

# Topics in Current Chemistry

# 129

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of More Selective Antitumorals



## Photochemistry and Organic Synthesis

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With Contributions by  
G. S. Cox, K. Dimroth, J-F. Labarre,  
M. A. Paczkowski, M. B. Rubin, N. J. Turro

With 91 Figures and 50 Tables



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P. F. Gordon, P. Gregory

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# Recent Photochemistry of $\alpha$ -Diketones

**Mordecai B. Rubin**

Department of Chemistry, Technion-Israel Institute of Technology, Haifa, Israel

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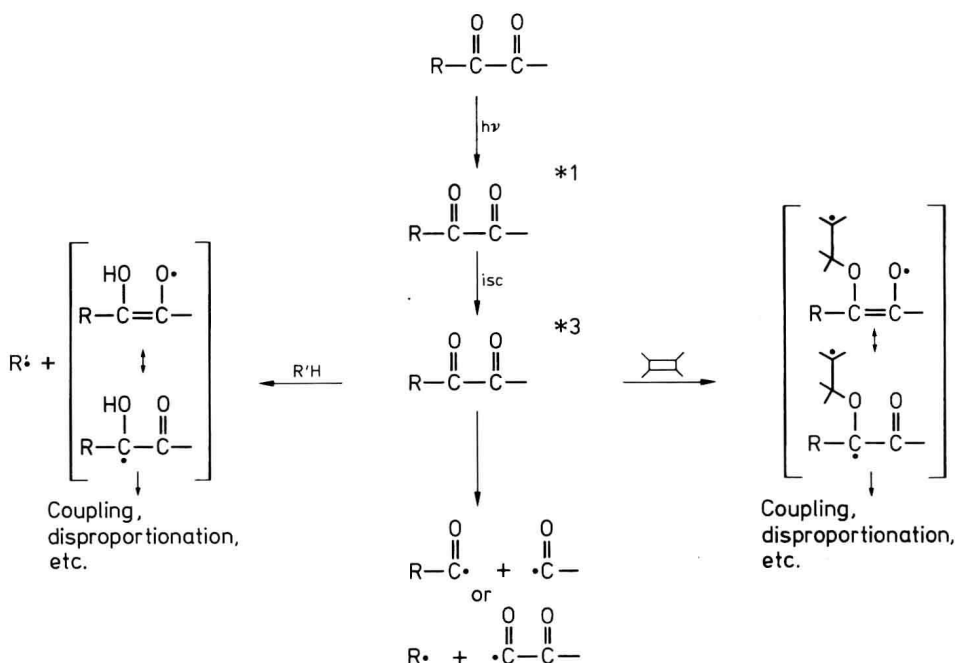
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Activity in the photochemistry of  $\alpha$ -diketones has continued unabated in the past decade. In addition to special attention to absorption and emission spectra, photoelectron spectroscopy has been applied widely. Areas of recent emphasis include (1) cyclobutene- and (2) cyclobutanediones, (3) bridged cyclohexenediones, and (4) reactions in the presence of oxygen, particularly epoxidation of olefins. The more venerable aspects such as inter- and intramolecular hydrogen atom abstraction reactions and additions to multiple bonds continue to receive attention. A considerable number of examples of synthetic applications have accumulated in recent years. In parallel, mechanistic understanding has broadened considerably.

## I Introduction

The photochemistry of  $\alpha$ -diketones has been a subject of interest for about a century. Since the appearance of comprehensive review articles <sup>1)</sup> in 1969 and 1971, activity in this area has continued with investigation of a number of new systems, particularly unsaturated diketones and diketones incorporated in a four-membered ring. New types of chemistry of synthetic and mechanistic interest have been revealed. The purpose of this review is to summarize these newer developments with briefer reference to some significant developments in the older reactions.

The Scheme below summarizes the "classical" photochemistry of saturated and aryl diketones. These undergo efficient intersystem crossing (very weak fluorescence, strong phosphorescence) to the chemically reactive triplet state ( $n_+$ ,  $\pi^*$ ) which may (inter- or intramolecularly) abstract a hydrogen atom of a wide variety of types or add to a multiple bond; in both cases two new radical centers are formed. The resulting radical pair or 1,4-biradical will proceed to product(s) or revert to starting material(s) by appropriate free radical processes which are of considerable intrinsic interest but whose only relation to photochemistry may be the multiplicity deriving from the excited state precursor. In addition to the two very common reaction types mentioned above, two possible  $\alpha$ -cleavages, as illustrated in Scheme I, might occur and will be recognizable by fragmentation or loss of carbon monoxide. These cleavages are generally of negligible importance <sup>2)</sup> and are observed mainly with



Scheme I Photochemistry of Saturated and Aryl Diketones

seven-membered cyclic systems, particularly those containing a heteroatom, or in irradiations in inert medium.

Most of the newer photochemistry, with the exception of open-chain unsaturated diones and recent results with the older reactions, is very different from that described in Scheme I. Reactions occur from the singlet state; bond cleavage, either with rearrangement or loss of carbon monoxide, is the major process.


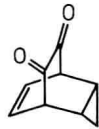
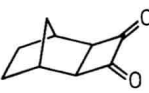
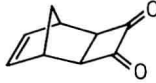
## II Spectroscopy

On the basis of extended Huckel and CNDO/2 calculations, Swenson and Hoffmann<sup>3)</sup> proposed in 1970 that through-bond interaction between non-bonding orbitals  $n_1$  and  $n_2$  of the two carbonyl groups of  $\alpha$ -diketones would result in two molecular orbitals  $n_+$  and  $n_-$  with clearly split orbital energies (rather than two orbitals of identical energies as had been assumed previously). The effect of through-space interactions was estimated to be negligible. Experimental confirmation was forthcoming one year later<sup>4)</sup> from vertical ionization potentials (IP) determined by photoelectron (PE) spectroscopy. PE spectra of many dicarbonyl compounds have been measured since; representative results are presented in Table I together with long wavelength absorption maxima. Assignments were based on theoretical calculation and analogy.

As can be seen in the Table, the splitting of  $n_+$  and  $n_-$  orbitals lies in the range 1.5–2.1 eV for a large number of dicarbonyl compounds of differing ground state conformations. Typical are planar biacetyl (entry 1,  $\lambda_{\max}$  440 nm,  $\Delta$ IP 1.84 eV) and tetramethylcyclobutanedione (entry 5, 492 nm, 2.08 eV) on the one hand and skewed di-*t*-butyldiketone (entry 2, 362 nm, 1.99 eV) and tetramethylcyclooctanedione (entry 7, 348 nm, 2.08 eV) on the other. Introduction of homoallylic conjugation in cyclic systems (entries 12, 15) results in a small hypsochromic shift of the absorption maximum and a much larger splitting of  $n_+$  and  $n_-$  energies. This has been attributed to through-bond effects. Much smaller effects are observed with more remote double bonds. The combination of PE, absorption, and emission spectra provides a powerful tool for detailed characterization of excited states.

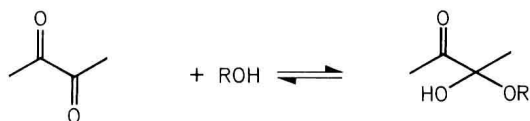
Turning to absorption spectra, the long-standing generalization<sup>14)</sup> that long wavelength ( $n_+$ ,  $\pi^*$ ) absorption maxima of  $\alpha$ -diketones vary as a function of torsion angle (maximum values for  $0^\circ$  ( $\sim$ 500 nm) and  $180^\circ$  ( $\sim$ 450 nm), minimum for  $90^\circ$  ( $\sim$ 330 nm)) continues to receive support. This generalization was originally based on absorption spectra in ethanol solution of the Leonard series of  $\alpha,\alpha,\alpha',\alpha'$ -tetramethyldiones of varying ring size where the ring provides a conformational constraint. Repetition of these measurements<sup>8,9)</sup> in cyclohexane solution confirmed the earlier results but with higher extinction coefficients due to the absence of a perennial problem with  $\alpha$ -diketones, hemiketal (or hydrate) formation. The four methyl groups introduced to prevent enolization apparently lead to conformational complications in larger rings since the value of 384 nm for a tetramethyl substituted 16-membered ring is much lower than the range 442–448 nm observed for the maxima of four compounds of similar ring size lacking methyl substitution<sup>15,16)</sup>. Long wavelength absorption maxima (band of highest intensity) will be included wherever possible in the sections to follow.

**Table 1.** Long Wavelength Absorption Maxima<sup>a</sup> and Vertical Ionization Potentials<sup>b</sup> of Selected  $\alpha$ -Diketones

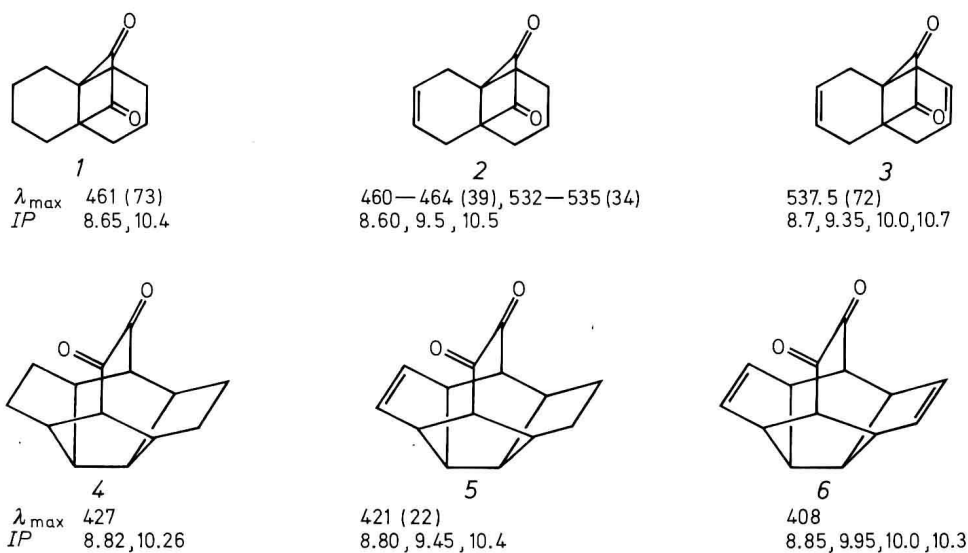
Entry	Compound	$\lambda_{\max}(\text{nm})$	I.P. (eV)			Ref.
			$n_+$	$n_-$	$\pi$	
1	Biacetyl	440	9.57	11.41		4)
2	Di- <i>t</i> -butyldiketone	362	8.66	10.65		5)
3	Benzil	370	9.1	11.1		6)
4	Cyclobutanedione	489	9.61	11.71	12.83	7)
5	Tetramethylcyclobutanedione	492	8.79	10.87		8, 9)
6	3,3,7,7-Tetramethylcycloheptanedione	337	8.67	10.55		5, 8, 9)
7	3,3,8,8-Tetramethylcyclooctanedione	348	8.61	10.59		9)
8	Cyclobutenedione	340	9.79	11.87	11.55, 13.61	7)
9	Benzocyclobutenedione	420	9.23	11.23	10.14, 10.43	10)
10	Camphorquinone	470	8.80	10.40		4)
11	Bicyclo[2.2.1]heptanedione	484	9.0	10.5		11, 12)
12	Bicyclo[2.2.1]heptenedione	460	8.7	11.1	10.6	11, 12)
13	7-Oxabicyclo[2.2.1]heptenedione	486	8.9	11.7	10.8	11)
14		460	8.9	11.5	10.3, 10.7 <sup>c</sup>	11)
15		450	8.7	11.8	10.3, 10.5 <sup>c</sup> , 10.9 <sup>c</sup>	11)
16		526	8.85	10.65		13)
17		546	8.65	10.80		13)

<sup>a</sup> In hydrocarbon solvent. Values are for the most intense maximum.<sup>b</sup> Vertical ionization potentials obtained from He(I) photoelectron spectra.<sup>c</sup> IP assigned to Walsh orbital of cyclopropane ring.

The intriguing observation<sup>17)</sup> that absorption maxima of [4,4,2]-propellanediones 1, 2, and 3 depended markedly on the presence of remote unsaturation has stimulated considerable activity. As summarized below, the saturated compound 1 had an absorption band of Gaussian shape with maximum at 461 nm, the most intense maximum of the diene 3 was at 537 nm with fine structure at shorter wavelengths, and the monoene 2 gave a composite spectrum. This remarkable effect was originally

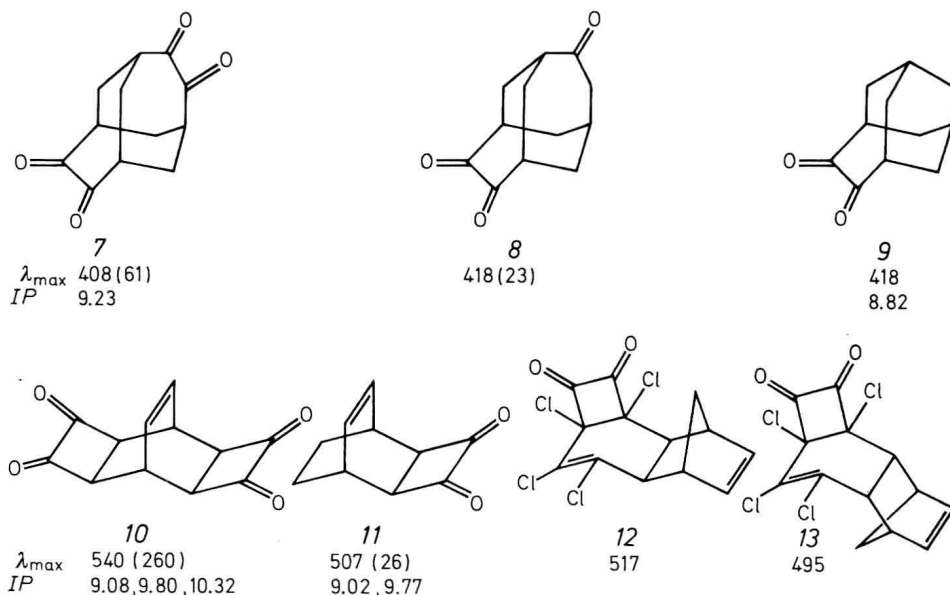


attributed <sup>17)</sup> to through-space interaction of the  $\pi$ -electrons with the dione moiety and subsequently <sup>18)</sup> to through-bond interaction. The present view <sup>19,20)</sup>, based on low-temperature absorption, PE, and fluorescence spectra and on calculation, is simply that the shift in absorption in going from *1* to *3* reflects conformational factors, specifically increasing rigidity of the system with introduction of double bonds. The questions posed by the spectra of *1*, *2*, and *3* prompted synthesis of the diketones *4-6* (and a cyclopropane analogue) in which conformational flexibility is not a problem <sup>19)</sup>. As can be seen below, the presence of unsaturation results in a small hypsochromic shift of the absorption maximum while PE spectra were similar. Calculated values for  $\lambda_{\text{max}}$  in this series were in good agreement with observed values. Quite good agreement between observed and calculated absorption has also been obtained with a number of bicyclic diketones <sup>21)</sup>. Additional examples <sup>22)</sup> pertinent to



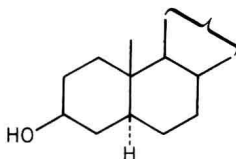
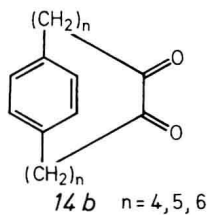
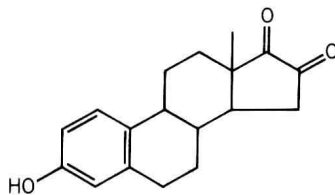
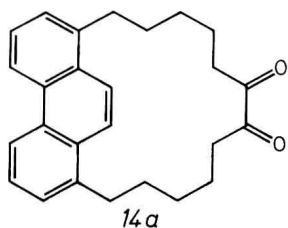
the question of long-range interactions are the bis- $\alpha$ -diketones *7* and *10*. Comparison of *7*, where the two diketo-chromophores are approximately orthogonal, with *8* and *9* possessing a single diketone function, shows little difference in absorption spectra but a considerable one in ionization potentials. On the other hand, the biscyclobutanedione *10*, with the two chromophores approximately parallel, shows opposite behaviour when compared to *11*. The geometry of *10* is considered to be particularly favorable for through-bond interactions. In general, absorption maxima of cyclobutanediones exhibit large variation as a result of relatively minor structural change as can be seen from the examples cited. Another illustration is the pair of stereoisomers *12* and *13* shown below, both of which appear to possess very rigid

structures<sup>23</sup>). While cyclobutanedione itself has been shown to have a planar structure in the gas phase<sup>24,25</sup>), the small deviations from planarity possible as a result of substituent effects do not seem sufficient to account for the considerable variation in absorption spectra in solution.

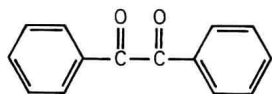


$\alpha$ -Diketones exhibit weak fluorescence and strong phosphorescence. In addition to their usefulness in characterizing excited states, these properties have frequently been exploited, particularly using biacetyl, as mechanistic probes in many types of photoreactions using the diketone either as a sensitizer or as a quencher<sup>1,2</sup>). An interesting application is the macrocyclic compound *14a* incorporating separated phenanthrene and diketone chromophores<sup>26a</sup>). Excitation of the aromatic moiety resulted in dual fluorescence (and phosphorescence) arising from partial energy transfer. The rate of singlet energy transfer was relatively slow when excitation was in the O—O band of the phenanthrene moiety and much faster upon shorter wavelength excitation. The direction of energy transfer could be reversed by two-photon excitation. This work has been extended<sup>26b</sup>) to series of analogous compounds such as *14b* where the efficiency of singlet energy transfer from the aromatic moiety to the dione depended markedly on the length of the polymethylene chains separating the chromophores. A successful theoretical treatment of this Dexter type of energy transfer has been achieved<sup>26c</sup>). Comparison of the solvent-dependence of emission spectra of the two steroidal diketones shown has been interpreted in terms of a long range interaction between ring A and the dione chromophore<sup>27</sup>).

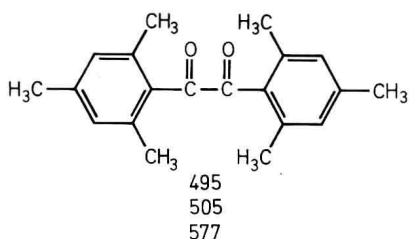
Conformational factors can play an important role in emission properties. The earlier view that, no matter what their ground state conformations, excited  $\alpha$ -diketones assume a coplanar (s-trans if possible) conformation is generally accepted<sup>6,8,9,28-34</sup>). This is based in part on observations that diketones having skewed ground states show marked lack of mirror image symmetry between absorption and fluorescence



spectra with large differences in energy between O—O states but fairly constant differences between fluorescence and phosphorescence transition energies. The comparison between benzil, whose ground state consists of two nearly planar benzoyl groups in an approximately orthogonal relationship, and mesitil<sup>29)</sup>, which consists of an s-trans coplanar dicarbonyl system with orthogonal aromatic rings, is an instructive one. Benzil has a broad absorption band with a maximum at 370 nm and a



$\lambda_{\max}$	370
$\lambda_{fl}$	505
$\lambda_{phos}$	562



separation of about  $5500\text{ cm}^{-1}$  between absorption and fluorescence while mesitil has a structured absorption spectrum with maximum at 495 nm and a separation of  $400\text{ cm}^{-1}$  between O—O bands of absorption and fluorescence. Both compounds have similar separation ( $\sim 2300\text{ cm}^{-1}$ ) between fluorescence and phosphorescence maxima. This has been interpreted in the following way<sup>30)</sup>. Excitation of skewed ground-state benzil results in formation of skewed singlet which then relaxes to the lower energy singlet having an s-trans planar dione system. This may require rotation of phenyl groups out of the plane of the dione. The relaxed singlet may emit or undergo intersystem crossing to a triplet of the same conformation which is again the most stable one for that state. It has been pointed out<sup>30)</sup> that the energy required to promote stable, skewed benzil to its (higher energy) skewed triplet state will be higher than that released by transformation of the relaxed planar (lower energy) triplet to planar (higher energy) ground state benzil. In other words, ground state benzil acting as a triplet quencher will have a higher apparent triplet energy than triplet benzil acting as a sensitizer.



Differences in low temperature emission spectra of benzil in methylcyclohexane and in isopentane have been ascribed to inhibition of the conformational changes involved in the skewed to planar relaxation in isopentane <sup>33)</sup>. Emission spectra were identical in both solvents at temperatures above the glass-forming temperature. Preference for an *s-cis* conformation in ethylene glycol solution has been suggested <sup>33b)</sup> to account for anomalous emission spectra of benzil in that medium. Other aspects of benzil emission have been examined <sup>33c)</sup>.

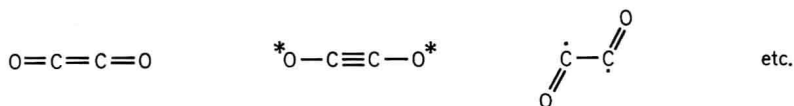
In the Leonard series of four- to eight-membered tetramethyl-cycloalkane diones mentioned earlier in connection with the angular dependence of  $\lambda_{\max}$ , the four-membered compound gave no emission, five- and six-membered showed only fluorescence, and the two larger ring members exhibited both fluorescence and phosphorescence <sup>9)</sup>. The separation between absorption and fluorescence varied as expected from the assumption of planar emitting and non-planar absorbing species.

We note that cyclobutanediones and unsaturated diketones which form the major part of this review show only fluorescence, often with very low yield.

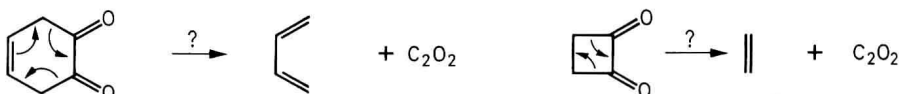
Circular dichroism provides an additional spectroscopic tool for characterization of excited states <sup>35)</sup>. Considerable interest has also been extended to esr-spectra of anion radicals of  $\alpha$ -diketones <sup>36)</sup>. Circular polarization of the phosphorescence of camphorquinone has been determined <sup>151)</sup>. Biacetyl has been the subject of a CIDNP study <sup>152)</sup>, of fluorescence quenching by a variety of substrates <sup>153)</sup>, and of steric effects in quenching of triplet states of alkylbenzenes <sup>154)</sup>.

### III Ethylenedione

Ethylenedione, the dimer of carbon monoxide, has attracted chemists' interest since at least 1913 when its synthesis by dechlorination of oxalyl chloride was unsuccessfully attempted <sup>37)</sup>. This substance, which lies between carbon dioxide and carbon suboxide in the series of oxycumulenes, is the simplest possible unsaturated diketone. It can be represented by a number of canonical structures as shown below:



Interest in the possibility of detecting  $\text{C}_2\text{O}_2$  received special impetus as a result of the photobisdecarbonylation reactions of bridged cyclohexenediones and of cyclobutanediones to be discussed later. Concerted cycloelimination to give ethylenedione and olefin was envisaged as a reaction pathway. Observation of a fragment corresponding to  $\text{C}_2\text{O}_2^{+}$  in mass spectra of such diketones was taken as an indication that similar fragmentation might occur from electronically excited states. As a result, a considerable

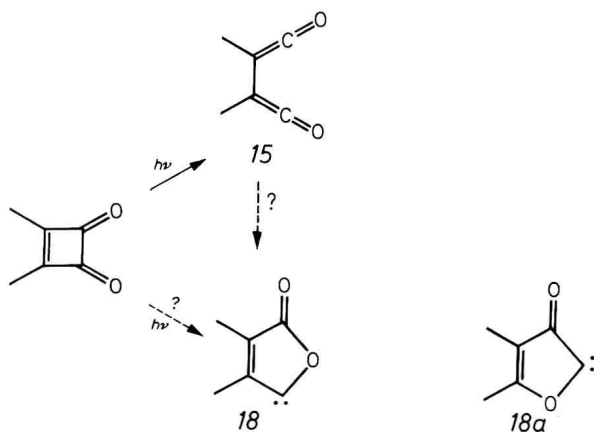


number of papers have appeared <sup>38)</sup> presenting results of calculations of the structure and properties of  $C_2O_2$ . In the first detailed theoretical paper <sup>38a)</sup> it was concluded that "ethylenedione is kinetically (singlet) and thermodynamically (singlet and triplet) unstable with respect to two molecules of carbon monoxide". The latest treatment <sup>38b)</sup> concludes that, because of spin restrictions, the triplet ground state is a minimum on the potential energy hypersurface and that metastable  $C_2O_2$  "should be detectable in a carefully designed experiment". The analogous ethylenedithione ( $C_2S_2$ ) was predicted to be of significantly greater stability.

On the experimental side,  $C_2O_2$  has never been observed by physical methods nor has it been possible to trap it (e.g. by reaction with dienes or with chlorine <sup>39)</sup>). Its existence remains an interesting question.

## IV Cyclobutenediones

In view of the destabilization resulting from incorporation of four trigonal carbon atoms in a four-membered ring and the juxtaposition of dipolar carbonyl groups in an *s-cis* arrangement, it is not surprising that all of the known photochemistry of 1,2-cyclobutenediones involves unimolecular reactions with ring cleavage or ring enlargement. The major primary process is ring opening to bis-ketenes (15). Formation of 15 is supported by observation of ketene bands in the infrared upon photolysis of dimethyl- <sup>40)</sup> (16a) and diphenylcyclobutenedione <sup>40, 41)</sup> (16b) (and a monoimine derivative <sup>41)</sup>) at 77 K. Intermediacy of 15 had been proposed earlier on the basis of isolation of the derived succinic diester from irradiation of phenylcyclobutenedione



in alcohol solution and of a Diels-Alder adduct when benzocyclobutenedione (17) was irradiated in the presence of dienophile. A number of additional examples of isolation of substituted succinic esters from photolyses in the presence of alcohols are summarized below, as well as an intramolecular case <sup>42)</sup>.

Additional examples of trapping of the bis-ketene from benzocyclobutenedione (in low yield) by Diels-Alder reactions have also been reported <sup>44)</sup>.

In addition to products derived from bis-ketenes, reactions of 17 <sup>45)</sup> and of diethyl