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PHOTOCHEMISTRY OF 1,2-DIKETONES:

1,2-CYCLODECANEDIONE AND 2,3-PENTANEDIONE

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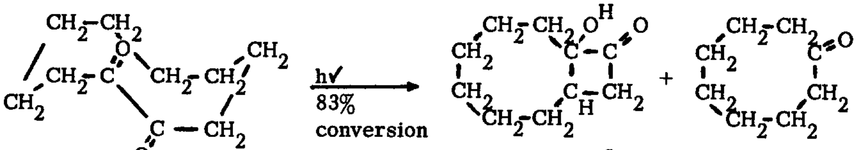
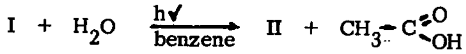
As with the symmetrical, acyclic vicinal-diones previously investigated[1], the photocyclizations of these substances give predominantly 2-hydroxycyclobutanones. Further mechanism studies have shown that the triplet state gives this reaction since it is photosensitized by benzophenone, and that with 4358 A° light quantum yields of this reaction with 2,7-dimethyl-4,5-octanedione may be higher than unity.

With 1,2-cyclodecanedione, an excellent yield (74%) is obtained of a substance otherwise difficult to prepare----1-hydroxybicyclo-[6.2.0]-decan-10-one (I) that undergoes novel photochemical cleavage concurrently to give cycloöctanone (II, 9%) and ketene.



I II



$$\text{I} + H_2O \xrightarrow[\text{benzene}]{h\nu} \text{II} + CH_3-C{\overset{O}{\underset{OH}{\lessgtr}}}$$

This result is unexpected since the photolysis of cyclodecanone gives decalols[2], and

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[1] W. H. Urry and D. J. Trecker, *J. Am. Chem. Soc.* **84**, 118 (1962).

[2] M. Barnard and N. C. Yang, *Proc. Chem. Soc.* 302 (1958). The irradiation (2537 A°) of cyclodecanone at 15° for 132 hours gives a 70% conversion to products containing *cis*-9-decalol (42%, based upon ketone consumed) and *trans*-9-decalol (10%). N. C. Yang, private communication.

"proximity" considerations with Fischer and Dunitz[3] models suggest that mixtures of hydroxybicyclodecanones should form.

1,2-Cyclodecanedione (15.0 g., 0.089 mole, b.p. 104-108° at 10 mm, m.p. 41-42°, prepared from ethyl sebacate[4] via 2-hydroxycyclodecanone[5,6]) in benzene (200 ml) in a Pyrex flask was irradiated (G. E. Sunlamp, 275 watts from 15 cm ; 70 hrs) until the yellow color faded. Analysis[7] of the reaction mixture gave cycloöctanone II (retention time 20.8 min , 9.3%), unreacted 1,2-cyclodecanedione (retention time 30.2 min , 16.7%), and 1-hydroxybicyclo-[6.2.0]-decan-10-one I (retention time 52.0 min , 74%). Distillation gave fractions containing mixtures of II and the dione, and then I (4.66 g, 0.028 mole, b.p. 75-79° at 1 mm, m.p. 49-50° from ligroin, i.r. 3400 and 1775 cm^{-1}. Anal. Calc'd for $C_{10}H_{16}O_2$: C, 71.4; H, 9.6. Found: C, 71.3; H, 9.4.). I gave a *p*-nitrophenylhydrazone (m.p. 204-205°. Calc'd for $C_{16}H_{21}N_3O_3$: N, 13.9. Found: N, 13.9.).

I (1.5 g., 0.0089 mole) was identified further by its reaction with periodic acid (2.1 g., 0.0092 mole) to give 2-oxocycloöctaneacetic acid[8] (1.35 g, 0.0074 mole, 83%, m.p. 70-71°. Anal. Calc'd for $C_{10}H_{16}O_3$: C, 65.2; H, 8.8. Found: C, 65.2; H, 8.6.). It gave the known phenylhydrazone[8] (m.p. 107-108°. Anal. Calc'd for $C_{16}H_{22}N_2O_2$: N, 10.2. Found: N, 10.4.).

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[3] E. Huber-Buser and J. D. Dunitz, *Helv. Chim. Acta*. **43**, 760 (1960). In these models, the two carbonyl groups were arranged as near to a trans coplanar configuration as possible. This detail is suggested by the long wavelength (λ_{max}, 395 mμ) of the A-band of the absorption spectrum of 1,2-cyclodecanedione. N. J. Leonard and P. M. Mader, *J. Am. Chem. Soc.* **72**, 5388 (1950).

[4] N. L. Allinger, *Organic Syntheses* **36**, 79 (1956).

[5] A. T. Blomquist, R. E. Burge and A. C. Sucsy, *J. Am. Chem. Soc.* **74**, 3636 (1954).

[6] A. T. Blomquist and A. Goldstein, *Organic Syntheses* **36**, 77 (1956).

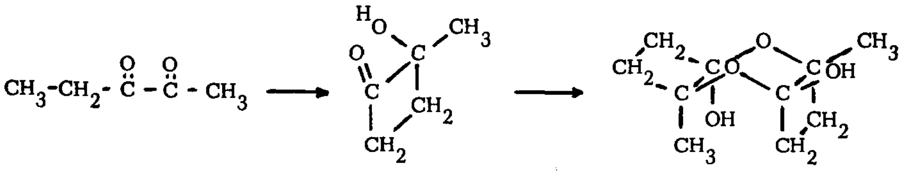
[7] Perkin-Elmer Vapor Fractometer, Model 154, 10ft. column with 30% Dow-Corning #710 Silicone oil on firebrick at 200° with a helium flow of 100 ml per minute.

[8] O. Schlichting and G. Scheuer, U.S. Patent 2,882,292 (1959). *Chem. Abst.* **53**, 21721 (1959).

Cycloöctanone (b.p. 50-52° at 1 mm, $n^{20}D$ 1.4718, i.r. 1695 cm^{-1}) was isolated by distillation in a subsequent experiment in which photolysis was continued (120 hrs) until the dione was consumed (its u.v. absorption at 395 $m\mu$ disappeared). Its 2,4-dinitrophenylhydrazone (m.p. 174-175°; m.p. of mixture with authentic sample 174-176° [9]) and p-nitrophenylhydrazone(m.p. 109-110°; mixed m.p. 109-111°. Anal. Calc'd for $C_{14}H_{19}N_3O_2$: N, 16.1. Found: N, 16.2.) were prepared.

Cycloöctanone and ketene probably are formed by photolysis of I since its long wavelength absorption band (λ_{max}, 3130 A°; ϵ, 35.5) extends into the available light (G. E. Sunlamp through Pyrex). I (2.0 g, 0.015 mole) in benzene (50 ml.) with added water (2.0 g) was irradiated (15 cm from Sunlamp, 44 hrs, 50°) with stirring. Water (25 ml) then was added, and titration with standard base (0.0821 N, 39.5 ml required, 0.0032 mole of acid) indicated that 22% of I had undergone this cleavage reaction. II (b.p. 53-55° at 1 mm, 2,4-dinitrophenylhydrazone m.p. 174-176°, no depression of mixed m.p.) was obtained by distillation of the benzene solution. The sodium acetate in the aqueous solution gave p-bromophenacyl acetate (m.p. 85-86°; m.p. of mixture with authentic sample 85-86°). Acetic acid similarly was shown to be a product when 1,2-cyclodecanedione in benzene was irradiated in the presence of water.

2,3-Pentanedione is the simplest of these diketones that can give this photocyclization reaction. Diminished statistics and the reduced reactivity of the primary hydrogens involved are manifest in the longer irradiation time required (224 hrs), the lower yield of 2-hydroxy-2-methylcyclobutanone (III, 49%), and enhanced side reactions. III upon standing gave a solid dimer, predominantly stereoisomer IVa.



III

IVa

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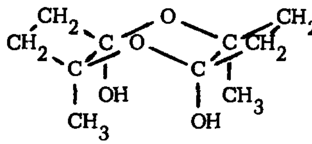
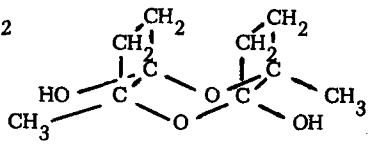
[9] P. J. Hamrick, C. F. Hauser and C. R. Hauser, J. Org. Chem. 24, 683 (1959).



IVb



IVc

2,3-Pentanedione (15.0 g, 0.15 mole, Matheson, b.p. 108-110°, $n^{25}D$ 1.4019) in benzene (0.75 M) was irradiated as in the above experiments. Analysis (vpc) and distillation gave recovered 2,3-pentanedione (3.6 g., 0.036 mole, 83%conversion), III (5.6 g, 0.056 mole, b.p. 75° at 6 mm, $n^{20}D$ 1.4524, i.r. 3400 and 1788 cm^{-1}. Anal. Calc'd for $C_5H_8O_2$: C, 60.1; H, 8.1. Found: C, 60.1; H, 8.0.), and a residue (5.7 g, i.r. indicated some III, average m.w. 306). A 2,4-dinitrophenylhydrazone (m.p. 169-170°. Anal. Calc'd for $C_{11}H_{10}N_4O_4$: N, 21.4. Found: N, 21.8.) was prepared from III. III with periodic acid gave 4-ketopentanoic acid (2,4-dinitrophenylhydrazone m.p. 205-207°[10]; p-nitrophenylhydrazone[11] m.p. 173-174°).

III solidified upon standing. Pure IV (white plates, m.p. 171-172°. Anal. Calc'd for $C_{10}H_{16}O_4$: C, 60.0; H, 8.1; m.w. 200. Found: C, 60.1; H, 8.3; m.w. 209.) was obtained by washing with ligroin and drying. The infrared spectrum of IV had no carbonyl absorption band (no 1788 cm^{-1}; OH at 3400 cm^{-1} present), but this band reappeared when IV was melted (IV → 2 III). IV gave the same 2,4-dinitrophenylhydrazone (m.p. 170-171°; mixed m.p. 170-171°) as III. These properties of IV indicate the dimeric, lactolide structure suggested above. Such products have been obtained from 2-hydroxycyclohexanone[12], 2-hydroxyethanal[13], 3-hydroxybutanone[14], and 2,2-diphenyl-2-hydroxyethanal[15].

The stereochemistry of this dimer IV is interesting. Since the two ring fusions are cis, the central dioxane ring is in the boat conformation in all of its stereoisomers. If conformational interconversion (boat-boat) were sufficiently slow,

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[10] M. A. Cowley and H. A. Schuette, J. Am. Chem. Soc. 55, 4365 (1933).

[11] F. Feist, Ber. 33, 2099 (1900).

[12] J. C. Sheehan, R. C. O'Neill and M. A. White, J. Am. Chem. Soc. 72, 3376 (1950).

[13] R. P. Bell and J. P. H. Hirst, J. Chem. Soc. 1777 (1939).

[14] W. Dirscherl and A. Schollig, Ber. 71B, 418 (1938).

[15] H. Wasserman, private communication.

three d,l-pairs (IVa, IVb, IVc and their respective antipodes) might be separated. However, it is likely that boat-boat inversion occurs so rapidly in liquids at ordinary temperatures that only an optically-inactive form (d-IVa $\rightleftarrows$ l-IVa; K = 1 since the antipodes are of equal energy), and an optically-active form (d-IVb, d-IVc, l-IVb, and l-IVc at equilibrium) would exist.

Nuclear magnetic resonance studies with IV (10% in dimethylsulfoxide: 2 equal CH_3peaks, τ, 8.86 and τ, 8.80; a CH_2 multiplet, τ_{center}, 8.26; and 2 equal OH peaks, τ, 3.5 and τ, 1.1. 20% in dimethylsulfoxide: CH_3 and CH_2 the same; and 2 equal OH peaks, τ, 4.3 and τ, 1.6. Relative peak areas: CH_3, 6; CH_2, 8; and OH, 2.) suggest that its structure is the equilibrium mixture of IVa and its antipode with the boat-boat inversion between them being too slow at room temperature for the methyl peaks or the hydroxyl peaks to coalesce[16]. Alternative explanations for these NMR results (IVb $\rightleftarrows$ IVc, $K \sim 1$; III $\rightleftarrows$ IV, $K \sim .75$ to give equal methyl or hydroxyl peaks) seem unlikely.

When the photocyclization is effected by triplet 4,5-octanedione (V) obtained predominantly with triplet-triplet conversion via benzophenone sensitization, its quantum yield is 1.6 times that involving the direct excitation of the dione[17,18]. Three matched pyrex tubes containing 1) V, 0.49 M, in benzene; 2) V, 0.49 M, and benzophenone, 0.49 M, in benzene; and 3) benzophenone, 0.66 M, in 2-propanol were sealed under vacuum after three freeze-pump-melt cycles, and were irradiated with equal intensities of 3660 A^{o} light (200 watt Hanovia high pressure lamp #54A36-S with cupric nitrate and Wratten 18A filters) until the yellow color of 2 had faded (132 hrs). Analysis of 1 (vpc) gave V (40 mole %) and 2-hydroxy-3-methyl-2-propylcyclobutanone (VI, 60 mole %), and of 2 showed V (3 mole %) and VI (97%). In 2, 93% of the 3660 A^{o} light was absorbed by the benzophenone. Benzpinacol (2.9 g., m.p. 186-187^{o}, 96%) was obtained from 3, and none was found in 2.

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[16] G. Claeson, G. Andros and M. Calvin, J. Am. Chem. Soc. **83**, 4357 (1961).

[17] H. L. J. Bäckström and K. Sandros, Acta Chem. Scand. **14**, 48 (1960).

[18] G. S. Hammond and P. A. Leermakers, J. Am. Chem. Soc. **84**, 207 (1962).

Quantum yields in ethanol at 25° determined with uranyl oxalate actinometry[19,20] are: with 4358 A° light; 2,7-dimethyl-4,5-octanedione → 3,3-dimethyl-2-hydroxy-2-[2-methylpropyl]-cyclobutanone, $\Phi = 1.13 \pm .12$; and 5,6-decanedione → 2-butyl-3-ethyl-2-hydroxycyclobutanone, $\Phi = 1.01 \pm .06$.

These results suggest two interesting alternatives. With the conservative view that the quantum yields are nearly unity within the experimental error, the process is overwhelmingly efficient with little quenching, or radiative or non-radiative decay, of excited states. With more liberal interpretation and to the extent that the aforementioned other fates of the excited states occur, the actual quantum yield of the photocyclization reaction may be appreciably higher than one. In the latter event, a short energy chain reaction may occur in which part of the ring closure reactions yield 2-hydroxycyclobutanone in its triplet state that then excites another dione molecule by triplet-triplet conversion.

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[19] W. G. Leighton and G. S. Forbes, J. Am. Chem. Soc. 52, 3139 (1930).

[20] For experimental details see D. J. Trecker, Doctoral Dissertation, University of Chicago, May 1962.