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A SYNTHESIS OF γ-ALKYLIDENEBUTENOLIDES PHOTOCHEMICAL REARRANGEMENT OF 2,3-EPOXY-1,4-CYCLOHEXANEDIONES

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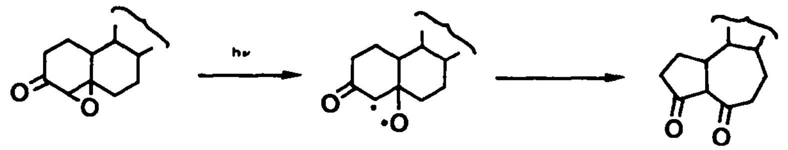
Abstract—Photo-induced rearrangement of 2,3-epoxy-1,4-cyclohexanediones was investigated for a synthesis of γ-alkylidene-γ-butyrolactones and γ-alkylidenebutenolides. Irradiation of epoxy diketones **1** and **4** in acetone gave γ-lactones, **2** and **5**, and triketones, **3** and **6**. On the other hand, in CH_2Cl_2, EtOAc, or PhH solution epoxy diketones **1** and **4** gave only triketones, **3** and **6**. Retro-Diels-Alder reaction of γ-lactones **5aE** or **5aZ** at 230° (20 mmHg) afforded γ-alkylidenebutenolides **7aE** and **7aZ** in addition to anthracene. According to the procedure, butenolide **7bZ**, a key intermediate for the synthesis of freelingyne, was prepared. The dramatic solvent effect in the photochemical rearrangement was also discussed.

The structural unit of γ-alkylidenebutenolide occurs in a variety of natural products, such as patulin,[1] protoanemonin,[2] tetrenolin,[3] freelingyne,[4] and matricarialactone,[5] possessing a wide range of biological activity. Although in recent years a number of methods for the syntheses of the γ-alkylidenebutenolides were reported,[6a] there is still a need for further, possibly less complicated synthetic routes. Furthermore, recent reports [6b] described the use of the γ-alkylidenebutenolides in synthesis of complex compounds. These facts prompted us to develop a convenient method of constructing this structural unit.[7]

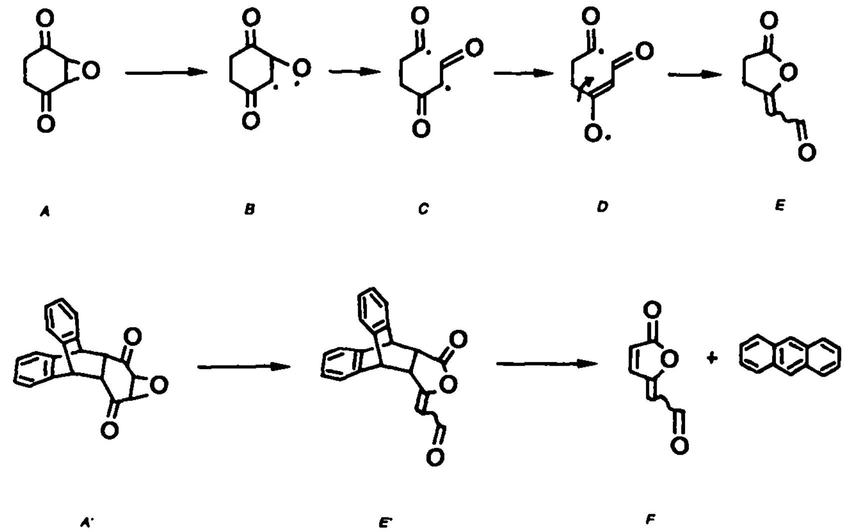
In this paper, we describe a method for the preparation of γ-alkylidenbutenolides based on the photoinduced rearrangement of 2,3-epoxy-1,4-cyclohexanediones into γ-alkylidene-γ-butyrolactones,[8] combined with retro-Diels-Alder reaction.

One of the most efficient photochemical reactions is the rearrangement of α,β-epoxy ketones into β-diketones.[9] Since this reaction is known to be initiated by homolysis of the oxirane ring to give a biradical and subsequent β-alkyl migration with an odd electron (Scheme 1), we have envisioned that photolysis of epoxycyclohexanedione A would produce biradical B, which would undergo subsequent ring opening to C and further rearrange to D, in view of the relative stability of acyl and alkoxyl radicals. Cyclization of this biradical would result in the formation of γ-alkylidene-γ-butyrolactones E.

γ-Alkylidenebutenolides F would be prepared by irradiation of epoxy diketone A′ followed by retro-Diels-Alder reaction[10] of E′ (Scheme 2).



Scheme 1.



Scheme 2.

RESULTS AND DISCUSSION

Irradiation of epoxy diketone **1a** in CH_2Cl_2, using a high pressure Hg lamp, gave only tricarbonyl compound **3a** (m.p. 131–134°) in 42% yield, a product in a similar line to the photochemical rearrangement of α,β-epoxy ketones.[9]

On the other hand, irradiation of **1a** in acetone and subsequent short-path distillation gave a 3:1 mixture of lactones **2aE** and **2aZ** in 38% yield, which were separable by preparative glc (Scheme 3).

The formation of **2** can obviously be interpreted by the coupling of acyl radical and O radical (C–O coupling) in the biradical **D**, and that of **3** can be explained by the coupling of acyl radical and C-radical (C–C coupling) in the biradical **C** (Scheme 2).

On irradiation in benzene, unsymmetrically substituted epoxy diketone **1b** gave triketone **3b** (m.p. 52–53°) in 43% yield as the sole product.

Irradiation of **1b** in acetone and preparative tlc separation afforded ketonic lactones, **2bE** (20%) and **2bZ** (19%), and an unseparable mixture of aldehydic lactones, **2cE** and **2cZ**, together with triketone **3b**. Another possible product **3c** was not found. NMR analysis of the crude reaction mixture showed that the ratio of **2bE**, **2bZ**, **2cE**, **2cZ**, and **3b** was 1:1.3:0.4:0.2:1.9. The ratio of (**2bE** + **2bZ** + **3b**)/(**2cE** + **2cZ** + **3c**) becomes to be 7/1, indicating the formation of the intermediate I rather than II (Scheme 4) on the basis of relative stability of the C-radical part in the intermediate biradicals, since I_a (tertiary) to give **2b–3b** is of lower energy than I_b (secondary) to give **2c–3c**, whereas II_a (secondary) to give **2b–3b** is less stable than II_b (tertiary) to give **2c–3c**.

As an extension of this study, we attempted to apply the photochemical rearrangement to the synthesis of γ-alkylidenebutenolides.

Irradiation of epoxy diketone **4a** derived from the adduct of anthracene and *p*-benzoquinone gave a mixture of γ-lactones, **5aE** and **5aZ**, triketone **6a**, and **4a** in a ratio of 1:1:2.5:1 (NMR). Preparative tlc separation gave lactones **5aE** [10%; m.p. 198°(dec)] and **5aZ** [13%; m.p. 191°(dec)], with recovered **4a** (13%). The triketone **6a**, too labile to survive the tlc conditions was the sole product on irradiation of **4a** in AcOEt [80%; m.p. 163%(dec)].

Retro-Diels-Alder reaction of **5aE** at 230° (20 mmHg) followed by preparative tlc separation gave a 1:1 mixture of butenolides **7aE** and **7aZ** in 80% yield, along with anthracene (90%). The same ratio of the products was obtained from the reaction of **5aZ**, indicating the stereomutation of **7aE** and **7aZ** under the reaction conditions (Scheme 5).

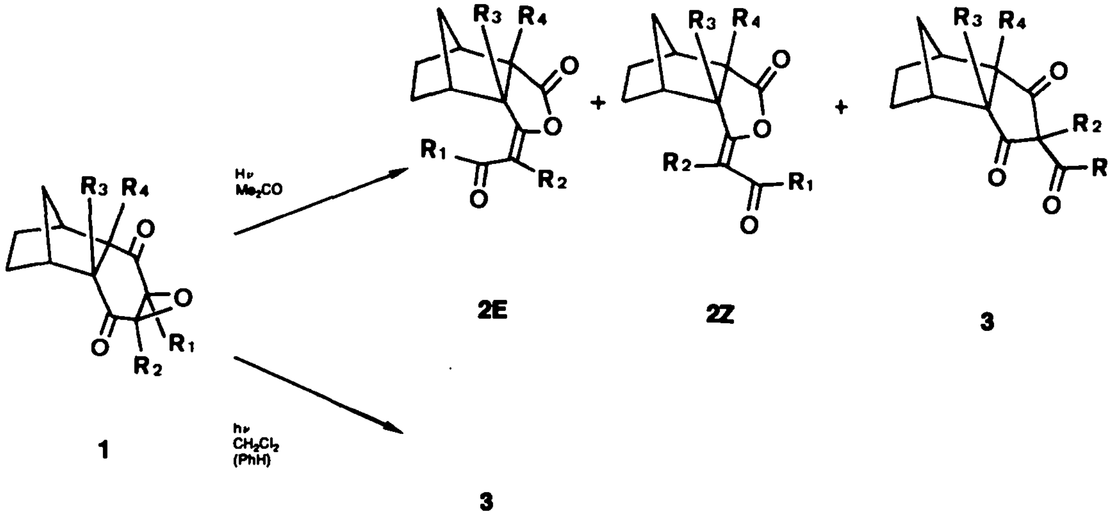
This success, combined with the regioselectivity in the reaction of **1b**, encouraged us to apply this method to the synthesis of the butenolide **4bZ**,[11] a key intermediate for synthesis of freelingyne,[4] a furanosesquiterpenoid. Irradiation of **4b** in acetone gave a mixture of **5bE**, **5bZ**, and **6c** in a ratio of 1:1.4:2.5. Other possible products, aldehydes **5cE**, **5cZ**, and **6c** were not detected. Preparative tlc separation gave **5bE** (12%; m.p. 174–176°), **5bZ** (15%, m.p. 167–168°), and **6b** (13%).

Pyrolytic treatment of the crude photolysate gave butenolides **7bE** (17% from **5b**; m.p. 88.5–89.5°, lit.[11] m.p. 88–89°) and **7bZ** (6%; m.p. 124–125°, lit.[11] m.p. 124–125°), in addition to anthracene. The other product **6b** remained as the still residue.

The stereochemistry of each of the *E,Z*-isomers (**2**, **5**, and **7**) could easily be assigned on the basis of the facts that allylic protons (R_3) *cis* to the CO function in α,β-unsaturated carbonyl compounds resonate at a lower field than their *trans* counterparts.[12] The NMR data are shown in Table 1.

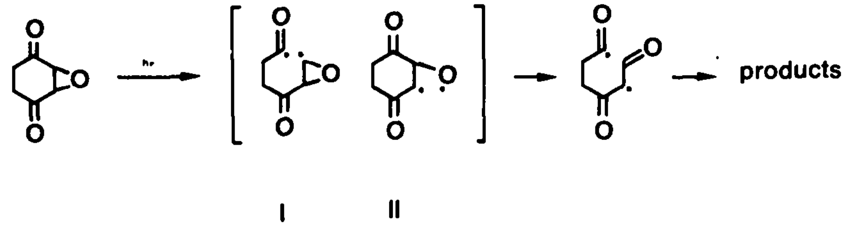
All of the triketones **3** and **6** were shown to exist in their enol forms, and **6b** as a tautomeric mixture of **i** and **ii** (1:1), on the basis of their ^1H and ^{13}C NMR spectra (Scheme 6).

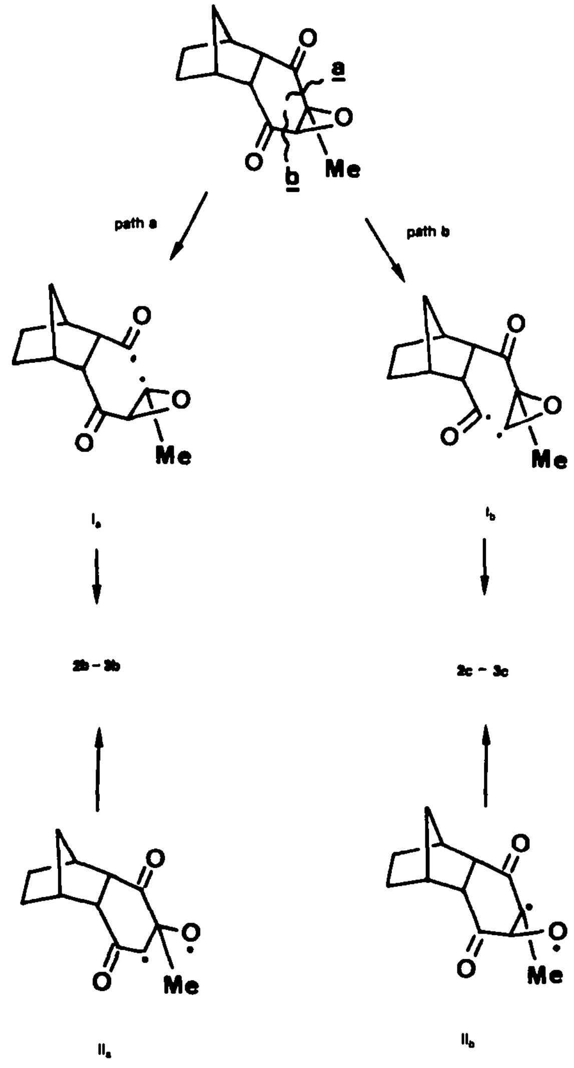
In these reactions, it was found that the reaction



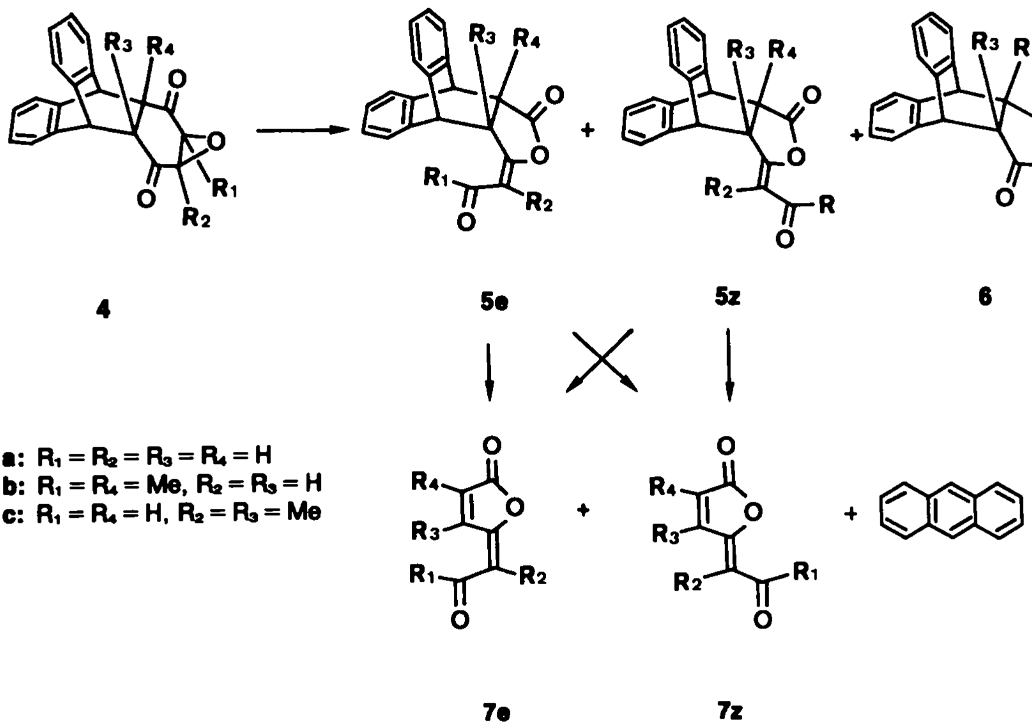
a: $R_1 = R_2 = R_3 = R_4 = H$
a: $R_1 = Me$, $R_2 = R_3 = R_4 = H$
c: $R_1 = R_3 = R_4 = H$, $R_2 = Me$

Scheme 3.





Scheme 4.



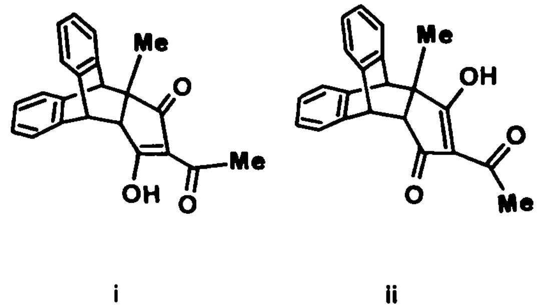
a: $R_1 = R_2 = R_3 = R_4 = H$
b: $R_1 = R_4 = Me$, $R_2 = R_3 = H$
c: $R_1 = R_4 = H$, $R_2 = R_3 = Me$

Scheme 5.

Table 1. NMR chemical shifts of 2, 5 and 7

		R_1	R_2	R_3	R_4
2aE	($R_1 = R_2 = R_3 = R_4 = H$)	9.78	5.93	3.92	3.22
2aZ		10.02	5.28	3.58	3.16
2bE	($R_1 = Me$, $R_2 = R_3 = R_4 = H$)	2.20	6.10	3.88	3.06
2bZ		2.42	5.23	3.50	3.13
5aE	($R_1 = R_2 = R_3 = R_4 = H$)	9.99	5.80	4.02	3.36
5aZ		9.68	5.49	3.65	3.28
5bE	($R_1 = R_4 = Me$, $R_2 = R_3 = H$)	2.28	5.95	3.54	1.20
5bZ		2.15	5.45	3.03	1.23
7aE	($R_1 = R_2 = R_3 = R_4 = H$)	9.93	8.14	6.63	6.15
7aZ		10.23	7.59	6.48	5.62
7bE		2.31	7.96	6.13	2.06
	($R_1 = R_4 = Me$, $R_2 = R_3 = H$)	(2.3)	(8.0)	(6.1)	(2.1)
7bZ		2.60	7.16	5.50	2.13
		(2.5)	(7.1)	(5.4)	(2.15)

The values in parentheses are from the Ref. 10.



Scheme 6.

course in the irradiation of epoxy diketones 1 and 4 changed dramatically by the solvents used. To disclose the origin of the solvent effect and to raise the selectivity of the rearrangement, we examined the photoinduced reactions of 1a and 4a in a variety of solvents. Irradiation of 1a (or 4a) in solvents with a wide variety of polarity, such as hexane, benzene, ethyl acetate, acetonitrile, nitromethane, dichloromethane, methanol, and ethanol gave only triketone 3a (or 6a) as the photoproduct. Furthermore, in acetic acid 1a gave also 3a, with a small amount of 2a. On irradiation in pyridine, 1a gave a small amount of 2a, but 3a was not found probably because of the reaction of 3a with pyridine.

Both of γ-lactones and triketones were proved to be the primary photo-products, because (i) the irradiation of triketone **3a** in acetone did not produce any photoproduct, and (ii) in the earlier stages of the irradiation of **4a** in acetone the ratios of photo-products **5aE**, **5aZ**, and **6a** were similar to those of the final products.

Radical property of the reactive species is suggested on the basis that the irradiation of **1a** in diethyl ether gave two 1:1 adducts of **1a** and diethyl ether. The structural elucidation of the adducts having 1-ethoxyethyl moiety was actively attempted, but the partial structure originated from **1a** could not be clarified.

In the presence of an efficient triplet quencher such as 1,3-pentadiene or oxygen, the photochemical rearrangement of **4a** to **5a** and **6a** was completely suppressed, resulting in the recovery of the starting material **4a**. These results suggest that the reaction occurred from a triplet state of **4a**.

Possibility of sensitization of the reaction by acetone was next investigated, since acetone was known as an efficient triplet sensitizer ($E_T = 80$ kcal/mol).[13] Irradiation of **4a** in a solution of benzene ($E_T = 84$ kcal/mol),[13] *m*-xylene ($E_T = 80$ kcal/mol),[13] and in the presence of acetophenone ($E_T = 74$ kcal/mol),[13] however, gave only triketone **6a**. Consequently, the possibility of acetone acting as a sensitizer may be ruled out.

The possibility of internal filter effect caused by acetone in the formation of γ-lactone then attracted our attention. Filtration of the exciting light with acetone or with 10% aq $CuSO_4$ (> 350 nm),[13] did not change the product ratios, although the reaction was slower than that in the absence of filters.

Other carbonyl or carbonyl-like compounds were found to be unsuitable as solvent for the formation of γ-lactones. On irradiation of **4a** in a cyclohexanone solution, a reaction of cyclohexanone occurred preferentially and the formation of γ-lactones **5a** was completely suppressed. A similar result was obtained on irradiation in propionaldehyde as solvent. Moreover, irradiation in acid (acetic acid), ester (ethyl acetate), and olefin (trichloroethylene) resulted in the formation of triketone **6a**. Epoxy diketone **1a** was also irradiated in dimethylformamide, dimethyl sulfoxide, or hexamethylphosphoric triamide (HMPT), but γ-lactone was not found and only polymeric compounds were obtained.

At present, acetone is the only solvent that has been found suitable to produce γ-lactones. Although the reaction was proved to proceed through the triplet state of the epoxy diketone, no satisfactory explanation can be offered where the observed solvent effect operates in the reaction steps.

The present new method of γ-alkylidenebutenolide synthesis is apparently an advantageous one because it requires only short reaction paths and is simple to carry out and also because the starting materials are easily obtained. Furthermore, the facile transformation of epoxy diketone to γ-alkylidenebutenolide is noteworthy in connection with the recently reported enzyme-catalyzed transformation[14] of phyllostine (epoxy diketone structure) into isopatulin and further into patulin (both having γ-alkylidenebutenolide moiety).

EXPERIMENTAL

All the m.ps were uncorrected. IR spectra were measured using a Shimadzu IR-27 spectrometer. UV spectra were recorded using a Hitachi EPS-2 spectrophotometer. ¹H NMR spectra were obtained with a Varian EM-360 or −390 spectrometer, using TMS as an internal standard. ¹³C NMR spectra were obtained with a Varian CFT-20 spectrometer with 16K memory, using TMS as an internal standard. Mass spectra were obtained using a Hitachi RMS-4 mass spectrometer with a nominal ionizing energy of 70 eV. Analytical glc was accomplished on a Shimadzu GC-4BPT using a 3 mm × 1.5 m column [10% APIEZON GREASE L on Chromosorb W-AW (80–100 mesh)]; preparative work was conducted on a Varian Model 920 using a 6 mm × 1 m column [10% APIEZON GREASE L on Chromosorb W-AW (80–100 mesh)]. Elemental analyses were carried out at the Elemental Analyses Center of Kyoto University. Irradiation was effected by means of a Fuji Glass 100-W high pressure Hg lamp.

Preparation of epoxy diketones **1a** *and* **1b**. The Diels-Alder adduct of cyclopentadiene and *p*-benzoquinone or methyl-*p*-benzoquinone was prepared and epoxidized by the method of Alder.[15] The epoxides were hydrogenated by using 10% Pd–C catalyst in EtOH.[16]

Preparation of epoxy diketone **4a**. The Diels-Alder adduct[17] of anthracene and *p*-benzoquinone was epoxidized by a modified method of FIESER.[18] To a soln of 2.40 g anhydrous Na_2CO_3 in 60 ml of water was added 12 ml 30% H_2O_2, and the mixture was added to a soln of 12.71 g of the above Diels-Alder adduct in 500 ml dioxane. After stirring of the mixture for 4 hr at room temp, water was poured into the soln and the ppt was collected by filtration to give **4a** quantitatively. Recrystallization from benzene gave pure **4a**: m.p. 216°(dec); UV(CH_3CN) λ_{max} 251(ε 1031), 265(1280), 272(1390), and 299(50, shoulder); MS *m/e* 302(M^+, 10%) and 178(100%); ¹H NMR($CDCl_3$) δ3.34(s,2H,CHCO), 3.49(s,2H,COCHO), 4.89(s,2H,PhCH̲), 6.9–7.4(m, 8H, ArH); ¹³C NMR($CDCl_3$) δ43.6(ArÇH), 48.8(COÇH), 58.6(COÇH), 123.8(CH), 126.0(CH), 126.1(CH), 126.5(CH), 140.7(C), 142.0(C), and 202.2(CO). (Found: C, 79.53; H, 4.43. Calcd for $C_{20}H_{14}O_3$: C, 79.45; H, 4.67%).

Preparation of epocy diketone **4b**. The Diels-Alder adduct of anthracene and 2,6-dimethyl-*p*-benzoquinone was prepared according to a modified method.[19] To an ice-cooled soln of 2,6-dimethyl-*p*-benzoquinone[20] (1.431 g). and anthracene (1.294 g) in 110 ml CH_2Cl_2 was added $AlCl_3$ (0.708 g). After stirring for 6 hr at the same temp, the reaction was quenched with $NaHCO_3$aq. The aqueous phase was extracted with CH_2Cl_2, and the extract was dried (Na_2SO_4) and concentrated *in vacuo*. The resulting crystalline product crystalline product was recrystallized from MeOH to give 1.630 g (71%) of 2,9a-dimethyl-1,4-dioxo-1,4,4a,9a-tetrahydrotriptycene as yellow crystals: m.p. 150.5–151.5°; MS *m/e* 178 and 136; ¹H NMR($CDCl_3$) δ1.05(s,3H,CH_3), 1.63(d,3H,CH_3,J = 1.3 Hz), 2.61(d,1H,CH,J = 2.6), 4.47(s,1H,CH), 4.58(d,1H,CH, J = 2.6), 6.19(q,1H,=CH,J = 1.3), and 6.9–7.4(m, 8H, ArH). (Found: C, 84.01; H, 5.96. Calcd for $C_{22}H_{18}O_2$: C, 84.05; H, 5.77%).

The above Diels–Alder adduct was epoxidized by a modified method.[18] To a soln of 195 mg anhydrous Na_2CO_3 in 5 ml water was added 0.9 ml 30% H_2O_2, and the mixture was added to a soln of 1.574 g of the above Diels–Alder adduct in 13 ml dioxane. After stirring for 1 hr at room temp., water was poured into the soln and the ppt was collected by filtration and recrystallized from benzene to give 1.450 g (88%) of **4b** as colorless crystals: m.p. 185–186°; MS *m/e* 330(M^+); IR(KBr) 1700 cm^{-1}; ¹H NMR δ1.27(s,3H,CH_3), 1.42(s,3H,CH_3), 2.77(d,1H,CH,J = 2.6 Hz), 3.38(s,1H,CHO), 4.60(s,1H,CH), 4.83(d,1H,J = 2.6) and 6.9–7.4(m,8H,ArH); ¹³C NMR($CDCl_3$), δ15.2(CH_2), 28.4(CH_3), 44.8(CH), 51.1(CH), 57.0(CH), 52.4(C), 65.3(CH), 69.5(C), Calcd for $C_{22}H_{18}O_3$: C, 79.98; H, 5.49%).

Irradiation of **1a** *in acetone*. A soln of **1a** (100 mg) in acetone (130 ml) was irradiated for 5 hr using a 100-W high pressure Hg lamp (pyrex) under N_2. Evaporation of the solvent and short-path distillation [150° (bath)/2 mmHg] gave 38 mg (38%) of **2aE** and **2aZ** (3:1 by NMR assay), which were separated by preparative glc (APIEZON GREASE L).

2aE: MS *m/e* 192(M^+); ¹H NMR($CDCl_3$) δ1.3–1.8(m,6H,CH_2 × 3), 2.82(m,2H,CH_2), 3.22(ddd,1H,CH,J = 10.7,5.8, and 1.2 Hz), 3.92(dd,1H,CH,J = 10.7 and 5.0), 5.93(dd,1H,=CH,J = 7.1 and 1.7), and 9.78(d,1H,CHO,J = 7.1). (Found: C, 68.53; H,6.31. Calcd for $C_{11}H_{12}O_3$: C, 68.73; H, 6.29%).

2aZ: MS *m/e* 192(M$^+$); ^{1}H NMR($CDCl_3$) δ 1.3–1.8(m,6H,$CH_2 \times 3$), 2.65(m.2H,CH_2), 3.16(m,1H,CH), 3.58(dd,1H,CH,J = 10.4 and 5.2), 5.28(dd,1H,=CH,J = 8.0 and 1.3), and 10.02(d,1H,CHO,J = 8.0). (Found: C,68.64; H, 6.33. Calcd for $C_{11}H_{12}O_3$: C, 68.73; H, 6.29%).

Irradiation of **1a** *in* CH_2Cl_2. A soln of **1a** (200 mg) in CH_2Cl_2(120 mg) was irradiated for 17 hr using a 100-W high pressure Hg lamp (pyrex) under N_2. Evaporation of the solvent and short-path distillation [150° (bath)/4 mmHg] gave 83 mg (42%) of **3a**: m.p. 131–134°; MS *m/e* 192(M$^+$, 21%) and 164(M$^+$–CO,100%); IR(nujol) 1695 cm^{-1}; ^{1}H NMR($CDCl_3$) δ 1.38(m,4H,$CH_2 \times 2$), 1.67(m,2H,CH_2), 2.78(m,2H,$CH \times 2$), 9.56(s,1H,CHO), and 10.19(bs,1H,OF); ^{13}C NMR($CDCl)_3$ δ 24.8($CH_2 \times 2$), 39.1($CH \times 2$), 42.6(CH_2), 51.0($CH \times 2$), 117.7(C), 166.7(COH), 189.4(CHO), and 202.1(CO). (Found: C, 68.44; H, 6.23. Calcd for $C_{11}H_{12}O_3$: C, 68.73; H, 6.29%).

Irradiation of **1a** *in other solvents*. Solns of **1a** in several solvents were irradiated under similar conditions. The crude photolysates were analyzed by NMR: in hexane, PhH, CH_3CN, CH_3NO_2, and trichloroethylene, only triketone **3a** was detected in MeOH and AcOH, triketone **3a** and a trace amount of **2a** were detected; in pyridine, a trace amount of **2a** was detected; in DMSO, Et_3N, HMPT, and DMF, only a polymeric material resulted.

Irradiation of **1a** *in diethyl ether*. A soln of **1a** (300 mg) in Et_2O (40 ml) was irradiated for 15 hr using a 100-W high pressure Hg lamp (pyrex) under N_2. Evaporation of the solvent and separation with plc over silica gel with hexane–Et_2O (1:1) as eluent to give 1:1 adduct of **1a** and Et_2O: ^{1}H NMR($CDCl_3$) δ 1.0–1.5(m,10H), 1.60(M,2H), 2.58(m,2H) 2.7–3.1(m,2H), 3.50(m,2H), and 3.91(m,1H); ^{13}C NMR($CDCl_3$ δ 15.3(ÇH$_3$CH$_2$OCHCH$_3$), 17.8(CH$_3$CH$_2$OCHÇH$_3$), 18.4(CH), 24.6(CH_2), 25.0(CH_2), 38.1(CH), 38.6(CH), 42.5(CH_2), 45.3(CH), 47.5(CH), 53.9(CH$_3$CH$_2$OÇHCH$_3$), 63.9(CH$_3$ÇH$_2$OCHCH$_3$), and 76.1(CH).

Irradiation of **1b** *in acetone*. A soln of **1b** (189 mg) in acetone (34 ml) was irradiated using a 100-W high pressure Hg lamp (pyrex) under N_2. After 11 hr irradiation the solvent was removed *in vacuo*. The crude products were separated by means of preparative tlc over phosphate-buffered silica gel, with hexane–Et_2O (1:2) as eluent to give three zones. In the absence of the buffer, the products decomposed completely. The fastest moving zone contained 38 mg (20%) of an oily substance, whose structure was assigned as **2bE** on the basis of its spectra: MS *m/e* 206(M$^+$); IR(film) 1800, 1685, and 1615 cm^{-1}: ^{1}H NMR($CDCl_3$) δ 1.1–1.7(m,6H,$CH_2 \times 3$), 2.20(s,3H,CH_3), 2.72(m,1H,CH), 3.06(m,2H,$CH \times 2$), 3.88(ddd,1H,CH,J = 10.0 and 2.5 Hz), and 6.10(d,1H,CH,J = 2.0); ^{13}C NMR($CDCl_3$) δ 23.7(CH_2), 25.5(CH_2), 31.9(CH_3), 40.3(CH), 40.8(CH), 41.9(CH_2), 46.6(CH), 48.9(CH), and 105.1(CH). (Found: C, 69.78; H, 7.10. Calcd for $C_{12}H_{14}O_3$: C, 69.88; H, 6.84%).

The second zone contained 40 mg of a mixture of **2cE** [^{1}H NMR δ 10.15(s,1H,CHO) and 1.70(s,3H,CH_3)], **2cZ** [^{1}H NMR δ 9.85(s,1H,CHO) and 1.81(s,3H,CH_3)], and **3b** [^{1}N NMR δ 2.50(s,CH_3)].

The third zone contained 36 mg (19%) of **2bZ** together with a small amount of **3b**. Further purification with plc gave pure **2bZ**: MS *m/e* 206(M$^+$); IR(film) 1800, 1680, and 1645 cm^{-1}; ^{1}H NMR($CDCl_3$) δ 1.1–1.7(m,6H,$CH_2 \times 3$), 2.42(s,3H,CH_3), 2.75(m,2H,$CH \times 2$), 3.13(dd,1H,CH,J = 10.5 and 4.5 Hz), 3.50(dd,1H,CH,J = 10.5 and 4.5), and 5.23(s,1H,=CH); ^{13}C NMR($CDCl_3$) δ 23.2(CH_2), 25.2(CH_2), 31.0(CH_3), 39.9(CH), 39.9(CH), 42.1(CH_2), 46.1(CH), 48.5(CH), and 107.6(CH). (Found: C, 69.73; H, 7.03. Calcd for $C_{12}H_{14}O_3$: C, 69.88; H, 6.84%).

Irradiation of **1b** *in benzene*. A soln containing 95 mg of **1b** in 43 ml benzene was irradiated for 8 hr with a 100-W high pressure Hg lamp (pyrex) under N_2. Removal of the solvent followed by short-path distillation [100–106° (bath)/3 mmHg] gave 41 mg (43%) of **3b**: m.p. 52.5–53.0°; MS *m/e* 206(M$^+$); IR (nujol) 1700, 1615, and 1595 cm^{-1}; ^{1}H NMR($CDCl_3$) δ 1.1–1.6(m,4H,$CH_2 \times 2$), 1.63(m, 2H,CH_2), 2.50(s,3H,CH_3), 2.6–2.9(M,3HCH × 3), 3.15(dd,1H, CH,J = 5.1 and 7.5 Hz), and 12.0(bs,1HOH); ^{13}C NMR($CDCl_3$) δ 24.8(CH_2), 24.8(CH_2), 26.3(CH_3), 36.2(CH), 36.2(CH), 42.5(CH_2), 48.8(CH), and 53.9(CH). (Found: C, 69.64; H, 6.75. Calcd for $C_{12}H_{14}O_3$: C, 69.88; H, 6.84%).

Irradiation of **4a** *in acetone*. A soln of **4a** (1 g) in acetone (270 ml) was irradiated for 20 hr, using a 100-W high pressure Hg lamp (pyrex) under N_2. Evaporation of the solvent and separation with plc over buffered silica gel with hexane–Et_2O (2:3) as eluent gave 100 mg (10%) of **5aE** and 128 mg (13%) of **5aZ**, together with 128 mg of starting material **4a**. NMR analysis of the crude photolysate indicated a ratio of **5aE**:**5aZ**:**6a**:**4a** = 1:1:2.5:1.

5aE: m.p. 198°(dec); ^{1}H NMR($CDCl_3$) δ 3.36(dd,1H,CH,J = 9.3 and 3.7 Hz), 4.02(ddd,1H,CH,J = 9.3,3.2, and 1.8), 4.76(d,1H,CH,J = 3.7), 4.80(d,1H,CH,J = 3.2), 5.80(dd,1H,=CH,J = 5.4 and 1.8), 7.0–7.6(m,8H,ArH), and 9.90(d,1H,CHO,J = 5.4); ^{13}C NMR($CDCl_3$) δ 45.4(CH), 45.4(CH), 46.3(CH), 48.4(CH), 107.0(CH), 124.3(CH), 124.3(CH), 125.0(CH), 125.6(CH), 127.0(CH), 127.0(CH), 127.4(CH), 127.4(CH), 138.0(C), 138.4(C), 140.8(C), 141.0(C), 188.6(CHO). (Found: C, 79.19; H, 4.57. Calcd for $C_{26}H_{14}O_3$: C, 79.45, H, 4.67%).

5aZ: m.p. 191°(dec); ^{1}H NMR ($CDCl_3$) δ 3.28(dd,1H,CH,J = 9.7 and 3.5 Hz), 3.65(ddd,1H,CH,J = 3.5), 5.49(dd,1H,CH,J = 7.9 and 1.3), 7.0–7.5(m,8H,ArH), and 9.68(d,1H,CHO,J = 7.9); ^{13}C NMR($CDCl_3$) δ 45.4(CH), 46.0(CH), 46.0(CH), 46.3(CH), 106.7(CH), 124.3(CH), 124.5(CH), 125.0(CH), 125.4(CH), 127.0(CH), 127.0(CH), 127.4(CH), 127.4(CH), and 189.0(CHO). (Found: C, 79.54; H, 4.44. Calcd for $C_{20}H_{14}O_3$: C, 79.45; H, 4.67%).

Irradiation of **4a** *in ethyl acetate*. A soln of **4a** (50 mg) in AcOEt (120 ml) was irradiated for 7 hr using a 100-W high pressure Hg lamp (pyrex) under N_2. Evaporation of the solvent and washing the residue with Et_2O gave 40 mg (80%) of **6a** as colorless crystals, which were recrystallized from benzene to give pure **6a**: m.p. 163°(dec); ^{1}H NMR($CDCl_3$) δ 3.14(m,2H), 4.70(m,2H) 6.9–7.5(m,8H,ArH), 8.74(bs,1H), and 9.13(s,1H,CHO); ^{13}C NMR($CDCl_3$) δ 45.8(CH), 49.3(CH), 124.2(CH), 124.7(CH), 126.3(CH), 126.6(CH), 138.6(C), 142.0(C), 188.4(CHO), and 199.7(CO). (Found: C, 79.44; H, 4.54. Calcd for $C_{20}H_{14}O_3$: C, 79.45; H, 4.67%).

Irradiation of **4a** *in other solvents*. Solns of **4a** in several solvents were irradiated in a similar manner. The crude photolysate was analyzed by NMR: in PhH, CH_2Cl_2, CH_3CN, and EtOH, only **6a** was detected; in cyclohexanone and propional dehyde, only polymeric materials derived from solvents were detected.

Quenching studies of **4a** *in the presence of oxygen or* 1,3-*pentadiene*. A soln of **4a** (300 mg) in acetone (130 ml) was irradiated under O_2 using a 100-W high pressure Hg lamp (pyrex). After 4 hr irradiation, the solvent was evaporated *in vacuo*. NMR analysis of the crude photolysate indicated that the formation of γ-lactones (**5aE** and **5aZ**) and **6a** was completely suppressed, and only starting material **4a** was recovered.

The reaction of **4a** (60 mg) in acetone (40 ml) was similarly quenched by added 1,3-pentadiene (186 mg).

Irradiation of **4a** *through a* $CuSO_4$aq *filter*. A soln of **4a** (20 mg) in acetone (5 ml) was irradiated externally with a 100-W high pressure Hg lamp through $CuSO_4$aq (1 cm,10%) for 48 hr. NMR analysis of the crude photolysate showed the ratio of **5aE**:**5aZ**:**6a** was 1:2:2.4.

Irradiation of **4a** (20 mg) in CH_2Cl_2 (5 ml) through the filter resulted in the formation of **6a**.

Irradiation of **4a** *through acetone filter*. A soln of **4a** (20 mg) in acetone (5 ml) was irradiated externally with a 100-W high pressure Hg lamp through acetone filter (1 cm) for 48 hr. NMR analysis of the crude photolysate showed the ratio of **5aE**:**5aZ**:**6a** was 1:1:2.4.

Irradiation of **4a** (20 mg) in CH_2Cl_2 (5 ml) through the filter resulted in the formation of **6a**.

Retro-Diels-Alder reaction of **5aE** *and* **5aZ**. γ-Lactone **5aE** (50 mg) was pyrolyzed at 230° (20 mmHg) using a short-part distillation apparatus. The crude products were chromatographed on silica gel layer using hexane–Et_2O (2:1) as eluent to give 15 mg (80%) of a 1:1 mixture (by NMR assay) of butenolides **7aE** and **7aZ**, accompanied by 28 mg of anthracene. γ-Lactone **7aZ** (65 mg) was also pyrolyzed and chromatographed to give 19 mg (77%) of a mixture of **7aE** and **7aZ** (1:1), in addition to 36 mg of anthracene. Butenolides **7aE** and **7aZ** were separated by preparative glc (APIEZON GREASE L).

7aE: MS *m/e* 124(M$^+$,87%) and 96(100%); ^{1}H NMR($CDCl_3$)

δ6.15(ddd,1H,J = 6.4,1.8, and 0.8 Hz), 6.63(dd,1H,J = 5.6 and 1.8), 8.14(dd, 1H,J = 5.6 and 1.8), and 9.96(d,1H,J = 6.4). (Found: C, 57.95; H, 3.35. Calcd for $C_6H_4O_3$: C, 58.07; H, 3.24%).

7aZ: MS *m/e* 124(M^+,80%) and 96(100%); ^{1}H NMR($CDCl_3$) δ5.62(d,1H,J = 7.8 Hz), 6.48(dd,1H,J = 5.6 and 0.7), 7.59(d,1H,J = 5.6), and 10.23(d,1H,J = 7.8). (Found: C, 58.07; H, 3.24. Calcd for $C_6H_4O_3$: C, 58.07; H, 3.24%).

Irradiation of **4b** *in acetone followed by pyrolysis.* A soln of **4b** (640 mg) in acetone (140 mg) was irradiated for 9 hr using a 100-W high pressure Hg lamp (pyrex) under N_2. Removal of the solvent *in vacuo* left 666 mg of a mixture of products. NMR analysis of the crude photo-products showed the presence of lactones **5bE**, **5bZ**, triketone **6b** and recovered **4b** in a ratio of 1:1.4:2.5:1.2. Preparative tlc of 250 mg of the crude photolysate over buffered silica gel with hexane–Et_2O (2:3) as eluent resulted in separation of **5aE** (29 mg,12%), **5bZ** (36 mg,15%), **6b** (22 mg,11%), and **4b** (29 mg).

5bE: m.p. 174–176°, MS *m/e* 178(100%); IR(KBr) 1800, 1695, and 1615 cm^{-1}; ^{1}H NMR($CDCl_3$) δ1.20(d,3H,CH_3), 2.28(s,3H,CH_3), 3.53(dd, 1H,CH,J = 3.3 and 1.5 Hz), 4.29(s,1H,CH), 4.93(d,1H,CH,J = 3.3), 5.95(d,1H,CH,J = 1.5), and 7.0–7.5(m,8H,ArH). (Found: C, 79.99; H, 5.72. Calcd for $C_{22}H_{18}O_3$: C, 79.88; H, 5.49%).

5bZ: m.p. 167–169°; MS *m/e* 178(100%) ; IR(KBr) 1795, 1680, and 1650 cm^{-1}; ^{1}H NMR($CDCl_3$) δ1.23(s,3H,CH_3), 2.15(s,3H,CH_3), 3.03(dd,1H,J = 3.3 and 1.2 Hz), 4.23(s,1H,CH), 4.35(s,1H,CH,J = 3.3), 5.45(d,1H,CH,J = 1.2), and 7.0–7.5(m,8H,ArH). (Found: C, 79.81; H, 5.69. Calcd for $C_{22}H_{18}O_3$: C, 79.98; H, 5.49%).

6b: ^{1}H NMR($CDCl_3$) δ1.03 and 1.20(s, 3H, CH_3), 2.20(s,3H,$COCH_3$), 2.42 and 2.73(d,1H,COCH), 4.63(d,1H), 4.32 and 4.27(s,1H), and 6.9–7.5(m,8H,ArH).

Pyrolytic treatment (190°,15 mmHg) of the above crude photolysate (232 mg) followed by plc separation (buffered silica gel) gave **7bE** (17 mg,17%), **7bZ**(6 mg,6%), and anthracene (63 mg,37%).

7bE: m.p. 88–89° (lit.[11] m.p. 88–89°); MS *m/e* 152(M^+); IR(nujol) 1785, 1685, 1630, and 1610 cm^{-1}; ^{1}H NMR($CDCl_3$) δ2.06(dd,3H,CH_3,J = 1.5 and 0.6 Hz), 2.31(s,3H,$COCH_3$), 6.13(s,1H,=CH), and 7.96(qd,1H,=CH,J = 1.5 and 0.7).

7bZ: m.p. 124–125° (lit.[11] m.p. 124.5–125.5°); MS *m/e* 152(M^+); IR(nujol) 1775, 1635, and 1620 cm^{-1}; ^{1}H NMR($CDCl_3$) δ2.13(d,3H,CH_3,J = 1.5 Hz), 2.60(s,3H,$COCH_3$), 5.50(s,1H,=CH), and 7.16(q,1H,=CH,J = 1.5).

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