

Table I. Bond Distances (Å) and Angles (deg)

Bond	Std dev, Å	Angle	Std dev, deg
Fe-Fe	0.006	As-Fe-As	0, 2
Fe-As	0.005	Other \angle s at Fe	1.0-1.3
Fe-C	0.03	\angle s at As	1.0-1.3
As-C	0.03	\angle s at C	2-3
C-O	0.04		
C-C	0.04		
C-F	0.03		

Bond	Distance, Å	Bond	Distance, Å
Fe(1)-Fe(2)	2.89	Fe(2)...C(9)	2.09
Fe(1)-As(3)	2.47	Fe(2)...C(10)	1.99
Fe(1)-As(4)	2.35	C(9)	
Fe(2)...As(3)	3.09	Fe(2)...	1.90
Fe(2)...As(4)	3.05	C(10)	
Fe(1)-C(17)	1.74	C(17)-O(18)	1.21
Fe(1)-C(19)	1.75	C(19)-O(20)	1.16
Fe(1)-C(21)	1.78	C(21)-O(22)	1.25
Fe(2)-C(23)	1.71	C(23)-O(24)	1.21
Fe(2)-C(25)	1.68	C(25)-O(26)	1.27
Fe(2)-C(27)	1.79	C(27)-O(28)	1.25
Mean Fe-C	1.74	Mean C=O	1.23
As(3)-Me(5)	1.95	As(3)-C(9)	1.91
As(3)-Me(6)	1.93	As(4)-C(10)	1.91
As(4)-Me(7)	2.01		
As(4)-Me(8)	1.89	C(9)=C(10)	1.51
Mean As-Me	1.95		
C(9)-C(12)	1.52	C(11)-F(13)	1.37
C(10)-C(11)	1.57	C(11)-F(14)	1.38
C(11)-C(12)	1.53	C(12)-F(15)	1.41
Mean C-C	1.54	C(12)-F(16)	1.31
		Mean C-F	1.37

Angle	Deg	Angle	Deg
At Fe(1)		At Fe(2)	
C(17)-Fe(1)-As(3)	96	Fe(1)-Fe(2)-C(9)	80
C(17)-Fe(1)-As(4)	98	Fe(1)-Fe(2)-C(10)	78
C(17)-Fe(1)-C(19)	98	Fe(1)-Fe(2)-mid-pt ^a	78
C(17)-Fe(1)-C(21)	96	Fe(1)-Fe(2)-C(25)	92
Fe(2)-Fe(1)-As(3)	70	Fe(1)-Fe(2)-C(27)	89
Fe(2)-Fe(1)-As(4)	70	C(23)-Fe(2)-C(9)	97
Fe(2)-Fe(1)-C(19)	93	C(23)-Fe(2)-C(10)	99
Fe(2)-Fe(1)-C(21)	97	C(23)-Fe(2)-mid-pt ^a	99
As(3)-Fe(1)-As(4)	86	C(23)-Fe(2)-C(25)	91
As(3)-Fe(1)-C(19)	90	C(23)-Fe(2)-C(27)	93
As(4)-Fe(1)-C(21)	88	C(25)-Fe(2)-C(27)	103
C(19)-Fe(1)-C(21)	93	C(25)-Fe(2)-mid-pt ^a	127
C(17)-Fe(1)-Fe(2)	162	C(27)-Fe(2)-mid-pt ^a	128
As(3)-Fe(1)-C(21)	167	C(25)-Fe(2)-C(9)	106
As(4)-Fe(1)-C(19)	164	C(25)-Fe(2)-C(10)	149
		C(27)-Fe(2)-C(9)	149
		C(27)-Fe(2)-C(10)	106
		C(9)-Fe(2)-C(10)	43
At As			
Fe(1)-As-Me	119, 119, 119, 120		
Fe(1)-As-C(9,10)	94, 8, 94, 2		
Me-As-Me	102, 101		
Me-As-C(9,10)	112, 110, 111, 111		
Fe-C-O	168, 174, 177, 178, 178, 179		
As(3)-C(9)-C(10)	116		
As(4)-C(9)-C(12)	120		
As(3)-C(9)-C(12)	136		
As(4)-C(10)-C(11)	136		
In cyclobutene ring	96, 85, 93, 86		
F-C-F	103, 104		

Displacement of Fe atoms

Fe(1) from plane As(3), As(4), C(19), C(21), O(20), O(22),
0.3 Å away from Fe(2)

Fe(2) from plane C(9), C(10), C(25), C(27), O(26), O(28),
0.2 Å away from Fe(1)

^a Mid-pt = center of C(9)-C(10) bond.

Fe-Fe bonds³⁻⁵ but is still short enough to indicate bonding, especially when viewed in conjunction with the over-all structure of the molecule. The bonding is most simply described in valence bond terms, the Fe-Fe bond involving overlap of an electron pair in a d^2sp^3 orbital of the octahedral iron atom with a dsp^3 orbital of the five-coordinate iron; each iron atom thus attains the krypton configuration. A description could also be given in terms of bonding between the second iron atom and a delocalized system in the five-membered ring of first iron, arsenic, and carbon atoms; however, the general arrangements around both iron atoms suggest that the valence bond description is more appropriate.

The compound probably arises from the addition of an $Fe(CO)_3$ fragment to the $LFFe(CO)_3$ molecule.

(3) L. F. Dahl and J. F. Blount, *Inorg. Chem.*, **4**, 1373 (1965).

(4) C.-H. Wei and L. F. Dahl, *J. Am. Chem. Soc.*, **88**, 1821 (1966).

(5) A. A. Hock and O. S. Mills, *Acta Cryst.*, **14**, 139 (1961).

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On the Photodimerization of Cyclopentenone

Sir:

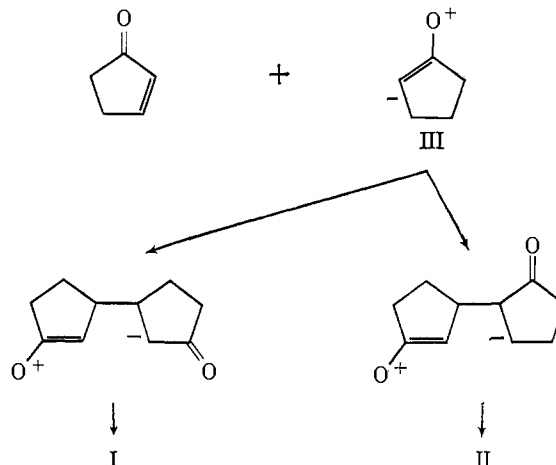
Eaton¹ has shown that on irradiation with wavelengths above 3000 Å cyclopentenone, neat or in "a variety of solvents," produces the two dimer forms I and II in high yield and in approximately equal amounts.



(1) P. E. Eaton, *J. Am. Chem. Soc.*, **84**, 2344 (1962).

(2) J. Calvert and J. Pitts, Jr., "Photochemistry," John Wiley and Sons, Inc., New York, N. Y., 1965, p 407.

(3) To summarize earlier work Eaton⁴ stated that although the initial excitation is presumably to the singlet state ($n-\pi^*$) at 3080 Å for neat solution, the charge distribution of the excited molecule taking part in the reaction is not known. However, taking the polarized form III as an adequate representation,⁵ Eaton argued that if the dimerization takes place via a two-step mechanism, the reaction may be pictured as follows:



Eaton then reasoned that this mechanism would result in a favoring of I due to the interaction of the adjacent carbonyl with the negative charge in the intermediate.

(4) P. E. Eaton, *J. Am. Chem. Soc.*, **84**, 2454 (1962).

(5) Eaton³ cites H. E. Zimmerman and D. I. Schuster, *ibid.*, **83**, 4486 (1961).

Table I

Cyclopentanone concn, <i>M</i> Solvent ^a	Neat	6.2				1.2				0.12			
		A	B	C	D	A	B	C	D	A	B	C	D
Dimer II/dimer I	1.1	2.0	1.6	1.4	1.9	4.3	2.2	1.7	1.9	6.4	2.1	4.3	1.9

^a A = cyclohexane, B = propanol, C = ethanol, D = methanol.

The quantum yield for photodecomposition of cyclopentenone is very small.^{2,3}

We shall now address our attention to the nature and multiplicity of the excited state. Turro⁶ suggests the possibility that *two* excited states, singlet and triplet, participate in the reaction. Thus the ratio of I to II might be expected to prove a function of the cyclopentenone concentration as singlet dimerization would become less competitive with triplet dimerization as the concentration decreased.

We have studied the ratio dimer II/dimer I as a function of concentration in cyclohexane, 2-propanol, ethanol, and methanol as solvents. The samples were irradiated for 3 hr at 3130 Å by a 450-w Hanovia mercury arc lamp. The reaction mixtures were analyzed by vpc, using a Carbowax 20M column (Table I).

That one of the dimers should be favored strongly suggests (but does not prove) a nonconcerted mechanism of some sort, though apparently not the one shown above.³ Furthermore, the concentration dependence of this effect in cyclohexane provides support to Turro's suggestion that both triplet and singlet states may be involved in the reaction. The apparent inertness of cyclohexane makes the results in that solvent the most relevant to this question. In the alcohols, dimer yield was markedly reduced as compared with cyclohexane solutions, and side reactions (including, perhaps, the triplet photoreduction of the enone) were decidedly enhanced.

Next, reactions identical with those in cyclohexane were carried out, except the solutions were made 0.1 *M* in the triplet quencher *cis*-piperylene (Table II). Absorption of 3130-Å light by the quencher was negligible.

Table II

Cyclopentenone concn, <i>M</i>	Neat	6.2	1.2	0.12
Factor of dimer yield suppressed	1.34	1.45	3.34	7.9

This provides excellent evidence that some and possibly all the dimerization is accounted for by a triplet-state intermediate.

Energy-transfer attempts were carried out using a variety of sensitizers. Cyclohexane solutions, 0.12 *M* in cyclopentenone and 0.1 *M* in sensitizer, were irradiated for 3 hr at 3130 Å. The dimer yield was then compared to that obtained without sensitizer (Table III). It would appear that the table establishes a minimum value on the triplet state of the enone.

Our efforts to establish the triplet sensitization of the photodimerization of cyclopentenone leave us less than fully satisfied that the reaction proceeds *via* a triplet-state mechanism, although Eaton's very recent demonstration of the piperylene quenching of the reaction with high concentrations of piperylene⁷

(6) N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, Inc., New York, N. Y., 1965, pp 203-204.

(7) P. E. Eaton, private communication.

Table III

Sensitizer	<i>E</i> ₁ , kcal/mole	% adsorption due to sensitizer	Effect on dimer yield
Acetophenone	73.6	52	None ^a
Benzophenone	69	80	Uncertain ^b
Naphthalene	61	<30	85% reduction
Nitrobenzene	60	>95	>95% reduction
2-Acetonaphthone	59	100	>90% reduction

^a That the quantum yield for dimerization is considerably less than unity was demonstrated by the fact that acetophenone drastically increased the yield of an unidentified by-product without affecting the yield of dimer. ^b Benzophenone appeared on the vpc at the same point as dimer II; however, dimer I was reduced by about 65%.

is most impressive. Our failure to demonstrate actual increase in dimer yield by sensitization (even though all "sensitization" experiments are somewhat ambiguous) is difficult to reconcile with a wholly triplet mechanism, provided the quantum yield for dimerization is substantially less than unity, as it almost certainly is.

In addition, *the very sensitive stereospecific dependence upon concentration (see Table I) suggests that more than one intermediate is involved in the dimerization; i.e., that the singlet state may be important at high concentrations of cyclopentenone.*

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The Lifetime of Triplet Acetone in Solution¹

Sir:

In 1958 Yang reported that irradiation of acetone in cyclohexane yields 50% isopropyl alcohol plus other reduction products.² Walling and Gibian have since shown that ketones are photoreduced in a variety of hydrocarbon as well as alcoholic solvents.³ Very recently Borkman and Kearns described the acetone-photosensitized isomerization of the 2-pentenes in solution.⁴ In interpreting their data, these authors concluded that triplet acetone has an unusually short intrinsic lifetime in solution, and that in neat acetone as solvent, triplet energy transfer may be faster than dif-

(1) Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. Research Corporation and NSF grants are also gratefully acknowledged.

(2) N. C. Yang and D.-H. Yang, *J. Am. Chem. Soc.*, **80**, 2913 (1958).

(3) C. Walling and M. J. Gibian, *ibid.*, **87**, 3361 (1965).

(4) R. F. Borkman and D. R. Kearns, *ibid.*, **88**, 3467 (1966).