radical is strongly suggested by the observation that in the presence of added iodide ion the iodine atom transient is again observed. No halogen atom transient appears when added bromide ion is present, however; this is consistent with our earlier report that iodide but not bromide inhibited nitrogen gas production in the photolysis of this complex.[2]

Less expected were the results for aqueous $PtBr_6^{-2}$ and PtI_6^{-2}. Again, concentrations of 10^{-4} M were used; all solutions were air saturated unless otherwise noted. Previous work in this laboratory showed that a chain mechanism acted to provide very high quantum yields for the photoexchange of bromide ion with $PtBr_6^{-2}$, and a mechanism was suggested for which the initial step was

$$PtBr_6^{-2} \longrightarrow PtBr_5^{-2} + Br \qquad (1)$$

analogous to the one proposed for the chloride system.[6] The complete mechanism accounted for the small amount of net decomposition observed, the square root dependence of the exchange quantum yield on light intensity, and its dependence on bromide ion concentration.

Our flash photolytic results for $PtBr_6^{-2}$ are as follows: (a) extensive decomposition occurs in either a quartz or a Pyrex cell to give what may be a hydrated form of $PtBr_6^{-2}$ (this is partially repressed by added bromide ion); (b) no indication of any bromine atom transient was present; (c) no free electrons were observed in the degassed system even though we do detect such with dilute ferrocyanide[7]; (d) if 10^{-4} M hydroquinone at pH 5 (itself not affected by flashing) was also present, a new permanent absorption at 244 mμ resulted; however, addition of the hydroquinone immediately after flashing gave no effect; (e) PtI_6^{-2} plus iodide solutions showed a long-lived transient with a half-life of about 0.1 sec. absorbing at 410 mμ.

Observation d indicates that a short-lived oxidizing species is present and therefore that the primary photochemical act is in nature oxidation–reduction. Observation b rules out reaction 1 and c, the possibility of free electron production, so that the primary reaction apparently must be

$$PtBr_6^{-2} \longrightarrow [PtBr_4^{-2}] + Br_2 \qquad (2)$$
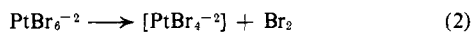
Reaction 2 is a two-electron oxidation–reduction step which although new is not implausible. From the structure of H_2PtBr_6,[8] the Br–Br distance is 3.41 Å., or less than the van der Waals distance of 3.90 Å.[9] We are thus supposing that the concerted departure of two bromine atoms with conmitant development of a Br–Br bond is easier than for process 1 to occur.

It also appears that the $[PtBr_4^{-2}]$ formed has a geometry which allows it to react rapidly with bromine to form $PtBr_6^{-2}$. The planar form will not do this either in the presence or the absence of added bromide ion. A likely configuration is a trigonal pyramid, or, in the presence of bromide, a trigonal bipyramid; these must live long enough to serve as chain carriers in

the exchange of bromide ion with $PtBr_6^{-2}$ and to react with some bromine derivative (Br_3^- or BrOH) to give the net reaction noted under a above. Conformational isomers in tetracoordinated systems are, of course, known, but it seems generally assumed that their interconversion is rapid.[10] In fact, the 0.1-sec. half-time species observed with PtI_6^{-2} may be the analog of our $[PtBr_4^{-2}]$ isomer. We are in the process of obtaining more complete data so as to be able to decide on this interesting possibility.

(10) R. H. Holm, A. Chakravorty, and G. O, Dudek, *J. Am. Chem. Soc.*, **86**, 379 (1964).

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The Radical Fragmentation Route on Photolysis of 2,5-Cyclohexadienones. 4-Methyl-4-trichloromethyl-2,5-cyclohexadienone[1,2]

Sir:

Considerable attention has been given recently to the mechanisms of phototransformations of unsaturated ketones in solution, particularly of 2,5-cyclohexadienones.[3] In almost all the reactions studied[3] the product-determining intermediates are best understood as being ionic in character, and Chapman[3c] has proposed that consideration of "polar state intermediates" II derived from dienones I allows for rationalization of the structures of the various products of these reactions.

Chart I
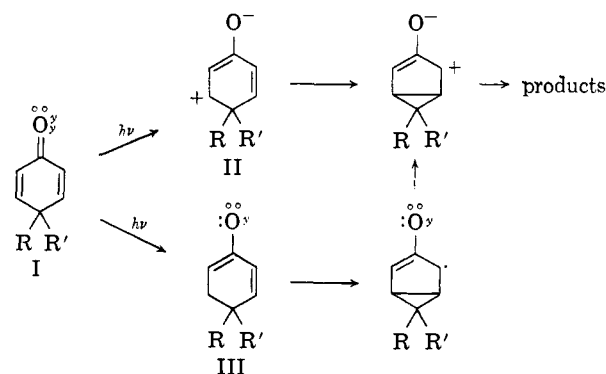
The mode of formation of the "polar state" II has not been explicitly outlined, although it has been suggested[4] that II may be an adequate representation of the excited state. Zimmerman has proposed[3a,b,d] an

(1) Part V. Photochemistry of Unsaturated Ketones. Part IV: D. I. Schuster, F.-T. Lee, A. Padwa, and P. G. Gassman, *J. Org. Chem.*, in press.
(2) Supported in part by Grant No. DA-ARO(D)-31-124-G425 from the Army Research Office (Durham).
(3) For reviews of recent studies, see (a) H. E. Zimmerman and D. I. Schuster, *J. Am. Chem. Soc.*, **84**, 4527 (1962); (b) H. E. Zimmerman, *Advan. Photochem.*, 1, 183 (1963); (c) O. L. Chapman, *ibid.*, 1, 323 (1963); (d) H. E. Zimmerman, *Tetrahedron Suppl.*, 2, 393 (1963); (e) P. J. Kropp, *J. Am. Chem, Soc.*, **86**, 4053 (1964).
(4) M. H. Fisch and J. H. Richards, *J. Am. Chem. Soc.*, **85**, 3029 (1963).

(6) R. L. Rich and H. Taube, *J. Am. Chem. Soc.*, **76**, 2608 (1954).
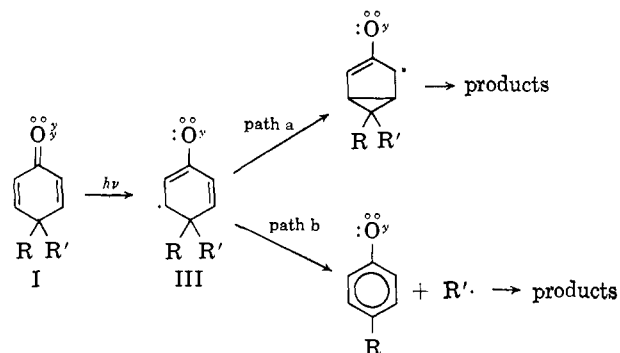(7) M. S. Matheson, W. A. Mylac, and J. Rabani, *J. Phys. Chem.*, **67**, 2613 (1963).
(8) P. A. Vaughan, J. H. Sturdivant, and L. Pauling, *J. Am. Chem. Soc.*, **72**, 5477 (1950).
(9) L. Pauling, "The Nature of the Chemical Bond," 3rd Ed., Cornell University Press, Ithaca, N. Y., 1960, p. 260.
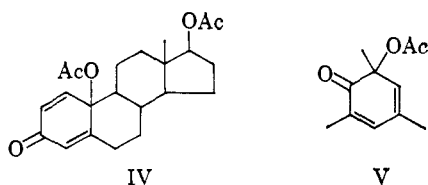
Chart II

elaborate scheme which accounts for the formation of ionic intermediates (and hence the products of these reactions) by considering the fate of initial excited state diradicals. These two schemes are outlined in Chart I. There has been no direct evidence, however, for radical precursors to the ionic product-determining intermediates.[5]

We wish to present evidence that diradical intermediates (presumably in the excited state) do in fact precede the ionic intermediates, since in the case of appropriate substituted dienones an alternate radical reaction path competes effectively with the ionic reactions. The general scheme is outlined in Chart II. It is suggested that the excited state, represented as III, can react by one of two routes: (a) 3,5-bond formation, followed by electron demotion to give product-determining ionic intermediates, and (b) expulsion of one of the 4-substituents as a radical, with concomitant formation of a *para*-substituted phenoxy radical. We are suggesting that path b is an activated process, and would only be observed in cases where the resulting radical, R′·, is minimally stabilized electronically. It is not surprising that path b has not been observed in the photochemistry of dienones in which R and R′ are phenyl or primary and secondary alkyl, which comprise the great bulk of studied systems.[3]

Some reactions have been reported, however, which can now be satisfactorily interpreted in terms of the radical fragmentation path (b). Thus, the steroid derivative 1V[6] and the conjugated dienone V[7] give the corresponding phenols on photolysis by loss of acetoxy (presumably as a radical). A case (VI) in which paths a and b seem to be neatly balanced and in which products from both sequences are observed has been reported by Matsuura.[8] A case of fragmentation by carbon–carbon cleavage was recently reported by Schuster and Polowczyk[9] on photolysis of the spiro-

IV   V

dienone VII. However, the interpretation in this case is complicated because of the conjugative properties and strain of the cyclopropane ring.

An investigation into the photochemistry of 4-methyl-4-trichloromethyl-2,5-cyclohexadienone (VIII)[10] was undertaken to verify the fragmentation route suggested above and to establish a case for C–C homolytic fragmentation without the objections inherent in spirodienone VII.[9] Irradiation[11] of dienone VIII using a Pyrex filter in ethereal or hydrocarbon solvents gave *p*-cresol as a major product (40–80% yield[12]). The photolysis was followed by ultraviolet spectroscopy and was essentially complete in 30–60 min. The products were analyzed by infrared and nuclear magnetic resonance spectroscopy and gas–liquid chromatography. *p*-Cresol was isolated and its properties were identical with those of an authentic sample. In ethereal solvents, chloroform was identified as a product by n.m.r. and g.l.c.; no hexachloroethane could be detected. In hydrocarbon solvents, however, hexachloroethane was also formed. The thermal stability of dienone VIII is indicated by its recovery after reflux in Diethyl Carbitol (b.p. 188°) for 3 hr.; no *p*-cresol was detected. Irradiation (Pyrex filter) of dienone VIII in piperylene for 4 hr. gave only a trace of *p*-cresol, the dienone being recovered in high

VIII
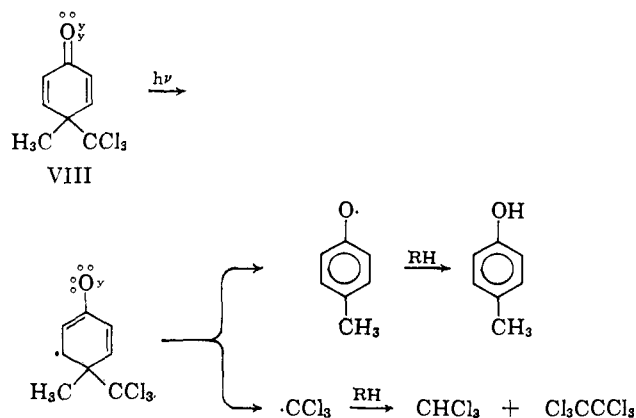
yield. This observation of quenching indicates that the reaction proceeds through a triplet excited state.[13,14]
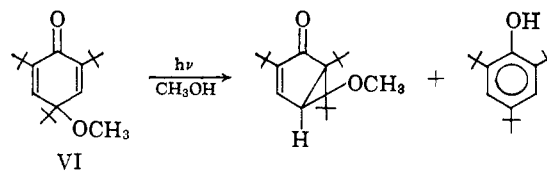
(5) For recent work which has been interpreted as evidence for such a distinction, see H. E. Zimmerman, R. C. Hahn, H. Morrison, and M. C. Wani, *J. Am. Chem. Soc.*, **87**, 1138 (1965).

(6) R. Warszawski, K. Schaffner, and O. Jeger, *Helv. Chim. Acta*, **43**, 500 (1960).
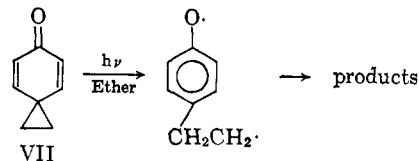
(7) D. H. R. Barton and G. Quinkert, *J. Chem. Soc.*, 1 (1960).

(8) T. Matsuura, *Bull. Chem. Soc. Japan*, **37**, 564 (1964).

(9) D. I. Schuster and C. J. Polowczyk, *J. Am. Chem. Soc.*, **86**, 4502 (1964).

(10) For synthesis, see M. S. Newman and A. G. Pinkus, *J. Org. Chem.*, **19**, 978 (1954). We are indebted to Professor D. J. Hennessy of Fordham University for suggesting this compound to us.

(11) High-pressure mercury arc (450-w.) in a conventional Hanovia immersion apparatus.

(12) Determined by ultraviolet spectroscopy; confirmed by g.l.c. using an internal standard.

(13) G. S. Hammond, J. Saltiel, A. A. Lamola, N. J. Turro, J. S. Bradshaw, D. O. Cowan, R. C. Counsell, V. Vogt, and C. Dalton, *J. Am. Chem. Soc.*, **86**, 3197 (1964).

(14) A decision between $^3(n,\pi^*)$ and $^3(\pi,\pi^*)$ excited states must await the results of further experiments.

It is clear that the "polar state" rule gives incorrect results in whole or in part when applied to dienones IV–VIII. We therefore doubt that the rule has theoretical significance; it would be useful only in those cases where structural features exclude path b (Chart II). Moreover, these results also cast doubt on suggestions that the excited state produced on photolysis of cross-conjugated cyclohexadienones is adequately represented by dipolar structures such as II. Ionic intermediates are most consistently regarded as arising from further transformations of the excited state.

We are now investigating the scope and mechanistic details of the photochemical fragmentation reactions of a variety of substituted cyclohexadienones.

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Diene Complexes from the Reaction of Activated Vinylcyclopropanes with Iron Pentacarbonyl

Sir:

In this communication we show that vinylcyclopropanes bearing para-substituted phenyl groups (Ia–Ic)[1,2] can enter into reaction with iron pentacarbonyl to yield π-complexes of the structure of 2-aryl-1,3-trans-pentadieneiron tricarbonyl (IIa–IIc). A mixture of equimolar quantities of iron pentacarbonyl and α-cyclo-

of IIa in 61% yield. Similar reactions of Ib and Ic with iron pentacarbonyl furnished the respective products IIb (57% yield) and IIc (55% yield). The properties and analysis of products are summarized in Table I.

The structural assignments follow from: (i) analysis, (ii) solubility in nonpolar solvents (petroleum ether), (iii) infrared spectrum, and (iv) n.m.r. spectrum[3] (Table II). An examination of the n.m.r. spectrum of IIa reveals that the transformation Ia → IIa is accompanied by a disappearance of the cyclopropane protons (H-1 and H-2 in Ia), leaving behind the anisyl group protons, at 3.78 and 7.20 p.p.m., essentially unchanged. Instead new signals appeared as a doublet at 1.49 p.p.m. (three protons) assigned to methyl group hydrogens linked to a diene metal complex (H-5),[4] a double quartet at 1.07 p.p.m. (single hydrogen) assigned to a terminal dienic proton endo to the metal (H-1),[5,6] and a broad doublet at 5.55 p.p.m. (single hydrogen) assigned to a central dienic proton (H-2).[6] The two vinylic hydrogens of the substrate (H-3 in Ia) are differentially shifted toward higher field on Ia → IIa conversion so that the proton exo to the metal (H-4 in IIa) now appears at 2.19 p.p.m., whereas the endo-oriented proton (H-3) appears at the highest field of the spectrum, at 0.35 p.p.m.[6]

A trans relationship between the vinylic hydrogens at the 3,4- double bond in IIa is inferred both from the chemical shift of H-1[7] and from the coupling constant, $J_{\text{H-1,H-2}} = 9$ c.p.s.[8] Final proof of structure follows

Table I

Product	M.p., °C	$\bar{\nu}$ (CO),[a] cm.$^{-1}$	Formula	Calcd., % C	H	Fe	Found, % C	H	Fe
IIa	70–71.7	1975,[b] 2051[c]	$C_{15}H_{14}O_4Fe$	57.3	4.4	17.8	57.3	4.4	17.6
IIb	Oil[d]	1996,[b] 2079[c,e]	$C_{14}H_{12}O_3Fe$	59.1	4.2	…	59.6	4.4	…
IIc	28.0	1998,[b] 2079[c]	$C_{14}H_{11}O_3ClFe$	52.7	3.4	…	51.7	3.3	…

[a] In KBr. [b] Broad. [c] Sharp. [d] Distilled at 10^{-5} mm. at room temperature. [e] In sandwich cell.

Table II

N.M.R. Spectrum of Free Ligand and Metal Complex

	Chemical Shift (p.p.m.)	Relative Intensity	Splitting	Chemical Shift (p.p.m.)	Relative Intensity	Splitting	Coupling constants
H(1)	0.69	6	multiplet centered 0.89 o.o.m	1.07	1	double quartet	$J_{H(1),H(2)}$ = 9 c.p.s.
H(2)	1.56	1	multiplet	5.55	1	b'ood doublet	
H(3)	4.92 / 5.25	1 / 1	singlet / singlet	0.35	1	doublet	$J_{H(3),H(4)}$ = 2.5 c.p.s.
H(4)	7.29	6	AB quartet centered 7.29 o.p.m.	2.19	1	double doublet	
H(5)	3.45	3	singlet	1.49	3	doublet	
H(6)				7.20	4	AB quartet centered 7.70 o.p.m.	
H(7)				3.78	3	singlet	

propyl-p-methoxystyrene (Ia)[2] in di-n-butyl ether was refluxed for 10 hr. in an atmosphere of pure nitrogen. The reaction mixture was filtered, the solvent was removed in vacuo, and the residue was chromatographed over alumina, using petroleum ether (b.p. 40–60°) as eluent. The first fraction eluted provided yellow plates

from an unambiguous synthesis of IIa and IIb involving predisposed geometry of the 3,4- double bond, following the path III[9a,b] → IV → V[10] → VI → II,[11] as outlined in Chart I.

The free ligands VI (not isolated), resulting from the thermal dehydration–decarboxylation of V, are highly unstable.[12] They presumably react with iron pentacarbonyl as soon as they are formed.

The alternative syntheses of IIa–IIb provide not only

(1) S. Sarel and E. Breuer, J. Am. Chem. Soc., 81, 6522 (1959).
(2) S. Sarel and E. Breuer, Israel J. Chem., 1, 451 (1963).

(3) The n.m.r. spectrum in CDCl₃ was obtained on a Varian A-60 spectrometer.
(4) Compare R. B. King, T. A. Manuel, and F. G. A. Stone, J. Inorg. Nucl. Chem., 16, 233 (1961).
(5) M. L. H. Green, L. Pratt, and G. Wilkinson, J. Chem. Soc., 3753 (1959).
(6) R. Pettit and G. F. Emerson, Advan. Organometal. Chem., 1, 12 (1964).
(7) Compare J. E. Mahler and R. Pettit, J. Am. Chem. Soc., 85, 3955 (1963).
(8) Compare E. Weiss, et al., Helv. Chim. Acta, 46, 288 (1963); see S. Sternhell, Rev. Pure Appl. Chem., 14, 15 (1964).
(9) (a) S. Dev, J. Indian Chem. Soc., 33, 703 (1956); (b) T. M. Patrick, Jr., J. Org. Chem., 17, 1269 (1952).
(10) R. Kuhn and M. Hoffer, Chem. Ber., 66, 1263 (1933).
(11) The physical properties and infrared and n.m.r. spectra of metal complexes obtained by this route proved to be identical with IIa and IIb.
(12) The reaction of IIIa with triphenylphosphinemethylene (Wittig reaction) leads to the formation of polymeric forms of VIa.