the absence of any single molecular orbital having a continuous electron density around the barrel, or is due to the nodes present at each carbon nucleus so that electron density is necessarily discontinuous, or results from the relatively poor overlap noted in ref. 1.

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Mechanistic Organic Photochemistry. VIII. Identification of the n–π* Triplet Excited State in the Rearrangement of 4,4-Diphenylcyclohexadienone[1]

Sir:

We proposed a mechanistic approach to organic photochemistry and noted that this treatment is applicable to transformations of both n–π* singlets and triplets.[2a,c] Despite our choice of investigating molecular and gross electronic details first, the singlet *vs.* triplet question in the reactions we studied is an intriguing problem. As noted[2c] we have been investigating this point in the 4,4-diphenylcyclohexadienone (I) to 6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one (VII) reaction.[2b,c] In the interim Richards[3] has studied the problem in the related santonin rearrangement.
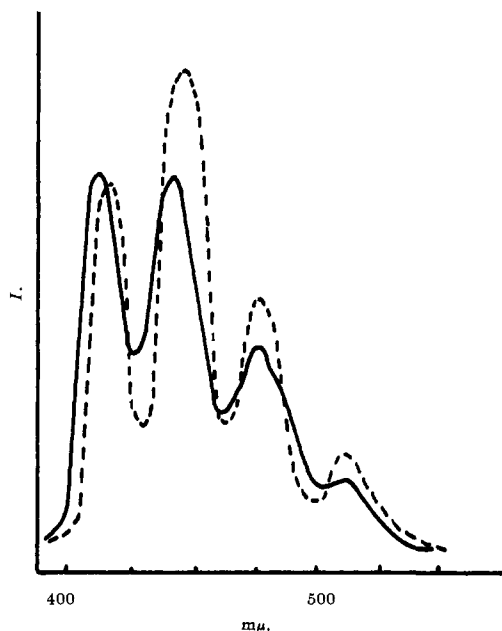

Fig. 1.—Triplet emission spectra: ———, dienone; – – – –, benzophene.

We now report that: (1) This reaction proceeds *via* a triplet state (III). (2) This triplet state undergoes molecular rearrangement at a rate rapid enough to

(1) Presented in preliminary form at the Gordon Research Conference in Organic Reactions, July, 1963, Tilton, N. H.

(2) (a) H. E. Zimmerman, Abstracts of the 17th National Organic Chemistry Symposium of the American Chemical Society, p. 31; (b) H. E. Zimmerman and D. I. Schuster, *J. Am. Chem. Soc.*, **83**, 4486 (1961); (c) *ibid.*, **84**, 4527 (1962); (d) H. E. Zimmerman, *et al.*, *ibid.*, **86**, 947 (1964) (paper VII).

(3) M. H. Fisch and J. H. Richards, *ibid.*, **85**, 3029 (1963).

invalidate one of the usual criteria for detecting triplets. (3) The triplet is of the n–π* variety, more electron rich at the β-carbon than is the ground state.[2b] Our, conclusions 1 and 2 are compatible with the findings of Richards.[3]
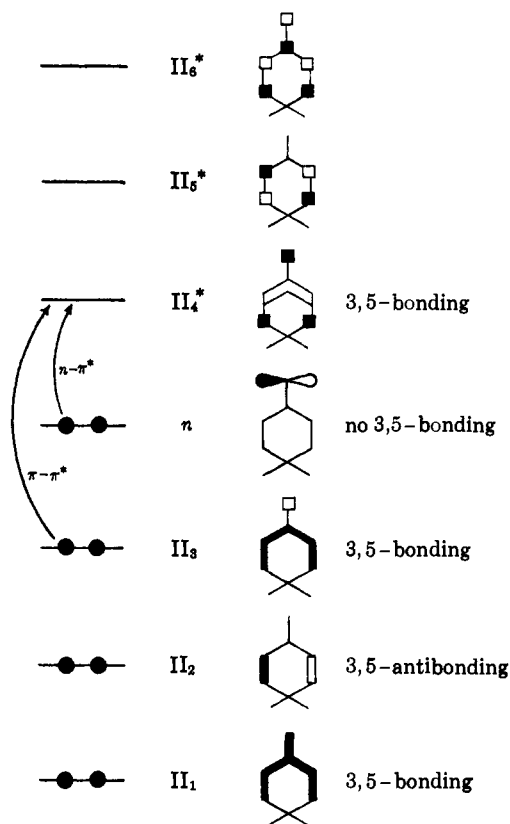

Fig. 2.— Cyclohexadienone molecular orbitals: ■, wave function positive; □, wave function negative.

Regarding the first point, we determined the 4,4-diphenylcyclohexadienone (I) to 6,6-diphenylbicyclo-[3.1.0]hex-3-en-2-one (VII) conversion (Table I) to

TABLE I

RELATIVE CONVERSIONS

Conditions[a,d,h]	Dienone disappearance	VII formation
Dienone alone[e]	11	8.3
Dienone alone[f]	11	7.7
Dienone + acetophenone[c,e,g]	50	38
Dienone + naphthalene[b,f,g]	11	8.4

[a] Dienone, 0.005 M. [b] Naphthalene, 0.1 M. [c] Acetophenone, 0.09 M. [d] All runs in benzene. [e] 310–360-mμ filter. [f] 335–420-mμ filter. [g] Beers' law adherence assured no ground state complexation. [h] Standardized for constant light.

be independent of minor wave length changes. With acetophenone present in concentration to absorb 98% of the light (Table I, entry 3) a fourfold increase resulted despite the negligible direct excitation of dienone, providing strong evidence for photosensitization by acetophenone forming 4,4-diphenylcyclohexadienone triplet (III). Since the same product (VII) resulted as in the ordinary irradiation, it is reasonably assumed that the dienone triplet (III) is also an intermediate in the unsensitized reaction (see Chart I).

CHART I
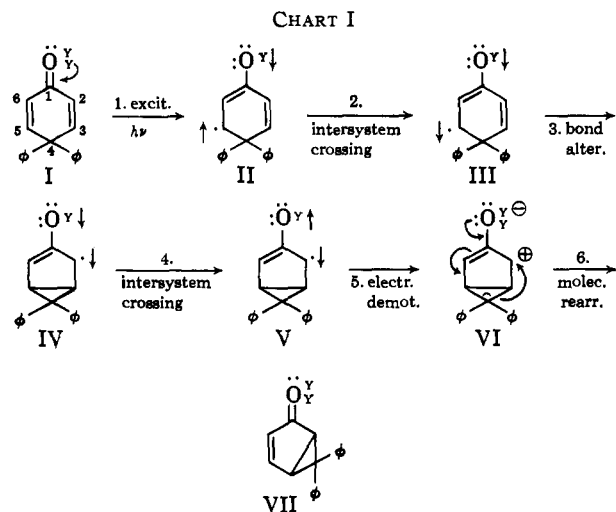
Now we direct attention to entry 4 of Table I showing the efficiency undiminished by 0.1 M naphthalene. This is remarkable in that the energy of 4,4-diphenylcyclohexadienone triplet is 68.8 kcal./mole, 8 kcal./mole higher than for naphthalene triplet[4] (61 kcal./mole). Presently we restrict comment to a note of caution that absence of quenching by triplet acceptors is inconclusive evidence against a triplet mechanism; the triplet intermediate may react rapidly enough to preclude quenching.[5]

Finally, we provide evidence that the reacting triplet is n–π* rather than π–π*. The phosphorescence (i.e., triplet) emission spectrum of 4,4-diphenylcyclohexadienone in EPA at 77°K. is accompanied in Fig. 1 by that of benzophenone for comparison. (A) The vibrational pattern is characteristic of n–π* emission[6]; band separation averages 1647 cm.$^{-1}$ (ground state C=O or C=C stretching). (B) The dienone triplet energy (68.8 kcal./mole, 415-mμ O–O band) approximates that of benzophenone triplet (68.8 kcal./mole, 415-mμ O–O band), which has been assigned[4b,6] the n–π* structure. (The full argument depends on the singlet system energies. n–π* O–O 392 mμ, 73 kcal./mole vs. 375 mμ, 76 kcal./mole for (C₆H₅)₂C=O; π–π* 220 mμ, 129 kcal./mole, plus benzenoid absorption, vs. 248 mμ, 115 kcal./mole for (C₆H₅)₂C=O.) (C) The 77°K. lifetime was determined as ca. 0.5 msec., consonant with an n–π* assignment[7]; π–π* lifetimes are generally much longer.

Our conclusion that the lowest energy triplet is n–π* differs with Richards' suggestion[3] that the santonin rearrangement proceeds via a π–π* triplet.

(4) The role of triplets in a number of reactions has been nicely demonstrated: (a) G. S. Hammond, M. J. Turro, and P. A. Leermakers, J. Phys. Chem., 66, 1148 (1962); (b) G. S. Hammond and P. A. Leermakers, J. Am. Chem. Soc., 84, 207 (1962).

(5) Quenching via naphthalene triplet is especially inefficient. The 310–360-mμ filter used with naphthalene and dienone allowed 30 (±10) % of the light to be absorbed by naphthalene; here quantum yields of 0.29 resulted. This remarkable "uphill" sensitization may be due to slow naphthalene triplet to ground state degradation compared with the 8 kcal./mole uphill sensitization and rapid subsequent rearrangement of dienone. Alternatively, a nonvertical energy transfer as considered recently [G. S. Hammond and J. Saltiel, ibid., 85, 2515 (1963)] is possible. A most interesting rationale is singlet–triplet sensitization (intersystem crossing of an excited singlet naphthalene–ground state dienone collisional pair).

(6) M. Kasha, Radiation Res. Suppl., 2, 265 (1960).

(7) Cf. 0.85 msec. for MeCOEt and 1.26 msec. for Et₂CO vs. 0.95 × 10³ msec. for MeCO(β-naphthyl) reported by D. S. McClure [J. Chem. Phys., 17, 905 (1949)]; of these only the last is π–π* (cf. ref. 4b) while the first three are certainly n–π*. Benzophenone triplet lifetime is similarly short. The reliability of this generalization will be discussed in our full paper along with full referencing.

Finally, an n–π* intermediate being demonstrated, we comment that as for n–π* singlets, n–π* triplets of such unsaturated ketones should have an electron-rich π-system and more electron-rich β-carbons than in the ground state. That this rationalizes observed dienone photochemistry has already been indicated.[1,2] The molecular orbitals are depicted in Fig. 2. We note that n–π* excitation leads to an augmented 3,5-bond order, augmented more than for π–π* promotion.[8] This accords with the step postulated for this reaction wherein a 3,5-bond is formed by excited state III followed by electron demotion and cyclopropylcarbinyl carbonium rearrangement by zwitterion VI. Our earlier mechanism thus requires refinement by addition of two intersystem (singlet–triplet) crossing steps.

(8) The MO ordering and this conclusion depend on oxygen Coulomb integral choice dictated by the necessity of n–π* excitation being lowest as experimentally found. Discussion of this and other parameter choices in the ordinary and self-consistent calculations is deferred.

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The Structure and Stereochemistry of α-Caryophyllene Alcohol

Sir:

α-Caryophyllene alcohol is obtained along with clovene and caryolan-1-ol by sulfuric acid treatment of crude caryophyllene.[1] Added interest in α-alcohol arose from the finding that photolysis of its nitrite ester was accompanied by epimerization of the C–O bond.[2] The present work establishes the structure and stereochemistry of α-alcohol as 6[3] and shows that, contrary to reports in the literature,[1b] caryophyllene is not the progenitor. A novel feature was the use of nitrite photolysis (Barton reaction[4]) to introduce remote ketonic groups for degradation.

Asahina and Tsukamoto found that α-alcohol (C₁₅H₂₆O, m.p. 117°, [α]D 0°) was saturated, tricyclic, and contained an OH group.[1a] Recently we[2] showed the OH was secondary by oxidation to a 5-membered ketone (ν 1742 cm.$^{-1}$),[5] which has no enolizable hydrogens and which was converted to α-alcohol and to an epimer (epi-α-alcohol) by suitable reduction. In the n.m.r. spectra of various esters of α-alcohol and

(1) (a) Y. Asahina and T. Tsukamoto, J. Pharm. Soc. Japan, 484, 463 (1922); (b) J. Bell and G. G. Henderson, J. Chem. Soc., 1971 (1930); (c) D. H. R. Barton, T. Brunn, and A. S. Lindsey, ibid., 2210 (1952), and references cited there.

(2) A. Nickon, J. R. Mahajan, and F. J. McGuire, J. Org. Chem., 26, 3617 (1961).

(3) Workers at Glasgow University have independently arrived at the same structure by X-ray crystallography, and simultaneous publication was arranged [K. W. Gemmell, W. Parker, J. S. Roberts, and G. A. Sim, J. Am. Chem. Soc., 86, 1438 (1964)].

(4) (a) D. H. R. Barton, J. M. Beaton, L. E. Geller, and M. M. Pechet, ibid., 82, 2640 (1960); (b) for a review see A. L. Nussbaum and C. H. Robinson, Tetrahedron, 17, 35 (1962).

(5) Unless stated otherwise, infrared spectra were taken in carbon tetrachloride, and n.m.r. spectra (60 Mc.) in deuteriochloroform, with peak positions (δ) expressed in p.p.m. downfield from internal tetramethylsilane.