 5,5-ethylene derivatives resulted in the recovery of the starting materials.

Previously, we have reported[2] the occurrence of a novel degradation process to form an epoxy norolefin, **B**, by the singlet oxygen oxidation of **A**, a spirocyclic vinylcyclopropane, in addition to the splitting into a dialdehyde, **C**. In considering this new process, we wanted to extend the reaction to other spiro olefins in order to ascertain its applicability and limitations. Looking for suitable substrates, we noticed a report by Tanida *et al.*[3] which described the Diels-Alder reaction of spiro[2.4]hepta-4,6-diene (**1**) with tropone (**2**)to form two *endo*-(4+2)π-adducts (**3** and **4**); we ourselves repeated the experiments to obtain some analogues from 2-chlorotropone (**5**) and 2-methoxytropone (**6**). Tropolone (**7**) was unreactive under similar conditions. We will herein describe the results of the photo-sensitized oxygenation of the adducts.



(**A**) (**B**) (**C**)

Diels-Alder Reaction of Troponoids and Spiroheptadiene (1). Slightly modifying Tanida's conditions, we have carried out the reaction with **5** and **6** and have confirmed the formation of similar types of adducts (**8**, **9**, **12**, and **13**), together with new 1 : 2-adducts (**10** and **14**). In addition, an *exo*-(4+2)π-adduct, **11**, was obtained from **1** and **5**.[4]

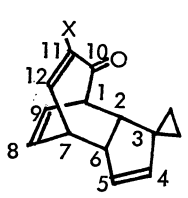
Sensitized Photooxidation of the Adducts. When a chloroform solution of **3** was irradiated by means of a 500 W tungsten lamp in the presence of Methylene Blue for 86 h, a single compound, colorless crystals (**15**), was obtained in a 79% yield. The NMR [δ: 2.73 (2H, br s), 3.31 (1H, d, J=2.5 Hz), 3.45 (2H, m), 3.60 (1H, d, J=2.5 Hz), 5.24 (1H, br s), 5.41 (1H, d, J=2 Hz), 5.64 (1H, dd, J=11, 2.5 Hz), 5.97 (1H, t, J=8 Hz), 6.31 (1H, t, J=8 Hz), and 7.13 (1H, dd, J=11, 9 Hz)] spectrum revealed the formation of an epoxy group and a terminal ethylene group, suggesting an oxidative fragmentation product related to **B**. Thus, the carbonyl group in the molecule suppressed the formation of a dialdehyde.

On the other hand, the isomer (**4**) afforded no product when similarly irradiated for 144 h.

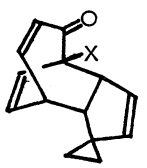
When a chloroform solution of **8** and Methylene Blue was similarly irradiated for 77 h, the sole product (**16**), also a vinyloxirane, was obtained in a 64% yield. The NMR [δ: 3.03 (2H, br s), 3.45 (1H, dd, J=9, 8 Hz), 3.54 (1H, d, J=3 Hz), 3.75 (1H, d, J=3 Hz), 3.82 (1H, d, J=8 Hz), and 7.50 (1H, d, J=9 Hz)] and the IR [ν: 925, 880 cm^{-1}] spectra indicated the structure of **16**. **9** was inert against the oxygenation.

Similarly, **12** afforded only **17** in an 89% yield, but **13** was inert. The NMR [δ: 2.95 (2H, br s), 3.50 (3H, s), 3.38—3.72 (4H, m), 5.25 (1H, br s), 5.45 (1H, br s), 5.95 (1H, dd, J=9, 8 Hz), 6.17 (1H, dm, J=10 Hz), and 6.38 (1H, t, J=8 Hz)] and IR [ν: 930, 890 cm^{-1}] spectra of **17** indicated the structure.

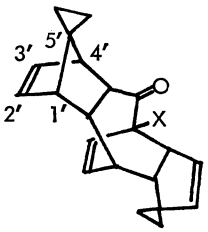
The continuous exposure of the adducts to oxygen in the dark caused no reaction; thus, the formation of vinyloxiranes is photochemical. Meanwhile, we have recently shown[6] that, during the oxygenation of **A**, a quenching of singlet oxygen by sodium azide has resulted in the complete suppression of both **B** and **C**, with the alternative production of free radical products. Therefore, the vinyloxiranes must be related to the singlet-oxygen oxidation,[7] and the location of the carbonyl group in the spirocyclic vinylcyclopropanes controlled the whole oxidation reaction. We have to admit that, compared to the reaction with a hydrocarbon, **A**, the reaction with the present series has revealed a critical rate decrease for usual singlet-oxygen oxidation, but this might be explained in terms of a quenching effect by the carbonyl group, as has already been described in connection with the photooxidation of tropinone derivatives.[8] Together with this quenching



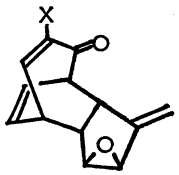
3: X=H
8: X=Cl
12: X=OMe



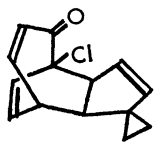
4: X=H
9: X=Cl
13: X=OMe



10: X=Cl
14: X=OMe



15: X=H
16: X=Cl
17: X=OMe



11

effect, the observed change in the product controle is probably also attributable to the carbonyl group, but these remote effects are not fully understandable at the present stage.

Experimental

Addition Reaction of Tropone (2) and Spiro[2.4]hepta-4,6-diene (1). A mixture of **2** (355 mg) and **1** (0.4 g) were heated in a sealed tube at 110—115 °C for 72 h, with a slight modification of the reported conditions.[3] A work-up of the mixture gave **3** (232 mg (35%)), and **4** (185 mg (28%)).

Addition Reaction of 2-Chlorotropone (5) and 1. **1** (2.5 ml) and **5** (1.00 g) were mixed in a sealed tube and then heated at 130—135 °C for 72 h. Repeated chromatography of the mixtures with benzene to benzene–ether afforded **8** (741 mg, 44%) as colorless needles; mp 133—135 °C (from benzene)[Found: C, 72.45; H, 5.62%. Calcd for $C_{14}H_{13}OCl$: C, 72.26; H, 5.63%. δ: 0.5—0.9 (4H, m), 2.61 (1H, dd, J=9, 2 Hz), 3.46 (1H, dddm, J=9.5, 8, 2 Hz), 3.52 (1H, ddm, J=2, 1 Hz), 3.74 (1H, dq, J=9, 2 Hz), 5.17 (1H, dd, J=5.5, 2 Hz), 5.37 (1H, dd, J=5.5, 2 Hz), 6.10 (1H, tt, J=8, 1 Hz), 6.40 (1H, tm, J=8 Hz), and 7.45 (1H, d, J=9.5 Hz); ν: 1680 cm^{-1}; λ_{max}^{MeOH}: 237 nm (ε: 3100), 273 (2200)], **9** (303 mg, 18%); pale yellow needles, mp 67—68 °C (from ethanol)[Found: C, 72.42; H, 5.70%. δ: 0.5—1.0 (4H, m), 2.93 (1H, dd, J=8.5, 2 Hz), 2.94 (1H, td, J=8, 2 Hz), 3.65 (1H, dt, J=8.5, 2 Hz), 5.29 (1H, dd, J=5.5, 2 Hz), 5.85 (1H, dd, J=5.5, 2 Hz), 5.94 (1H, dd, J=11, 0.7 Hz), 6.08 (1H, dt, J=9, 0.7 Hz), 6.36 (1H, ddm, J=9, 8 Hz), and 7.04 (1H, dd, J=11, 8 Hz); ν: 1680 cm^{-1}], **11** (16.8 mg, 1%); a pale yellow oil[Found: *M. W.*, 232.0645 (M$^+$). Calcd for $C_{14}H_{13}OCl$: 232.0655. δ: 0.76 (4H m). 2.71 (1H, dd, J=10, 5 Hz), 3.27 (1H, dddm, J=8, 7.5, 5 Hz), 4.02 (1H, dt, J=10, 2 Hz), 5.26 (1H, dd, J=6, 2 Hz), 5.63 (1H, dd, J=6, 2 Hz), 5.92 (1H, d, J=11 Hz), 6.07 (1H, d, J=9 Hz), 6.42 (1H, dd, J=9, 7.5 Hz), and 6.96 (1H, dd, J=11, 8 Hz); ν: 1690 cm^{-1}], and **10** (as a mixture with **8**), 78.3 mg.

Isolation of 10. A mixture (75 mg) of **8** and **10** was dissolved in chloroform (20 ml) and was then irradiated by means of a tungsten lamp in the presence of Methylene Blue (20 mg) under an oxygen stream. The mixture was then chromatographed on a silica gel column to give **10** as colorless needles; mp 150—151 °C, 21 mg (0.9% overall from **5**) [Found: *M. W.*, 324.1295. Calcd for $C_{21}H_{21}OCl$: 324.1281. δ: 0.3—0.9 (8H, m), 2.12 (1H, br s), 2.26 (1H, ddm, J=8, 2.5 Hz), 2.75 (1H, dt, J=9, 2.5 Hz), 2.88 (1H, dm, J=4 Hz), 2.98 (1H, ddm, J=9, 2.5 Hz), 3.28 (1H, dd, J=9, 4 Hz), 3.78 (1H, dt, J=9, 1.5 Hz), 5.36 (1H, dd, J=6, 1.5 Hz), 5.37 (1H, d, J=9.5 Hz), and 5.8—6.2 (4H, m, 3-H, 12-H, 2′-H, and 3′-H); ν: 1710 cm^{-1}; λ_{max}^{MeOH}: 225 nm (ε: 5000, sh), 254 (1800)].

Addition Reaction of 2-Methoxytropone (6) with 1. A mixture of **1** (2.5 ml) and **6** (1.00 g) was heated in a sealed tube at 130—135 °C for 94 h. The mixture thus formed, a dark brownish oil, was fractionated by chromatography using silica gel to give **12**, 395 mg (23.5%) of a pale yellow oil[Found: C, 77.12; H, 6.98%. Calcd for $C_{15}H_{16}O_2$: C, 78.92; H, 7.06%. δ: 0.50—0.90 (4H, m), 2.62 (1H, dm, J=9 Hz), 3.35—3.82 (3H, m), 3.56 (3H, s), 5.16 (1H, dd, J=6, 2 Hz), 5.40 (1H, dd, J=6, 2 Hz), 6.00 (1H, t, J=8 Hz), 6.17 (1H, d, J=9 Hz), and 6.43 (1H, t, J=8 Hz); ν: 1670 cm^{-1}, λ_{max}^{MeOH}: 234 nm (ε: 9200), 282 (8050)], **13**, 160 mg (9.5%), pale yellow needles, mp 123—125 °C (from ethanol) [Found: C, 78.72; H, 7.12%. δ: 0.50—0.80 (4H, m), 2.82 (1H, dd, J=9, 2 Hz), 2.99 (1H, ddm, J=9, 7 Hz), 3.59 (3H, s), 3.66 (1H, dt, J=9, 2 Hz), 5.24 (1H, dd, J=6, 2 Hz), 5.66 (1H, dd, J=6, 2 Hz), 5.80 (1H, d, J=11 Hz), 6.01 (1H, dm, J=9 Hz), 6.37 (1H, dd, J=9, 7 Hz), and 7.00 (1H, dd, J=11, 9 Hz); ν: 1680 cm^{-1}; λ_{max}^{MeOH}: 225 nm (δ: 7800), 250 (6500)], and **14**, 246 mg (10.5%), colorless needles, mp 148—150 °C (from ethanol) [Found: *M. W.*, 230. δ: 0.20—0.90 (8H, m), 2.08 (1H, tm, J=3 Hz), 2.24 (1H, ddm, J=8, 3 Hz), 2.66 (1H, dt, J=10, 3 Hz), 2.84 (1H, dd, J=4, 3 Hz), 2.89 (1H, dm, J=10 Hz), 3.13 (1H, dd, J=10, 4 Hz), 3.38 (3H, s), 3.88 (1H, dt, J=10, 2Hz), 5.19 (1H, d, J=9 Hz), 5.32 (1H, dd, J=6, 2 Hz), 5.63 (1H, dd, J=6, 2 Hz), 5.91 (1H, dd, J=9, 8 Hz), 5.94 (1H, dd, J=6, 3 Hz), and 6.10 (1H, dd, J=6, 3 Hz); ν: 1710 cm^{-1}].

An Attempted Addition Reaction of Tropolone (7) and 1. **7** (214 mg) and **1** (0.6 ml) were mixed in a sealed tube and heated for 72 h at 130—135 °C. The mixture was then treated with acetic anhydride (0.5 ml) and evaporated *in vacuo*; the residual mass was chromatographed through a silica gel column with benzene. Only **7** as the acetate (203 mg (93%)), and the dimer of **1** (355 mg) were obtained.

Sensitized Photooxidation of 3. **3** (690 mg) was dissolved in chloroform (40 ml), and was irradiated by a 500-W tungsten lamp in the presence of Methylene Blue (20 mg) under oxygen bubbling. After 86 h, the mixture was chromatographed to give colorless needles (**15**) (mp 82—83 °C (from methanol); 386 mg (79%) [Found: C, 77.67; H, 6.07%. Calcd for $C_{13}H_{12}O_2$: C, 77.98; H, 6.04%]), together with **3** (195 mg). Inspections of every chromatographic fraction confirmed the absence of any other product.

Sensitized Photooxidation of 8. **8** (600 mg) and Methylene Blue (20 mg) were dissolved in chloroform (30 ml), and the mixture was irradiated by means of a 500-W tungsten lamp for 77 h, with a continuous bubbling of oxygen, at −5—0 °C. The mixture was then fractionated by chromatography to give **16** (colorless needles, mp 125—126 °C (from ethanol), 150 mg (64%) [Found: *M. W.*, 234.0474 (M$^+$). Calcd for $C_{13}H_{11}O_2Cl$: 234.0448. ν: 1680 cm^{-1}]), along with only **8** (365 mg).

Sensitized Photooxidation of 12. **12** (609 mg) and Methylene Blue (20 mg) were dissolved in chloroform (30 ml), and the mixture was irradiated by means of a 500-W tungsten lamp for 204 h with a bubbling oxygen stream at −5—0 °C. After a chromatography, the mixture gave a pale yellow oil, **17** (446 mg (89%) [Found: C, 73.55; H, 6.61%. Calcd for $C_{14}H_{14}O_3$: C, 73.02; H, 6.13%. ν: 1680 cm^{-1}]), together with **12** (110 mg). No other product was detectable.

References

1) Part XI: H. Takeshita, A. Mori, N. Yamamoto, and T. Fujita, *Kyushu Daigaku Seisan Kagaku Kenkyusho Hokoku*, **66**, 9 (1977).

2) H. Takeshita, T. Hatsui, and H. Kanamori, *Tetrahedron Lett.*, **1973**, 1697.

3) H. Tanida, T. Yano, and M. Ueyama, *Bull. Chem. Soc. Jpn.*, **45**, 946 (1972).

4) The formation of an *exo*-(4+2)π-adduct in the Diels-Alder reaction of **5** and cyclopentadiene has been recognized; *cf.* S. Itô, K. Sakan, and Y. Fujise, *Tetrahedron Lett.*, **1969**, 775.

5) S. Itô, H. Takeshita, and Y. Shoji, *Tetrahedron Lett.*, **1969**, 1815.

6) T. Hatsui and H. Takeshita, *Chem. Lett.*, **1977**, 603.

7) An irradiation of **A** using a high-pressure mercury lamp without the sensitizer under an oxygen atmosphere produced no isolable product other than the starting material.

8) M. H. Fisch, J. C. Gramain, and J. A. Oleson, *Chem. Commun.*, **1970**, 13.