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THE PHOTOREARRANGEMENT OF DIMETHYL β-KETOETHYL PHOSPHITES TO DIMETHYL VINYL PHOSPHATES

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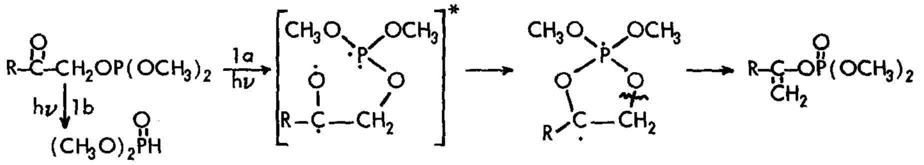
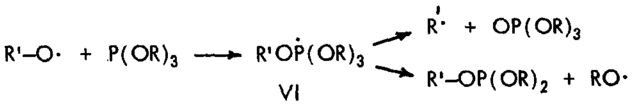
We wish to report the observation of a facile intramolecular photorearrangment (Eq. 1) of certain keto phosphites. Yields of the major photoproducts, IV and V, formed by the irradiation of Ia ($R = CH_3$) and Ib ($R = C_6H_5$) in various solvents are compiled in Table I.[1]

I  (1)

V II III IV

The yields of IV are reduced by the ready formation of tars on further irradiation. Although stable in the dark, IV ($R = CH_3$ or C_6H_5) was 39 to 68% consumed after 24 hr irradiation in acetone or benzene (0.1 M solutions of IV).

Reaction 1a represents a new intramolecular reaction pathway for photo-excited ketones. Such states (n,π^*) often exhibit the reactions characteristic of alkoxyl radicals.[2] In this regard the reactions of alkoxy radicals with phosphites (Eq. 2) are well known.[3] The similarities to reaction 1a are obvious.

 (2)

$$R'{-}O\cdot + P(OR)_3 \longrightarrow \underset{\text{VI}}{R'O\dot{P}(OR)_3} \begin{cases} \longrightarrow R'\cdot + OP(OR)_3 \\ \longrightarrow R'{-}OP(OR)_2 + RO\cdot \end{cases} \qquad (2)$$

We find it intuitively satisfying, therefore, to postulate that the rearrangement reported here may proceed <u>via</u> the excited state II and intermediate III. However, the reaction may in fact be concerted or involve some other intermediate. The corresponding *intermolecular* photoreactions of trialkyl phosphites with aryl or alkyl ketones failed to give ketone-derived products containing phosphorus.[4] Apparently, process 1a derives considerable driving force from its *intramolecular* nature and the concomitant formation of the carbon-carbon double bond.

Table I. Photolyses of Dimethyl β-Ketoethyl Phosphites[a]

					Yield (%) Products[d,e]		
Run No.	I, R =	Solvent[b]	Temp(°C)	Time (hr)[c]	IV	V	Comments
1	CH_3	neat	35	24	28(33)	(19)	
2	CH_3	Me_2CO	0-5	24	33(46)	(25)	
3	CH_3	Me_2CO	0-5	24	(8)	(1)	Pyrex filter; 80% Ia recovered.
4	CH_3	Me_2CO	0-5	6	(47)	(23)	Pyrex filter; 0.1 M benzophenone added.
5	CH_3	Me_2CO	0-5	24	(0)	(0)	0.1 M biacetyl added; 95% Ia recovered.
6	CH_3	C_6H_6	20-25	24	(41)	(22)	
7	CH_3	C_6H_6	20-25	24	(0)	(0)	Dark reaction; 98% Ia recovered.
8	CH_3	C_6H_6	20-25	24	(0)	(0)	0.1 M biacetyl added; 88% Ia recovered.
9	CH_3	cyclohexane	20-25	24	(18)	(32)	7% VIII isolated.
10	CH_3	cyclohexane	20-25	8	(38)	(41)	Pyrex filter; 0.1 M benzophenone added.
11	CH_3	cyclohexane	20-25	24	(0)	(0)	0.1 M biacetyl added; 95% Ia recovered.
12	CH_3	cyclohexene	20-25	24	(1.5)	(34)	34% VI isolated.
13	CH_3	cyclohexene	20-25	24	(0)	(0)	0.1 M biacetyl added; 90% Ia recovered.
14	C_6H_5	Me_2CO	0-5	24	21(24)	(37)	
15	C_6H_5	C_6H_6	20-25	24	13(17)	(29)	8% C_6H_5COCHO isolated.
16	C_6H_5	C_6H_6	20-25	24	(0)	(0)	Dark reaction; 98% Ib recovered.

[a] Unfiltered 400 watt lamp, quartz vessel.

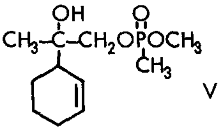
[b] Except for Run No. 1, [I] = 0.1 M.

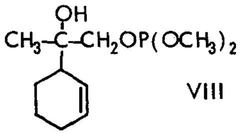
[c] Run Nos. 1, 2, 4, 6, 9, 10, 12, 14 and 15 followed by IR for disappearance of ν_{co} of I.

[d] Yields in parentheses determined by glpc analysis. Other indicated yields are for isolated products.

[e] Intractable tars formed in Run Nos. 1, 2, 4, 6, 9, 10, 12, 14 and 15.

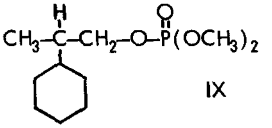
In solvents with more readily abstractable hydrogens, intermolecular reactions involving solvent become important. Photolysis of Ia in cyclohexane and cyclohexene gives yields of V comparable to or greater than those formed in acetone and benzene. However, only 1.5% of IV is formed in cyclohexene. The other major isolated product in this solvent is VII (34%),* presumably formed by the photo-Arbuzov rearrangement[5] of VIII.

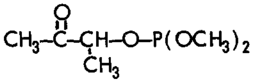

VII


VIII

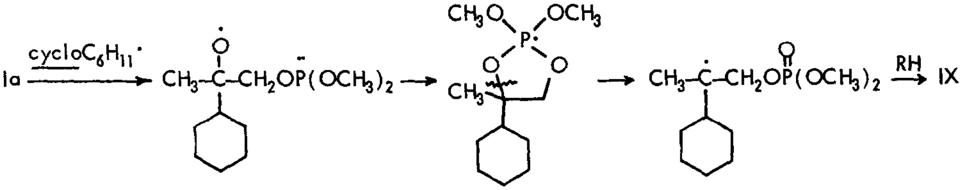
The formation of phosphite VIII is analogous to the formation of 2-(3-cyclohexenyl)-2-propanol in the photoreaction of cyclohexene and acetone.[6] In cyclohexane, the yield of IV (18%) is also reduced from that in acetone and benzene, but the effect is not nearly so dramatic as in cyclohexene which contains more readily abstractable hydrogens. In both cyclohexane and cyclohexene, large amounts of unidentified, high-boiling products are encountered. The fact that the yield of V is little affected by the changes in solvent which greatly decrease the amount of IV formed suggests that these products are generated in separate processes. The fate of the residual fragment formed when I undergoes cleavage to yield V is unknown despite attempts to detect its probable products.[7]

An additional product isolated from photoreaction in cyclohexane is IX (7%). This observation seems particularly interesting since it suggests the possibility that cyclohexyl radicals generated in these reactions


IX


X

add to I and then undergo intramolecular oxygen transfer (Eq. 3) in analogy to Ia.[8] All products were thoroughly characterized by quantitative elemental analysis and by their nmr, ir, and mass spectra. Photoreaction of X in cyclohexane at 0° gave V as the only product detectable by glpc.


(3)

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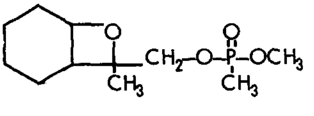
* In addition to VII, 7% of a product tentatively identified as the oxetane i was also isolated from this reaction.


i

Reactions Ia and Ib were both completely quenched by added biacetyl in acetone, benzene, and cyclohexane (Table I).[9] The reaction of Ia in acetone using unfiltered light is most likely photosensitized, as acetone should absorb nearly all the light under these conditions. The quantum yield (ϕ_{IV})[10] for the formation of IV, measured in acetone at 2537 Å, was 0.09 and using 3130 Å light was 0.003. However, the reaction in acetone at 3130 Å in the presence of 0.1 M benzophenone (0.1 M in Ia) has ϕ_{IV} = 0.28. For Ib, ϕ_{IV} = 0.12 at 2537 Å and 0.09 at 3130 Å (both in acetone).

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4. C. E. Griffin and R. B. LaCount, unpublished results.

5. R. B. LaCount and C. E. Griffin, Tetrahedron Letts., 3071 (1965).

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7. Only in Run No. 15 was such a product isolated.

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10. Quantum yields were determined at 0.1 M conc. of I using a $K_3Fe(C_2O_4)_3$ actinometer and were relatively constant for 5-25% consumption of I. Figures reported are average values for the range. Formation of IV was monitored by glpc.