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Photochemistry of bicyclo[2.2.2]Octene-2,3-dione. Intersystem crossing via an excimer

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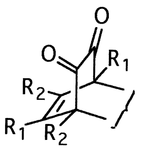
Abstract

Irradiations of the title compound (**10**) in the visible region of the spectrum resulted in competing allylic rearrangement to cyclobutanedione **11** and photobisdecarbonylation to cyclohexadiene (**12**). The product ratio depended on experimental variables including solvent, concentration, presence of added sensitizer or quencher, and temperature. It is suggested that rearrangement occurs from the singlet state and bisdecarbonylation via an excimer which undergoes intersystem crossing and decay to **12**. Comparison with the photochemistry of a variety of related α-diketones indicates that competition between the two processes is sensitive to a variety of structural factors. The cyclobutanedione **11** underwent bisdecarbonylation to **12** upon direct and sensitized irradiations. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: α-Diketones; Allylic rearrangement; Photobisdecarbonylation; Excimer

1. Introduction

Irradiation of homallylically conjugated, bi- or polycyclic α-diketones[1] of general type **1**, **2** or **3** (see Fixed graphic 1[2]) with a broad spectrum of light (λ>300 nm) results in elimination of two molecules of carbon monoxide (“photobisdecarbonylation”) with formation of cyclic conjugated dienes of general type **7**, **8** or **9**. This reaction has been of considerable synthetic utility.[1] It was originally suggested [2] that the photolysis might involve a concerted elimination of ethylenedione (C_2O_2), the elusive [3] dimer of carbon monoxide. However, low temperature (10 K), matrix isolation photolysis [4][3] at various wavelengths failed to provide any evidence in support of this hypothesis while confirming the formation of dienes. In fact, when irradiations of compounds of type **1**, **2**, or **3** were performed using monochromatic light (404 or 436 nm), it could be shown in a considerable number of cases[1] that the initial photochemical reaction was allylic rearrangement, via the excited singlet state, to homoallylic cyclobutenediones of type **4**, **5**, or **6**. An example of such behavior is shown in Fig. 1 for diketone **1g**. Cyclobutanediones, in turn, underwent photobisdecarbonylation upon direct irradiation to give the dienes. Here also, matrix isolation photolyses failed to provide any evidence for formation of ethylenedione; the only products observed from **4**, **5**, **6** were carbon monoxide and **7**, **8**, **9**. Triplet sensitized reactions of all the diketones proceeded directly to dienes with significantly higher quantum yields than the direct irradiations.



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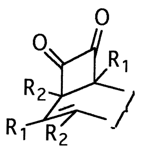
3 $R_1 =$ t-bu, $R_2 = H$



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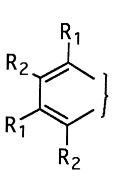

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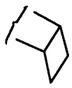
8 $R_1 = R_2 = Cl$
9 $R_1 =$ t-bu, $R_2 = H$


a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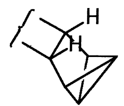

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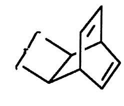
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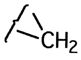

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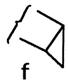
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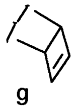
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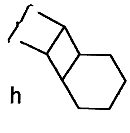
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[1] For a general reference see [1].

[2] The following notation has been used. The chromphoric part (left side) of each molecule is indicated by a bold numeral and the bridging moiety (right side) by a bold letter. Thus, for example, **1a** is **10**, **4a** is **11**, and **7a** is **12**. Similarly **1e** is bicyclo[2.2.1]heptene-2,3-dione.

[3] For a recent reference to ethylenedione see [5].

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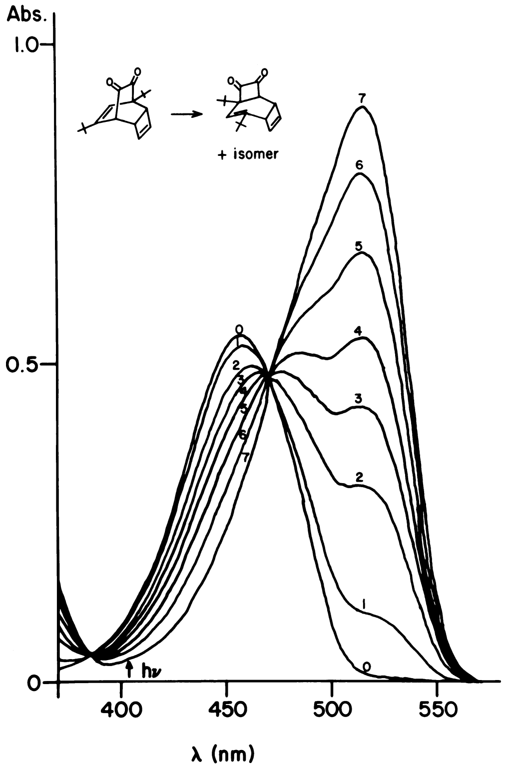
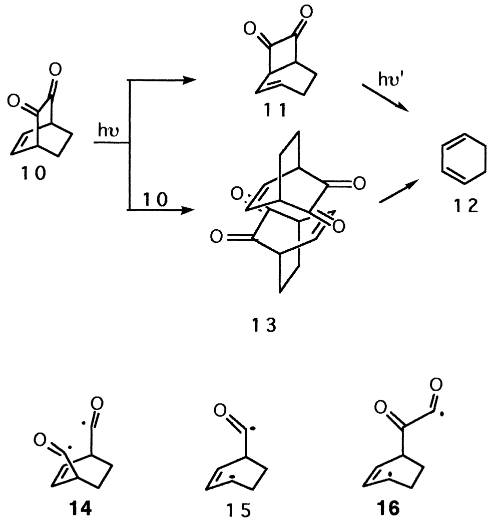


Fig. 1. Irradiation at 404 nm of 4.4×10^{-3} M **3g** in methylcyclohexane at 20°C.

Compounds **4**, **5**, **6** have maxima at significantly longer wavelengths than **1**, **2**, **3**, usually with higher extinction coefficients, and have much weaker absorption in the region 400–460 nm where maxima for **1**, **2**, **3** are observed. It is the latter property which allows observation of the isomerization **1**→**4**, etc. by permitting selective excitation of **1**, **2**, **3** in the presence of **4**, **5**, **6**. In ideal cases, proper choice of the irradiating wavelength results in quantitative isomerization with clean isosbestic behavior as can be seen in Fig. 1 for **1g**. A number of other examples of this behavior can be found in the literature cited in this report. In other cases, where significant absorption by the cyclobutanediones overlapped the absorption of starting material at the irradiating wavelength, isosbestic behavior could be observed at early stages of the reaction but was spoiled as the concentration of product increased with progress of reaction, and **4**, **5**, **6** began to undergo photobisdecarbonylation.

We now report a detailed study of the photochemistry of bicyclo[2.2.2]octene-2,3-dione (**10**) which does not exhibit the behavior described above. Instead loss of two molecules of carbon monoxide (bisdecarbonylation) competes with rearrangement. A number of other unsaturated diones, unsubstituted on the cyclohexenedione chromophore, have been shown to exhibit similar behavior; other unsubstituted compounds exhibited exclusive rearrangement (see Scheme 1).



Scheme 1.

2. Experimental

2.1. Materials

Bicyclo[2.2.2]octene-2,3-dione (**10**) was sublimed (70–80°C, 0.1 mm) immediately before use. Anthracene was purified by chromatography on alumina followed by crystallization. Analytical grade benzophenone was used as received. Spectro or reagent grade solvents were stored over 4A Molecular Sieves and boiled (to remove traces of moisture by azeotropic distillation) immediately before use. Cyclohexane and methylcyclohexane were shown to be free of aromatic contaminants by UV spectroscopy.

2.2. Irradiations

Solutions were irradiated at 20–22°C in standard 1 cm quartz or Pyrex cells which had been degassed by five freeze-pump-thaw cycles before being sealed off. Quantum yields at 436 nm were determined using a 125 W Phillips medium pressure mercury lamp with a voltage-stabilized power supply and a 436 nm Schott interference filter (total light intensity 2–3×10^{-7} Einstein/min on a 9×27 mm area of the cell) and at 454 nm using a 900 W Xenon lamp in conjunction with a Bausch and Lomb high intensity monochromator (total light intensity 3–4×10^{-7} Einstein/min). The photochromic fulgide, Aberchrom 540, was used in its colored form for actinometry at 436, 454 and 515 nm [6,7]. Quantum yields were calculated including a correction for the fraction of incident light absorbed by **11** (ϵ_{454}=30).

Infrared maxima at 1780 and 1800 cm^{-1} were observed when a solution of **10** in dry methylene chloride was irradiated at 454 nm in a standard IR cell.

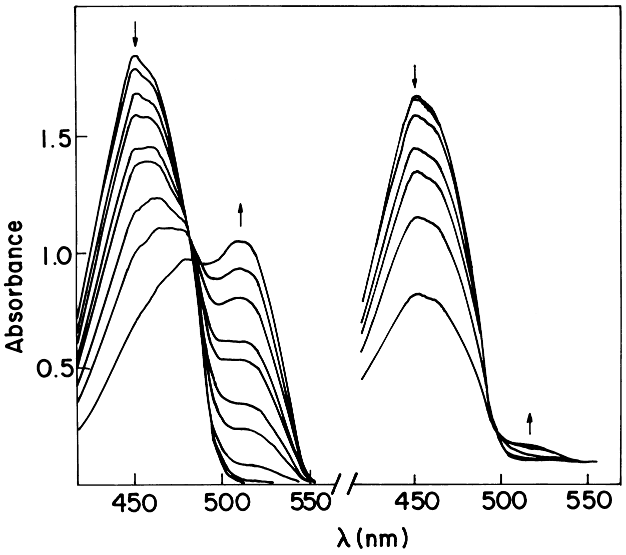


Fig. 2. Irradiations of **10** at 436 nm and room temperature. Right side: irradiation of 1.53×10^{-2} M **10** in cyclohexane at various time intervals. Left side: irradiation of 1.68×10^{-2} M **10** in cyclohexane containing 3.3×10^{-3} M anthracene at various time intervals.

2.3. Triazolinedione adduct of cyclohexadiene

A solution of diketone **10** (13 mg) in cyclohexane (spectro grade, free of cyclohexadiene by UV analysis) was irradiated through a 380 nm cut-off filter until the yellow color had passed through a pink coloration and then faded completely. A solution of *N*-phenylpyrazolinedione (15 mg) in a small volume of methylene chloride was added. After concentration on a rotary evaporator, a white solid (20 mg), m.p. 170–172°C (lit. [8] m.p. 172–4°); NMR and IR spectra were identical with those of an authentic sample.

3. Results

Irradiation of **10** [9] (λ_{max} 454 nm, ϵ 110) in dry cyclohexane or methylcyclohexane solution at 436 nm resulted in rearrangement to cyclobutanedione **11** (λ_{max} 513 nm, ϵ 105) with simultaneous bisdecarbonylation (cf. Fig. 2) to cyclohexadiene (**12**). Because of its thermal instability [10][4] and its high sensitivity to moisture and to light, **11** was not isolated but was characterized by its absorption maximum at 513 nm in the visible (cf. Fig. 2) and by its infrared spectrum in solution (1780, 1800 cm^{-1}), these being unique absorptions typical of the cyclobutanedione ring.[1] Formation of **12** was established by appearance of its characteristic absorption in the ultraviolet, by nmr spectra of irradiated solutions, and by isolation of the known Diels–Alder adduct of cyclohexadiene with *N*-phenyltriazolinedione. The spectroscopic results and GC analysis indicated that **11** and **12** were the only products of the photochemical reaction provided that anhydrous conditions prevailed throughout. This could be ensured by use of freshly sublimed **10**, carefully dried solvent, and measurement in sealed cuvettes.

Table 1
Quantum yields for irradiation of **10** in various solvents at 436 nm

Solvent	Concentration ($M\times10^3$)	ϕ_{-10}	ϕ_{11}	ϕ_{12}	Ratio (ϕ_{12}/ϕ_{11})
Cyclohexane [a]	4.62	0.21	0.105	0.105	1
Benzene	5.7	0.23	0.060	0.17	2.8
Toluene	6.43	0.19	0.052	0.17	3.3
Dimethoxyethane	6.93	0.25	0.063	0.18	2.9
Ethyl acetate	6.55	0.21	0.046	0.16	3.6

[a] Identical results with methylcyclohexane.

Monitoring spectroscopic changes in the visible provided a convenient method (cf. Figures) for determining quantum yields for disappearance of **10** (ϕ_{-10}) and formation of **11** (ϕ_{11}). Since **11** and **12** were the only detectable products of reaction, the quantum yield for formation of **12** (ϕ_{12}) was then obtained by difference. These quantum yields include a correction for absorption by product **11** at the irradiating wavelength. Further experiments showed that quantum yields for product formation depended markedly on a variety of experimental variables including solvent, concentration, presence of added anthracene or benzophenone, and temperature.

Results obtained in a number of solvents are summarized in Table 1. While ϕ_{-10} showed very little variation, the fraction of bisdecarbonylation to **12** increased with increased solvent polarity at the expense of rearrangement. We note that the range of solvents which can be used is limited by the sensitivity of **10** and particularly of **11** to moisture and to protic solvents.

Considerable variation in the ratio of products was observed as a function of diketone concentration. Results of a series of experiments in cyclohexane are summarized in Table 2. While the overall quantum yield for reaction (ϕ_{-10}) did not change significantly, the extent of rearrangement to **11** increases with decreasing concentration of **10**. At concentrations of **10** below 10^{-5} M, where quantum yield measurements were not practicable, rearrangement became the exclusive process ($\phi_{-10}=\phi_{11}$) and isosbestic behavior was observed at low conversions with isosbestic points at 227, 258, 358 and 487 nm. Spoiling of the isosbestic points

Table 2
Dependence of quantum yields on concentration of **10** irradiated at room temperature in cyclohexane at 454 nm

Concentration **10** (M)	ϕ_{-10}	ϕ_{11}	ϕ_{12}
1.16×10^{-2}	0.22	0.070	0.15
5.75×10^{-3}	0.20	0.086	0.11
3.45×10^{-3}	0.20	0.11	0.09
1.47×10^{-3}	0.20	0.11	0.09
8.48×10^{-4}	0.22	0.13	0.09

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[4] For a report on thermal reactions of compounds of this type: see [10].

Table 3
Quantum yields for 4.62×10^{-3} M **10** in cyclohexane at 454 nm (3.33×10^{-7} Einstein/min [a]) in the presence of anthracene

Anthracene ($M\times10^3$)	ϕ_{-10}	ϕ_{11}
3.3	0.11	0.11
1.1	0.14	0.10
0.33	0.16	0.11
0.11	0.19	0.11
0.033	0.21	0.10
0.011	0.22	0.10
0	0.21	0.10

[a] Total light intensity incident on a 9×27 mm area of a standard cuvette.

at higher conversions is due to subsequent photoreaction of **11** as discussed below.

Formation of **12**, but not of **11**, was quenched by anthracene (E_t 42 kcal/mol) as illustrated in the left side of Fig. 2. Results of a series of experiments at 454 nm in cyclohexane, giving quantum yields as a function of quencher concentration are presented in Table 3. Isosbestic behavior was observed at low conversions and the spoiling of isosbestic points is again attributed to further reaction of **11** because of its significant absorption at 454 nm (e_{454}=30). Similar results were observed in benzene solution containing anthracene.

With benzophenone as triplet sensitizer, on the other hand, exclusive formation of **12** was observed with quantum yield ϕ_{-10}=0.9.

The availability of solutions containing relatively high concentrations of **11** allowed investigation of its photochemical behavior at long wavelength. Irradiation of 3.3×10^{-3} M **11** in methylcyclohexane solution at room temperature and 515 nm resulted in appearance of the characteristic absorption of cyclohexadiene with a quantum yield of 0.3. Thus **11** reacts with a quantum yield 50% greater than that of **10**. Since it also has an extinction coefficient of 30 which is 27% that of **10** at the irradiating wavelength, it is not surprising that isosbestic behavior is not maintained as conversion **10**→**11** proceeds.

Both reactions of **10** showed temperature dependence in 3:1 methylcyclohexane–methylene chloride (added to increase solubility at low temperature). Rearrangement was much more sensitive to temperature than bisdecarbonylation as shown in Table 4. At 50°C rearrangement to **11** was close to quantitative but at temperatures below about −10°C, no rearrangement at all could be observed while formation of **12** was still observed at −55°C. Irradiation of **10** at 385 nm in an Argon matrix at 10 K resulted in slow photolysis to form **12** and carbon monoxide [15].[5]

Table 4
Temperature dependence of quantum yields for **10** relative to quantum yield for each process at 22°C in 3:1 methylcyclohexane–methylene chloride, 4.3×10^{-2} M **10**

	Temperature (°C)				
	50	22	−6	−30	−55
ϕ_{-10} (rel [a])	0.1	1	1	0.33	0.18
ϕ_{11} (rel [a])	2	1	0.1	–	–

[a] Quantum yields are relative to the value at 22°C taken as unity for each process.

The fluorescence spectrum of **10** exhibited the usual emission for such diketones at about 500 nm; no anomalous fluorescence was observed. Attempts to observe phosphorescence at 77 K gave negative results.[6]

4. Discussion

Direct irradiation of **10** into its long wavelength ($n_+\pi^*$) absorption band results in two competing photoreactions: allylic rearrangement to **11** and bisdecarbonylation to cyclohexadiene (**12**) as illustrated on the right side of Fig. 2. At 50% conversion of **10**, only a slight increase in absorption above 500 nm, due to formation of the rearrangement product **11**, is observed. These two competing reactions showed classical singlet vs. triplet behavior. In the presence of sufficiently high concentrations of the triplet quencher anthracene, rearrangement to **11** occurred exclusively. This behavior is shown in Fig. 2 which presents the results of irradiation of solutions of comparable concentration with (left side of Figure) and without (right side) added anthracene. The right side of the Fig. 2 contrasts markedly with the result of similar irradiation of **3g** shown in Fig. 1. The remaining product is cyclohexadiene (**12**) formed by bisdecarbonylation of **10**. Observations that: (1) added anthracene quenched bisdecarbonylation but not rearrangement as shown in the left side of Fig. 2, and (2) that benzophenone sensitization resulted only in bisdecarbonylation with enhanced quantum yield combine to indicate that rearrangement is an excited singlet state reaction and bisdecarbonylation proceeds from a quenchable triplet state. Involvement of the excited singlet state in rearrangement is consistent with a considerable body of work[1] on photorearrangement reactions of related compounds.

Further, it is noteworthy that the quantum yield for disappearance of **10** remained constant over a concentration range varying by a factor of 500 while the product ratio **12**:**11** changed by a factor of 3; rearrangement became the exclusive process at concentrations of **10** below about 1×10^{-5} M. Thus, in cyclohexane or methylcyclohexane solutions, 80% of the initially formed singlets decayed by a combination of radiative and non-radiative pathways to ground state **10** and the remaining 20% partitioned between formation of **11**, the singlet product and **12**, the triplet product, with **12** increasing with increasing concentration of **10**. Thus the formation of **12** involves an interaction

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[5] Conventional energy transfer procedures are not feasible in glasses at 10 K.

[6] We thank Dr. S. Hassoon of this laboratory for the emission measurements.

between singlet excited **10** and a molecule of **10** in the ground state. We suggest that this bimolecular process is formation of an excimer having a structure such as **13** which involves two sets of interactions between double bond and α-diketone moieties. The fact that ϕ_{-10} remained constant indicates that decay of excimer **13** to product **12** occurs with a quantum yield of unity.

The proposed dione–olefin interactions have been observed [11,12] between biacetyl and activated olefins; direct electron transfer was observed in esr spectra in some cases. The solvent effects observed, increased formation of **12** in benzene, toluene, dimethoxyethane and ethyl acetate as compared to cyclohexane or methylcyclohexane provide some support. Unfortunately, the sensitivity of **10** and particularly of **11** to traces of moisture or to protic solvents precluded examination of a wider range of solvents.

The temperature effects on quantum yields show that both photoreactions involved activated processes, and that the activation energy for rearrangement is larger than for bisdecarbonylation. The effect observed in rearrangement is consistent with earlier results on temperature effects [13,14] which have been interpreted in terms of reaction from higher vibrational states of the singlet excited state of diketone. It is noteworthy that the activation energy for rearrangement of tetrachloro (**3**) and tetrabromo substituted compounds is significantly smaller; appreciable quantum yields for rearrangement were observed even at liquid nitrogen temperature.[1]

Direct irradiation of **11** at 515 nm led to **12** with a quantum yield of 0.30 while benzophenone sensitized reaction proceeded with a quantum yield of unity.

We note that two mechanisms can be suggested for bisdecarbonylation proceeding from a triplet state of diketones **10** or **11**. One involves cleavage of the intercarbonyl bond[7] to form triplet diacyl biradical **14** which then stabilizes by successive losses of carbon monoxide (via a biradical such as **15**) and intersystem crossing to give a diene. Alternatively, the bridgehead bond to a carbonyl group could cleave to form triplet α-ketoacyl biradical **16** which would then terminate as diene and carbon monoxide. Conversion of **14** to triplet cyclobutanedione is unlikely on energetic grounds. As discussed in the Introduction, a concerted elimination to form C_2O_2 and ground state diene (singlet) is an intriguing possibility which has not been supported by low temperature, matrix isolation experiments. The failure of such experiments may be due to the fact that the ground state of ethylene dione is a triplet so that spin considerations require that the diketone be generated in its triplet state. This has not been possible to date [15][5]. The evidence clearly indicates that diketone triplet states do not undergo rearrangement to cyclobutanediones.

Results (concentration dependence, anthracene quenching, benzophenone sensitization) similar to those obtained with **10**, namely competing singlet state photorearrangement and triplet state photobisdecarbonylation, have been obtained with diketones **1b** [16][8], **1c** (see below)), and **1d** [17,18] although not investigated in the same detail as **10**. All of these compounds have only hydrogen substitution on the enedione chromophore. However, compounds, **1e** and **1f**, which have the same hydrogen substitution, underwent exclusive rearrangement in the measurable concentration range. The spectroscopic changes observed with **1e** [19] and **1f** [20] and are reproduced in the literature cited. All showed good isosbestic behavior indicative of exclusive photorearrangement. This was further confirmed for **1e** by gas chromatographic analysis of product at various stages of conversion. Since remote substitution should not affect excimer formation, we conclude that the rate of rearrangement is subject to subtle factors such as ring strain so that rearrangement competes successfully with excimer formation in some cases but not in others.

A considerable number of diketones having tetrachloro, tetrabromo, or 1,3-di-*t*-butyl substitution on the enedione chromophore have been studied.[1] In all cases, rearrangement was the exclusive process. The lovely spectroscopic behavior observed with **2h** is reproduced on page 17 of [1] and is characteristic of halo compounds in general. Since the dione moiety is the acceptor and the double bond the donor in excimer formation, the presence of electron withdrawing halogen groups may be important in reducing the possibility of excimer formation. A similar exquisite result for a 1,3-di-*t*-butyl derivative of **3e** has also appeared [21]. Steric hindrance to excimer formation may also be important in all of these substituted cases, particularly with *t*-butyl groups.

The compounds **1c**, **2c**, and **3c** were prepared by Christl et al. [22] and served as precursors for the corresponding dienes, new members of the interesting $C_{10}H_{10}$ family of compounds. In our laboratory, as noted above, **1c** behaved like **10** upon irradiation at 436 nm, producing a mixture of cyclobutanedione **4c** and diene **7c** with diene formation being quenched by added anthracene. On the other hand, both **2c** and **3c** underwent exclusive rearrangement to cyclobutanediones **5c** and **6c** under the same conditions, with isosbestic points at 235, 272, 386, and 467 and $\lambda_{\max}$ 490 nm for **5c** and isosbestic points at 385 and 485 and $\lambda_{\max}$ 523 nm for **6c**. We were able to grow crystals of **1c** and **2c** suitable for X-ray crystallographic analysis.[9] The values of selected bond lengths are given in Table 5. We note that the intercarbonyl bond lengths (C7–C8) are identical in both compounds but that there are significant differences (well outside the experimental standard deviations given in the

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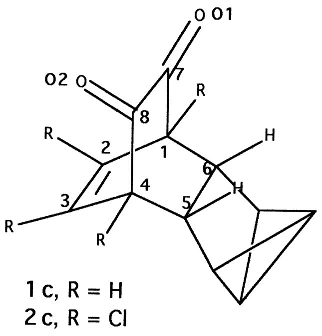
[7] Intercarbonyl bond cleavage is generally not observed with α-diketones in solution with the exception of cyclobutenediones, cf. [1].

[8] Work performed in this laboratory.

[9] M. Kapon has deposited atomic coordinates for structures **1c** (CCDC 113078) **2c** (CCDC 113079) with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK. Results of the X-ray analysis confirm the stereochemical assignments originally made ([22]) on the basis of nmr spectra.

Table 5
Selected bond lengths for **1c** and **2c**



1 c, R = H
2 c, R = Cl

Bond Lengths in Å (esd's in parentheses)

	1c	2c
C1–C2	1.503(5)	1.525(4)
C2–C3	1.305(5)	1.319(4)
C3–C4	1.516(5)	1.539(4)
C1–C7	1.501(4)	1.525(4)
C4–C8	1.495(4)	1.520(4)
C7–C8	1.553(4)	1.551(4)
C7–O1	1.208(3)	1.191(4)
C8–O2	1.202(3)	1.196(3)
C1–C6	1.539(4)	1.551(4)
C4–C5	1.549(4)	1.544(4)

Table) between all remaining C–C bond lengths in the enedione framework. These are consistently longer in **2c** than in **1c**. If a similar situation also exists in the excited state, this loosening of the molecule would appear to favor rearrangement and reinforce the inhibition of excimer formation due to the electronic effects of chlorine substitution. Bond angles in the chromophore region of both diones did not show significant differences.

We should note that direct spectroscopic evidence for the intermediacy of an excimer could not be obtained. Absorption spectra of **1c** and of **2c** were very similar. The fluorescence spectrum of **10** showed no unexpected bands which might be attributed to exciplex emission and no phosphorescence could be detected.

5. Conclusion

Photochemistry remains full of surprises. After two substances containing the bridged cyclohexenedione chromophore and a considerable number of additional compounds possessing halogen or *t*-butyl substituents on this chromophore had been shown to undergo reaction from their first excited singlet states to give cyclobutanediones, a number of examples in which more complex behavior was observed have been encountered. With bicyclo[2.2.2]octenedione (**10**), this behavior is due to competing formation of an excimer which undergoes intersystem crossing and bisdecarbonylation to a diene. The results emphasize the importance of experimental variables in deterimining the outcome of photochemical reactions.

Acknowledgements

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References

[1] M.B. Rubin, Top. Curr. Chem. 129 (1985) 1.
[2] J. Strating, B. Zwanenburg, A. Wagenaar, A.C. Udding, Tetrahedron Lett. (1969) 125.
[3] D. Schroder, C. Heinemann, H. Schwarz, J.N. Harvey, S. Dua, S.J. Blanksby, J.H. Bowie, Chem. Euro. J. (1998) 2550 and references therein.
[4] M.B. Rubin, A. Patyk, W. Sander, Tetrahedron Lett. 29 (1988) 6641.
[5] G. Maier, H.P. Reisenauer, B. Rother, J. Eckwert, Ann. (1996) 303.
[6] H.J. Kuhn, S.E. Braslavsky, R. Schmidt, Pure Appl. Chem. 61 (1989) 198.
[7] V. Wintgens, L.J. Johnston, J.C. Scaiano, J. Am. Chem. Soc. 110 (1988) 511.
[8] J.P. Snyder, V.T. Bandurco, F. Darack, H. Olsen, J. Am. Chem. Soc. 96 (1961) 5158.
[9] H.D. Scharf, P. Friedrich, A. Linckens, Synthesis (1976) 256.
[10] M.B. Rubin, Y. Harel, Tetrahedron Lett. 28 (1987) 5373.
[11] J. Mattay, J. Gersdorf, K. Buchkremer, Chem. Ber. 120 (1987) 307.
[12] J. Gersdorf, J. Mattay, H. Gorner, J. Am. Chem. Soc. 109 (1987) 1203.
[13] M.B. Rubin, M. Weiner, R. Katraro, S. Speiser, J. Photochem. 11 (1979) 287.
[14] S. Hassoon, M.B. Rubin, S. Speiser, J. Photochem. 26 (1984) 295.
[15] W. Sander, Bochum, personal communication.
[16] M. Kummer, Doctoral Dissertation, University of Düsseldorf, 1986.
[17] R. Braun, M. Kummmer, H.-D. Martin, M.B. Rubin, Angew Chem., Int. Ed. Engl. 24 (1985) 1059.
[18] J. Behr, S. Grimme, M. Kummer, H.-D. Martin, B. Mayer, M.B. Rubin, C. Ruck, Eur. J. Org. Chem. (1998) 2239.
[19] M.B. Rubin, M. Weiner, H.-D. Scharf, J. Am. Chem. Soc. 98 (1976) 5699.
[20] M.B. Rubin, J. Am. Chem. Soc. 103 (1981) 7791.
[21] M.B. Rubin, Tetrahedron Lett. 25 (1984) 4697.
[22] M. Christl, H.-J. Lüddeke, A. Nagyrevi-Neppel, G. Freitag, Chem. Ber. 110 (1977) 3745.