

Effect of Spiro Ring Size on the Photochemical Ring Expansion of Dispiro Substituted Cyclobutane-1,3-diones

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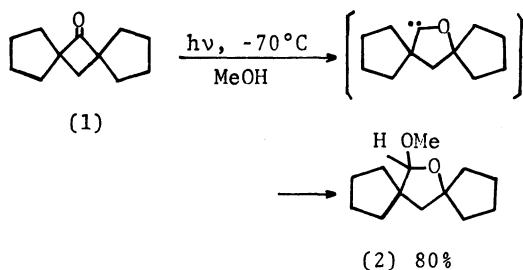
The photochemical ring expansion of dispiro substituted cyclobutane-1,3-diones in methanol has been investigated. The formation of ring expansion product was strongly dependent on the spiro ring size of dispiro substituent. The ring expanded acetal was obtained in a low yield when the spiro ring of dispiro substituted cyclobutane-1,3-diones was a five- or seven-membered ring. This is the first example of photochemical ring expansion from cyclobutane-1,3-diones. A mechanism is postulated.

Three primary photochemical processes, (a) decarbonylation (α -cleavage) (b) cycloelimination (β -cleavage) and (c) ring expansion, are usually observed in the photochemistry of simple cycloalkanones such as cyclobutanones¹⁾ and cyclopentanones.

Recently extensive studies have been carried out from an interest in photochemical ring expansion *via* an oxacarbene intermediate (c).^{1a,b,2,3)} However, in the photochemistry of cyclobutane-1,3-diones,⁴⁾ no photochemical ring expansion seems to have been found.^{1c,d)} In a previous communication,⁵⁾ a report was given on the first example of ring expansion in the photochemical reaction of dispiro[4.1.4.1]dodecane-6,12-dione. We now report the effect of the ring size on the photochemical ring expansion of spiro substituted cyclobutanones and cyclobutane-1,3-diones in methanol, and suggest a plausible mechanism.

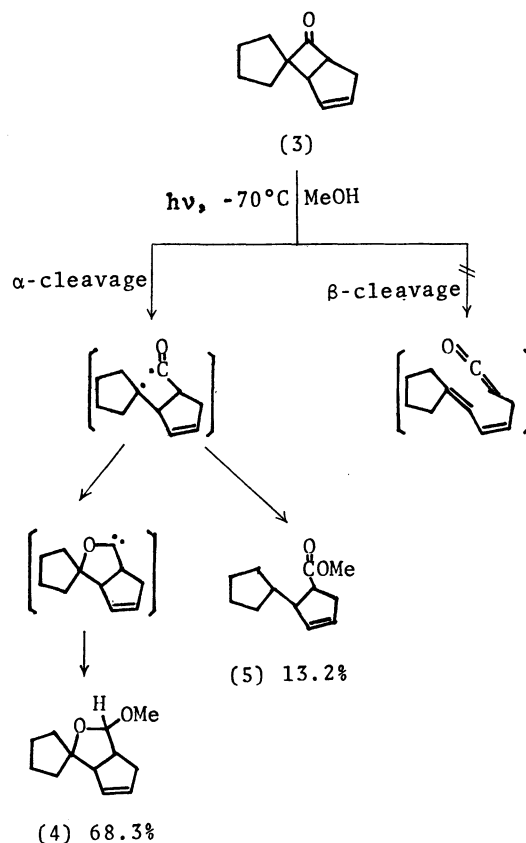
Results and Discussion

The photochemical reaction of cyclobutanone derivatives substituted by a spiro five-membered ring has been carried out to clarify the effect of spiro ring substituent on the photochemical processes. When dispiro[4.1.4.1]dodecane-6-one (1) was irradiated in methanol at -70°C for 10 hr with a Pyrex filter, a photochemical ring expansion *via* an oxacarbene intermediate took place smoothly to give ring expanded acetal (2) predominantly.



When 7-tetramethylene-bicyclo[3.2.0]hept-2-en-6-one (3) was irradiated in methanol, α -cleavage into only one of two possible directions occurred preferentially to yield a large quantity of ring expanded acetal (4) and an ester (5) without any formation of β -cleavage product.

In both cases, the ring expanded acetals were obtained predominantly. This is of great interest as compared with the cases of bicyclo[3.2.0]hept-2-en-6-one⁶⁾ and



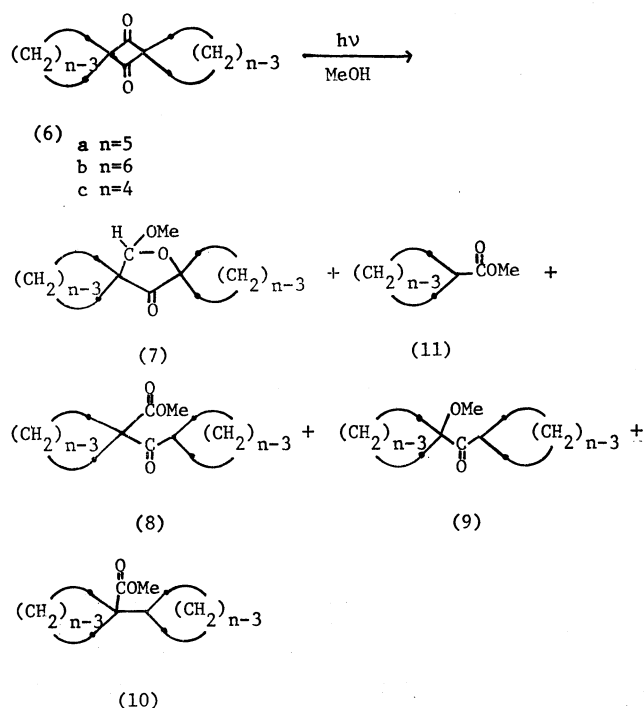
its 7,7-dimethyl derivative,⁷⁾ accompanied by comparable amounts of β -cleavage. This enhancement of ring expansion in 1 and 3 may be interpreted in terms of the nucleophilicity and stability of the carbon atom migrated to electron deficient oxygen atom. In connection with the stability of migratory carbon atom, it is not unreasonable to presume that the spiro five-membered ring substituent affects the stability of 1,4-biradical derived from initial α -cleavage in a striking manner. It can be anticipated that photo ring expansion would occur depending upon the selection of certain spiro substituents, even in the photochemical reaction of dispiro substituted cyclobutane-1,3-diones. A spiro five-membered ring substituent was chosen as a suitable substituent. As expected, irradiation of degassed methanolic solution of dispiro[4.1.4.1]dodecane-6,12-dione (6a) at -70°C for 2 h through a Pyrex filter gave ring expanded acetal (7a) in 6.1% yield.⁵⁾ The formation of 7a represents the first example of photo-

TABLE 1. PER CENT YIELDS OF PRODUCTS DERIVED FROM PHOTOLYSES OF CYCLOBUTANE-1,3-DIONES IN METHANOL

Compd	Irrad Temp	Acetal(%)	Other Products(%)			
6a	-70°C	7a (6.1)	8a (55.5)	9a (3.9)	10a ^a (1.1)	11a (3.6)
	0°C	(2.0)	(4.2)	(45.5)	(2.3)	(4.2)
	30°C	(1.4)	(1.6)	(54.6)	(3.8)	(3.6)
6b	-70°C		8b (3.4)		10b' (12.5) ^b	11b (41.7)
6c	-70°C		8c (54.9)		10c (5.6)	11c (4.9)

Besides the above products, cyclopentanone and cyclohexanone were obtained for both **6a** and **6b**, but not quantified. a) Compound (**10a**) was also produced by further irradiation of isolated compound (**8a**) in methanol. b) Methyl 1-(1-cyclohexenyl)cyclohexanecarboxylate.

chemical ring expansion from cyclobutane-1,3-diones. In analogy with cyclobutanones, the formation of **7a** from **6a** can be satisfactorily explained by a photochemical ring expansion reaction by way of an oxacarbene intermediate. As the major nongaseous product other than **7a**, methyl 1-(cyclopentylcarbonyl)cyclopentanecarboxylate (**8a**) was obtained in 55.5% yield, together with small amounts of α -methoxy dicyclopentyl ketone (**9a**), methyl 1-(cyclopentyl)cyclopentanecarboxylate (**10a**) and methyl cyclopentanecarboxylate (**11a**).

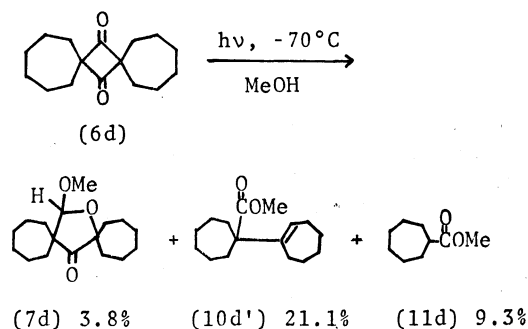


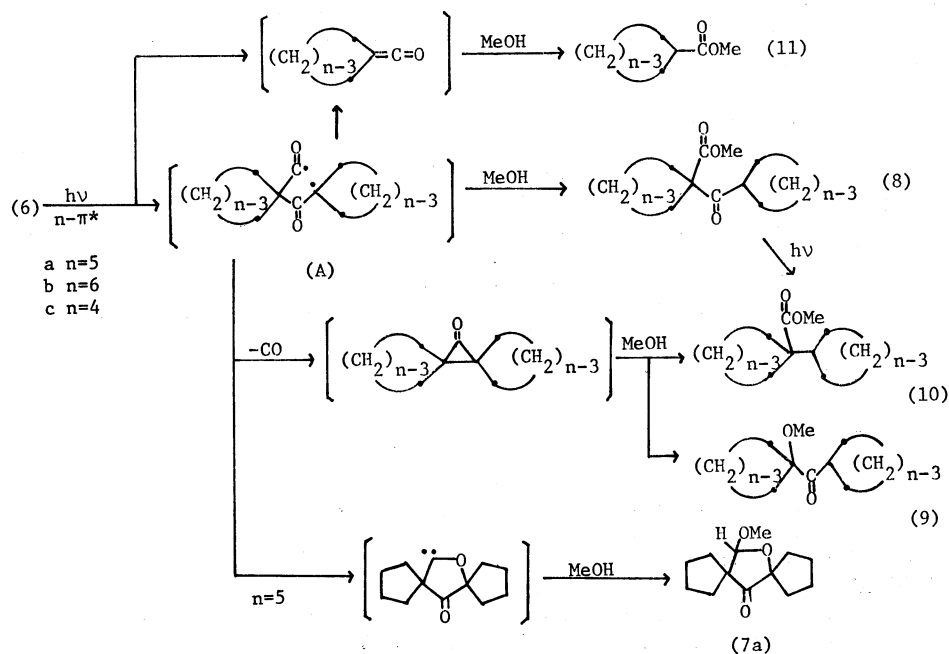
On the other hand, in a similar irradiation of dispiro[5.1.5.1]tetradecane-7,14-dione (**6b**) and dispiro[3.1.3.-1]decane-5,10-dione (**6c**), no ring expansion product could be detected by vapor phase chromatography. In these reactions, either β - or α -cleavage took place predominantly and, as the major products in each case, methyl cyclohexanecarboxylate (**11b**) and methyl 1-(cyclobutylcarbonyl)cyclobutanecarboxylate (**8c**) were obtained in 41.7% and 54.9% yields, respectively. It has been confirmed, however, that all or most of keto ester (**8c**) is easily formed by the dark reaction. This is perhaps due to the release of internal ring strain. The yields of photolysis products are given in Table 1.⁸⁾

The effect of spiro ring size on the photochemical

processes of cyclobutane-1,3-diones is remarkable. With the increase in temperature in the case of **6a**, the formation of **7a** and **8a** decreases and that of **9a**, which appears to be derived from intermediary unstable dispirocyclopropanone, increases markedly (Table 1). 1,3-Pentadiene is ineffective for the formation of **7a**, an attempt to sensitize with benzophenone being unsuccessful. It is thus assumed that a reactive species of **6a** is an $n-\pi^*$ singlet (or unquenchable triplet). From this excited state, the molecule undergoes α -cleavage to give a spin-conserved singlet biradical (1,4-acyl cycloalkyl biradical) (**A**). In these photochemical reactions, there are three primary photochemical processes (decarbonylation, β -cleavage, and ring expansion) which compete for the short-lived 1,4-acyl cycloalkyl biradical.⁹⁾ We would like to postulate that the stability of 1,4-acyl cycloalkyl biradical intermediate (**A**) is of importance in determining the subsequent path, though there is little evidence for the existence of 1,4-acyl cycloalkyl biradical. Increasing stability of intermediary biradical might increase the efficiency of ring expansion. The main path which describes the photochemical transformation of dispiro cyclobutane-1,3-diones is given in the Scheme.

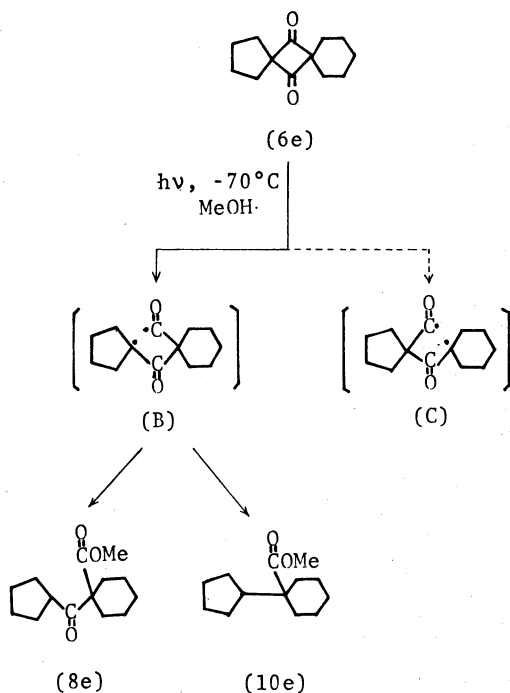
Since cycloalkyl radicals are stable in the sequence $\cdot C_5 > \cdot C_7 > \cdot C_8 > \cdot C_4$,¹⁰⁾ it may be reasonable to consider that an acyl cyclopentyl biradical derived from initial α -cleavage of excited **6a** is stable enough to undergo electronic rearrangement, and that the bonding between the carbonyl oxygen atom and cyclopentyl radical center in the biradical intermediate produces the oxacarbene intermediate. Dispiro[6.1.6.1]hexadecane-8,16-dione (**6d**) would undergo photochemical ring expansion, since the stability of an acyl cycloheptyl radical intermediate derived from initial α -cleavage may be comparable to that of an acyl cyclopentyl radical. As expected, ring expanded acetal (**7d**) was





obtained in 3.8% yield.

In order to obtain precise information on the effect of two different spiro ring sizes on the photochemical processes and, in particular, the direction of initial α -cleavage, the photolysis of dispiro[4.1.5.1]tridecane-6,13-dione (**6e**) in methanol has been examined.



The above reaction led to the preferential formation of methyl 1-(cyclopentylcarbonyl)cyclohexanecarboxylate (**8e**). The result can be explained by the difference in the stability of two 1,4-acyl cycloalkyl biradical intermediates (**B**) and (**C**) derived from the different directions of α -cleavage.

Experimental

All the melting points and boiling points are uncorrected. Infrared spectra were measured with a JASCO IR-G spectrometer, UV spectra with a Hitachi Two-wavelength Double Beam Spectrophotometer 356, and NMR spectra with a JEOL JNM-3H-60 or JEOL JNM-PS-100 spectrometer, tetramethylsilane being used as an internal standard. Mass spectra were taken on a Hitachi RMU-6E spectrometer. Gas chromatography was carried out on a Hitachi gas chromatograph 063 and on a Varian aerograph model 90-P.

Dispiro Substituted Cyclobutane-1,3-dione. Dispiro cyclobutane-1,3-diones (**6a**, **b**, **c**, **d**) were prepared by the procedure given by Erickson *et al.*¹¹ Dispiro[4.1.5.1]tridecane-6,13-dione (**6e**) was synthesized by the following procedure. To a stirred solution of cyclopentanecarbonyl chloride (7.6 mmol) and cyclohexanecarbonyl chloride (23.2 mmol) in 50 ml of ether under nitrogen was added triethylamine (46.5 mmol) over a period of 0.5 hr. The reaction mixture was stirred and refluxed for 24 hr, then worked up as usual to give dione (**6e**) in 37.7% yield, together with **6a** and **6b**. After diones had been chromatographed on silica gel, recrystallization from pentane gave white needles (**6e**). Dione (**6e**) was obtained in maximum yield, when the molar ratio of cyclopentanecarbonyl chloride to cyclohexanecarbonyl chloride was 1:3. The

TABLE 2. PROPERTIES AND SPECTRAL DATA FOR THE DISPIRO CYCLOBUTANE-1,3-DIONES

	Mp °C	Mass (<i>m/e</i>)	IR (C=O)cm ⁻¹	UV(in CH ₂ Cl ₂) nm(<i>e</i>)
6a	75	192 (M ⁺)	1727	347 (24), 306 (27)
6b	164—165	220 (M ⁺)	1721	342 (22), 313 (43), 302 (49)
6c	86—87	164 (M ⁺)	1730	359 (25), 312 (81)
6d	145—146	248 (M ⁺)	1730	333 (27), 312 (57)
6e^a	91—92	206 (M ⁺)	1736	345 (20), 309 (35)

^a Found: C, 75.56; H, 9.01%. Calcd for C₁₃H₁₈O₂: C, 75.69; H, 8.80%.

properties and spectral data for these dispiro cyclobutane-1,3-diones are given in Table 2. The ultraviolet absorption of the dispiro cyclobutane-1,3-diones showed two distinct $n\pi^*$ transitions due to 1,3 π interactions in the excited states and a small, regular increase in each absorption maximum with decreasing spiro ring size.

General Irradiation Procedure. A solution degassed by bubbling nitrogen slowly for 30 min was irradiated through a Pyrex filter using 500W high pressure mercury lamp. The reaction progress was monitored periodically by glpc analysis. Upon termination of the irradiation, the solvent was evaporated and the residue was purified by glpc. The yields were determined by glpc analysis (Poly Ethylene Glycol 20-M).

Synthesis of Dispiro[4.1.4.1]dodecane-6-one (1). A mixture of Raney nickel (80 g), ethanol (200 ml) and 12,12-di(ethylthio)dispiro[4.1.4.1]dodecane-6-one (2.5 g, 8.4 mmol)¹² was refluxed for 8 hr. Distillation of the residue gave **1** (753 mg, 50%), bp 81–82 °C/3 Torr; IR (neat) 2950, 2900, 1760, 1440, 1110, 1015 cm^{-1} ; NMR (CCl_4) δ 1.32–1.90 (m, 16H), 1.98 (s, 2H); Mass m/e 178 (M^+), 150, 96, 83, 68. Found: C, 80.62; H, 10.38%. Calcd for $\text{C}_{12}\text{H}_{18}\text{O}$: C, 80.85; H, 10.18%.

Photolysis of Dispiro[4.1.4.1]dodecane-6-one (1) in Methanol. A degassed solution of **1** (537 mg, 3.0 mmol) in 250 ml of methanol was irradiated at -70°C for 10 hr. Preparative glpc afforded cyclic acetal (**2**) (80%); IR (neat) 2980, 2910, 1450, 1330, 1190, 1160, 1095, 1030, 960 cm^{-1} ; NMR (CCl_4) δ 1.35–2.00 (m, 16H), 2.02 (s, 2H), 3.25 (s, 3H), 4.28 (s, 1H); Mass m/e 210 (M^+), 178, 160, 149, 137, 96, 81, 67.

Synthesis of 7-Tetramethylene-bicyclo[3.2.0]hept-2-en-6-one (3). Triethylamine (0.12 mol) was added to a solution of cyclopentanecarbonyl chloride (0.1 mol) and cyclopentadiene (0.7 mol) in 200 ml of dry ether under an atmosphere of nitrogen, and the resulting suspension was stirred and refluxed for 20 hr. The amine salt was removed by filtration. After distillation of the residue three times, spiro ketone (**4**) was obtained in 74.4% yield, bp 68–69 °C/9.5 Torr; IR (neat) 1775, 1600 cm^{-1} ; NMR (neat) δ 1.60 (m, 8H), 2.38 (m, 2H), 3.19 (d, 1H), 3.58–4.00 (three d or two t, 1H), 5.80 (m, 2H); Mass m/e 162 (M^+), 134, 119, 105, 96, 91, 68, 66. Found: C, 81.24; H, 8.78%. Calcd for $\text{C}_{11}\text{H}_{14}\text{O}$: C, 81.44; H, 8.70%.

Photolysis of Spiro Ketone (3) in Methanol. A solution of **3** (18.5 mmol) in 300 ml of methanol was irradiated at -70°C for 10 hr. Preparative glpc afforded acetal (**4**) in 68.4% yield, together with methyl 2-(cyclopentyl)-3-cyclopentene-1-carboxylate (**5**) (13.2%). For **4**, IR (neat) 3075, 2900, 1615, 1445, 1190 cm^{-1} ; NMR (neat) δ 1.60 (m, 8H), 2.48–2.80 (m, 2H), 3.08 (m, 1H), 3.20 (s, 3H), 4.30 (m, 1H), 4.50 (s, 1H), 5.60 (m, 2H); Mass m/e 194 (M^+), 162, 144, 133, 110, 105, 91, 79, 77, 67, 55. Found: C, 74.17; H, 9.32%. Calcd for $\text{C}_{12}\text{H}_{18}\text{O}_2$: C, 74.10; H, 9.34%. For **5**, IR (neat) 3075, 2900, 1725, 1615, 1445, 1360, 1190, 1100 cm^{-1} ; NMR (CCl_4) δ 1.40–2.10 (m, 8H), 2.20–2.80 (m, 4H), 3.10 (m, 1H), 3.25 (s, 3H), 5.60 (m, 2H); Mass m/e 194 (M^+), 163, 134, 120, 106, 91, 79.

Photolysis of Dispiro[4.1.4.1]dodecane-6,12-dione (6a) in Methanol.

A degassed solution of **6a** (18 mmol) in 200 ml of methanol was irradiated using a Pyrex filter at -70°C for 2 hr. Analysis of the photolysate by glpc revealed the following products: ring expanded acetal (**7a**, 6.1%), methyl 1-(cyclopentylcarbonyl)cyclopentanecarboxylate (**8a**, 55.5%). In addition, α -methoxydicyclopentyl ketone (**9a**, 3.9%), methyl 1-(cyclopentyl)cyclopentanecarboxylate (**10a**, 1.1%) and methyl cyclopentanecarboxylate (**11a**, 3.6%) were detected. Methyl cyclopentanecarboxylate (**11a**) was identified by comparison of glpc retention time with that of an authentic sample. For **7a**, IR (neat) 2950, 2890, 1742, 1445, 1090, 1015, 975 cm^{-1} ; NMR (CCl_4) δ 1.77 (b, 16H), 3.35 (s, 3H), 4.60 (s,

1H); Mass m/e 224 (M^+), 193, 165, 112, 96, 84, 67, 55, 41. Found: C, 69.34; H, 9.01%. Calcd for $\text{C}_{13}\text{H}_{20}\text{O}_3$: C, 69.61; H, 8.99%. For **8a**, IR (neat) 2960, 2890, 1740, 1707, 1447, 1435, 1335, 1230, 1160, 1120, 1080, 1010 cm^{-1} ; NMR (CCl_4) δ 1.30–2.30 (m, 16H), 2.50–3.30 (b, 1H), 3.68 (s, 3H); Mass m/e 224 (M^+), 193, 165, 128, 97, 69, 41. The structure of **8a** was confirmed also by its identity with an authentic sample prepared by treating **6a** with methanol containing a catalytic amount of sodium methoxide. For **9a**, IR (neat) 2950, 2870, 1700, 1440, 1360, 1070 cm^{-1} ; NMR (CCl_4) δ 1.70–2.00 (m, 16H), 2.50 (m, 1H), 3.05 (s, 3H); Mass m/e 196 (M^+), 164, 149, 135, 99, 67. For **10a**, IR (neat) 2950, 2890, 1724, 1440, 1155 cm^{-1} ; NMR (CCl_4) δ 1.40–2.30 (m, 17H), 3.60 (s, 3H); Mass m/e 196 (M^+), 194, 166, 137, 111, 97, 81, 69. Irradiation of **6a** at 0°C and 30°C gave the same photoproducts in somewhat different yields (Table 1).

Quenching with 1,3-Pentadiene. Three samples were prepared, each containing 250 ml of methanol solution of **6a** (18 mmol). One also contained 1,3-pentadiene (0.1 mol) and another contained 1,3-pentadiene (0.01 mol). All the samples were irradiated at -70°C for 2 hr. 1,3-Pentadiene has no quenching effect on the formation of cyclic acetal (**7a**).

Photolysis of Dispiro[5.1.5.1]tetradecane-7,14-dione (6b) in Methanol.

A solution of **6b** (41 mmol) in 300 ml of methanol was irradiated at -70°C for 5 hr. Isolation of products by preparative glpc afforded methyl cyclohexanecarboxylate (**11b**, 41.7%), dimethyl (bicyclohexyl)-1,1'-dicarboxylate (**12**, 15.4%), methyl 1-(1-cyclohexenyl)cyclohexanecarboxylate (**10b'**, 12.5%), and methyl 1-(cyclohexylcarbonyl)cyclohexanecarboxylate (**8b**, 3.4%). Methyl cyclohexanecarboxylate (**11b**) was identified by comparison of glpc retention time with that of an authentic sample. For **12**, mp 117–118 °C (lit.¹³ 116 °C); IR (KBr) 3030, 2970, 2900, 1720, 1450, 1435, 1350, 1300, 1210, 1130, 1060, 1030, 985 cm^{-1} ; NMR (CCl_4) δ 1.0–2.2 (m, 20H), 3.60 (mc, 6H); Mass m/e 282 (M^+), 251, 223, 169, 163, 142, 113, 109, 81. For **10b'**, IR (neat) 2950, 2890, 2700, 1728, 1450, 1298, 1260, 1212, 1200, 1175, 1155, 1130, 995 cm^{-1} ; NMR (CCl_4) δ 0.9–2.0 (m, 14H), 2.07 (m, 4H), 3.58 (s, 3H), 5.50 (m, 1H); Mass m/e 222 (M^+), 190, 163, 142, 95, 83, 81. For **8b**, IR (neat) 2940, 2820, 1730, 1703, 1445, 1365, 1210, 1130, 1110, 980 cm^{-1} ; NMR (CCl_4) δ 1.0–2.1 (m, 20H), 2.2–2.6 (b, 1H), 3.65 (s, 3H); Mass m/e 252 (M^+), 221, 193, 142, 111, 83, 55. The structure of **8b** was confirmed also by its identity with an authentic sample.

Photolysis of Dispiro[3.1.3.1]decane-5,10-dione (6c) in Methanol.

A solution of **6c** (8.2 mmol) in 250 ml of methanol was irradiated at -70°C for 2 hr. Preparative glpc gave methyl 1-(cyclobutylcarbonyl)cyclobutanecarboxylate (**8c**, 54.9%), dimethyl (bicyclobutyl)-1,1'-dicarboxylate (**14**, 17.1%), methyl 1-(cyclobutyl)cyclobutanecarboxylate (**10c**, 5.6%) and methyl cyclobutanecarboxylate (**11c**, 4.9%). For **8c**, IR (neat) 2950, 1734, 1700, 1430, 1350, 1273, 1245, 1220, 1118, 968 cm^{-1} ; NMR (CCl_4) δ 1.5–2.6 (m, 12H), 3.30 (m, 1H), 3.68 (s, 3H); Mass m/e 196 (M^+), 165, 141, 113, 83, 55. For **14**, IR (neat) 2970, 1728, 1430, 1283, 1215, 1195, 1120, 1070, 970 cm^{-1} ; NMR (CCl_4) δ 1.6–2.6 (m, 12H), 3.58 (mc, 6H); Mass m/e 226 (M^+), 194, 170, 166, 153, 139, 114, 107, 83, 79, 59, 55. Methyl cyclobutanecarboxylate (**11c**) was identified by comparison of glpc retention time with that of an authentic sample. However, when a solution of dione (**6c**) (100 mg) in methanol (20 ml) was allowed to stand at room temperature for 5 hr, **6c** underwent a facile ring opening to produce **8c** quantitatively. On the other hand, diones (**6a**, **b,d,e**) were stable in refluxing methanol.

Photolysis of Dispiro[6.1.6.1]hexadecane-8,16-dione (6d) in Methanol. A solution of dione (**6d**) (5.1 mmol) in 250 ml

of methanol was irradiated using a Pyrex filter at -70°C for 2 hr. Analysis of the photolysate by glpc revealed the following products: ring expanded acetal (**7d**, 3.8%), methyl 1-(1-cycloheptenyl)cycloheptanecarboxylate (**10d'**, 21.1%) and methyl cycloheptanecarboxylate (**11d**, 9.3%). Methyl cycloheptanecarboxylate (**11d**) was identified by comparison of glpc retention time with that of an authentic sample. For **7d**, IR (neat) 2930, 2850, 1725, 1440, 1100, 970 cm^{-1} ; NMR (CCl_4) δ 1.50–1.90 (m, 24H), 3.36 (s, 3H), 4.62 (s, 1H); Mass m/e 280 (M^+), 220, 140, 124, 108, 95. For **10d'**, IR (neat) 2930, 2850, 1725, 1440, 1240, 1190, 1170, 1060 cm^{-1} ; NMR (CCl_4) δ 1.30–1.80 (m, 18H), 1.94–2.20 (m, 4H), 3.56 (s, 3H), 5.62 (t, 1H); Mass m/e 250 (M^+), 191, 180, 156, 109, 95.

Photolysis of Dispiro[4.1.5.1]tridecane-6,13-dione (6e) in Methanol. A solution of **6e** (1.84 mmol) in 300 ml of methanol was irradiated at -70°C for 1 hr. Preparative glpc afforded keto ester (**8e**) and methyl 1-(cyclopentyl)cyclohexanecarboxylate (**10e**) in 20.5% and 15.2% yields, respectively. For **8e**, IR (neat) 2950, 2900, 1730, 1705, 1445, 1295, 1220, 1120 cm^{-1} ; NMR (CCl_4) δ 1.27–2.30 (m, 18H), 2.50–2.78 (b, 1H), 3.66 (s, 3H); Mass m/e 238 (M^+), 206, 195, 178, 142 (vs), 110, 96, 85, 67. For **10e**, IR (neat) 2950, 2900, 1725, 1450, 1200, 1170, 1130, 1000 cm^{-1} ; NMR (CCl_4) δ 1.20–2.65 (m, 19H), 3.64 (s, 3H); Mass m/e 210 (M^+), 208, 176, 151, 149, 142, 128, 95, 87, 83, 81, 69.

References

- 1) (a) D. R. Morton and N. J. Turro, *J. Amer. Chem. Soc.*, **95**, 3947 (1973) and references therein; (b) G. Quinkert, P. Jacobs, K. H. Kaiser, G. Weich, and W. -D. Stohrer, *Angew. Chem. Intern. Ed.*, **13**, 197, 198, 199, 200 (1974); (c) O. L. Chapman and O. S. Weiss, "Organic Photochemistry," Vol. III, ed. by O. L. Chapman, Marcel Dekker, New York, N. Y. (1973), pp. 197–280; (d) G. Quinkert, "Topics in Current Chemistry," Vol. 46, "Photochemistry," Springer-Verlag, Berlin, Heidelberg, New York (1974).
- 2) P. M. Collins, N. N. Oparaeché, and B. R. Whitton, *Chem. Commun.*, **1974**, 292.
- 3) It has been shown that some cyclobutane-1,2-diones also undergo the photochemical ring expansion. J. M. Conia and J. M. Denis, *Tetrahedron Lett.*, **1973**, 461.
- 4) (a) N. J. Turro, P. A. Leermakers, H. R. Wilson, D. C. Neckers, G. W. Byers, and G. F. Vesley, *J. Amer. Chem. Soc.*, **87**, 2613 (1965); (b) R. C. Cookson, M. J. Nye, and Subrahmanyam, *Proc. Chem. Soc., London*, **1964**, 144; (c) H. G. Richey, J. M. Richey, and D. C. Clagett, *J. Amer. Chem. Soc.*, **86**, 3906 (1964); (d) I. Haller and R. Srinivasan, *ibid.*, **87**, 1144 (1965); (e) N. J. Turro, G. W. Byers, and P. A. Leermakers, *ibid.*, **86**, 955 (1964); (f) P. A. Leermakers, G. F. Vesley, N. J. Turro, and D. C. Neckers, *ibid.*, **86**, 4213 (1964); (g) N. J. Turro, D. C. Neckers, P. A. Leermakers, D. Seldner, and P. D'Angelo, *ibid.*, **87**, 4097 (1965); (h) A. P. Krapcho and F. J. Waller, *J. Org. Chem.*, **37**, 1079 (1972); (i) A. P. Krapcho and B. Abegaz, *ibid.*, **39**, 2251 (1974).
- 5) K. Kimura, M. Takamura, A. Kunai, and Y. Odaira, *Chem. Comm.*, **1974**, 685.
- 6) G. Jones II and S. A. Zalk, *Tetrahedron Lett.*, **1973**, 4095.
- 7) H. U. Hostettler, *ibid.*, **1965**, 687.
- 8) No ring expansion reaction is mentioned by Krapcho and Abegaz in their report on the photochemistry of cyclobutane-1,3-diones.⁴ⁱ⁾
- 9) As an alternative mechanism, there is one involving concerted reaction from excited S_1 . In the photolysis of some 3-methylene cyclobutanones, Quinkert *et al.*^{1b)} recently reported that the oxacarbene intermediate is formed directly from the electronic excited state but not *via* 1,4-acyl alkyl biradical intermediate.
- 10) (a) C. G. Overberger, A. B. Finestone, H. Bilech, J. Lilker, and J. Herbert, *J. Amer. Chem. Soc.*, **75**, 2078 (1953); (b) C. Rüchardt, *Angew. Chem. Intern. Ed.*, **9**, 830 (1970).
- 11) J. L. Erickson, F. E. Collins, Jr., and B. L. Owen, *J. Org. Chem.*, **31**, 480 (1966).
- 12) H. M. Walborsky and E. R. Buchman, *J. Amer. Chem. Soc.*, **75**, 6339 (1953).
- 13) M. Kitabatake and M. Ogawa, *Nippon Kagaku Zasshi*, **85**, 450 (1964).