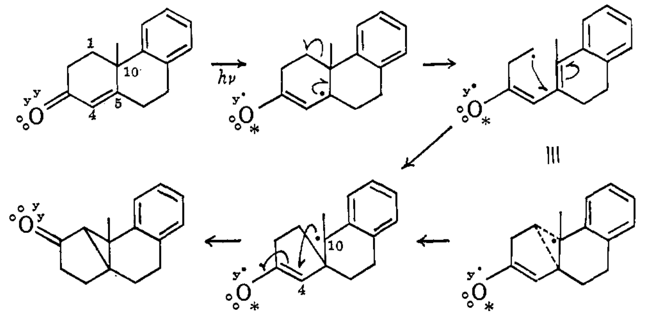
In runs in isopropyl alcohol the pinacol of phenanthrone **7** was formed *ca.* one-fifth as fast as **8**. Photoketone and pinacol formation were quenched equally by naphthalene, signifying that the same triplet is responsible for both reactions, or alternatively that two exceedingly rapidly equilibrating states are involved, one in each reaction. The rate of hydrogen abstraction calculated from this data is $k_h^{bi} = 3 \times 10^3$ l. mole^{-1} sec^{-1}, which is slow compared to the acetophenone abstraction rate in the same solvent,[14] suggesting either that a π–π* triplet is the dominant species, that hydrogen abstraction is reversible, or that n–π abstraction rates vary.

The rearrangement is only slightly solvent dependent and not suggestive of the reaction of a polar species. This accords with our recent finding that the β carbon of the enone moiety is not electron deficient.[15] The very low rate and efficiency of rearrangement contrast with the dienone case and a different, less efficient mechanism is required. Such a mechanism is shown in Scheme I. The 4–10 bond formation of the last step may be concerted with the 10–5 migration of the carbon-1 methylene, and MO calculations indicate this to be favorable. The inefficiency is then seen to derive either solely from the requirement for σ bond (1–10) fission and lack of a second double bond for interaction in the excited state or from this factor coupled with the intervention of a low energy π–π* triplet. Both factors differ in the dienone case.

Scheme I



* = y, if n-π*, or ·, if π-π*

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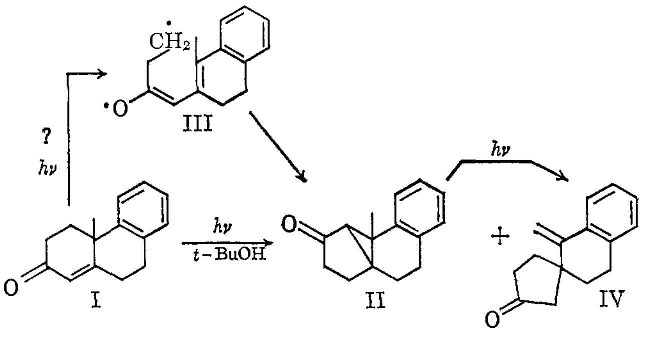
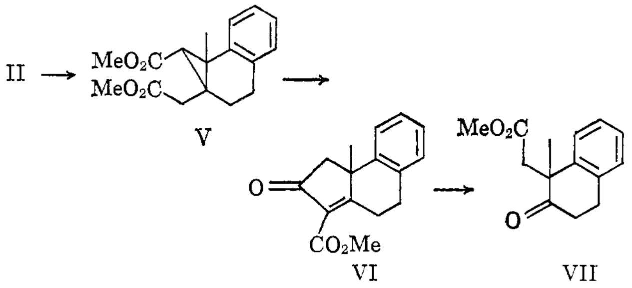
Stereospecific Rearrangement of an Excited Triplet Ketone[1]

Sir:

Various attempts have been made to rationalize the photochemical rearrangements of conjugated cyclohexenones.[2–4] Among these attempts, it has been suggested[2] that the rearrangements observed can be accounted for on the basis of homolytic fission of the 1,10 bond (steroid numbering) with concomitant formation of a 5,10 double bond (giving an intermediate such as III) followed by readdition at C-5 and cyclization. This view suggests that for a cyclic enone (I) with a single suitably disposed asymmetric center, photorearrangement should give an optically inactive product. Alternate possibilities[3,4a] suggest retention of optical activity.



Irradiation (λ >290 mμ) of I in *t*-butyl alcohol gives II [70%; mp 86–87°; 5.82 and 1.65 μ; $\lambda_{\max}^{95\%\ \mathrm{EtOH}}$ 238 mμ (ε 9380)] and IV [1.5%; 5.73, 6.15, and 11.15 μ; $\lambda_{\max}^{95\%\ \mathrm{EtOH}}$ 245 mμ (ε 10,900) and 282 mμ (ε 1200), τ 4.56 and 5.12 (1 H, singlets, $C{=}CH_2$)].[5] Irradiation of II in *t*-butyl alcohol gives IV as does acid treatment of II. The structures of II and IV were established by degradation to known compounds. Treatment of II with ethyl formate and base followed by hydrogen peroxide oxidation and treatment with diazomethane gave V [5.75 and 5.80 μ; $\lambda_{\max}^{\mathrm{MeOH}}$ 228 mμ (ε 8650)]. Treatment of V with sodium methoxide gave VI [5.75 and 6.15 μ; $\lambda_{\max}^{95\%\ \mathrm{EtOH}}$ 233 mμ (ε 10,300)]. Ozonolysis of VI followed by treatment with hydrogen peroxide and diazomethane gave VII, identical in infrared absorption, v.p.c. retention time, and 2,4-dinitrophenylhydrazone with an authentic sample.[6]



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(1) (a) Portions of this work were described at the Reaction Mechanisms Conference, Corvallis, Ore., June 1964. (b) Related work on the same system is being published simultaneously (H. E. Zimmerman, R. G. Lewis, J. J. McCullough, A. Padwa, S. Staley, and M. Semmelhack, *J. Am. Chem. Soc.*, **88**, 159 (1966).

(2) H. E. Zimmerman, *Advan. Photochem.*, **1**, 183 (1963).

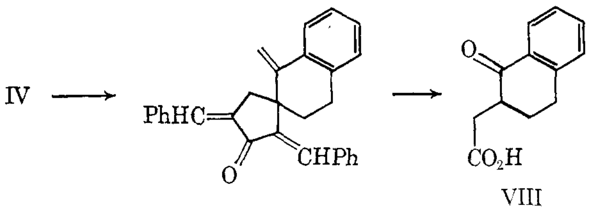
(3) H. E. Zimmerman and J. W. Wilson, *J. Am. Chem. Soc.*, **86**, 4036 (1964).

(4) (a) O. L. Chapman, T. A. Rettig, A. A. Griswold, A. I. Dutton, and P. Fitton, *Tetrahedron Letters*, No. **29**, 2049 (1963); (b) W. W. Kwie, B. A. Shoulders, and P. D. Gardner, *J. Am. Chem. Soc.*, **84**, 2268 (1962); (c) B. Nann, D. Gravel, R. Schorta, H. Wehrli, K. Schaffner, and O. Jeger, *Helv. Chim. Acta*, **46**, 2473 (1963); (d) O. Jeger and K. Schaffner, *Chem. Weekblad*, **60**, 389 (1964); (e) O. Jeger, *Angew. Chem. Intern. Ed. Engl.*, **3**, 318 (1964); (f) O. Jeger, *Angew. Chem.*, **76**, 275 (1964).

(5) Satisfactory analyses were obtained for all new compounds except VI and IV (crystalline derivatives of IV were analyzed).

(6) Prepared by treatment of 1-methyl-2-tetralone with sodium hydride and methyl bromoacetate.

Treatment of IV with benzaldehyde and base gave two isomeric dibenzal derivatives, mp 136.5–138.5°; 5.94, 6.19, and 11.18 μ; $\lambda_{\max}^{95\%\ \text{EtOH}}$ 239 mμ (ε 24,000) and 347 mμ (ε 30,100); mol wt 388; and mp 173–175°; 5.93, 6.17, and 11.10 μ; $\lambda_{\max}^{95\%\ \text{EtOH}}$ 239 mμ (ε 20,400) and 347 mμ (ε 30,400); mol wt 388). Ozonolysis of each dibenzal derivative separately gave VIII, isolated as the 2,4-dinitrophenylhydrazone which was compared with an authentic sample.



VIII

The rearrangement of I to II proceeds *via* an excited triplet state.[1b,7] The reaction proceeds at a comparable rate in the presence of dibenzothiophene as sensitizer (greater than 90% of the light absorbed by dibenzothiophene) and in the absence of the sensitizer. Furthermore, the reaction is almost completely quenched by 0.03 *M* piperylene.[8]

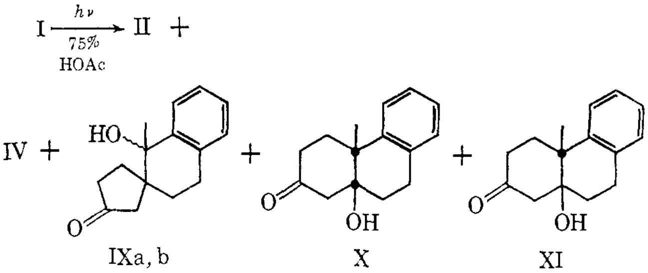
Complete resolution of I and II was accomplished *via* the corresponding pyrrolidinium *d*-camphor-10-sulfonates, a new method for resolution of racemic ketones.[9] The rotations of the ketones were I, $[\alpha]^{27}\text{D}$ +332 and −332°, and II, $[\alpha]^{27}\text{D}$ +42.5 and −42.3°. Table I summarizes the results of irradiation of the enantiomers of I. The rotations of the product were taken on the solid product II after chromatography on silica gel and treatment with charcoal in solvent, but without crystallization. The rotation of II is opposite in sign to that of I so that slight contamination of II with I would lower the apparent retention of optical activity. In all runs using both enantiomers a minimum of 95% retention of optical activity was observed. The photochemical rearrangement thus is stereospecific, and mechanisms which involve complete fission of the 1,10 bond with concomitant formation of an intermediate having a plane of symmetry (*e.g.*, III) can be excluded for the photochemical rearrangement of I to II.

Table I. Summary of Irradiations of Optically Active I[a]

Run	$[\alpha]^{27}\text{D}$, deg I	$[\alpha]^{27}\text{D}$, deg II	Duration of irradiation, hr[b]	Yield of II, %	Retention of opt. act., %
1	+332	−40.2	5	65	95
2	+332	−40.5	18.5	27	96
3	−332	+40.9	6	80	96
4	−332	+41.0	18.5	37	96

[a] All rotations were measured at *c* 1. [b] All irradiations were carried out in *t*-butyl alcohol at 28–30° using a 550-w Hanovia type A mercury lamp filtered through Pyrex.

Irradiation (λ >290 mμ) of I in aqueous acetic acid (75%) gives several new products, IXa,b (30%),



IXa, b X XI

X (1%), and XI (3%), in addition to II (<2%) and IV (5%). Control experiments show that IXa,b and IV are produced from II in the dark under the conditions of the experiment. Control experiments suggest that X and XI are derived from I in a photochemical step, but the small amounts of these compounds in the crude product render this conclusion tenuous. The structures of IXa,b (2.88 and 5.75–5.80μ), which we have been unable to separate, rest on dehydration by phosphorus oxychloride in pyridine to IV, which has been degraded to a known compound. Keto alcohols X and XI were identified by comparison with authentic samples.

The relationship of the photochemistry of the cross-conjugated cyclohexadienones[2,4d,10] to the photochemistry of the 2-cyclohexenones is now more clearly in focus. The two series show structurally similar types of rearrangement (alkyl shifts) and similar stereospecificity and nucleophilic solvent incorporation (in the case of the cyclohexenones, at least, this is often the result of a subsequent dark reaction).[4] They differ substantially in quantum efficiency[1b,7] and the rate of reaction of the triplet (*i.e.*, triplets of 2-cyclohexenones can be quenched while those from cyclohexadienones cannot).[1b,7]

Acknowledgment. This investigation was supported by Public Health Service Research Grant AM0720 from the National Institute of Arthritis and Metabolic Diseases.

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(7) H. E. Zimmerman, *J. Pure Appl. Chem.*, **9**, 493 (1964). See also ref 1b.

(8) This quenching involves reaction with piperylene in addition to energy transfer.

(9) W. R. Adams, O. L. Chapman, J. B. Sieja, and W. J. Welstead, Jr., *J. Am. Chem. Soc.*, **88**, 162 (1966).

(10) For reviews see (a) P. J. Kropp, chapter in "Organic Photochemistry," Vol. I, O. L. Chapman, Ed., Marcel Dekker, Inc., New York, N. Y., in press; (b) P. de Mayo, *Advan Org. Chem.* **2**, 367 (1960); (c) O. L. Chapman, *Advan. Photochem.*, **1**, 323 (1963); (d) see ref 1f.

(11) Public Health Service Fellow (5-Fl-GM-21, 687-02) National Institute of General Medical Sciences.

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Received October 11, 1965

A New Method for the Resolution of Ketones

Sir:

Resolution of racemic ketones and aldehydes, though of frequent interest in mechanism studies and synthesis, remains a difficult problem. Several approaches to this problem have been suggested, prominent among which are optically active carbonyl reagents such as hydrazines,[1] semicarbazides,[2] diols,[3] dithiols,[4] semi-

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(1) C. Neuberg, *Chem. Ber.*, **36**, 1192; (1903); C. Neuberg and M. Federer, *ibid.*, **38**, 866 (1905).