

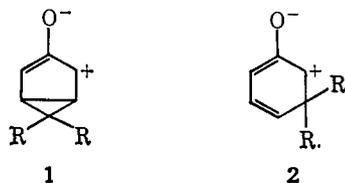
Mechanistic and Exploratory Photochemistry. XV.¹ The Relation of Cyclohexenone to Cyclohexadienone Rearrangements

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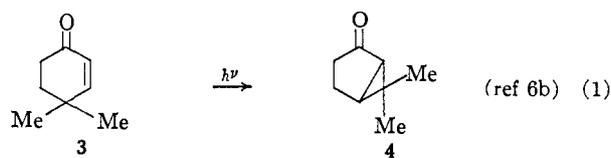
Abstract: The photochemical rearrangements of 4a-methyl-4,4a,9,10-tetrahydro-2(3H)phenanthrone and $\Delta^{1,9}$ -10-methyl-2-octalone are described as giving products formally analogous to those arising in cyclohexadienone photolyses. In the former case the product structure was proven by degradation and in the latter by synthesis. The cyclohexenone rearrangement was shown to proceed by way of a triplet excited state. The electronic configuration of this species is discussed. In striking contrast to the extraordinarily rapid (*i.e.*, $k_r \geq 10^9 \text{ sec}^{-1}$) and efficient dienone rearrangement, the cyclohexenones were found to rearrange with very low quantum efficiency and of the order of four powers of ten more slowly. In isopropyl alcohol the pinacol was formed. It was demonstrated that this and the photoketone are formed from the same or very rapidly equilibrated excited states.

In order to rationalize the intriguing photochemical rearrangements of cross-conjugated cyclohexadienones, we proposed some time ago^{3,4a,b} the intervention of the mesoionic intermediates **1** and **2**. These



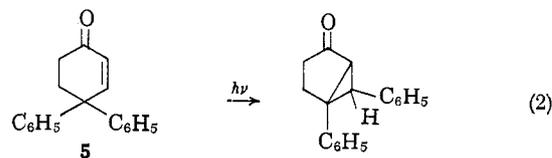
intermediates are in accord with a large number of literature photochemical rearrangements and have found extensive subsequent acceptance.⁵ Nevertheless, there remained the problem that the mechanistic pathway which we proposed, affording intermediate **1** and leading to a 6,6-disubstituted 2-ketobicyclo[3.1.0]hexane skeleton (conveniently termed a type A process), is inapplicable to monoenones since the mechanism invokes participation of the second double bond of the dienones. Yet, 4,4-disubstituted monoenones rearrange in a manner formally analogous⁶ (*i.e.*, type A)

as is depicted in eq 1. This posed the reasonable questions whether the existence of the enone rearrangement invalidated the mechanism for dienones and secondly what the relationship between the two reactions might be.



(formally analogous to a type A dienone rearrangement)

However, subsequently we found⁷ that in the case of



4,4-diphenylcyclohexenone (**5**), photolysis did not afford a type A product but rather phenyl migration intervened. In 4,4-diphenylcyclohexadienone this phenyl rearrangement thus had been an *a priori* possibility which did not occur. From this it was possible to draw the likely but not necessary conclusion that the dienone rearrangement is a more efficient process than the phenyl migration of monoenone. Additionally, since 4,4-diphenylcyclohexenone had the possibility of undergoing the type A skeletal change followed by its completely aliphatic analogs and yet underwent phenyl migration, a similar inference could be drawn, namely, the type A rearrangement of 4,4-disubstituted cyclohexenones is the least efficient of the processes studied. The reaction of dienones is the most efficient and a totally different process of intermediate efficiency (*i.e.*, phenyl migration) is interposed. This logic is, however, imperfect for it utilizes comparisons between two processes available to each given molecule of interest to predict the reaction efficiencies of the different molecules relative to each other. The evidence can be taken to suggest but not to prove

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

(1) For paper XIII in the series *cf.* H. E. Zimmerman, *Pure Appl. Chem.*, **9**, 493 (1964); paper XIV: H. E. Zimmerman, R. G. Lewis, J. J. McCullough, A. Padwa, S. W. Staley, and M. Semmelhack, *J. Am. Chem. Soc.*, **88**, 159 (1966).

(2) (a) National Institutes of Health Predoctoral Fellow 1961-1964; National Science Foundation Summer Fellow 1961; (b) Postdoctoral Research Associate 1963-1965; (c) National Science Foundation Postdoctoral Fellow 1962-1963; (d) Postdoctoral Research Associate 1963-1964; (e) Senior Honors Thesis Research Student.

(3) H. E. Zimmerman, 17th National Organic Chemistry Symposium, June 1961, Abstracts, p 31.

(4) (a) H. E. Zimmerman and D. I. Schuster, *J. Am. Chem. Soc.*, **83**, 4486 (1961); (b) H. E. Zimmerman and D. I. Schuster, *ibid.*, **84**, 4527 (1962).

(5) (a) O. L. Chapman, *Advan. Photochem.*, **1**, 323 (1963); (b) O. L. Chapman and L. F. Englert, *J. Am. Chem. Soc.*, **85**, 3029 (1963); (c) P. J. Kropp and W. F. Erman, *ibid.*, **85**, 2456 (1963); (d) P. J. Kropp, *ibid.*, **85**, 3779 (1963); **86**, 4053 (1964); (e) C. Gantner, E. C. Utzinger, K. Schaffner, D. Arigoni, and O. Jeger, *Helv. Chim. Acta*, **45**, 2403 (1962); (f) P. J. Kropp, *J. Org. Chem.*, **29**, 3110 (1964); (g) D. Caine and J. B. Dawson, *ibid.*, **29**, 3108 (1964); (h) C. Gantner, F. Greuter, D. Kagi, K. Schaffner, and O. Jeger, *Helv. Chim. Acta*, **47**, 627 (1964); (i) G. Bozzato, H. P. Thronsdon, K. Schaffner, and O. Jeger, *J. Am. Chem. Soc.*, **86**, 2073 (1964); (j) C. Gantner, R. Warszawski, H. Wehrli, K. Schaffner, and O. Jeger, *Helv. Chim. Acta*, **46**, 320 (1962).

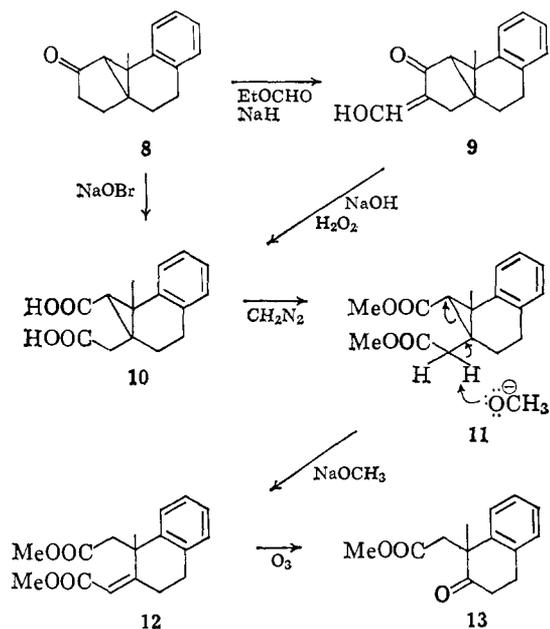
(6) (a) W. W. Kwie, B. A. Sholders, and P. D. Gardner, *J. Am. Chem. Soc.*, **84**, 2268 (1962); (b) O. L. Chapman, T. A. Rettig, A. I. Dutton, and P. Fitton, *Tetrahedron Letters*, 2049 (1963); (c) B. Nann, D. Gravel, R. Schorta, H. Wehrli, K. Schaffner, and O. Jeger, *Helv. Chim. Acta*, **46**, 2473 (1963).

that the type A skeletal rearrangements in the dienones and aliphatic monoenones are fortuitously similar while actually deriving from fundamentally different reaction routes. The goal of the presently reported investigations was to ascertain the validity of this view.

Exploratory, Structural, and Synthetic Aspects. The two cyclohexenones selected for the present study were 4a-methyl-4,4a-9,10-tetrahydro-2(3H)-phenanthrone⁸ (6) and $\Delta^{1,9}$ -10-methyl-2-octalone⁹ (7).

Photolysis in the $n-\pi^*$ region of the phenanthrone 6 either in *t*-butyl alcohol or in methanol afforded as the virtually exclusive product an isomeric ketone (8), mp 88.5–89.5°. In benzene the same product was formed with comparable ease; but, in addition, by-products were found. The spectral data (nmr, infrared, and ultraviolet) summarized in the Experimental Section were consonant with and tended to point to structure 8. Solid confirmation was obtained from the degradation outlined in Chart I. This led to 1-methyl-1-carbomethoxymethyl-2-ketotetrahydronaphthalene (13) which was synthesized for comparison.^{10,11}

Chart I



In parallel studies the photolysis of $\Delta^{1,9}$ -10-methyl-2-octalone (7) was found on irradiation in the $n-\pi^*$ region to afford an isomeric ketone 14 as the virtually exclusive product when the irradiations were run to low conversion in methanol or in *t*-butyl alcohol. This photoproduct was isolated by preparative vpc and characterized as the semicarbazone, mp 170.5–171.0°. The infrared, ultraviolet, and nmr evidence (*cf.* the Experimental Section) was in agreement with the assigned structure 14 of the photoproduct. An unambiguous structure proof was found in the independent synthesis¹² of 14 as outlined in Chart II.

(8) E. Wenkert and T. E. Stevens, *J. Am. Chem. Soc.*, **78**, 2318 (1956).

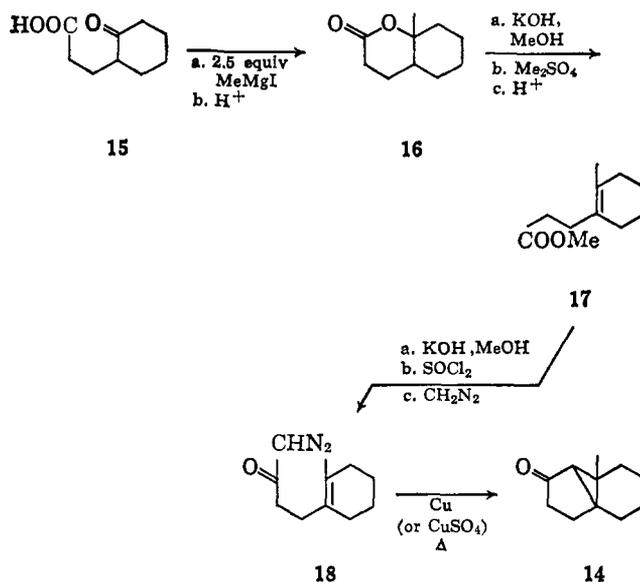
(9) E. C. du Feu, F. J. McQuillin, and R. Robinson, *J. Chem. Soc.*, 53 (1937).

(10) This degradative scheme is quite similar to that employed by H. Dutler, C. Ganter, H. Ryl, E. C. Utzinger, K. Weinberg, K. Schaffner, D. Arigoni, and O. Jeger, *Helv. Chim. Acta.*, **45**, 2346 (1962), and that of Zimmerman and Wilson.⁷ The hypobromite oxidation of photoketone 8 to diacid 10 has precedent in the latter reference.

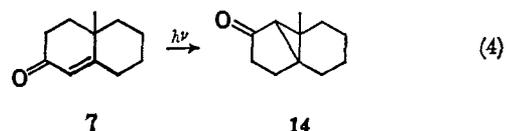
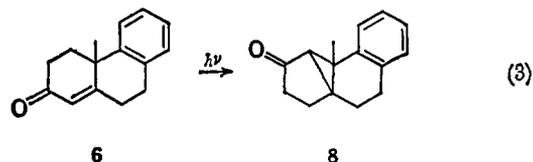
(11) Independent studies by O. L. Chapman (private communication) arrive at the same structural conclusions.

(12) A nonphotochemical synthesis of 14 utilizing an essentially identical last step has been reported by M. M. Fawzi and C. D. Gutsche,

Chart II



Thus the photochemical rearrangements of the phenanthrone 6 and octalone 7 may be pictured as



These reactions can be seen to be of type A.^{13a,b}

Mechanistic Results and Discussion. In initial agreement with the logic deriving from the rearrangement of 4,4-diphenylcyclohexenone (*vide supra*), it was observed that the preparative rearrangements of monoenones 6 and 7 proceeded much more slowly than the photochemical transformations of 4,4-diphenylcyclohexadienone and 4,4-diphenylcyclohexenone. More quantitative evidence was obtained from quantum yield studies (note Tables I and II) of the two rearrangements. The efficiency of the phenanthrone conversion (6 \rightarrow 8, eq 3) was only 0.0084 and that of the octalone reaction (7 \rightarrow 14, eq 4) was 0.0038 and thus also low. These reactions thus contrast with the rearrangement of 4,4-disubstituted cyclohexadienones¹⁴ where virtually every quantum of light is utilized in product formation, this despite both the reactions of the

J. Org. Chem., in press. We are indebted to Professor Gutsche for communicating these results to us prior to publication.

(13) (a) In contrast to the present results, M. B. Rubin, D. Glover, and R. G. Parker, *Tetrahedron Letters*, 1075 (1964), report irradiation of octalone 6 to give only high molecular weight material. Note also a similar report by Butenandt;^{33c} (b) O. Jeger and co-workers^{6c} have isolated an additional product in smaller yield. No corresponding product could be found in the present work, and it is conceivable that in their study this material was a product of further transformation; such a transformation would be mechanistically reasonable.

(14) For example, the rearrangement of 4,4-diphenylcyclohexadienone to 6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one (*cf.* ref 4a,b) has been shown (unpublished research by H. E. Zimmerman and J. S. Swenton) to have a quantum efficiency of 0.86. Parallelwise, M. H. Fisch and J. H. Richards, *J. Am. Chem. Soc.*, **85**, 3029 (1963), report the santonin to lumisantonin reaction to have a nearly unit efficiency.

Table I. Representative Phenanthrone Quantum Yields

Run ^a	Enone, <i>M</i>	Sensitizer or quencher, <i>M</i>	Quantum yield, Φ
1	1.42×10^{-2}	None	$8.40 \pm 0.84 \times 10^{-3}$
2	1.39×10^{-2}	Naphthalene, 9.90×10^{-3}	$4.93 \pm 0.49 \times 10^{-3}$
3	1.60×10^{-2}	Naphthalene, 3.2×10^{-2}	$2.32 \pm 0.23 \times 10^{-3}$
4	1.42×10^{-2}	Naphthalene, 6.19×10^{-2}	$2.00 \pm 0.20 \times 10^{-3}$
5	1.49×10^{-2}	Naphthalene, 6.79×10^{-2}	$1.74 \pm 0.17 \times 10^{-3}$
6	1.31×10^{-2}	Naphthalene, 7.79×10^{-2}	$1.41 \pm 0.14 \times 10^{-3}$
7	1.39×10^{-2}	Naphthalene, 9.60×10^{-2}	$1.23 \pm 0.12 \times 10^{-3}$
8	2.44×10^{-2}	Naphthalene, 7.78×10^{-2}	$1.18 \pm 0.18 \times 10^{-3}$
9	1.28×10^{-2}	Biphenyl, 9.37×10^{-2}	$6.70 \pm 0.67 \times 10^{-3}$
10	2.87×10^{-2}	(<i>t</i> -Bu) ₂ NO, 4.32×10^{-2}	$2.54 \pm 0.25 \times 10^{-3}$
11	1.65×10^{-2}	(<i>t</i> -Bu) ₂ NO, 2.19×10^{-2}	$2.90 \pm 0.29 \times 10^{-3}$
12	6.70×10^{-3}	Acetophenone, 0.200	$8.64 \pm 0.86 \times 10^{-3}$

^a All runs in *t*-butyl alcohol with filter A with $\lambda_{\max}(\text{trans})$ 337 m μ and transmission mainly 320–370 m μ . Inappreciable absorption by naphthalene and biphenyl quenchers; 10% by (*t*-Bu)₂NO taken into account.

Table II. Representative Octalone Quantum Yields^a

Run ^f	Solvent	Sensitizer or quencher, <i>M</i>	Quantum yield
1	<i>t</i> -BuOH	None	$3.8 \pm 0.4 \times 10^{-3}$
2	<i>t</i> -BuOH	Biphenyl, 5.90×10^{-4}	$3.8 \pm 0.4 \times 10^{-3}$
3	<i>t</i> -BuOH	FDM, ^b 4.40×10^{-4}	$3.2 \pm 0.3 \times 10^{-3}$
4	<i>t</i> -BuOH	Acetophenone, 0.267 ^c	$5.5 \pm 0.6 \times 10^{-3}$
5	MeOH	None	$4.0 \pm 0.4 \times 10^{-3}$
6	Benzene	None	$6.1 \pm 0.7 \times 10^{-3}$ ^d
7	Benzene	Acetophenone, 0.187 ^e	$13.4 \pm 1.3 \times 10^{-3}$
8	Benzene	Naphthalene, 2.90×10^{-4}	$4.30 \pm 0.4 \times 10^{-3}$

^a All runs with filter B with $\lambda_{\max}(\text{trans})$ 327 m μ and transmission mainly 305–365 m μ . ^b Ferric dipivaloylmethide. ^c C₆H₅COCH₃ absorbing 97% of the light. ^d Quantum yields of photoketone formation; by-products formed in benzene photolysis not included. ^e C₆H₅COCH₃ absorbing 99% of the light. ^f Octalone concentrations ranged from 0.006 to 0.011 *M*.

mono-enones and the dienones being structurally the same (*i.e.*, of type A).

In both the phenanthrone and octalone cases the reaction was found to proceed *via* the triplet excited state in analogy with the dienone examples.¹⁵ This may be seen by inspection of Tables I and II. In Table I it is seen that in run 12 under conditions where the acetophenone is absorbing virtually all of the light, the phenanthrone reaction (eq 3, 6 \rightarrow 8) proceeds with its usual efficiency (note run 1 in Table I). In the case of the octalone rearrangement (eq 4, 7 \rightarrow 14) the sensitized reaction (runs 4 and 7 Table II) has a greater efficiency than the ordinary unsensitized runs (1 and 6, same table). Were the acetophenone, which is absorbing essentially all the light in the sensitized runs, wasting this energy, then the quantum yields in these runs would be zero. This is not the case and we can conclude that an acetophenone excited state is transferring its excitation to the enone reactants. Now the concentration of enones used in the sensitization experiments was of the order of 7×10^{-3} *M*, a concentration sufficiently low so that acetophenone singlet excited-state species could not survive long enough to collide with enone molecules and excite

(15) Thus, 4,4-diphenylcyclohexadienone has been demonstrated to rearrange by way of its triplet excited state¹⁶ and santonin has been shown by Richards (note reference cited in footnote 14) to rearrange *via* the triplet.

(16) H. E. Zimmerman and J. S. Swenton, *J. Am. Chem. Soc.*, **86**, 1436 (1964).

these to enone singlet species. This assumes short-range energy transfer as seems likely for small molecules with weak transitions and in view of evidence²⁰ for absence of singlet transfer from acetophenone to biacetyl. The concentration is, however, sufficiently large to allow acetophenone triplets to collide with enone prior to their spontaneous decay.¹⁷ This is the basis of the original statement that the photosensitization is by triplet transfer.

Furthermore, the efficiency with which acetophenone singlets form acetophenone triplet molecules (*i.e.*, intersystem crossing) is known²² to be unity. Since the quantum yield of phenanthrone photoproduct 8 in sensitization runs is the same within experimental error as in the direct photolysis (note runs 1 and 12 in Table I), we can conclude that intersystem crossing in this case is very close to unit efficiency. Inspection of Table II shows that in the case of the octalone rearrangement there was an up to twofold increase in efficiency with photosensitization suggesting that intersystem crossing here was less than perfectly efficient. Nevertheless, in both systems the efficiency on sensitization did not change sufficiently to account for the very low quantum efficiency of the enone reactions on the basis of poor intersystem crossing. It is therefore certain

(17) The enone concentration in the sensitization experiments was of the order of 7×10^{-3} *M*. The bimolecular rate of diffusion in benzene has been estimated as *ca.* 10^{10} l. mole⁻¹ sec⁻¹;¹⁸ similarly, using the Debye equation,¹⁹ one can estimate the same constant for *t*-butyl alcohol as 2×10^9 l. mole⁻¹ sec⁻¹. Consequently the estimated pseudomolecular rates of collision of acetophenone excited states with enone become *ca.* 7×10^7 and 1.4×10^7 sec⁻¹ in benzene and *t*-BuOH, respectively. Since intersystem crossing to the triplet has been found²⁰ to be over 10^{11} sec⁻¹ for acetophenone, the destruction of singlet acetophenone is seen to be too fast for collision with enone. However, the rate of collision is seen to be larger than the rate of unimolecular decay of triplet acetophenone which has been measured²¹ as *ca.* 1×10^6 sec⁻¹ in *i*-PrOH at room temperature.

(18) (a) H. L. J. Bäckstrom and K. Sandros, *J. Chem. Phys.*, **23**, 2197 (1955); (b) note also F. Wilkinson, *Advan. Photochem.*, **3**, 241 (1964).

(19) P. Debye, *Trans. Electrochem. Soc.*, **82**, 205 (1942).

(20) F. Wilkinson and J. T. Dubois, *J. Chem. Phys.*, **39**, 377 (1963).

(21) S. G. Cohen, D. A. Laufer, and W. Sherman, *J. Am. Chem. Soc.*, **86**, 3060 (1964).

(22) (a) F. Wilkinson, *J. Phys. Chem.*, **66**, 2569 (1962), has shown that the benzophenone and acetophenone triplets sensitized the photodecomposition of 1-iodonaphthalene equally efficiently; from this we may conclude that, since benzophenone has an intersystem crossing efficiency of unity acetophenone does also; (b) C. A. Parker and C. G. Hatchard, *Analyst*, **87**, 664 (1962), have found the acetophenone phosphorescence quantum yield to be unity; (c) in the photoreduction of acetophenone by phenethyl alcohol a plot²¹ of $1/\Phi$ vs. $1/(\text{alcohol})$ gave an intercept of unity, again in agreement with a unity quantum yield of intersystem crossing; (d) G. S. Hammond, Vanderbilt University Photochemistry Symposium, May 14, 1965.

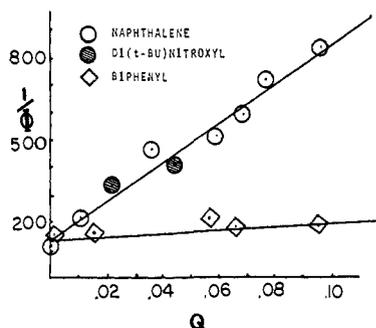


Figure 1. Reciprocal of quantum yield vs. quencher concentration (mole/l.).

that the low quantum efficiency may be attributed to inefficient reaction of the enone triplet once formed. In agreement, we find that the triplet is quenched by naphthalene at modest concentrations; note run (e.g.) 7 in Table I where the quantum yield of phenanthrone photoproduct is reduced to *ca.* one-seventh by the addition of 0.096 *M* naphthalene. In contrast the 4,4-diphenylcyclohexadienone rearrangement is unquenched by such naphthalene addition.¹⁶ Thus, even the rate of diffusion of naphthalene quencher is too slow to compete with the unimolecular rearrangement of the dienone while such diffusion (*ca.* 10^9 l. mole⁻¹ sec⁻¹) is rapid enough to destroy triplets in the enone case.²³

We might be tempted immediately to attempt to correlate the observed inefficient enone triplet rearrangement to some molecular feature. However, there remained the possibility that the low quantum yield was due to unusually rapid triplet degradation competing effectively with the rearrangement. As a consequence the rate of rearrangement of the triplet seemed important.

A plot of the reciprocal of the quantum yield of phenanthrone photoproduct *vs.* quencher concentration is given in Figure 1. If k_r is the unimolecular rate of rearrangement, k_q is the bimolecular rate of quenching, k_d is the unimolecular rate of triplet decay to ground state, E^* is the enone triplet concentration, and Q is the quencher concentration, we can see that $1/\Phi$ is given by

$$\frac{1}{\Phi} = \frac{\overbrace{k_r E^* + k_d E^* + k_q Q E^*}^{\text{all triplet processes}}}{\underbrace{k_r E^*}_{\text{only triplet process leading to product}}} = \frac{k_r + k_d}{k_r} + \frac{k_q Q}{k_r} \quad (5)$$

Hence the slope of the plot gives (k_q/k_r) and the intercept gives $(k_r + k_d)/k_r$. Quenching by naphthalene (triplet energy 61 kcal/mole) should be reasonably exothermic and diffusion controlled since the energy of the enone triplet appeared to be *ca.* 70 kcal/mole. To check this point, di-*t*-butylnitroxide²⁵

(23) In both the dienone and monoene examples, the quencher (naphthalene) triplet energy is sufficiently low (61 vs. 68.8 kcal/mole for dienone¹⁶) to ensure diffusion control of triplet destruction. Thus it has been estimated^{22a,24} that triplet transfers exothermic by more than *ca.* 3 kcal/mole are diffusion controlled.

(24) G. Porter and F. Wilkinson, *Proc. Roy. Soc. (London)*, **A264**, 1 (1961).

(25) A. K. Hoffmann, A. M. Feldman, E. Gelblum, and W. Hodgson, *J. Am. Chem. Soc.*, **86**, 639 (1964).

was used as a quencher²⁶ and it can be seen in Figure 1 that the efficiency of di-*t*-butylnitroxide quenching is the same as that of naphthalene within experimental error, a result reasonably understood if both quenching processes are diffusion controlled. If we now assume that $k_q = 2 \times 10^9$ l. mole⁻¹ sec⁻¹, the diffusion-controlled rate,¹⁷ we can solve for the unimolecular rate of rearrangement as $k_r = 2.9 \times 10^5$ sec⁻¹. Knowing k_r and the intercept we obtain $k_d = 3.9 \times 10^7$ sec⁻¹.

Thus, the relatively low quantum efficiency of the enone rearrangement does correlate with a relatively slow rate of rearrangement, one which is over four orders of magnitude slower than the dienone rearrangement.

It is interesting to note (Figure 1) that biphenyl quenches very inefficiently if at all. Biphenyl has been reported to have a triplet energy of 65.5 kcal/mole^{27a} (also 64 kcal/mole,^{27b} 65 kcal/mole^{27c}). A phosphorescence emission spectrum was obtainable²⁸ from the phenanthrone 6. This showed a 0-0 band at 401 m μ (*i.e.*, 71 kcal/mole) and poorly defined but discernable vibrational spacing of 1600 and 1760 cm⁻¹, corresponding to the ground-state stretching frequency of the C=O or C=C. Thus, one might have expected the transfer of triplet excitation to be sufficiently exothermic to occur efficiently.²⁹

Having established the dramatic inefficiency of the type A rearrangement of enones relative to dienones, both in terms of quantum yields and rearrangement rates, we felt it worthwhile to explore the reactivity of the phenanthrone 6 toward hydrogen abstraction. There was literature evidence that cyclohexenones formed pinacols in solvents having abstractable hydrogen atoms. The early work of Bergmann,^{33a} Inhoffen,^{33b} and Butenandt and co-workers^{33c} established the formation of pinacolic and cyclobutane dimeric products from the irradiation of 4-en-3-one steroids. Such dimers were also found in the more recent study of Jeger cited above.^{6c} This is in sharp contrast to the behavior of cyclohexadienones, for example, 4,4-diphenylcyclohexadienone,⁴ where rearrangement is much too fast to allow reaction of the excited triplet with an external species¹⁶ as a hydrogen donor, or for that matter, attack on an unexcited reactant molecule.

(26) It seems likely but not certain that quenching by this compound derives from its paramagnetic properties. It has a convenient "window" in the ultraviolet at 320-380 m μ (ϵ 3.1 in this region); the compound was unchanged under reaction conditions.

(27) (a) E. Clar, *Chem. Ber.*, **89**, 749 (1956); (b) A. Terenin and V. Ermolaev, *Trans. Faraday Soc.*, **52**, 1042 (1956); (c) G. N. Lewis and M. Kasha, *J. Am. Chem. Soc.*, **66**, 2100 (1944).

(28) The possibility invariably exists that such weak emission is due to a very small impurity; however, cyclohexenones have given, in our hands, weak emission ranging from 68 to 71 kcal/mole.

(29) One possibility is that the enone triplet is of lower energy or biphenyl of higher energy than estimated. A second rationale is that ground-state biphenyl, being twisted partially, is a nonvertical and slow energy acceptor.³⁰

(30) In contrast an interesting quenching by ferric dipivaloylmethide at *ca.* 10^{-5} *M* in benzene was observed for the octalone; this quenching to a quantum yield of 2.4×10^{-3} for 1.51×10^{-5} *M* quencher and 1.5×10^{-3} for 2.7×10^{-5} *M* quencher contrasts with the lack of quenching in *t*-BuOH. It finds some analogy in the work of Hammond^{31,32} with chelates where anomalously low concentrations were effective in quenching singlets.

(31) G. S. Hammond and R. P. Foss, *J. Phys. Chem.*, **68**, 3739 (1964).

(32) R. P. Foss, D. O. Cowan, and G. S. Hammond, *ibid.*, **68**, 3747 (1964).

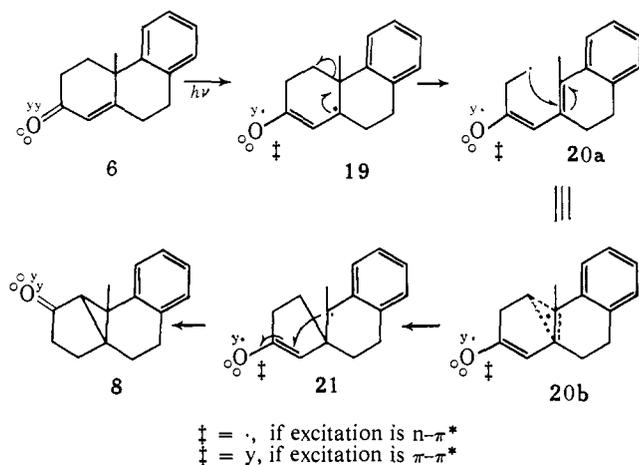
(33) (a) E. Bergmann and Y. Hirschberg, *Nature*, **142**, 1037 (1938);

(b) H. H. Inhoffen and Huang-Minlon, *Naturwiss.*, **27**, 1121 (1939);

(c) A. Butenandt, L. K. Poschmann, G. Failer, U. Schiedt, and E. Biekert, *Ann.*, **575**, 123 (1952).

We have proposed the mechanism in Chart III,^{1,44,45} however, with the assumption that the rearranging species is $n-\pi^*$.⁴⁶ The scheme in Chart II is written

Chart III



so that the symbol \ddagger , will represent a p_y , nonbonding electron if the excited species 19 is $\pi-\pi^*$ or instead will signify a π -system electron if triplet 19 has an $n-\pi^*$ configuration. In either case the mechanism requires at least partial fission of the 1-10 σ bond and is likely to be inefficient as observed.⁴⁷

Experimental Section

Synthetic and Structural Aspects Pertaining to Phenanthrone Photochemistry.⁴⁸ **4a-Methyl-4,4a,9,10-tetrahydro-2(3H)-phenanthrone.** A solution of 20.0 g (0.125 mole) of 1-methyl-2-tetraolone,⁴⁹ 10.5 g (0.15 mole) of methyl vinyl ketone, and 75 ml of *t*-butyl alcohol was stirred with cooling by an ice-water bath and a solution of 20.0 ml of 40% Triton B methoxide was slowly added over a period of 45 min. The deep red solution was stirred with cooling for an additional 2 hr and then for 12 hr at room temperature. One liter of water was added and the solution was extracted three times with ether. The combined ether extracts were extracted six times with water and the solvent was removed on a rotary evaporator. The orange-yellow solid (27.3 g) was recrystallized four times from ether with charcoal treatment and twice from hexane to give 4a-methyl-4,4a,9,10-tetrahydro-2(3H)-phenanthrone, mp 90–91° (lit⁸ mp 89–90°). A 2,4-dinitrophenylhydrazone, mp 200–202°, was prepared (lit⁸ mp 203–204°). The ultraviolet spectrum in 95% EtOH of the phenanthrone had a maximum at 237 m μ (log ϵ 4.15) with a shoulder at 273 m μ (log ϵ 2.69). In *t*-butyl alcohol a clearly separated $n-\pi^*$ maximum at 320 m μ (ϵ 48.5) was discernible.

(44) This mechanism was presented at the 9th Reaction Mechanisms Conference, Brookhaven, N. Y. June 1962; the stereochemistry was discussed; cf. also H. E. Zimmerman, *Advan. Photochem.*, **1**, 183 (1963).

(45) Species 20b in Chart III is merely species 20a in which the methylenic radical center is bonded to the 5-10 (steroid numbering) bond; simple MO considerations indicate some driving force for such bonding (*i.e.*, methyl radical + ethylene vs. cyclopropenyl radical). To the extent that species 20b intervenes to the exclusion of 20a, the reaction will proceed stereospecifically as has been noted by us earlier.⁷ The reaction is depicted in discrete steps for simplicity. However, a likely possibility is the beginning of 4-10 bonding in the penultimate step concerted with 1-5 bonding.

(46) There is an interesting point regarding rearrangements originating with $n-\pi^*$ species. There may be some cases in which, as the molecular transformation proceeds, the system subject to electron delocalization becomes sufficiently lengthened that the $\pi-\pi^*$ state becomes of lower energy resulting in internal conversion to this configuration.

(47) Another factor contributing to the low efficiency derives from the poor overlap of the C-5 orbital of the excited state with the 1-10 σ bond being broken. A distorted ring B is required for optimum overlap.

(48) All melting points were taken on Fisher-Johns or Monoscope hot stage apparatus corrected with compounds of known melting point.

(49) G. Stork, A. Brizzolara, H. Landesman, J. Szmuzkovic, and R. Terrel, *J. Am. Chem. Soc.*, **85**, 207 (1963).

Preparative Irradiation of 4a-Methyl-4,4a,9,10-tetrahydro-2(3H)-phenanthrone. In a typical run 2.65 g (12.5 mmoles) of the phenanthrone in 700 ml of anhydrous methanol was irradiated for 63 hr with a 450-w medium pressure Hanovia immersion well apparatus and using a Pyrex filter. Oxygen-free nitrogen was passed through the solution for 45 min prior to irradiation and a positive pressure was maintained during the run. The reaction was followed using silica gel thin layer chromatography (25% EtOAc-benzene) and by appearance of a new peak at 5.83 μ and disappearance of the 5.98- μ phenanthrone peak in the infrared. The reaction product was chromatographed on a 4 \times 86 cm silica gel column slurry packed in 2% ethyl acetate in benzene and eluted with 16 250-ml fractions of 3% ethyl acetate in benzene followed by ten such fractions using 5% ethyl acetate. Fractions 8-15 totalled 1.51 g (57% yield) of essentially pure photoproduct 8. Fraction 16 was essentially empty while fractions 17-25 contained 1.03 g (39% recovery) of phenanthrone reactant. Recrystallization of the material from fractions 8-15 raised the melting point slightly to 88.5–89.5°. In another run, separation was attempted using liquid-liquid partition chromatography;^{4b} although separation was imperfect, only two overlapping peaks were discernable and these afforded phenanthrone reactant and the same photoproduct 8. Thus silica gel rearrangement is precluded. Physical data on the product was as follows: infrared (carbonyl) 5.83 μ ; ultraviolet (95% EtOH) 240 m μ (log ϵ 3.89) maximum; nmr (CCl₄) τ 2.91 multiplet (4 H, aromatic), 7.42 multiplet (2 H, benzylic), 7.83 broad singlet (4 H, five ring), 7.99 singlet (1 H, methine), 8.07 singlet (2 H, β to aromatic), 8.50 singlet (3 H, methyl).

Anal. Calcd for C₁₅H₁₆O: C, 84.86; H, 7.60. Found: C, 84.60, 84.56; H, 7.56, 7.48.

Formylative Peroxide Degradation of Photoketone 8. To a solution of 250 mg of photoketone 8 and 4.7 ml of ethyl formate in 40 ml of anhydrous benzene was added in portions 900 mg of a 54% dispersion of sodium hydride in mineral oil. The mixture was stirred vigorously under nitrogen at room temperature for 14 hr followed by addition of 2 ml of methanol and dilution with ether. The solution was poured onto ice and the ether layer was extracted with 50 ml of ice-cold 2 *N* sodium hydroxide. The combined aqueous solution was acidified to pH 2 with 10% hydrochloric acid and extracted with ether. The dried extracts afforded 288 mg (99%) of an orange oil which solidified on standing. Recrystallization from hexane-chloroform gave a material: mp 149–150°; infrared (CHCl₃) 3.31, 6.01, 11.1, and 11.9 μ ; nmr singlet at τ -1.67 (1 H, hydroxyl), multiplet centered at 2.85 (5 H, aromatic + =CHO-), multiplet centered at 7.38 (4 H, five ring CH₂ + benzylic CH₂), singlet at 7.88 (2H, CH₂ β to aromatic), singlet at 7.97 (1 H, methine), singlet at 8.49 (3 H, methyl). This accords with formula of the hydroxymethylene derivative 9.

To 500 mg of the hydroxy ethylene photoketone in 75 ml of 2 *N* sodium hydroxide and 53 ml of methyl alcohol was added 18.7 ml of 30% hydrogen peroxide. There was slight warming on addition. The mixture was stirred for 13 hr at room temperature. The cooled solution was acidified to pH 3 with cold 50% sulfuric acid and diluted to 750 ml with water. The aqueous solution was extracted with ether and the ether extracts were washed with 2 *N* sodium hydroxide. The basic layer was acidified to pH 3 with cold 50% sulfuric acid and was extracted with ether. The dried ethereal extracts on concentration left 490 mg (91%) of a solid, mp 214–222°. Recrystallization from methanol-water gave 460 mg of material, mp 213–218°. Further recrystallization did not change the melting point. The material analyzed for 1-methyl-2,3-benzo-6-(carboxymethyl)-7-carboxybicyclo[4.1.0]heptane.

Anal. Calcd for C₁₅H₁₆O₄: C, 69.22; H, 6.20. Found: C, 68.85; H, 6.46.

The neutralization equivalent of the crystalline compound is in accord with its assignment as dicarboxylic acid 10.

Anal. Calcd for C₁₅H₁₆O₄: 130.15. Found: 130.7.

The infrared spectrum (KBr) of the diacid had an intense band at 5.91 μ ; nmr (hexadeuterioacetone) multiplet centered at τ 2.75 (4 H, aromatic), singlet at 6.97 (2 H, CH₂COO-), multiplet centered at 7.33 (2 H, benzylic CH₂), singlet at 8.42 (3 H, CCH₃). The remaining portion of the spectrum was obscured by solvent impurity.

Hypobromite Oxidation of Photoketone 8. To a 0° solution of 11.2 g of potassium hydroxide in 45 ml of water was added 3.5 ml of bromine. The cold mixture was added to a solution of 500 mg of photoketone in 250 ml of dioxane and the homogeneous solution was stirred at room temperature for 16 hr. Removal of most of the solvent *in vacuo* followed by addition of water (300 ml) and extraction with methylene chloride gave a basic aqueous layer which was

acidified to pH 3 with 10% hydrochloric acid and ether extracted. The extracts were dried and concentrated leaving 261 mg of acidic residue. This was taken up in chloroform and concentrated to 10 ml, and hexane was added to the warm solution to the point of cloudiness, whereupon solid crystallized. The solid (185 mg, 37%), mp 210–216°, was recrystallized from methanol–water to give material, mp 213–217°, whose infrared spectrum (KBr) was identical in every detail with the acid obtained in the preceding degradation.

1-Methyl-2,3-benzo-6-(carbomethoxymethyl)-7-carbomethoxybicyclo[4.1.0]heptane (11). Distilled ethereal diazomethane was added to 320 mg of 1-methyl-2,3-benzo-6-(carbomethoxymethyl)-7-carboxybicyclo[4.1.0]heptane in 85 ml of ether until the yellow color persisted. The mixture was allowed to stand for 45 min and the bulk of the ether and excess diazomethane was distilled, leaving 334 mg (100%) of a colorless oil which crystallized from hexane–chloroform: mp 143–145°; infrared (CCl₄) broad absorption 3–5, carbonyl band at 5.83 μ ; nmr (CCl₄) broad band at τ –1.31 (1 H, COOH), multiplet centered at 2.86 (4 H, aromatic), singlet at 6.42 (3 H, ester methyl), doublet at 6.95 (2 H, CH₂COO), a multiplet centered τ 7.34 (2 H, benzyl CH₂), multiplet centered at 7.91 (3 H methine + CH₂ β to aryl), singlet at 8.35 (3 H, methyl). This evidence indicates that the compound is the monomethyl ester of 1-methyl-2,3-benzo-6-(carboxymethyl)-7-carboxybicyclo[4.1.0]heptane.

To 300 mg of the monomethyl ester in 75 ml of ether was added a 4-mole excess of diazomethane in ether, and the mixture was allowed to stand for 18 hr at room temperature. Removal of the ether and excess diazomethane left 314 mg (100%) of a white solid, mp 93.0–95.0°. Recrystallization from hexane–ether gave white crystalline material, mp 94.0–95.0°.

Anal. Calcd for C₁₇H₂₀O₄: C, 70.81; H, 6.99. Found: C, 70.56, 70.68; H, 6.94, 7.06.

The infrared spectrum (CCl₄) showed bands at 3.30, split carbonyl at 5.75 and 5.78 μ ; nmr (CCl₄) pattern centered at τ 2.86 (4 H, aromatic), sharp singlet at 6.38 (3 H, COOMe⁵⁰), sharp singlet at 6.42 (3 H, COOMe⁵⁰), doublet at 7.04 (2 H, CH₂COO), quartet at 7.34 (2 H, benzyl CH₂), multiplet centered at 8.19 (3 H, methine + CH₂ β to aryl), singlet at 8.35 (3 H, CCH₃).

1-Methyl-1-carbomethoxymethyl-2-carbomethoxymethylenetetrahydronaphthalene (12). A 600-mg sample of 1-methyl-2,3-benzo-6-carbomethoxymethyl-7-carbomethoxybicyclo[4.1.0]heptane was refluxed in 10 ml of methanol with sodium methoxide (48 mg of sodium) for 4 hr. The mixture was cooled, diluted with water, and ether extracted, and the extracts were dried over sodium sulfate. Concentration *in vacuo* left 460 mg (77%) of a pale yellow oil. Liquid–liquid partition chromatography^{4b} was run using a 4.5 \times 150 cm thermostated column and 100:40:25:3 cyclohexane–DMF–ethyl acetate–water solvent system with 40% by weight of lower phase on Celite. There were two major peaks in the chromatogram. The first peak (retention volume 1500 ml) was identified as starting material by infrared and mixture melting point comparison. The second peak (retention volume 1720 ml) afforded 110 mg (59% based on recovered starting material) of a colorless oil which solidified on standing. Recrystallization of the solid from hexane–chloroform gave white crystalline material, mp 109–110°.

Anal. Calcd for C₁₇H₂₀O₄: C, 70.81; H, 6.99. Found: C, 70.65, 70.78; H, 6.93, 6.89.

The infrared spectrum (CCl₄) showed split carbonyl 5.76, 5.79, also 6.09 μ ; ultraviolet (95% EtOH): at 216 m μ maximum (4.17), 265 m μ shoulder (2.96), 273 m μ maximum (2.50); nmr (CCl₄) τ 2.94 multiplet (4 H, aromatic), 4.21 singlet (1 H, =CH–), 6.34 singlet (3 H, COOMe), 6.55 singlet (3 H, COOMe), quartet centered at 6.92 (4 H, six ring CH₂'s), 7.14 singlet (2 H, –CH₂COO), 8.38 singlet (3 H, CH₃C).

Ozonolysis of Unsaturated Diester 12. A Welsbach ozonizer operating at 0.045 mmole of ozone/min and the ozonization procedure of Turner⁵¹ were used. In 24 ml of ethyl acetate and 6 ml of glacial acetic acid was dissolved 375 mg (1.3 mmoles) of unsaturated diester 12. Ozone was passed for 26 min (1.3 mmoles) to the solution cooled to –20 to –30°. Then 15 ml of water and 6 ml of a 40% solution of peracetic acid in acetic acid were added and the mixture was allowed to stand at room temperature for 18 hr. The mixture was diluted with 200 ml of ether and washed successively with water and 5% sodium hydroxide. The ethereal

solution was dried over sodium sulfate and concentrated *in vacuo* leaving 267 mg of an oil. This was chromatographed on a 1.7 \times 46 cm silica gel chromatography column slurry packed in 2% ethyl acetate–benzene. The column was eluted with 500 ml of 2% ethyl acetate in benzene, 350 ml of 3% ethyl acetate–benzene, and 350 ml of 5% ethyl acetate–benzene. The crystalline solid (141 mg) from elution with 3% ethyl acetate–benzene was identical with starting material as judged by infrared and mixture melting point comparison. The clear oil obtained by elution with 5% ethyl acetate amounted to 79 mg (42% based on reacted diester) and declined to crystallize: infrared (CCl₄) 3.37, 3.49, 5.74, 5.81, and 6.90 μ ; nmr (CCl₄) τ 2.90 singlet (4 H, aromatic), 6.59 singlet (3 H, COOMe), multiplet centered at 6.99 (6 H, CH₂COO and six ring CH₂'s), 8.71 singlet (3 H, CH₃).

The 2,4-dinitrophenylhydrazone of 1-methyl-1-carbomethoxymethyl-2-ketotetrahydronaphthalene was prepared as yellow needles, mp 149–150°.

Anal. Calcd for C₂₀H₂₀N₄O₈: C, 58.25; H, 4.89; N, 13.59. Found: C, 58.43; H, 5.02; N, 13.50.

The infrared spectrum of the 2,4-dinitrophenylhydrazone derivative has bands at 2.98 and 5.78 μ . The identity of the ozonolysis product as 1-methyl-1-carbomethoxymethyl-2-ketotetrahydronaphthalene was confirmed by infrared and nmr comparison with a sample independently synthesized as described below as well as by infrared, nmr, and mixture melting point comparison of the 2,4-DNP derivatives.

1-Carbomethoxymethyl-2-ketotetrahydronaphthalene. A mixture of 2-tetralone (11.9 g, 0.0816 mole) and 9.00 g (0.127 mole) of pyrrolidine in 240 ml of anhydrous benzene was refluxed in a nitrogen atmosphere for 4.5 hr, the water formed in the reaction being removed with a Dean–Stark apparatus. The crude pyrrolidine, which was obtained on removal of the solvent, was refluxed for 12 hr with methyl bromoacetate (14 g, 0.913 mole) in 120 ml of anhydrous methanol. Addition of 25 ml of water and further heating for 1 hr was followed by dilution with 250 ml of water and ether extraction. The ethereal extracts were dried over sodium sulfate and concentrated, and the residue was distilled to give 10.3 g (56%) of 1-carbomethoxymethyl-2-ketotetrahydronaphthalene, bp 119–120° (0.1 mm), infrared split carbonyl at 5.74 and 5.81 μ ; nmr (CCl₄) τ 2.90 singlet (4 H, aromatic), 6.21 triplet (1 H, benzylic), 6.41 singlet (3 H, COOMe), multiplet centered at 6.99 (4 H, benzylic CH₂ + CH₂COO), multiplet centered at 7.56 (2 H, CH₂ α to C=O). The semicarbazone of 1-carbomethoxymethyl-2-ketotetrahydronaphthalene formed colorless monoclinic needles, mp 163–164°, from ethanol.

Anal. Calcd for C₁₄H₁₇N₃O₃: C, 61.08; H, 6.22; N, 15.26. Found: C, 60.91; H, 6.23; N, 15.29.

1-Methyl-1-carbomethoxymethyl-2-ketotetrahydronaphthalene (13). Following the general procedure of Bloomfield,⁵² 500 mg (0.0023 mole) of 1-carbomethoxymethyl-2-ketotetrahydronaphthalene dissolved in 5.0 ml of dimethyl sulfoxide was added to a mixture of 105 mg (0.0023 mole) of a 54.2% dispersion of sodium hydride in mineral oil in 10 ml of dimethyl sulfoxide. The mixture was stirred at room temperature for 45 min. To the dark red solution was added 392 mg (0.0028 mole) of methyl iodide in 2.0 ml of dimethyl sulfoxide. The reaction mixture was stirred for 17 hr at room temperature. The cooled, pale yellow solution was diluted with water and ether, and extracted, and the ethereal extracts were washed with water and dried over sodium sulfate. Evaporation of the solvent left 541 mg of a pale yellow oil. The residue was chromatographed on a 1.7 \times 47 cm alumina chromatography column (Fisher alumina, 80–200 mesh) slurry packed in 75% benzene–hexane. Elution was with 800 ml of 75% benzene–hexane followed by 700 ml of 90% benzene–hexane. The latter yielded 325 mg of a colorless oil (60%) whose homogeneity was demonstrated by the identity of the infrared of adjacent 200-ml fractions.

The infrared and nmr spectra of the colorless oil were identical in every detail with that of 1-methyl-1-carbomethoxymethyl-2-ketotetrahydronaphthalene obtained from the degradation of photoketone. The 2,4-dinitrophenylhydrazone of the compound formed yellow needles, mp 149–150°.

Anal. Calcd for C₂₀H₂₀N₄O₈: C, 58.25; H, 4.89; N, 13.59. Found: C, 58.06; H, 4.96; N, 13.68.

The mixture melting point of this material with the 2,4-DNP of 1-methyl-1-carbomethoxymethyl-2-ketotetrahydronaphthalene prepared by the degradation route (148–149°) was undepressed at 147.5–148.5°. The infrared and nmr spectra of the two derivatives were identical in all respects.

(50) G. V. D. Tiers, "Characteristic Nuclear Magnetic Resonance Shielding Values for Hydrogen in Organic Structures," Minnesota Mining and Mfg. Co., St. Paul, Minn., 1958.

(51) R. B. Turner, *J. Am. Chem. Soc.*, **72**, 579 (1950).

(52) J. Bloomfield, *J. Org. Chem.*, **26**, 4112 (1961).

Synthetic and Structural Aspects Pertaining to Octalone Photochemistry. $\Delta^{1,9}$ -10-Methyl-2-octalone. This was prepared by a modification of the method of Robinson.⁹ From 41.0 g (1.8 g-atoms) of sodium, 1600 ml of absolute ethanol, 200 g (1.8 moles) of 2-methylcyclohexanone, and 250 g (3.6 moles) of methyl vinyl ketone there was obtained 40.64 g (15.6%) of colorless $\Delta^{1,9}$ -10-methyl-2-octalone, bp 82–84° (0.5 mm).

Preparative Photolysis of $\Delta^{1,9}$ -10-Methyl-2-octalone. A solution of 5.00 g of $\Delta^{1,9}$ -10-methyl-2-octalone in 1850 ml of anhydrous methanol was irradiated for 72 hr through a Pyrex filter using a Hanovia type L 450-w mercury lamp and a positive pressure of oxygen-free nitrogen.

The colorless solution was concentrated *in vacuo* at 35° and the residue (4.73 g) was flash distilled through a 12-in. Vigreux column to give 3.81 g of colorless oil, bp 58–72° at 0.14 mm. This was subjected in portions to vpc on a 25 mm \times 2 m column packed with 15% Apiezon L grease on crushed firebrick at 170°. By this method 0.390 g (21% based on reacted starting material) of photoproduct, identified as 2-methyltricyclo[5.3.0^{1,7}.0^{2,7}]decan-10-one (14), was isolated.

Anal. Calcd for C₁₁H₁₆O: C, 80.44; H, 9.83. Found: C, 80.61; H, 9.85.

The semicarbazone had mp 170.5–171°. *Anal.* Calcd for C₁₂H₁₉N₃O: C, 65.13; H, 8.65; N, 18.99. Found: C, 65.07; H, 8.58; N, 19.06.

Retention time (argon as carrier gas, column pressure of 20 psi) was 36 min. Starting material (retention time 58 min) amounted to 3.16 g (63%). Two other photolysis products were obtained in yields of 2.5 and 1.6%. The retention times were 84 and 101 min, respectively.

2-Methyl-2-hydroxycyclohexanepropionic Acid Lactone. In a typical run, a solution of 23.28 g (0.136 mole) of 2-cyclohexanone-propionic acid,⁵³ mp 62.5–64.0°, in 260 ml of anhydrous ether was added with stirring over 1.5 hr to 2.5 equiv of methylmagnesium iodide prepared from 48.6 g (0.342 mole) of methyl iodide and 8.41 g (0.346 g-atom) of magnesium in 200 ml of ether. The addition was carried out at 0°, then the mixture was stirred at room temperature for 6 hr. The mixture was poured into ice, diluted with 1 l. of water, acidified to pH 2 with 10% hydrochloric acid, and ether extracted, and the ether extract was washed with 5% sodium bicarbonate solution to give after drying 16.62 g (72%) of the δ -lactone 16.^{54,55} The lactone was not further purified since distillation tended to cause rearrangement to what was believed to be the corresponding γ -lactone.

Methyl 2-Methyl-1-cyclohexene-1-propionate. In a typical run, 9.53 g (0.056 mole) of δ -lactone and 3.25 g (0.058 mole) of potassium hydroxide in 50 ml of methanol was refluxed for 10 min. The solution was concentrated *in vacuo* to 25 ml, then heated with stirring to 40°. Without further heating of the solution, 10.7 g (0.085 mole) of dimethyl sulfate was added dropwise during 1 hr, the mixture becoming acidic (pH 2) near the completion. The mixture refluxed slightly from the exothermic reaction. It was allowed to stir at 50° for 1 hr more and then poured into 200 ml of water, and ether extracted. The ether extracts were washed with 5% sodium bicarbonate solution and concentrated *in vacuo* to yield 8.77 g of colorless oil. The oil was chromatographed on a 4.3 \times 75 cm column slurry packed with silica gel (650 g) in 5% ether in hexane. Elution of fractions 1 and 2 was with 1000 ml each of 1:10 ether-hexane, 3–5 with 500 ml each of 3:100 ether-hexane, 6–10 with 500 ml each of 3:50 ether-hexane, 11–14 with 500 ml each of 1:10 ether-hexane, 15 with 1000 ml of ether, and 16–18 with 1000 ml each of 1:10 chloroform-ether. Fractions 7–9 afforded 0.906 g (8.9%) of methyl 2-methyl-1-cyclohexene-1-propionate,^{54,55–57} 15–17, 7.23 g of the δ -lactone (76% recovery). The lactone was recycled to obtain a total yield of 2.25 g (21.8%) of the desired ester. In another run a boiling point 48–50° (0.005 mm) was observed for the ester.

Methyl 2-methyl-1-cyclohexene-1-propionate showed a single, sharp absorption maximum at 5.82 μ in the infrared carbonyl region. The nmr spectrum revealed a singlet at τ 6.38 (3 H, COOMe) and 7.73 (4 H) and complex absorption between τ 7.83 and 8.95 (11 H).

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(55) C. Chuang, Y. Tien and C. Ma, *Chem. Ber.*, **69**, 1494 (1933).

(56) A. A. Plentl and M. T. Bogert, *J. Org. Chem.*, **6**, 669 (1941).

(57) C. D. Nenitzescu and V. Prezemetzky, *Chem. Ber.*, **74**, 676 (1951).

Anal. Calcd for C₁₁H₁₆O₂: C, 72.49; H, 9.96. Found: C, 72.23; H, 9.66.

2-Methyl-1-cyclohexene-1-propionic Acid. In a typical run, a solution of 0.940 g (0.0052 mole) of methyl 2-methyl-1-cyclohexene-1-propionate and 0.45 g (0.008 mole) of potassium hydroxide in 30 ml of methanol was refluxed for 2 hr. The mixture was poured into water and ether extracted, and the aqueous phase was cooled in an ice bath and carefully acidified to pH 5 with 5% hydrochloric acid. Ether extraction gave 0.794 g (90.5%) of 2-methyl-1-cyclohexene-1-propionic acid. A 74.7-mg portion was further purified by gradient temperature molecular distillation in a 100 cm \times 8 mm tube. The material (49.3 mg) collected at 110° (0.005 mm) had the same infrared spectrum as the crude acid.

Anal. Calcd for C₁₀H₁₆O₂: C, 71.39; H, 9.59. Found: C, 71.11; H, 9.53.

2-Methyl-1-cyclohexene-1-propionyl diazomethane. In a typical run, a solution of 0.794 g (0.0047 mole) of 2-methyl-1-cyclohexene-1-propionic acid in 30 g (0.025 mole) of thionyl chloride was stirred at room temperature for 30 min and then refluxed for 15 min. Excess thionyl chloride was removed *in vacuo*, leaving 0.811 g (92.5%) of 2-methyl-1-cyclohexene-1-propionyl chloride characterized from its infrared spectrum and used directly.

A solution of 0.811 g (0.0043 mole) of 2-methyl-1-cyclohexene-1-propionyl chloride in 75 ml of ether was added dropwise to 150 ml of ether containing an excess of distilled ethereal diazomethane prepared from 8.5 g of DuPont EXR-101 bis(N-methyl-N-nitroso)-terephthalamide 509 in mineral oil and 70 ml of 40% aqueous potassium hydroxide. The mixture was stirred at room temperature for 1 hr. Removal of the ether under nitrogen left 0.743 g (88.9%) of the diazoketone characterized by infrared analysis and used directly in the following experiments.

2-Methyltricyclo[5.3.0^{1,7}.0^{2,7}]decan-1-one (14). A. Using **Copper Bronze.** The general method of Stork⁵⁸ was used. A solution of 0.467 g (0.0025 mole) of crude 2-methyl-1-cyclohexene-1-propionyl diazomethane in 50 ml of cyclohexane was stirred with a suspension of 0.101 g of copper bronze (Luco No. 16, Leo Uhlfelder Co., New York, analyzed for 99.5+ % copper) under reflux for 12 hr. After cooling, the mixture was filtered and concentrated under reduced pressure to afford 0.400 g of brown oil.

This was subjected to preparative vapor phase chromatography on a 25 mm \times 2 m column packed with Apiezon L grease on crushed firebrick at 170°. By this method 0.187 g (46.8%) of 2-methyltricyclo[5.3.0^{1,7}.0^{2,7}]decan-1-one was isolated; retention time 32.5 min (helium carrier gas, column pressure 20 psi).

Anal. Calcd for C₁₁H₁₆O: C, 80.44; H, 9.83. Found: C, 80.35; H, 9.68.

The semicarbazone had mp 170–171°. *Anal.* Calcd for C₁₂H₁₉N₃O: C, 65.13; H, 8.65; N, 18.99. Found: C, 65.20; H, 8.48; N, 19.14.

B. Using **Copper Sulfate.** The general method of Sorm⁵⁹ was employed. A solution of 0.312 g (0.0016 mole) of 2-methyl-1-cyclohexene-1-propionyl diazomethane in 50 ml of cyclohexane was stirred with a suspension of anhydrous cupric sulfate under reflux for 12 hr. After filtration, the solvent was evaporated under reduced pressure, leaving 0.284 g of brown, oily residue. Vapor phase chromatography as described in A afforded 0.095 g (35.4%) of 2-methyltricyclo[5.3.0^{1,7}.0^{2,7}]decan-1-one with a retention time of 35.5 min.

Pinacol of 4a-Methyl-4,4a,9,10-tetrahydro-2(3H)-phenanthrone. To 1.10 g (5.19 mmoles) of the phenanthrone in 150 ml of equal parts of acetic acid and isopropyl alcohol was added over 30 min with stirring sodium amalgam from 6.0 g of sodium and 300 g of mercury. An exothermic reaction ensued. The organic layer was poured into 600 ml of water and the solid which separated was filtered. This solid was dissolved in 50 ml of hot benzene and 100 ml of acetone was added. After 12 hr at 0°, crystals separated. The filtrate on concentration afforded after crystallization from benzene-acetone 400 mg (47%) of pinacol, mp 212–217°. Recrystallization from ethyl acetate brought the melting point to 219.0–222.5°. The infrared and silicic acid thin layer behavior was identical with that of the pinacol from photolysis.

Anal. Calcd for C₂₀H₃₄O₂: C, 84.46; H, 8.03. Found: C, 84.55; H, 7.98.

Photolysis in Isopropyl Alcohol. The phenanthrone (1.212 g, 5.71 mmoles) in 25 ml of isopropyl alcohol was irradiated for 24

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hr with a 100-w medium pressure lamp (GE A-100-H4, without envelope) in an immersion apparatus of Pyrex. A filter solution of 100 ml of 0.01 *M* bismuth trichloride in 10% hydrochloric acid, 17.5 g of copper sulfate pentahydrate, and 100 ml of 10 *N* hydrochloric acid and 2 l. of water was used. This had 3% transmission at 330 μ and zero at 320 and below. Positive pressure of oxygen-free nitrogen (below 20 ppm) was used. Following irradiation for 24 hr it was ascertained that the solution had remained transparent in the ultraviolet. The concentrated solution gave 1.253 g which was chromatographed on 500 g of acetic acid-deactivated⁶⁰ alumina slurry packed in benzene in a 4.0 \times 90 cm column which was then eluted with 1 l. of benzene, 1.5 l. of 5% ether-benzene, 2 l. of 10% ether, and 5 l. of 50% ether; 250-ml fractions were taken. Fractions 4-7 gave 816 mg of photoketone, mp 80-88°, 8 and 9 afforded reactant enone, mp 75-85° (96.0 mg). Fractions 27-38 gave 114 mg of pinacol-containing material; tlc (silicic acid, 50:50 EtOAc-benzene) showed little additional material. The later fractions were crystalline, mp 195-210°, and recrystallization from ethyl acetate gave 45 mg of pinacol, mp 217-220°.

Anal. Calcd for C₃₀H₃₄O₂: C, 84.46; H, 8.03. Found: C, 84.39; H, 8.23. Fractions 11-25 contained noncrystalline material free of the pinacol and were not investigated.

Lead Tetraacetate Cleavage of the Pinacol. The pinacol (75.5 mg, 0.177 mmole) in 10.0 ml of acetone was added all at once to recrystallized lead tetraacetate (104.4 mg, 0.236 mmole). Stirring was continued for 2.5 hr at 24° and the mixture was poured into water, ether extracted, and the solution dried. The residue after concentration weighed 78.1 mg and had an infrared almost identical with that of 4a-methyl-4,4a,9,10-tetrahydro-2(3H)-phenanthrone. Chromatography was on a 2 \times 50 cm column of silica gel slurry packed in 3% ethyl acetate in benzene; 200-ml fractions were collected. Fractions 7-11 contained the phenanthrone, mp 88-92° (58.0 mg), identified by infrared. Then 10% MeOH-benzene (500 ml) eluted the pinacol (9.7 mg, mp 190-210°) which was identified by infrared and tlc.

Photolysis of 4a-Methyl-4,4a,9,10-tetrahydro-2(3H)-phenanthrone. Determination of Product Ratio. The enone (1.697 g, 8.00 mmoles) in 35.0 ml of isopropyl alcohol was irradiated as described above in the preparative run, however, for 39 hr. The reaction was followed by the infrared of aliquots and at the end the reaction appeared to be 90% complete. The concentrate weighing 1.651 g was chromatographed on deactivated (with HOAc) alumina using a 4.0 \times 90 cm column slurry packed with 1% EtOAc-benzene. Elution was with 3 l. of 1%, 1 l. of 4%, 1 l. of 10%, and 2 l. of 25%, and 250-ml fractions were collected. Fractions 3-8 contained enone and the photoketone (total 1.208 g). Fractions 21-28 had pinacol as evidenced by infrared and tlc but only some of the fractions were crystalline (mp 195-210°, 295 mg).

The mixed fractions 5-8 of enone and photoketone were chromatographed on 450 g of silica gel on a 4.0 \times 90 cm column slurry packed in 3% EtOAc-benzene with 250-ml fractions. Photoketone was obtained in the first 4 l. of solvent and the total yield was 979 mg, mp 80-87°. Further elution from the silica gel column (1.5 l. of 10% EtOAc-benzene) gave 163 mg of recovered phenanthrone. The fractions containing pinacol were assayed (fractions 21-28, alumina column product, 285 mg) by solution in 35.0 ml of acetone and addition over 15 min to 300 mg (0.677 mmole) of lead tetraacetate at 25° with stirring for 2.5 hr. The usual work-up gave material which was impure enone. Chromatography as above on silica gel with 3% EtOAc-benzene afforded 161 mg of enone. Methanol eluted noncrystalline material which was shown by tlc not to be pinacol. Thus 57.7% photoketone, 9.5% pinacol, and 9.6% enone were obtained. In a run with 1.7965 g of enone in 130 ml of isopropyl alcohol, 48.4% photoketone, 10.9% pinacol, 31.0% enone were obtained.

Photolysis of the Phenanthrone in Isopropyl Alcohol with Naphthalene Present. A solution of the phenanthrone (1.751 g, 8.25 mmoles) and 284 mg (2.216 mmoles) of naphthalene was photolyzed as described for the unquenched run except that the time was 84 hr.

(60) Fisher alumina treated with 5% by weight 10% aqueous acetic acid.

An infrared spectrum showed the reaction to be about 60% complete and a ultraviolet spectrum indicated transparency in the region of initial absorption by the enone. Separation following the procedure outlined above gave 772 mg of photoketone, mp 80-97°, and 254 mg of pinacol-containing fractions which were assayed by lead tetraacetate cleavage to give 159 mg of enone. Thus 44.1% photoketone, 10.4% pinacol, and 28.6% enone were obtained.

Quantum Yield Determinations. The apparatus used was that described earlier⁶¹ using a 1000-w AH6 lamp and parabolic reflector, three-compartment filter cells, and double-compartment reaction and actinometric cells. The nitrogen atmosphere was purified by the vanadous ion method of Meites.⁶² Monitoring of nitrogen purified in this way showed⁶³ it to contain less than 10 ppm of oxygen. Quantum yields were carried out at 25 \pm 0.04° and 27 \pm 0.04°. Each determination consisted of a first and third run with actinometer solution in cells 1 and 2 and a second run with reactant in cell 1 and actinometer in cell 2. Uranyl oxalate and potassium ferrioxalate actinometry was used and these were cross checked. The constancy of light was monitored with a phototube following the filters.

In both the octalone and phenanthrone studies the filter solutions were preceded by a Corning Corex D (9700) filter cutting off below 276 μ . In the phenanthrone work the three 2.4-cm filter cells contained in order: distilled water, a solution of 300 g of CoSO₄·7H₂O plus 50 g of NiSO₄·6H₂O per liter of 3 *N* H₂SO₄, 16 g of SnCl₂·2H₂O per liter of 15% HCl. This filter had a maximum transmission of 55% at 340, zero transmission at 315 and 385, and main transmission 320-270 μ . In the octalone study the three compartments contained in order: a solution of 300 g of CoSO₄·7H₂O per liter of 10% H₂SO₄, 56.3 g of NiSO₄·6H₂O per liter of 10% H₂SO₄, and 50 g of CuSO₄·5H₂O per liter of 10% H₂SO₄. Since some variation was observed in absorption of filters prepared as above these were adjusted prior to use to standard transmission. The filter solution transmission properties were checked immediately after use.

In the phenanthrone study analysis was by quantitative column chromatography using silica gel (Davidson, 60-200 mesh) and 3% ethyl acetate in benzene after removal of solvent and acetophenone when used. With a 2.5 \times 100 cm column and 250-ml fractions, naphthalene was found in fractions 2-3, photoproduct in 9-16, and 17-24 were eluted to 25% EtOAc-benzene. The conversions in the phenanthrone series were run to 5% or less. The mass balance in *t*-butyl alcohol runs was generally better than 99%. Thus in run 1 of Table I 2.2558 g of enone was photolyzed. Chromatography gave 103 mg of photoketone and 2.150 g of recovered enone. In run 3, 2.5440 g of enone gave 35 mg of photoketone plus 2.506 g of recovered enone. The conversion to photoketone was thus essentially quantitative here.

For the octalone work the solvent was distilled and the residue analyzed by vpc with 15% Apiezon L on firebrick. Propiophenone was used as an internal standard to allow determination of the absolute amount of each component. Known mixtures were analyzed to calibrate the method and preparative runs were made in which the product corresponding to each peak was actually isolated and identified by infrared spectroscopy. In all cases the essentially exclusive volatile product under the low conversion conditions was the photoketone. This was formed quantitatively in *t*-butyl alcohol while some nonvolatile by-product formed in benzene. For example, in one run corresponding to 1 in Table II, 4.49% photoketone and 96.70% of recovered octalone were obtained with no other significant vpc peaks.

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