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PHOTOCYCLOADDITION OF $\Delta^{\alpha,\beta}$-γ-BUTYROLACTONE WITH OLEFINS AND ITS QUENCHING BY DIMETHOXYETHYLENE

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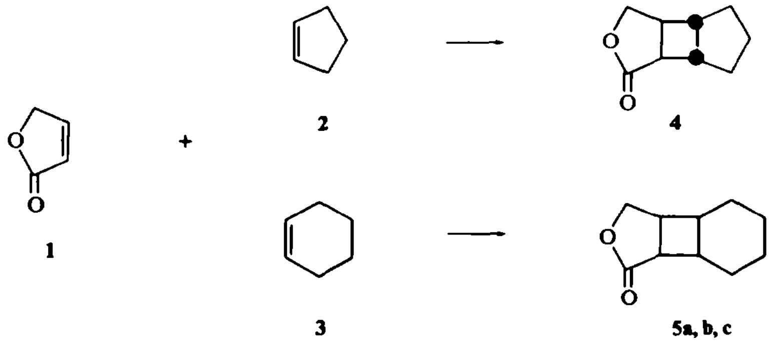
Abstract—Photocycloaddition of $\Delta^{\alpha,\beta}$-γ-butyrolactone (**1**) to cyclopentene or cyclohexene giving cyclobutane derivatives **4** and **5** proceeds through the triplet excited state of lactone **1**. The cycloaddition is quenched by dimethoxyethylene, and the formation of exciplex between **1** and dimethoxyethylene is proposed for the mechanism of the quenching.

PHOTOCYCLOADDITION of the enol form of acetylacetone to olefins has been reported by de Mayo and Takeshita.[1] We have shown that the enol form of acetoacetic ester is inactive for photocycloaddition to olefins.[2] These results indicate the possible difference in the cycloaddition of cyclopent-2-enone and $\Delta^{\alpha,\beta}$-γ-butyrolactone (**1**) to olefins.*

It is the purpose of this work to investigate the photochemical behaviours of lactone **1** in the cycloaddition with olefins.

Irradiation of $\Delta^{\alpha,\beta}$-γ-butyrolactone (**1**) ($\varepsilon^{end}_{210nm} = 2580$, $\varepsilon^{infl}_{266nm} = 22$, MeCN) in the presence of excess cyclopentene (**2**) or cyclohexene (**3**) by a 10 W low pressure mercury lamp for 20 hr gave 1:1 adducts in 36 and 42% yields, respectively, along with the unchanged lactone **1** (*ca.* 30%).

The single adduct from cyclopentene has the proper physical constants for structure **4** (experimental), whose stereochemistry (*cis–anti–cis*) is tentatively assigned by an analogy to the adduct between cyclopent-2-enone and cyclopentene.[3] Adducts from cyclohexene consist of three stereoisomers, **5a**, **5b**, and **5c** in the ratio of 1·0:3·2:2·1, all of which have similar physical constants.



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* Photodimerization of lactone **1** has been reported by Ohga and Matsuo without discussions on a detailed mechanism. K. Ohga and T. Matsuo, *Bull. Chem. Soc. Japan* **43**, 3505 (1970)

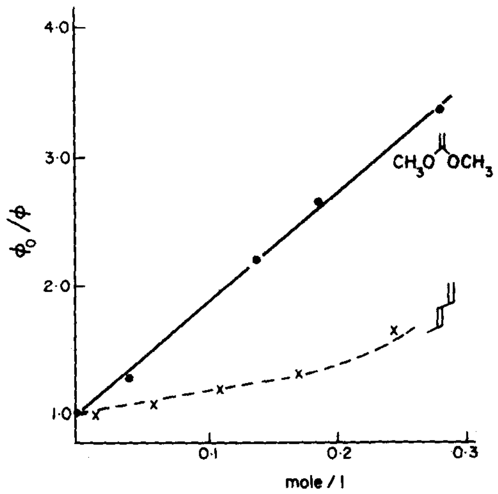

FIG 1. Quenching of the cycloaddition by 1,3-pentadiene and dimethoxyethylene

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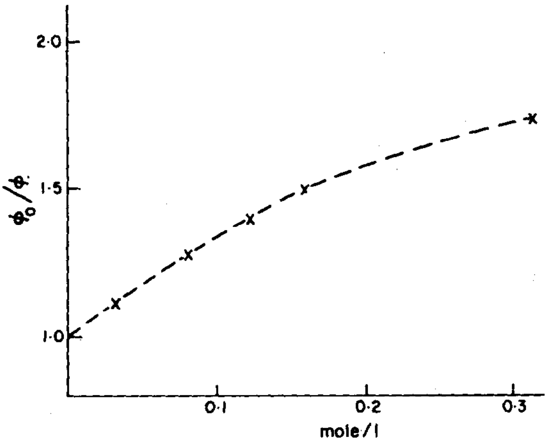

FIG 2. Quenching of the oxetane formation from acetone and dimethoxyethylene by 1,3-pentadiene

One of the strongest peaks in the mass spectra of these adducts is seen at $m/e = 85$ ($C_4H_5O_2^+$, 94% for **4**, 100% for **5a**, 100% for **5b**, and 100% for **5c**, respectively) which is due to the lactone part having a hydrogen migrated from the alicyclic system. Other strong peaks are seen at $m/e = 68$ ($C_5H_8^+$, 100% for **4**) and $m/e = 82$ ($C_6H_{10}^+$, 85% for **5a**, 85% for **5b**, and 84% for **5c**) which represent cyclopentene and cyclohexene moieties, respectively. These features in the mass spectra are characteristic of carbonyl compounds fused in such a ring system as **4** and **5**.[4]

Cycloaddition between lactone **1** and cyclopentene is sensitized by acetone (E_t = 80 kcal/mol)[5] and quenched by 1,3-pentadiene (E_t = *ca.* 58 kcal/mol).[6] The deviation of the Stern–Volmer plot (Fig 1) from a straight line, in the range of high concentration of 1,3-pentadiene, originates from the absorption of incident light by the diene. Acetophenone (E_t = 73·6 kcal/mol)[7] and chromone (E_t = 75·1 kcal/mol),[8] however, cannot sensitize the cycloaddition. Dimethoxyethylene, which is one of the most reactive olefins in the cycloaddition with cyclopent-2-enone and cyclohex-2-enone,[9] does not give adducts with lactone **1**. Unexpectedly, dimethoxyethylene quenches the cycloaddition between lactone **1** and cyclopentene, more efficiently than 1,3-pentadiene, to give a linear Stern–Volmer plot (Fig 1). Sensitization by acetone and quenching by 1,3-pentadiene suggest that the cycloaddition of lactone **1** with olefins proceeds *via* a triplet excited state, and the energy of active triplet state of **1** lies between 75 and 80 kcal/mol in MeCN.

There are two possible mechanisms involving energy transfer for the quenching by dimethoxyethylene, a triplet energy transfer and a singlet energy transfer. For an efficient triplet energy transfer, the triplet energy of an acceptor must be lower by a few kilo-calories than that of a donor. The lowest triplet energy of dimethoxyethylene, however must be higher than that of acetone, since the formation of oxetane **6** from acetone and dimethoxyethylene proceeds, at least partly, through the triplet excited state of acetone.[10] This was shown by the quenching experiment of the oxetane formation by 1,3-pentadiene (Fig 2). The Stern–Volmer plot implies that the formation of oxetane proceeds mainly from a singlet state and partly from a triplet state.[11] These facts exclude the possibility that the quenching of the cycloaddition of lactone **1** by dimethoxyethylene proceeds through a triplet energy transfer.

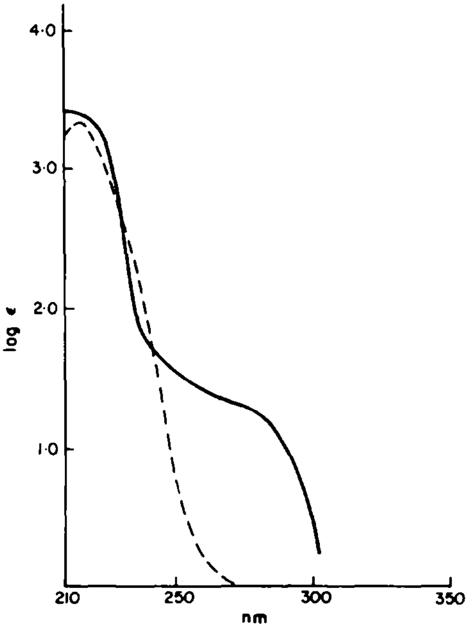

Fig 3. Absorption spectra of $\Delta^{\alpha,\beta}$-γ-butyrolactone, ———, and dimethoxyethylene, - - - - -, in MeCN

Dimethoxyethylene has no absorption over 260 nm, and we cannot expect the substantial spectral overlap between the absorption of dimethoxyethylene and the emission of lactone **1**, which is required for an efficient singlet energy transfer.[12] Though we cannot observe the fluorescence emission from lactone **1**, the hypothetical emission spectrum from the lowest excited singlet state must have a mirror image structure with the absorption band at the longest wavelength.[13] These considerations exclude a singlet energy transfer as a possible mechanism of the quenching of the cycloaddition.

The absorption spectrum of the mixture of lactone **1** and dimethoxyethylene does not show any sign of the formation of a charge-transfer complex at ground state. We infer that the annihilation of the excited state of lactone **1** is caused by the formation of the exciplex between the excited lactone **1** and dimethoxyethylene. Unfortunately, we could not succeed in detecting the fluorescence emission from lactone **1**, and cannot provide rigorous evidence for the formation of the exciplex. The mechanism of quenching by exciplex formation, however, is quite reasonable when we take into account the electronegative character of the lactone **1** and the electron releasing nature of dimethoxyethylene, and is further supported by the efficient formation of a charge-transfer exciplex between acetone and dimethoxyethylene.[14]

One of the modes of efficient deactivation of the exciplex is an ionic dissociation to give the anion radical of lactone **1** and the cation radical of dimethoxyethylene, in such a polar solvent as MeCN.[15] An electron transfer between the ion radicals results in regeneration of the starting lactone and olefin.

EXPERIMENTAL

Irradiation of $\Delta^{\alpha,\beta}$*-γ-butyrolactone* (**1**) *with cyclopentene* (**2**). $\Delta^{\alpha,\beta}$-γ-Butyrolactone (**1**) (5·88 g, 0·07 mol) and cyclopentene (6·20 g, 0·09 mol) in 70 ml of MeCN were irradiated with a 10 W low pressure mercury lamp through quartz for 20 hr under N_2, when a polymeric film was formed on the wall of a reaction vessel and *ca.* 70% of the starting lactone disappeared. Concentration of the mixture *in vacuo* gave the crude product (7·30 g), which contained the starting lactone and the adduct **4** from VPC analysis (10% PEG-2OM on Shimalite W). The starting lactone was removed from the product by passing it through a silica gel column (12 mm × 55 cm) with $CHCl_3$ and purified by distillation to give 3·83 g (36%) of adduct **4**, b.p., 93–95°/0·5 mm. (Found: C, 71·16, H, 7·86. Calc. for $C_9H_{12}O_2$: C, 71·02, H, 7·95%). MS (80 eV); 152 (M^+, 23%), 107 ($M^+—CO_2 - H$, 94%), 85 ($C_4H_4O_2^+ + H$, 94%), and 68 (C_5H_8, 100%). IR (neat); 1770, 1175, 1064, 1009, and 982 cm^{-1}. NMR (CCl_4); 4·28 (diffused q, 2H), 2·68 (diffused, 2H), 2·47 (diffused, 2H), and 1·2–2·0 ppm (6H).

Irradiation of $\Delta^{\alpha,\beta}$*-γ-butyrolactone* (**1**) *with cyclohexene* (**3**). $\Delta^{\alpha,\beta}$-γ-Butyrolactone (**1**) (4·20 g, 0·05 mol) and cyclohexene (24·6 g, 0·30 mol) in 70 ml of MeCN were irradiated in essentially the same way as in the case of cyclopentene. Silica gel chromatography followed by distillation gave 3·47 g (42%) of adducts, b.p., 120–130°/5 mm. VPC analysis (10% PEG-20M on Shimalite W) of the adducts showed three peaks due to **5a, 5b**, and **5c** in the ratio of 1·0:3·2:2·1. Each component was isolated by prep. VPC for the measurement of physical constants. Since the isolation of each product for analysis was difficult, the mixture of **5a**, **5b**, and **5c** was analysed. (Found: C, 72·41, H, 8·72. Calc. for $C_{10}H_{14}O_2$: C, 72·26, H, 8·49%). **5a**: MS (80 eV); 166 (M^+, 2%), 121 ($M^+—CO_2 - H$, 89%), 85 ($C_4H_4O_2^+ + H$, 100%), and 82 (C_6H_{10}, 85%). IR (neat); 1770, 1156, 1032, and 956 cm^{-1}. NMR (CCl_4); 4·15 (diffused, 2H, AB part of ABK system), 3·10 (diffused, 2H), and 1·2–2·0 ppm (10H).

5b: MS (80 eV); 166 (M^+, 11%), 121 ($M^+—CO_2 - H$, 26%), 85 ($C_4H_4O_2^+ + H$, 100%), and 82 (C_6H_{10}, 85%). IR (neat); 1760, 1164, 1028, and 967 cm^{-1}. NMR (CCl_4); 4·20 (heptet, 2H, AB part of ABK system), 2·4–3·3 (m, 4H), and 1·1–2·1 ppm (8H).

5c: MS (80 eV); 166 (M^+, 5%), 121 (M^+—CO_2 − H, 26%), 85 ($C_4H_4O_2^+$ + H, 100%), and 82 (C_6H_{10}, 84%). IR (neat); 1765, 1158, 1045, and 976 cm^{-1}. NMR (CCl_4); 4·33 (sextet, 2H, AB part of ABK system), 2·4–3·4 (m, 4H), and 1·0–2·1 ppm (8H).

Sensitization of the cycloaddition between $\Delta^{\alpha,\beta}$*-γ-butyrolactone* (**1**) *and cyclopentene* (**3**). Varying amounts of acetone and acetophenone as sensitizer (5×10^{-2} − 1·0 mol/l) were added to solution of $\Delta^{\alpha,\beta}$-γ-butyrolactone (**1**) (164 mg, 0·002 mol) and cyclopentene (680 mg, 0·01 mol) in MeCN and the mixtures (total 10 ml) were externally irradiated with a 450 W high pressure mercury lamp through Pyrex filter for 1 hr under N_2. The reference solution without sensitizer was irradiated under the same conditions and no adduct formed. The adduct **3** between lactone **1** and cyclopentene was determined by VPC analysis. 1·5% of the starting lactone **1** was converted to the adduct within this period when sensitized by acetone (1·0 mol/l). On the other hand, no adduct was formed when acetophenone or chromone was used as sensitizers.

Quenching of the cycloaddition by 1,3-*pentadiene*. A solution of $\Delta^{\alpha,\beta}$-γ-butyrolactone (**1**) in MeCN (0·2 mol/l) was added with varying amount of 1,3-pentadiene ($1{\cdot}6 \times 10^{-2}$–$2{\cdot}4 \times 10^{-1}$ mol/l), and the mixture (total 5 ml) mounted in a rotating apparatus was irradiated externally with a 100 W high pressure mercury lamp through quartz tube (distance between the lamp and the quartz tube; *ca.* 5 cm) for 5 hr under N_2. Relative quantum yields (Φ_0/Φ) were determined by VPC analysis using internal standard.

Quenching of the cycloaddition by dimethoxyethylene. Quenching experiments using dimethoxyethylene were carried out in the same way as in the case of 1,3-pentadiene by using varying amount of dimethoxyethylene ($2{\cdot}8 \times 10^{-2}$–$2{\cdot}3 \times 10^{-1}$ mol/l).

Quenching of the oxetane formation from acetone and dimethoxyethylene by 1,3-*pentadiene*. A solution of dimethoxyethylene in acetone (880 mg, 2·0 mol/l) was added with a varying amount of 1,3-pentadiene ($3{\cdot}1 \times 10^{-2}$–$3{\cdot}1 \times 10^{-1}$ mol/l) and the mixture (total 5 ml) was mounted in a rotating apparatus. The mixture was irradiated externally with a 100 W high pressure mercury lamp through quartz tube (distance between the lamp and the quartz tube; *ca.* 5 cm) under N_2. Relative quantum yields (Φ_0/Φ) were determined by VPC analysis using an internal standard.

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REFERENCES

[1] P. de Mayo and H. Takeshita, *Can. J. Chem.* **41**, 440 (1963)

[2] M. Tada, T. Kokubo and T. Sato, *Bull. Chem. Soc. Japan* **43**, 2162 (1970)

[3] P. E. Eaton, *J. Am. Chem. Soc.* **84**, 2454 (1962)

[4] P. Singh, *Tetrahedron Letters* 1071 (1971)

[5] R. F. Borkman and D. R. Kearns, *J. Chem. Phys.* **44**, 945 (1966)

[6] N. J. Turro, *Technique of Organic Chemistry*, Vol. XIV, *Energy Transfer and Organic Photochemistry*, p. 193. Edited by P. L. Leermakers and A. Weissberger, Interscience Publ., New York (1969)

[7] p. 92, ref 6.

[8] J. W. Hanifin and E. Cohen, *J. Am. Chem. Soc.* **91**, 4494 (1969)

[9] E. J. Corey, J. D. Bass, R. LeMahieu and R. Mitra, *Ibid.* **86**, 5570 (1964)

[10] N. J. Turro and P. Wriede, *Ibid.* **90**, 6863 (1968)

[11] p. 338, ref 6.

[12] N. J. Turro, *Molecular Photochemistry*, p. 98 and 102. W. A. Benjamin, Inc. New York (1965)

[13] H. H. Jaffe and M. Orchin, *Theory and Applications of Ultra-violet Spectroscopy*, p. 536. John Wiley and Sons, Inc., New York, (1962)

[14] N. J. Turro, C. Lee, N. Schore, J. Barltrop and H. A. J. Carless, *J. Am. Chem. Soc.* **93**, 3079 (1971)

[15] H. Masuhara, M. Shimada and N. Mataga, *Bull. Chem. Soc. Japan* **43**, 3316 (1970)