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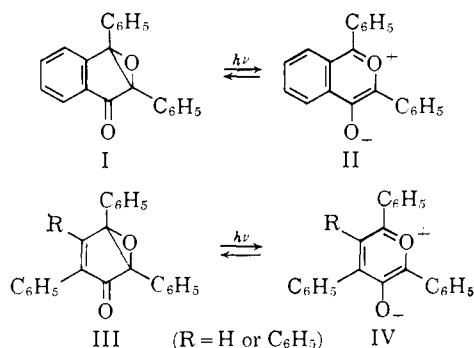
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RECEIVED AUGUST 13, 1964

Photochemical Valence Tautomerization Mechanism of Indenone and Cyclopentadienone Oxides. III

Sir:

Reversible photochemical valence tautomerizations have recently been described for 2,3-diphenylindenone oxide (I)^{1a} and the cyclopentadienone oxides III, R = H^{1b} and R = C₆H₅,^{1c} with the red pyrylium oxides II and IV, R = H and C₆H₅, respectively. We now describe data bearing on the mechanism of these reactions.



The indenone oxide I exists in thermal equilibrium with II ($K_{II/I}^{25^\circ} = 7 \times 10^{-5}$) in deoxygenated benzene. Irradiation (365 m μ) in this solvent produces a photostationary state, II/I = 0.097, which slowly diminishes on prolonged exposure. Addition of enough benzophenone (triplet energy, $E_T = 68.7$ kcal.)² to absorb initially most of the light produces shifts in the photostationary state, up to II/I = 0.35, which appear limited by the direct unsensitized photochemical reconversion to I of the strongly absorbing II ($\epsilon_{365\text{m}\mu}$ 7800) and by thermal reconversion of II to I. Sensitizers of lower triplet energies (<68 kcal.) in sufficient quantities to absorb nearly all the light no longer sensitize the forward reaction and thus produce complete bleaching by sensitized reaction of II.³ These data suggest that II can be formed from triplet

(1) (a) E. F. Ullman and J. E. Milks, *J. Am. Chem. Soc.*, **84**, 1316 (1962); *ibid.*, **86**, 3814 (1964); (b) E. F. Ullman, *ibid.*, **85**, 3529 (1963); (c) J. M. Dunston and P. Yates, *Tetrahedron Letters*, 505 (1964).

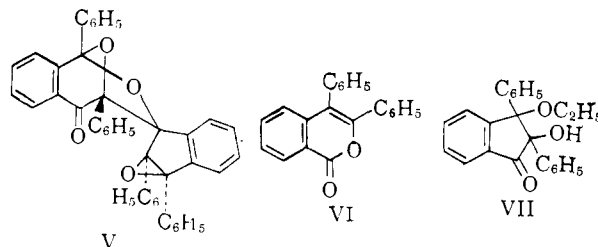
(2) G. S. Hammond and J. Saltiel, *J. Am. Chem. Soc.*, **84**, 4883 (1962).

(3) Additives having $E_T \leq 68$ kcal. which did not absorb light such as fluorene (E_T 68 kcal.)⁴ and naphthalene ($E_T = 60.5$ kcal.)⁵ were without effect, showing that the described phenomena are due to sensitization rather than quenching processes. As would be expected, when benzophenone was also added, these additives in high concentration competed successfully with I for triplet energy and behaved similarly to other low-energy sensitizers.

(4) D. S. McClure, *J. Chem. Phys.*, **17**, 905 (1949).

I (T_1) which is populated by sensitizers having $E_T > 68$ kcal., i.e., $E_{T_1} \geq 68$ kcal. Moreover, I can be formed from T_{II} , where $E_{T_{II}} < 50$ kcal. since T_{II} must be less energetic than singlet II ($E_{S_{II}} \leq 50$ kcal. = 570 m μ).⁵

On prolonged unsensitized irradiation (365 m μ) of benzene or ethanol solutions of I there were formed the dimer V,^{1a} 3,4-diphenylisocoumarin (VI) and, in ethanol, the stereoisomeric ethers VII. The isocoumarin VI was found to arise exclusively from II. Thus on irradiation of a thermally equilibrated mixture



of I and II in hot (125°) ethanol using light (>450 m μ) absorbed only by II (i.e., population of S_{II}), high conversions to VI were obtained. Moreover, VI was not formed by irradiation (365 m μ) of I alone (i.e., population of S_I).⁶⁻⁸ Therefore, S_I does not rearrange to S_{II} , a precursor of the isocoumarin VI.

A less rigorous argument suggests that similarly T_I does not rearrange to T_{II} . On using sensitizers with progressively lower triplet energies an abrupt drop in the efficiency of sensitization of reaction I \rightarrow II is observed at $E_{T(\text{sens})} \sim 68$ kcal. Thus, for example, a sharp change is observed in the benzophenone ($E_T = 68.7$ kcal.) sensitized photostationary state from II/I ≥ 0.35 down to II/I ≤ 0.001 on addition of fluorene ($E_T = 68$ kcal.).⁹ This striking behavior of reaction I \rightarrow II toward small changes in sensitizer triplet energy stands in sharp contrast to the slow, erratic dropoff in sensitizer efficiency observed for reactions capable of sensitization by a process described as "nonvertical" energy transfer.¹⁰ This process, which probably involves sensitized triplet excitation and concerted rearrangement of the reactant to give a new triplet species, appears to be characteristic of photochemical reactions which proceed by exothermic triplet rearrangements.^{10,11} Since the process $T_I \rightarrow T_{II}$ is highly exothermic ($\Delta E_T > 12$ kcal.), such a nonvertical energy transfer process to give the lower energy T_{II} might be expected. The absence of this abnormal

(5) The lowest observable absorption maximum at -190° is given. This represents a maximum energy for the 0-0 band, since II showed no vibrational structure in the long wave length band.

(6) This was shown by irradiation of tritium-labeled indenone oxide (I) in the presence of norbornadiene, an efficient scavenger for T_{II} .¹² An isotopic dilution method was used to detect small quantities of isocoumarin VI in the presence of up to 98% yields of the norbornadiene adduct of II.

(7) These results cannot presently be reconciled with the assumption of H. E. Zimmerman and R. D. Simkin [*Tetrahedron Letters*, 1847 (1964)] that 3-methyl-4-phenylisocoumarin is formed by direct photochemical rearrangement of 2-methyl-3-phenylindenone oxide.

(8) The ethers VII were likewise produced only from II but in a multistep process which does not shed light on the present problem.

(9) Cf. ref. 3.

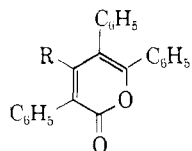
(10) G. S. Hammond and J. Saltiel, *J. Am. Chem. Soc.*, **85**, 2516 (1963).

(11) 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, *ibid.*, **86**, 3197 (1964).

sensitizer behavior suggests that this reaction pathway is not available.¹²

In summary, these data suggest that electronically excited states of the pyrylium oxide II are not intermediates in the photochemical reaction $I \rightarrow II$, nor are electronically excited states of the indenone oxide I intermediates in the reverse process.¹³ Thus by elimination, both reactions probably proceed by way of vibrationally excited ground electronic states formed by isoenergetic crossing from T_1 , T_{11} , and possibly also S_1 and S_{11} .¹⁴

Similar though less complete data have been obtained for the photointerconversions $III \rightleftharpoons IV$. The effects of sensitizers are parallel to those described above, while direct irradiation of III but not IV causes rearrangement to the pyrone VIII.^{1b,c,15} Arguments similar to those given again point to reaction by way of a vibrationally excited ground state.



Of particular interest is the observation that lowering the temperature reduces the quantum yields for reactions $II \rightarrow I$ and $IV \rightarrow III$.^{1b} An attractive but not unique interpretation of these results may be made in terms of the relative energies of the transition states in the thermal isomerizations and of the vibrationally excited ground states of II and IV formed by isoenergetic crossing from the electronically excited states. Thus the energies of the electronically excited states and transition states are probably sufficiently close to each other that collisional deactivation of the vibrationally excited states may compete with rearrangement to the corresponding epoxides. At increased temperatures more successful competition with collisional deactivation should occur since more energetic vibrationally excited ground states would be produced by internal conversion from thermally populated higher vibrational levels of the electronically excited states.

This reasoning suggests that successful competition with collisional deactivation should also become more likely on lowering the thermal transition state energies. A rough parallel between the quantum yields and thermal rates of reactions $II \rightarrow I$ and $IV \rightarrow III$ would be expected, since the energies of at least the singlets of II and IV are very similar. The observed order of quantum yields at 77°K., $II \gg IV$ (R = C₆H₅) > IV (R = H), and the thermal fading rates

(12) Additional evidence that nonvertical energy transfer does not play a role in sensitized reaction $I \rightarrow II$ is found in the absence of energy transfer from sensitizer triplets of energies substantially below the maximum possible triplet energy of I ($E_{T1} < E_{S1} = 74$ kcal.). By contrast relatively large apparent uphill energy transfers are frequently associated with the nonvertical energy transfer process; cf. ref. 10 and 11.

(13) Rearrangement of S_{11} or T_{11} to S_1 or T_1 is energetically forbidden, for E_{S11} (50 kcal.) is at least 12 kcal. less than E_{T1} (~68 kcal.) when related to the energy difference of the ground states ($\Delta F = 6$ kcal.). Thus $E_{S11} > E_{S1}$ and $E_{T1} > E_{T2}$, both by more than 12 kcal.

(14) Since the preparation of this manuscript it has been found that quenching of reaction $I \rightarrow II$ approaches a limit (quantum yield reduced by 11%) with increasing naphthalene concentrations. This strongly suggests that 89% of II is formed directly from S_1 without the intermediacy of T_1 .

(15) We are indebted to Professor P. Yates for providing a generous supply of III (R = C₆H₅).

$k_{II}^{25^\circ} \approx 5 \times 10^{-6}$ sec.⁻¹, $k_{IV(R=C_6H_5)}^{25^\circ} \approx 8 \times 10^{-7}$ sec.⁻¹, and $k_{IV(R=H)}^{25^\circ} \approx 0$, are in accord with this prediction.

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A Novel Reaction of Transition Metal Alkyls and Aryls. Sulfur Dioxide Insertion

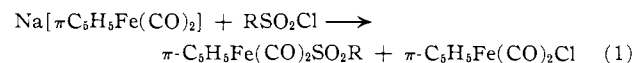
Sir:

Extensive investigations of organic reactions catalyzed by transition metal carbonyls resulted in the discovery of interesting and intriguing carbon monoxide insertion¹ and decarbonylation processes.^{2,3} Subsequent experiments by Kebly and Filbey,⁴ Booth and Chatt,⁵ and Heck and Breslow,⁶ as well as mechanistic studies of interconversion of acetyl- and methylmanganese carbonyl complexes by Calderazzo and Cotton,⁷ and, more recently, by Mawby, Basolo, and Pearson,⁸ point to a facile migration of the methyl group directly bonded to a number of transition metals.

These observations and a general interest in catalysis by complexes prompted us to commence a detailed investigation of the versatility of low-valent metals in effecting insertion and migration processes of small groups or fragments, similar in nature to carbon monoxide. This note describes some preliminary results which indicate that such reactions may be much more general than has been hitherto realized.

A recent report⁹ of the synthesis of sulfur dioxide derivatives of iron carbonyls suggested to us an interesting analogy. There is a remarkable structural similarity between the acyl (CO + alkyl) and unknown sulfonyl (SO₂ + alkyl) metal complexes, and therefore it appeared reasonable that the latter might exhibit certain aspects of the chemical behavior characteristic of the former systems.

Investigation of cyclopentadienyliron dicarbonyl complexes has shown that this is indeed the case. Reaction of $Na[\pi-C_5H_5Fe(CO)_2]$ with alkyl (CH₃, C₂H₅) and aryl (C₆H₅) sulfonyl chlorides affords, in addition to $\pi-C_5H_5Fe(CO)_2Cl$, small amounts of iron sulfonyl carbonyls (eq. 1). The sulfonyl complexes,



which may be separated from the carbonyl chloride by alumina chromatography, are yellow, crystalline com-

(1) The word *insertion* is not to be interpreted literally from a mechanistic point of view. In this paper, *insertion* has structural significance only; see R. J. Mawby, F. Basolo, and R. G. Pearson, *J. Am. Chem. Soc.*, **86**, 5043 (1964).

(2) T. H. Coffield, J. Kozikowski, and R. D. Closson, Special Publication No. 13, The Chemical Society, London, 1959, p. 126.

(3) R. D. Closson, T. H. Coffield, and J. Kozikowski, *J. Org. Chem.*, **22**, 598 (1957).

(4) K. A. Kebly and A. H. Filbey, *J. Am. Chem. Soc.*, **82**, 4204 (1960).

(5) G. Booth and J. Chatt, *Proc. Chem. Soc.*, 67 (1961).

(6) R. F. Heck and D. S. Breslow, *J. Am. Chem. Soc.*, **83**, 4023 (1961).

(7) F. Calderazzo and F. A. Cotton, *Inorg. Chem.*, **1**, 32 (1962).

(8) R. J. Mawby, F. Basolo, and R. G. Pearson, *J. Am. Chem. Soc.*, **86**, 3994 (1964).

(9) E. H. Bray and W. Hübel, *Angew. Chem.*, **75**, 345 (1963).