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PHOTOCHEMISTRY OF CERTAIN NON-ENOLIZABLE β-DIKETONES

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Abstract—Photochemical rearrangement of 2,2,5,5-tetramethyl-1,3-cyclohexanedione (I) yields predominantly an enol δ-lactone V with an exocyclic olefinic bond. A small amount of its more stable isomer VIII is also produced. Similar treatment of 2,2-dimethyl-1,3-cyclohexanedione (II) exclusively affords an exocyclic enol δ-lactone VI. These enol lactones V and VI are reconverted photochemically into the respective diketones I and II in low yields, while VIII gives fragmentation products. Photolysis of an open-chain diketone, 3,3-dimethyl-2,4-pentanedione (XVI), gives the isomeric enol ester XXI along with biacetyl and 1,4-diketone XX, whereas photolysis of 2-acetyl-2-methylcyclohexanone (XXII) involves the so-called Type II reaction leading to a ring-cleavage product XXVI. The mechanistic implications of the photochemistry of I, V and VIII have been discussed.

PHOTOCHEMICAL cycloaddition of enols of β-diketones such as acetyl-acetone has been investigated and has opened a valuable route to 1,5-diketones.[1] The photochemistry of non-enolizable β-diketones has been studied by several groups with respect to tetrabenzoylethylene[2] and dimethylketene dimer.[3] The present paper is mainly concerned with photochemical behaviour of three types of non-enolizable β-diketones as represented by I, XVI and XXII.

Photorearrangement of 2,2-dimethylated 1,3-cyclohexanediones. Irradiation of 2,2,5,5-tetramethyl-1,3-cyclohexanedione (I)[4] in benzene at room temp (high-pressure Hg arc, no filter, N_2 atmosphere) caused rearrangement giving a mixture of I and two isomeric enol lactones V and VIII (3:95:2) in 85% yield.[5-7] Similar treatment of 2,2-dimethyl-1,3-cyclohexanedione (II)[8] gave exclusively an enol δ-lactone VI in 70% yield. The structures of these lactones were established by the comparison with the specimens independently synthesized according to the published method[4a] in

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[1] [a] P. deMayo, H. Takeshita and A. B. M. A. Sattar, *Proc. Chem. Soc.* 119 (1962); [b] P. deMayo and H. Takeshita, *Canad. J. Chem.* **41**, 440 (1963); [c] G. Kornis and P. deMayo, *Ibid.* **42**, 2822 (1964); [d] H. Hikino and P. deMayo, *J. Am. Chem. Soc.* **86**, 3582 (1964).

[2] H. Schmid, H. Hochweber and H. von Halban, *Helv. Chim. Acta* **30**, 1135 (1947) and Refs cited therein.

[3] [a] N. J. Turro, P. A. Leermakers, H. R. Wilson, D. C. Neckers, G. W. Byers and G. F. Vesley, *J. Am. Chem. Soc.* **87**, 1613 (1965), and Refs. cited therein; [b] H. G. Richey, J. M. Richey and D. C. Clagett, *Ibid.* **86**, 3906 (1964); [c] I. Haller and R. Srinivasan, *Ibid.* **87**, 1144 (1965); [d] R. C. Cookson, M. J. Nye and G. Subrahmanyam, *Proc. Chem. Soc.* 144 (1964).

[4] [a] R. D. Desai, *J. Chem. Soc.* 1079 (1932); [b] $\lambda_{max}^{cyclohexane}$ 292 mμ (ε 52).

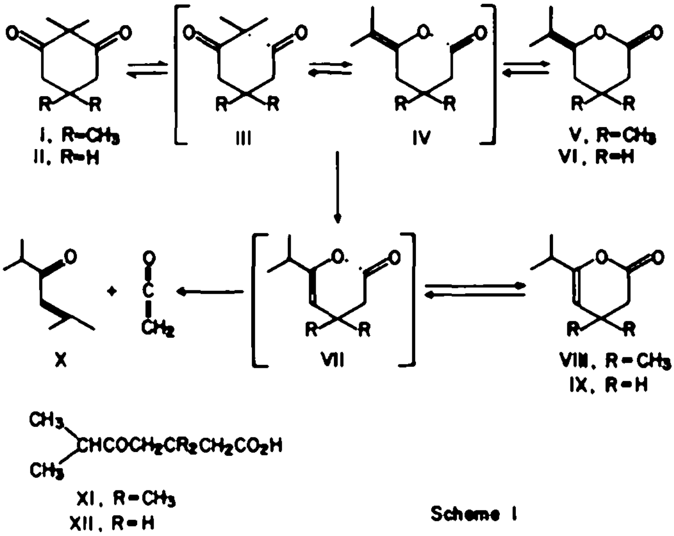
[5] The result has been briefly reported in a communication form: H. Nozaki, Z. Yamaguti and R. Noyori, *Tetrahedron Letters* 37 (1965).

[6] Similar results have been disclosed independently: [a] R. C. Cookson, A. G. Edwards, J. Hudec and M. Kingsland, *Chem. Commun.* 98 (1965); [b] H. U. Hostettler, *Tetrahedron Letters* 1941 (1965).

[7] Cookson *et al.* (Ref 6*a*) reported V was the sole product on irradiation of I in ethanol or cyclohexane with Pyrex-filtered light, but we observed formation of VIII under the same conditions.

[8] [a] I. N. Nazarov and S. I. Zav'yalov, *Zh. Obshch. Khim.* **23**, 1703 (1953); *Chem. Anstr.* **48**, 13667 (1954); [b] $\lambda_{max}^{cyclohexane}$ 285 mμ (ε 55).

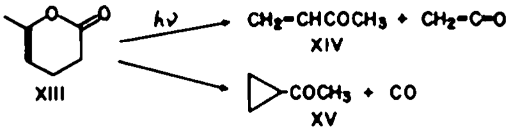
which the corresponding keto acids XI and XII were cyclized by means of acetyl chloride. This cyclization of XI and XII, however, has now been proved to give a mixture of V and VIII (38:62)[9] and a mixture of VI and IX (25:75), respectively. Thus, the preferential formation of the less stable exocyclic enol δ-lactone characterizes the photochemical rearrangement herein recorded.



Scheme I

Irradiation of the exocyclic enol lactone V[10] in benzene (high-pressure Hg lamp, Vycor, N_2 atmosphere) for 10 hr at room temp afforded a *pseudo*-equilibrium mixture of I, V and VIII, the product ratio being 3:95:2 which was notably similar to that obtained on photochemical transformation of I.

On the other hand 130 hr irradiation of the endocyclic enol lactone VIII under the same conditions yielded neither I nor the isomeric V, but 2,5-dimethyl-4-hexen-3-one (X) in 11% yield as an only isolable product. Irradiation of 0·1 molar cyclohexane solution of VIII gave a 46% yield of X. The structure of X was identified by IR, NMR and elemental analysis. The counterpart of this photo-cleavage product or ketene was not detected among the products, but irradiation conducted in the presence of ethanol gave ethyl acetate originating therefrom. Photolysis of an enol lactone XIII was reported to result in the decarbonylation along with loss of ketene molecule to afford XV and XIV, respectively,[11] but we did not observe the decarbonylation of VIII at all. The mechanism of these reactions will be discussed below.



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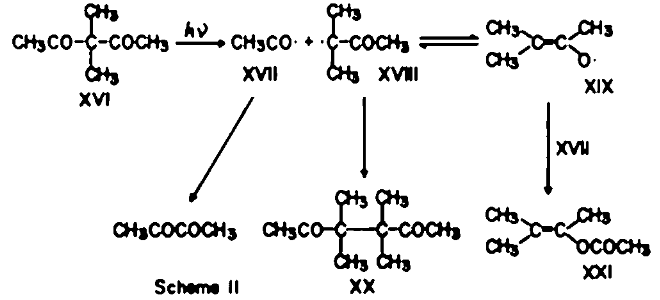
[9] Desai (Ref 4a) reported the simple formation of VIII in this cyclization, but with no proof. Both isomers are thermally stable and heating at 190° does not induce mutual interconversion.

[10] V: $\varepsilon_{220\,m\mu}^{cyclohexane}$ 5,250, VIII: $\varepsilon_{220\,m\mu}^{cyclohexane}$ 20,000.

[11] A. Yogev and Y. Mazur, *J. Am. Chem. Soc.* 87, 3520 (1965).

Photochemistry of 3,3-dimethyl-2,4-pentanedione. Attention was focused to the purely open-chain β-diketones. The photochemical reaction of 3,3-dimethyl-2,4-pentanedione (XVI)[12] was conducted as for I or II, but the results obtained were far more complicated. From the complex mixture the following products were isolated by GLC and identified (yields in parentheses): biacetyl (8%), 3,3,4,4-tetramethyl-2,5-hexanedione (XX; 33%), and the rearranged product, trimethylvinyl acetate (XXI; 20%). The structures were established by comparison with authentic specimens. The photolysis induces α-fission to produce radicals XVII and XVIII (Scheme II). The C-radical XVIII would be partly converted to the corresponding O-radical XIX, which subsequently recombines with acetyl radical to yield the enol ester XXI. Formation of biacetyl and the diketone XX is explained by assuming dimerization of the respective *free* radicals XVII and XVIII.



Scheme II

Photolysis of 2,2-dimethyl-1,3-diphenyl-1,3-propanedione and 2,2-dimethyl-1-phenyl-1,3-butanedione yielded intractable mixtures which were not further investigated.

Photochemistry of 2-acetyl-2-methylcyclohexanone. Another type of photochemical transformation was observed in the case of 2-acetyl-2-methylcyclohexanone (XXII).[13] Irradiation of the benzene solution of XXII (high-pressure Hg lamp, Vycor, N_2 atmosphere, 20 hr) at room temp followed by preparative GLC led to isolation of the following compounds (yields in parenthesis based on consumed XXII): biacetyl (trace amount), 2-methylcyclohexanone (XXIII; 6%), 3-methyl-7-octene-2,4-dione (XXVI; 14%) along with the starting material (35% recovery) and several unidentified components in small quantities. The open-chain diketone XXVI was identified by comparison with an authentic sample.[14] Rearrangement leading to 8-membered enol lactones could not be demonstrated.

In the photochemistry of XXII abstraction of the C_4—H by the excited carbonyl oxygen of the axial acetyl group (Scheme III) and the simultaneous cleavage of the C_2—C_3 bond supposedly yield the unsaturated β-diketone XXVI. This type of fission is reminiscent of Type II cleavage in aliphatic ketones.[15] To our best knowledge, this kind of ring-opening is without precedent. The α-fission products were

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[12] [a] C. R. Hauser and J. T. Adams, *J. Am. Chem. Soc.* 66, 345 (1944); [b] λ_{max}^{EtOH} 292 mμ (ε 173) [S. T. Yoffe, E. M. Popov, K. V. Vatsuro, E. K. Tulikova and M. I. Kabachnik, *Tetrahedron* 18, 923 (1962)].

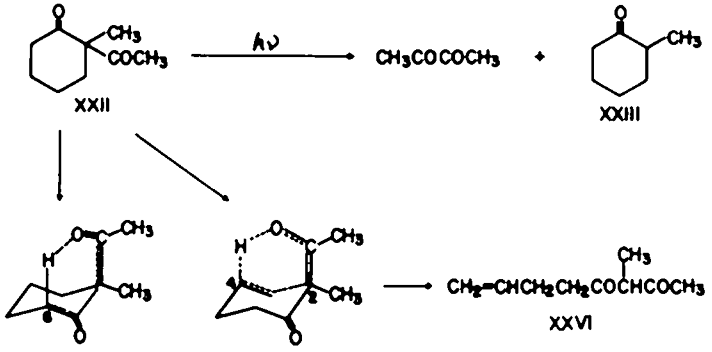
[13] [a] G. B. Payne, *J. Org. Chem.* 26, 4793 (1961); [b] $\lambda_{max}^{C_6H_6}$ 290 mμ (ε 400).

[14] G. Leser, *Bull. Soc. Chim. Fr.* (3) 27, 64 (1902).

[15] J. G. Calvert and J. N. Pitts, Jr., *Photochemistry* p. 382. Wiley, New York (1966).

also produced, but the ketene arising from possible abstraction of the C_6—H could neither be observed, nor trapped even in the presence of methanol.

Mechanistic studies on the photochemistry of I, V *and* VIII. The photorearrangement of cyclic β-diketones I and II would be consistently explained by Scheme I. The



XXV XXIV Scheme III

photoexcitation of I results in the fission of the C—CO bond (α-fission) giving the C,C-diradical III, which subsequently isomerizes to the C,O-diradical IV, and recyclizes to the enol lactone V. Rearrangement of III or IV to the C,O-diradical VII *via* 1,3-hydrogen migration occurs to a lesser extent and the subsequent radical recombination gives the isomeric lactone VIII. In order to obtain a further insight about this mechanistic interpretation the irradiation of I was carried out in certain solvents and the results were summarized in Table 1.

The involvement of n, π* triplet as a reactive species in this rearrangement was supported by the quenching effect of piperylene.[16, 17] Upon irradiation with light of wavelength longer than 350 mμ in the presence of benzophenone, however, the rearrangement did not proceed appreciably. The lack of benzophenone effect might be accounted for by assuming that the triplet energy of benzophenone (69 kcal/mole) is insufficient to excite I. On the other hand the direct photolysis was found to be remarkably accelerated in n-propyl bromide. This should be explained on the basis of the intermolecular heavy atom effect.[18] Finally, diketone I reacted about twice as fast in benzene as in cyclohexane under irradiation with Vycor filter. This would probably be rationalized by assuming the sensitization by benzene.[19]

Scheme I also involves the photochemistry of enol lactones V and VIII. In these

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[16] For piperylene as an efficient triplet energy acceptor, see [a] G. S. Hammond, P. A. Leermakers and N. J. Turro, *J. Am. Chem. Soc.* **83**, 2396 (1961); [b] P. Wagner and G. S. Hammond, *Ibid.* **88**, 1245 (1966).

[17] In the photochemistry of dimethylketene dimer, the chemically active excited state was claimed to be an n, π* singlet (Ref. 3*a*).

[18] [a] For the external heavy atom effects, see S. P. McGlynn, T. Azumi and M. Kasha, *J. Chem. Phys.* **40**, 507 (1964); [b] In the photodimerization of coumarin, *n*-propyl bromide as the solvent gave a high yield of triplet dimer; H. Morrison and H. Curtis, *Abstracts of Papers Presented at the Organic Chemistry Division, 151st National Meeting of the American Chemical Society* 55K. Pittsburgh, Pa., March (1966); [c] UV spectra of I in cyclohexane and in *n*-propyl bromide were compared but no appreciable change observed: $\lambda_{max}^{cyclohexane}$ 292 mμ (ε 52) and $\lambda_{max}^{n\text{-propyl bromide}}$ 292 mμ (ε 50).

[19] For the ability of benzene as a *solvent sensitizer*, see G. W. Griffin, J. Covell, R. C. Petterson, R. M. Dodson and G. Klose, *J. Am. Chem. Soc.* **87**, 1410 (1965).

latter cases, however, the interpretation is not so clear-cut as that of the β-diketone I. Upon irradiation in the presence of benzophenone (> 350 mμ, in cyclohexane), rearrangement of V and fragmentation of VIII did proceed to yield the same products as the ones obtained by the direct photolysis. The accurate comparison of the product distribution, however, could not be attained due to side reactions involved in the sensitized photolysis. These facts should imply that excited triplet states of V and VIII are able to induce chemical reactions, but the possibility of the direct photolysis proceeding *via* an excited singlet state cannot be excluded.

TABLE 1. PHOTOCHEMISTRY OF 2,2,5,5-TETRAMETHYL-1,3-CYCLOHEXANEDIONE (I)[a]

Solvent	Filter	Irradiation time (min)	Conversion[b] (%)	Distribution (%)[b]		
				I	V	VIII
Piperylene	Pyrex[c]	70	0	100	0	0[d]
Cyclohexane[e, f]	Pyrex[c] CuSO$_4$aq[g]	180	20	100	0	0[d]
n-Propyl bromide	Pyrex[c]	20	25	75	24	1
		40	61	39	58	3
		60	100	0	96	4[d, h]
Cyclohexane	Pyrex[c]	20	18	82	17	1
		40	44	56	43	1
		60	72	28	71	1
		130	85	15	84	1
		250	100	0	98	2[d]
Benzene	Vycor[i]	60	83	17	82	1
		120	94	6	92	2
		180	97	3	95	2[d]
Cyclohexane	Vycor[i]	60	43	57	41	2
		120	65	35	62	3
		180	73	27	70	3[d]

[a] Irradiation was effected externally on 0·1M soln in each solvent by means of a 200 W high-pressure Hg lamp.

[b] These values were obtained on the basis of peak areas of GLC.

[c] A Pyrex tube with 5 mm diameter and 40 mm length was used as a vessel.

[d] These values were practically unchanged even on prolonged irradiation.

[e] Benzophenone (2 mole ratio to I) was added.

[f] Benzopinacol was precipitated during irradiation.

[g] A 1·5 cm thick 10% CuSO$_4$soln was used as a filter.

[h] Formation of an unidentified product (ca. 15%) was observed.

[i] A Vycor tube with 15 mm diameter and 120 mm length was used as a vessel.

EXPERIMENTAL

All m.ps and b.ps are uncorrected. Microanalyses were performed at Elemental Analyses Centre of Kyôto University. NMR spectra were taken with Varian A 60 apparatus and chemical shifts are given in ppm from TMS internal standard. Unless otherwise stated, irradiation was effected externally by means of a 200 W high-pressure Hg lamp (quartz jacket) from a distance of 3 cm under N_2 atmosphere at room temp.

Photolysis of 2,2,5,5-tetramethyl-1,3-cyclohexanedione (I). A soln of I[4] (3·0 g; 18 mmoles) in benzene (400 ml) was irradiated without filter. Aliquots of the irradiated mixture were directly analyzed by GLC (High vacuum silicone grease 2 m; He as a carrier gas; 200°). After 2 hr irradiation a *pseudo*-photostationary state was attained, and there appeared two new peaks, *A* (relative retention time, 0·85; relative peak area, 2%) and *C* (1·66; 95%) along with *B* (1·00; 3%) which was shown to be the starting material. Trace amount of unidentified product (relative retention time, 1·10) was also formed. Concentration of the soln followed by distillation gave a colourless oil, b.p. 67–68°/2·5 mm, $n^{20}{}_D$ 1·4725, which was established to be *5-hydroxy-3,3,6-trimethyl-5-heptenoic acid δ-lactone* (V). IR (neat): 1760, 1692 and 1217 cm^{-1} (enol ester). NMR (CCl_4): δ 1·02 (6H, singlet, *gem*-dimethyl), 1·63 and 1·71 (6H, two singlets, isopropylidene methyl) and 2·26 (4H, singlet, methylene). (Found: C, 71·1; H, 9·3. $C_{10}H_{16}0_2$ requires: C, 71·4; H, 9·4%.)

The peak *A* was found to be 5-hydroxy-3,3,6-trimethyl-4-heptenoic acid δ-lactone (VIII) isomeric to V. IR (neat): 1770, 1683, 1240 and 1212 cm^{-1} (enol ester) and 1060 cm^{-1}. NMR (CCl_4): δ 1·03 and 1·08 (6H, two singlets, *gem*-dimethyl), 1·11 and 1·14 (6H, two singlets, isopropyl methyl), 1·90 2·70 (1H, multiplet, methine), 2·30 (2H, singlet, methylene) and 4·79 (1H, singlet, olefinic). (Found: C, 71·6; H, 9·7. Calc. for $C_{10}H_{16}O_2$: C, 71·4; H, 9·4%.) Independent synthesis of V and VIII was performed according to the method of Desai.[4e] Treatment of XI (18·6 g; 0·1 mole) and acetyl chloride (64 ml; 0·9 mole) afforded an oily mixture of V and VIII (38:62; 16·1 g; 90% yield). Fractional distillation through a spinning band column (theoretical 30 plates) yielded the lactone VIII (7·6 g), b.p. 103·5° 20·8 mm 102·6° 20·6 mm, n_D^{20} 1·4540 (lit.[4e] n_D^{19} 1·4547), and the lactone V (1·7 g), b.p. 120·6 121·2°/20·5 mm, n_D^{20} 1·4718. Their IR spectra were completely superimposable on those of photorearranged products from I.

The yield of the unidentified product (relative retention time, 1·10) reached ca. 15% when n-propyl bromide was used as the solvent.

Photolysis of I *in various solvents; general procedure*. A soln of I in various solvents was introduced to Pyrex or Vycor tube and irradiated under the conditions described in Table 1. The course of the reaction was monitored by GLC (Apiezon grease L 2 m; He as a carrier gas; 200°) with reference to the unirradiated samples. The results are summarized in Table 1.

Photolysis of the exocyclic enol lactone V. A 0·1 molar soln of V in benzene in a Vycor tube was irradiated. The course of the reaction was followed by GLC (High vacuum silicone grease; He; 200°). 10 hr irradiation yielded the same distribution of the products (I:V:VIII = 3:95:2) as the photolysis of I. A 0·1 molar soln of V in cyclohexane in a Vycor tube was similarly irradiated. After 2 hr the distribution of the products (I:V:VIII) was found to be 27:70:3 or in the same ratio as the photolysis of I in a Vycor tube. When 2 mole ratio of benzophenone was added to a 0·1 molar soln of V in cyclohexane and the mixture was irradiated by means of a 200 W high-pressure Hg arc (filtered by Pyrex glass and 10% $CuSO_4$ aq) at room temp for 1 hr, the same mixture (I:V:VIII = 10:87:3) was obtained, but low yields (35%) of this mixture should be attributed to side reactions.

Photolysis of the endocyclic enol lactone VIII. A soln of VIII (13·3 g; 79 mmoles) in benzene (220 ml) was irradiated in a Vycor tube. A new peak appeared at retention time of 0·33 relative to the starting material VIII. After 130 hr irradiation it amounted to 11%. At this point irradiation was intercepted and the mixture was concentrated. Distillation *in vacuo* gave an oil (2·0 g), b.p. 40 63°/70 mm, which was analyzed by GLC (High vacuum silicone grease 2 m; He; 150°) and a single component with retention time of 0·33 (VIII as standard) was isolated by preparative GLC. The following physical data established the structure of this component as X. IR (neat): 1690, 1623, 1380, 1175 and 1152 cm^{-1}. NMR (CCl_4): δ 0·98 and 1·09 (6H, two singlets, *gem*-dimethyl, 1·86 and 2·10 (6H, two doublets, isopropylidene methyl), 2·48 (1H, heptet, methine) and 6·00 (1H, multiplet, olefinic). (Found: C, 75·7; H, 11·3. Calc. for $C_8H_{14}O$: C, 76·7; H, 11·2%.) 2,4-Dinitrophenylhydrazone, m.p. 112° (lit.[20] 115-116°).

When 2 mole ratio of benzophenone was added to a 0·1 molar soln of VIII in cyclohexane and irradiated in a Pyrex tube with 10% $CuSO_4$ aq as a filter for 2 hr, the yield of X reached 6%.

Irradiation of VIII in cyclohexane (Vycor tube) for 2 hr gave 46% yield of X.

When a soln of VIII (0·17 g; 1 mmole) in EtOH (2 ml) was irradiated in a Vycor tube for 70 hr, AcOEt was detected among the reaction mixture by GLC (High vacuum silicone grease 2 m; He; 50°).

Hydrolysis of 5-hydroxy-3,3,6-trimethyl-5-heptenoic acid δ-lactone (V). A soln of V (0·54 g; 3·2 mmoles) in alcoholic KOH aq (100 ml) was heated under reflux for 1 hr. Working up the mixture followed by

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[20] C. J. Timmons, *J. Chem. Soc.* 2613 (1957)

distillation *in vacuo* afforded XI (0·31 g; 60% yield) as a colourless oil, b.p. 150–154°/15 mm (lit.[4e] 160°/15 mm), n_D^{20} 1·4461 (lit.[4e] 1·4473). (Found: C, 64·8; H, 9·9. Calc. for $C_{10}H_{18}O_3$: C, 64·5; H, 9·7%.) Semicarbazone of XI, m.p. 154–155° (dec) (lit.[4e] 155° (dec)). (Found: C, 54·4; H, 8·8. Calc. for $C_{11}H_{21}O_3N_3$: C, 54·3; H, 8·7%.)

Photolysis of 2,2-dimethyl-1,3-cyclohexanedione (II). A soln of II (2·0 g; 14 mmoles) in cyclohexane (70 ml) was irradiated in a Pyrex tube. The course of the reaction was followed by GLC (Apiezon grease L 2 m; He; 200°) and after 12 hr irradiation the starting material II was completely consumed and another single peak with relative retention time of 1·65 (II as standard) was obtained. Concentration followed by distillation *in vacuo* gave an oil (1·4 g; 70% yield), b.p. 121°/16 mm. This was found to be *5-hydroxy-6-methyl-5-heptenoic acid δ-lactone* (VI). IR (neat): 1760, 1695 and 1230 cm^{-1}. NMR ($CDCl_3$): δ 1·68 (6H, doublet, isopropylidene methyl), 1·80–2·00 (2H, multiplet, methylene) and 2·33–2·80 (4H, multiplet, methylenes). (Found: C, 68·6; H, 8·9. $C_8H_{12}O_2$ requires: C, 68·5; H, 8·6%.) Lactone VI was independently obtained from cyclization of XII.[4e] The isomeric mixture consisted of VI and IX in a ratio of 25:75. The IR spectrum of VI thus obtained was completely superimposable on that of the photorearrangement product.

Irradiation of VI in cyclohexane (Vycor tube) for 2 hr gave a mixture of II and VI in a ratio of 1:2.

Hydrolysis of 5-hydroxy-6-methyl-5-heptenoic acid δ-lactone (VI). Hydrolysis of VI by means of alcoholic KOH aq gave the corresponding keto acid, b.p. 135–137°/13 mm (lit.[21] 138–140°/5 mm). (Found: C, 60·8; H, 9·2. Calc. for $C_8H_{14}O_3$: C, 60·7; H, 8·9%). Semicarbazone melted at 186–187° (lit.[21] 177–178°). (Found: C, 50·2; H, 8·1; N, 19·2. Calc. for $C_9H_{17}O_3N_3$: C, 50·2; H, 8·0; N, 19·5%.)

Preparation of 3,3-dimethyl-2,4-pentanedione (XVI). The method was essentially based on the recorded methylation procedure.[22] 3-Methyl-2,4-pentanedione (24·4 g; 0·21 mole), MeI (51 g; 0·36 mole), abs acetone (40 ml) and anhyd K_2CO_3 (28 g; 0·21 mole) were heated under reflux with stirring for 48 hr. Solids were removed by filtration and washed several times with acetone. Combined filtrates were concentrated and treated with $CuSO_4$ aq to remove unchanged starting material. Distillation gave XVI (25·2 g; 92% yield), b.p. 168–171° (lit.[12a] 172°). IR (neat): 1725, 1703, 1358, 1133 and 1105 cm^{-1}. (Found: C, 65·4; H, 9·6. Calc. for $C_7H_{12}O_2$: C, 65·6; H, 9·4%.)

Photolysis of 3,3-dimethyl-2,4-pentanedione (XVI). A soln of XVI (35·4 g; 0·28 mole) in benzene (500 ml) was irradiated through a Pyrex filter. The reaction was monitored by GLC (High vacuum silicone grease; He; 150°). After 20 hr irradiation, 97% of the starting material was consumed. GLC analysis indicated that the reaction mixture consisted of at least 9 components. Isolation by preparative GLC gave the following products: *A*, biacetyl (8% yield; relative retention time, 0·30), *B*, XXI (20%; 0·67), *C*, XX (33%; 2·8) along with the starting material (3%; 1·0). Other components could not be further investigated.

The peak *A* had the same retention time as an authentic sample of biacetyl and had characteristic odour as well as yellow colour. The peak *B* showed IR (neat) absorptions at 1765, 1710 and 1220 cm^{-1} (enol ester). The IR spectrum was superimposable with the authentic sample of trimethylvinyl acetate (XXI). (Found: C, 66·0; H, 9·9. Calc. for $C_7H_{12}O_2$: C, 65·6; H, 9·5%). The authentic specimen was prepared according to the method of Man *et al.*[23] The GLC analysis showed the product of this independent synthesis consisting of XXI (70%) and an isomeric 1,2-dimethyl-2-propenyl acetate (30%).

The peak *C* showed IR (neat) absorptions at 1703, 1385 and 1357 cm^{-1} and NMR (CCl_4) signals at δ 1·21 (12H, singlet, methyl) and 2·03 (6H, singlet, acetyl methyl). The IR spectrum was superimposable with the one of an authentic sample of XX,[24] b.p. 101–111°/23 mm (lit.[24] 108–115°/22 mm).

Photolysis of 2-acetyl-2-methylcyclohexanone (XXII). Irradiation was carried out with a soln of XXII (15·4 g; 0·1 mole) in benzene (160 ml) in a Pyrex tube for 60 hr. The photolysate was subjected to GLC separation (Apiezon grease L 2 m; He; 200°) and the following products were isolated: *A*, biacetyl (trace; relative retention time 0·08), *B*, XXIII (6% yield based on the consumed XXII; 0·37) and *C*, XXVI (14% yield; 0·69) along with the starting material XXII (35% recovery; 1·00) and some unidentified products.

Biacetyl and the ketone XXIII were identified by comparison of retention time on GLC and IR spectra with ones of the authentic samples. The unsaturated ketone XXVI showed IR (neat) absorptions at 3030,

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2995, 1740, 1705, 1640, 1605 (broad), 1420, 1360, 990 and 907 cm^{-1}. NMR ($CDCl_3$) spectrum consisted of signals at δ 1·33 (9/4H, doublet, methyl of keto form), 1·84 (3/4H, singlet, methyl of enol form), 2·11 (3/4H, singlet, acetyl methyl of enol form), 2·16 (9/4H, singlet, acetyl methyl of keto form), 2·30–3·00 (4H, multiplet, methylenes), 3·69 (3/4H, quartet, methine of keto form), 4·95, 5·12 and 5·68 (2H and 1H, ABX type, terminal methylene) and 16·50 (1/4H, singlet, enolic proton). The contribution of enol form in $CDCl_3$ solution was estimated to be 25%. The independent synthesis[14] also established the structure assigned. (Found: C, 70·1; H, 9·2. Calc. for $C_9H_{14}O_2$: C, 69·9; H, 9·3%.)

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