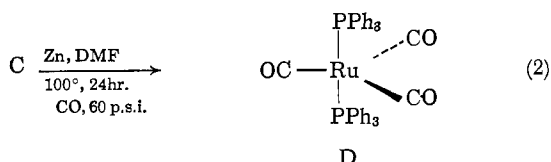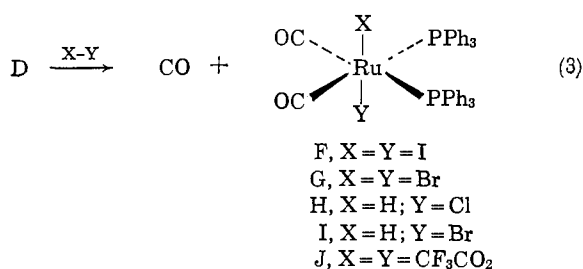configuration as the related dialkylphenylphosphine complexes described by Chatt, et al.[26] The stereochemistry of these complexes was elucidated by dipole moment and infrared measurements.

Treatment of C with zinc dust in hot DMF yielded intractable complexes of ruthenium(0) containing tightly bound DMF. This expected tendency of ruthenium(0) to attain the five-coordinate state[24] suggested reduction in the presence of CO. Such a process afforded pale yellow crystals of [Ru(CO)$_3$-(Ph$_3$P)$_2$] (D) in high yield (eq. 2). Anal. Calcd. for

$$C \xrightarrow[\substack{100°, 24hr. \\ CO, 60 \text{ p.s.i.}}]{Zn, DMF} \quad OC-Ru \overset{\overset{PPh_3}{|}}{\underset{PPh_3}{|}} \underset{CO}{\overset{CO}{<}} \quad (2)$$

D

$C_{39}H_{30}O_3P_2Ru$: C, 66.01; H, 4.26; P, 8.73; Ru, 14.24; mol. wt., 709.7. Found: C, 65.97; H, 4.15; P, 8.75; Ru, 14.45; mol. wt., 644 (Mechrolab osmometer, benzene). It is of interest that the over-all preparation of D requires CO pressures less than 100 p.s.i. obviating the need for high pressure CO equipment. The single carbonyl stretching frequency at 1895 cm.$^{-1}$ suggests the structure depicted with apical phosphines and equatorial CO ligands about a trigonal bipyramid. Cotton[27] reports that the iron(0) complex [Fe(CO)$_3$(Ph$_3$P)$_2$] exhibits a single CO stretch at 1887 cm.$^{-1}$. The related triphenylarsine complex [Ru(CO)$_3$(Ph$_3$As)$_2$] (E) having the same infrared spectrum as D was prepared in the same way. Anal. Calcd. for $C_{39}H_{30}O_3As_2Ru$: C, 58.72; H, 3.79. Found: C, 58.24; H, 4.08. The monomeric ruthenium(0) compounds D and E are soluble in common organic solvents and show no apparent tendency to trimerize.

As anticipated, D undergoes a series of oxidative additions with consequent loss of one CO ligand (eq. 3). Iodine reacts with D to form [RuI$_2$(CO)$_2$(Ph$_3$P)$_2$]

$$D \xrightarrow{X-Y} CO + OC \overset{\overset{X}{|}}{\underset{OC}{\cdot}} \underset{Y}{\overset{PPh_3}{Ru}} \overset{PPh_3}{\underset{}{}} \quad (3)$$

F, X = Y = I
G, X = Y = Br
H, X = H; Y = Cl
I, X = H; Y = Br
J, X = Y = CF$_3$CO$_2$

(F) having the same stereochemistry as C. Anal. Calcd. for $C_{38}H_{30}O_2I_2P_2Ru$: C, 48.79; H, 3.23. Found: C, 48.81; H, 3.51. Hydrogen chloride and hydrogen bromide also add to D to form the dihalides C and G, presumably by way of the intermediate hydrides H and I. Anal. Calcd. for $C_{38}H_{30}O_2Br_2P_2$-Ru (G): C, 54.24; H, 3.59. Found: C, 54.48; H, 4.08. In a similar manner trifluoroacetic acid combines with D to form the bistrifluoroacetate (J). Anal. Calcd. for $C_{42}H_{30}O_6F_6P_2Ru$: C, 55.56; H, 3.33. Found: C, 55.54; H, 3.77.

(26) J. Chatt, B. L. Shaw, and A. E. Field, J. Chem. Soc., 3466 (1964).
(27) F. A. Cotton and R. V. Parish, ibid., 1440 (1960).

Mercury halides and methyl iodide add to D affording mercury–ruthenium and carbon–ruthenium bonds. These and other reactions will be discussed subsequently. Currently we are extending this synthesis to osmium(0) analogs.

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Mechanism of Type II Photoelimination[1]

Sir:

Irradiation of aldehydes and ketones which bear hydrogen atoms attached to a γ-carbon atom often effects molecular cleavage to an alkene and the enol of a smaller carbonyl compound.[2,3] Frequently formation of cyclobutanols accompanies this photoelimination.[4,5] Both reactions may be visualized as arising from a common biradical intermediate.
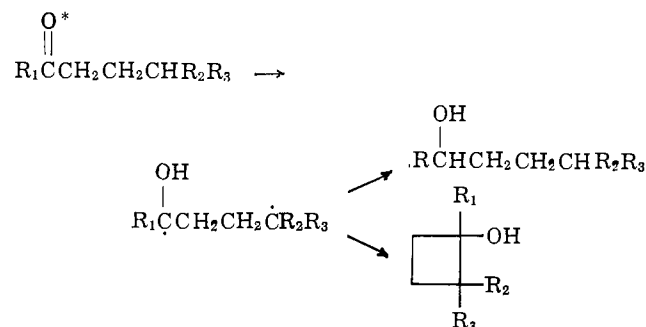
Identification of the excited state(s) responsible for this reaction is of considerable interest, but previous studies in the vapor phase have given seemingly equivocal results. Michael and Noyes[6] studied the effect of biacetyl on the photochemistry of both 2-pentanone and 2-hexanone. From the slight quenching observed, they concluded that excited singlets were primarily responsible for the photoelimination. Ausloos and Rebbert[7] also studied 2-pentanone and concluded that excited triplets were involved on the very reasonable grounds that addition of biacetyl quenches the type II reaction without affecting the weak fluorescence of pentanone.

We wish to report the results of study of the effect of piperylene (1,3-pentadiene) on the photoreactions of both ketones in solution. Piperylene was chosen as a quencher since it accepts only triplet energy from excited ketones, and that very efficiently.[8]

(1) Mechanisms of Photochemical Reactions in Solution. XXXV.
(2) R. Srinivasan, J. Am. Chem. Soc., 81, 5061 (1959).
(3) G. R. McMillan, J. G. Calvert, and J. N. Pitts, Jr., ibid., 86, 3602 (1964), and references cited therein.
(4) N. C. Yang and D. H. Yang, ibid., 80, 2913 (1958); Tetrahedron Letters, No. 4, 10 (1960).
(5) P. Ausloos and R. E. Rebbert, J. Am. Chem. Soc., 83, 4897 (1961).
(6) J. L. Michael and W. A. Noyes, Jr., ibid., 85, 1027 (1963).
(7) P. Ausloos and R. E. Rebbert, ibid., 86, 4512 (1964).
(8) G. S. Hammond, P. A. Leermakers, and N. J. Turro, ibid., 83, 2396 (1961).
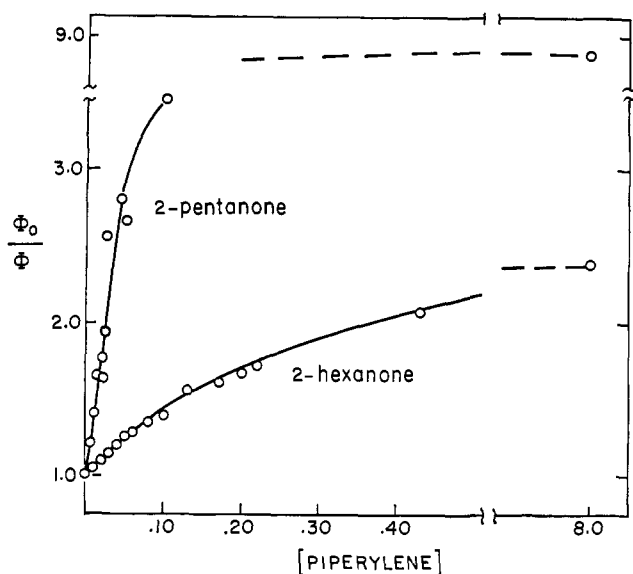
Figure 1. Ratio of quantum yield for disappearance of ketone with no quencher to quantum yield at given quencher concentration vs. quencher concentration.

Figure 1 shows plots of $(\Phi_{II})_0/\Phi_{II}$ against the concentration of piperylene for both ketones.[9] The simple Stern–Volmer relationship is obviously not followed in either case. Relatively low concentrations of piperylene do a good deal of quenching, but at higher concentrations the quantum yields for type II reaction level off to constant values. The most obvious interpretation of the results is that *the elimination reaction arises from both excited singlets and triplets.* If we take the quantum yields in 8 M piperylene as a measure of the amount of singlet reaction, the mechanism is dissected as shown in Table I.

Table I. Quantum Yields for Disappearance of Ketone and Appearance of Acetone[a]

| Ketone | —Ketone— | | | +Acetone— | | |
	Φ_0[b]	Φ_s[c]	Φ_t[d]	Φ_0[b]	Φ_s[c]	Φ_t[d]
2-Pentanone	0.44	0.05	0.39	0.30	0.04	0.26
2-Hexanone	0.50	0.21	0.29	0.44	0.18	0.26

[a] [Ketone]$_0$ = 0.20 M; cosolvent was n-hexane; irradiation at 3130 Å. [b] Quantum yield with no added piperylene. [c] Quantum yield in 8 M piperylene. [d] $\Phi_0 - \Phi_s = \Phi_t$.

The initial slopes of the curves in Figure 1 should be equal to k_q/k_r, where k_r is the sum of the rate constants for all of the reactions quenched by piperylene. The values are 5 and 40 l. mole^{-1} for 2-hexanone and 2-pentanone, respectively. Since the triplet excitation energy of either ketone should be much higher ($\sim$75 kcal./mole) than that of piperylene ($\sim$58 kcal./mole), we expect that energy transfer should be diffusion controlled in both cases. By analogy to many other cases in which rate constants have been measured by flash spectroscopy, this would place the values of k_q at about 5 $\times$ 10^9 l. mole^{-1} sec.$^{-1}$.[11] We therefore esti-

mate the values of k_r as 1 $\times$ 10^9 sec.$^{-1}$ for 2-hexanone and 1.2 $\times$ 10^8 sec.$^{-1}$ for 2-pentanone.

The results are very reasonable. The reactivity of excited singlets and triplets of unconjugated carbonyl compounds should be qualitatively similar since both states have the n,π* configuration.[12] The rates of the type II eliminations are faster with 2-hexanone than with 2-pentanone in both states if we assume that the intersystem crossing rates are similar. If the reaction involves abstraction of hydrogen to form a biradical, the relative reactivities would be expected to be sensitive to the substitution at the γ-carbon atom. Ausloos[13] has found that there is a 13:1 preference for attack on the secondary position in 4-methyl-2-hexanone. Walling and co-workers[14] have shown that hydrogen abstraction by alkoxy radicals is four–eight times as fast at secondary positions as at primary sites. They have also shown that the reactivity of benzophenone triplets toward various kinds of C–H bonds parallels the reactivity of alkoxy radicals very closely.[15]

It is difficult to imagine a result more genuinely compatible with all of the *apparently* conflicting earlier discussions (in which part of the discrepancy involves interpretation of results). Michael and Noyes[6] found the strongest evidence for a singlet mechanism with 2-hexanone which we find undergoes extensive elimination by that path even in solution where deactivation to the vibrationally relaxed singlet is very rapid. On the other hand, Ausloos and Rebbert[7] obtained seemingly unequivocal evidence for a triplet mechanism with 2-pentanone, which we find has only a small contribution from the singlet path in solution. It is not at all surprising that the singlet mechanism should be more important (in the vapor phase) at 2537 Å., where vibrational deactivation and intersystem crossing are likely to be slower, than at 3130 Å.

Our results do not, of course, establish the intermediacy of a biradical. One might expect that excited singlets could undergo the elimination reaction by a completely concerted mechanism. If this is true, cyclobutanol formation might occur from the excited singlet, although it has been pointed out that even this process may be concerted.[16] Yields of acetone do not equal the amounts of ketone reacted. With zero quencher our 65% yield of acetone from 2-pentanone agrees with the reported amount,[5] while with 2-hexanone the corresponding acetone yield is 88%. Peaks attributed to cyclobutanols appear in the vapor chromatograms of reaction mixtures and their formation is quenched by piperylene, although we are not yet prepared to compare quencher effects on the competition between elimination and cyclization reactions.

(9) The 3130 Å. line from the source was isolated by filters. Analyses were done by vapor-phase partition chromatography and the quantum yields were placed on an absolute basis by comparison with an acetophenone–isopropyl alcohol actinometer. The results are in good quantitative agreement with those of the group at the University of Chicago.[10]

(10) N. C. Yang, private communication.

(11) W. G. Herkstroeter, unpublished results.

(12) There has been a tendency to attribute "biradical" character solely to triplet states. Our results indicate that spin correlation need not be a very important determinant of chemical reactivity. If a singlet and triplet have similar electron distribution, they will probably show similar reactivity in any reaction in which spin conservation is not an important factor. We believe that carbonyl triplets are more frequently implicated in radical-producing reactions, such as hydrogen abstraction, merely because they have longer lifetimes than the corresponding singlets.

(13) P. Ausloos, J. Phys. Chem., 65, 1616 (1961).

(14) C. Walling and B. Jacknow, J. Am. Chem. Soc., 82, 6108 (1960); C. Walling and A. Padwa, ibid., 85, 1597 (1963).

(15) C. Walling and M. J. Gibian, ibid., 86, 3902 (1964).

(16) (a) I. Orban, K. Schaffner, and O. Jeger, ibid., 85, 3033 (1963); (b) K. H. Schulte-Elte and G. Ohloff, Tetrahedron Letters, 1143 (1964).

Peter J. Wagner,[17] George S. Hammond
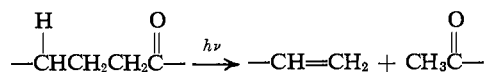Contribution No. 3270
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Received June 28, 1965

Type II Photolysis of 2-Octanone

Sir:

Considerable controversy exists as to the nature of the excited state responsible for photoelimination in ketones having γ-hydrogen atoms (type II photolysis). Michael and Noyes concluded that excited singlet

$$\underset{\text{H}}{|}\underset{|}{\overset{\text{O}}{\overset{\|}{}}} \quad \quad \overset{\text{O}}{\overset{\|}{}}$$

—CHCH$_2$CH$_2$C— $\xrightarrow{h\nu}$ —CH=CH$_2$ + CH$_3$C—

states were involved, based upon vapor-phase studies of 2-pentanone and 2-hexanone in the presence of biacetyl.[1] Ausloos and Rebbert[2] concluded that excited triplets were involved in 2-pentanone photolysis since biacetyl quenched the type II reaction without affecting the fluorescence yield.

Table I. Effect of Quencher Concentration on Rate of 1-Pentene Formation

Quencher, M	R(1-pentene) $\times 10^5$, M min.$^{-1}$	R(*trans*-DCE) $\times 10^5$, M min.$^{-1}$
0	11.8	...
cis-DCE, 0.81	8.5	6.25
cis-DCE, 0.83	8.03	5.68
cis-DCE, 1.80	5.80	7.66
cis-DCE, 3.05	4.46	11.35
cis-DCE, 3.99	3.57	11.55
cis-DCE, 5.53	2.81	14.55
cis-DCE, 11.20	2.12	...
cis-DCE, 12.49	2.12	...
Piperylene, 0.0109	8.54	
Piperylene, 0.0195	7.10	
Piperylene, 0.0417	5.45	
Piperylene, 0.0813	4.50	
Piperylene, 0.162	3.55	
Piperylene, 0.311	3.23	
Piperylene, 0.618	2.60	
Piperylene, 0.914	2.36	
Piperylene, 7.2	2.36	

The accompanying communication by Wagner and Hammond utilizing piperylene as triple state quencher for 2-pentanone and 2-hexanone provides convincing evidence that both excited singlets and triplets can be involved in these reactions.[3] Since our study closely parallels and confirms that of Wagner and Hammond we wish to communicate the results at this time.

We have studied the effect of both *cis*-dichloroethylene and piperylene (1,3-pentadiene) on the rate of 1-pentene formation from liquid 2-octanone under conditions of constant illumination. Both olefins are expected to

(1) J. L. Michael and W. A. Noyes, Jr., *J. Am. Chem. Soc.*, **85**, 1027 (1963).
(2) P. Ausloos and R. E. Rebbert, *ibid.*, **87**, 4512 (1964).
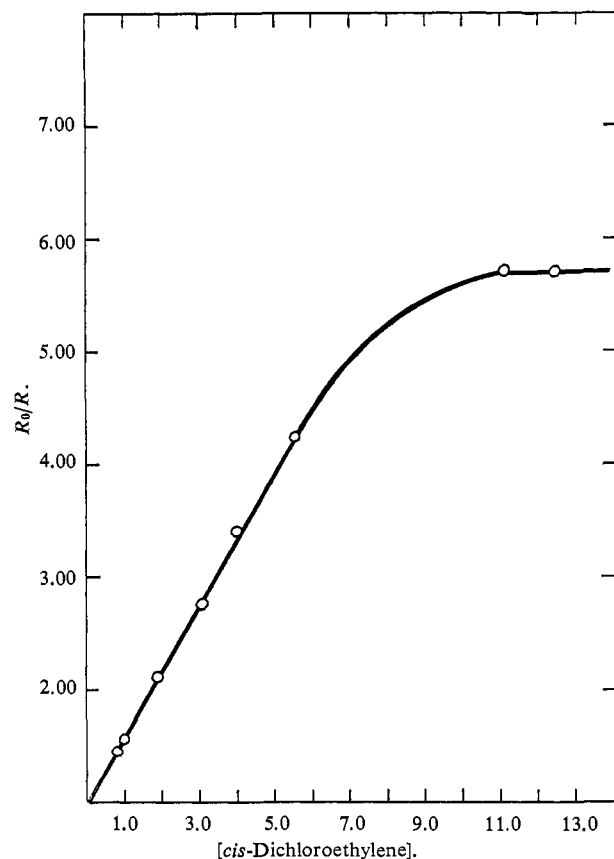(3) P. J. Wagner and G. S. Hammond, *ibid.*, **87**, 4009 (1965).

Figure 1. Ratio of rate of 1-pentene formation (neat) to rate in the presence of *cis*-dichloroethylene *vs.* concentration of *cis*-dichloroethylene.

act as triplet-state quenchers in this system, the latter being particularly efficient.[4]

Measured amounts of 2-octanone and quencher were sealed in quartz cells of approximately 1.8-ml. capacity, deoxygenated, and inserted in a quartz water bath at 1.5–3.5°. Photolysis was effected with a General Electric H100-A4/T lamp.[5] Analyses were carried out by gas chromatography. Concentrations of acetone, 1-pentene, and *trans*-dichloroethylene were followed with time.[6] The rates of acetone and 1-pentene formation were essentially the same, although the latter was most reliable. Table I summarizes the results.

Figures 1 and 2 show plots of R_0/R for 1-pentene against *cis*-dichloroethylene and piperylene concentrations, respectively (Stern–Volmer Plot). It is apparent that piperylene is a much more efficient quencher for this reaction than is *cis*-dichloroethylene by a factor of about 60, but significantly in both cases the maximum extent of quenching is approximately 80%. The amount of nonquenchable reaction ($\sim$20%) may reasonably be attributed to reaction through the excited singlet state with the remainder of the photoelimination occurring through the excited triplet state. This compares with Wagner and Hammond's results of

(4) G. S. Hammond, N. J. Turro, and P. A. Leermakers, *J. Phys. Chem.*, **66**, 1144 (1962).
(5) The effective absorption occurs between 300 and 315 mμ. In all cases 2-octanone absorbs essentially 100% of the incident light.
(6) Energy transfer from 2-octanone to *cis*-dichloroethylene results in isomerization to the *trans* olefin.[3] Although a similar isomerization occurs with piperylene, it could not be followed under the analytical conditions employed here.