Photochemistry of βγ-Unsaturated Carbonyl Compounds. 3,3-Dimethyl-5,5-diphenylpent-4-en-2-one and 2,2-Dimethyl-4,4-diphenylbut-3-enal

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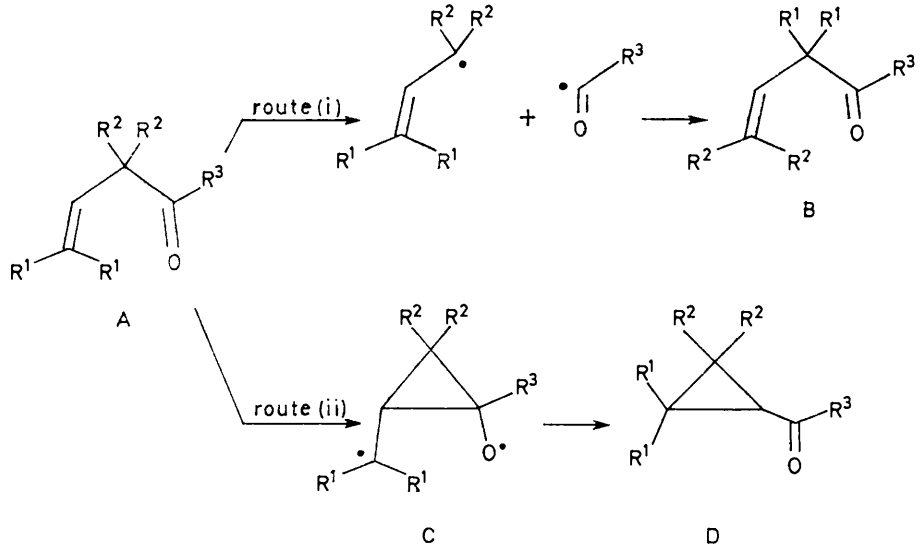
Irradiation of 3,3-dimethyl-5,5-diphenylpent-4-en-2-one (1) resulted in formation of 5-methyl-3,3-diphenylhex-4-en-2-one (3), an allylic rearrangement product arising from the singlet excited state. The product 2,2-dimethyl-3,3-diphenylcyclopropyl methyl ketone (8), was absent from both direct and acetophenone-sensitised irradiations. Irradiation of 2,2-dimethyl-4,4-diphenylbut-3-enal (2) resulted in decarbonylation.

THE photoreactions of βγ-unsaturated ketones have received considerable attention in recent years. Two major processes involving skeletal rearrangement [1] have been recognised for such systems (Scheme): (a) allylic rearrangement involving 1,3-acyl migration (A ⟶ B) and (b) cyclopropyl ketone formation involving 1,2-acyl migration (A ⟶ D). The singlet excited state appears to be responsible for the 1,3-acyl migration [1] whereas cyclopropyl ketone formation occurs from the triplet excited state.[1] Both rearrangements may be concerted, symmetry-allowed processes [1a] although it has been suggested that the 1,3-acyl shift involves α-cleavage followed by recombination of the intermediate acyl and allylic radicals [route (i)] [1b] and that an 'oxa-di-π-methane' intermediate (C) may be formed during the 1,2-acyl migration [route (ii)].[1c]



SCHEME

Most studies have been on cyclic systems and, when the work outlined here was begun, results for relatively few

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[1] (*a*) R. S. Givens, W. F. Oettle, R. L. Coffin, and R. G. Carlson, *J. Amer. Chem. Soc.*, 1971, **93**, 3957; (*b*) P. S. Engel and M. A. Schexnayder, *ibid.*, 1972, **94**, 4357; (*c*) W. G. Dauben, M. S. Kellogg, J. I. Seeman, and W. A. Spitzer, *ibid.*, 1970, **92**, 1786; (*d*) K. N. Houk, D. J. Northington, and R. E. Duke, jun., *ibid.*, 1972, **94**, 6233; (*e*) K. G. Hancock and R. O. Grider, *Tetrahedron Letters*, 1972, 1367; (*f*) J. Ipaktschi, *Chem. Ber.*, 1972, **105**, 1840.

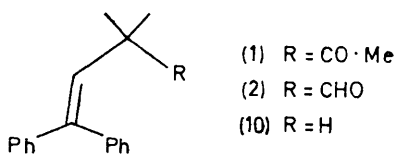
acyclic cases had been reported [2] and, except for some detailed studies with cyclopentenyl aldehydes,[3] little attention had been paid to the excited state reactions of βγ-unsaturated aldehydes. The solution photochemistry of the acyclic βγ-unsaturated carbonyl compounds 3,3-dimethyl-5,5-diphenylpent-4-en-2-one (1) and 2,2-dimethyl-4,4-diphenylbut-3-enal (2) was investigated. Treatment of aldehyde (2) [4] with methylmagnesium iodide followed by oxidation [5] of the resulting alcohol yielded (1).

RESULTS AND DISCUSSION

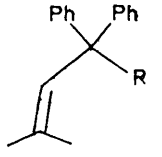
Irradiation of ketone (1) in benzene or propan-2-ol through a Pyrex filter resulted in the rapid production of a single ketonic photoproduct (3). More prolonged irradiation led to the formation of a complex hydrocarbon mixture with the simultaneous disappearance of both (1) and (3). The n.m.r. spectrum (Experimental section) indicated that photoketone (3) should be assigned the structure of the product arising from a 1,3-acetyl migration, 5-methyl-3,3-diphenylhex-4-en-2-one. Confirmation of this structure was obtained by catalytic hydrogenation of (3) to give ketone (4), which was obtained by an unambiguous route from the known carboxylic acid (5).[6] Catalytic hydrogenation of (5) provided the saturated acid (6) which was converted into the acid chloride (7). Subsequent treatment of (7) with dimethylcadmium yielded authentic ketone (4), identical with that derived from photoketone (3). Cyclopropyl ketone (8), synthesised for comparison purposes from 2,2-dimethyl-3,3-diphenylcyclopropanecarboxylic acid (9),[7,4b] could not be detected at any stage during the photochemical reaction.

Ketone (1) was irradiated in benzene in the presence of acetophenone as sensitiser under conditions where essentially all the light was being absorbed by the sensitiser. The βγ-unsaturated ketone (1) was consumed much more slowly than in the direct irradiations and a complex product mixture was obtained. Examination of the mixture at various stages during the reaction failed to reveal the presence of either photoketone (3) or cyclopropyl ketone (8).

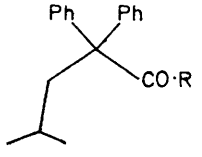
Irradiation of the aldehyde 2,2-dimethyl-4,4-diphenylbut-3-enal (2) in benzene yielded a mixture of the two possible isomeric decarbonylation products, 3-methyl-1,1-diphenylbut-1-ene (10) (major) [8] and 3-methyl-1,1-diphenylbut-2-ene (11) (minor),[9] identified by comparison with authentic specimens. Decarbonylation has been previously recognised as the major photoreaction of βγ-unsaturated aldehydes.[3]



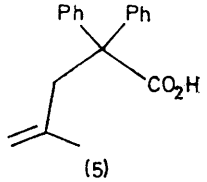
(1) R = CO·Me
(2) R = CHO
(10) R = H



(3) R = CO·Me
(11) R = H



(4) R = Me
(6) R = OH
(7) R = Cl



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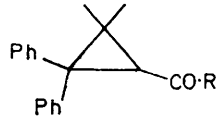
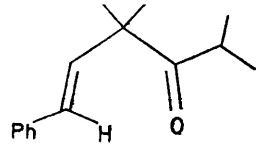


(8) R = Me
(9) R = OH

Attempted sensitised photoreaction of the βγ-unsaturated aldehyde (2) gave ambiguous results. Decarbonylation to a mixture of olefins (10) and (11) occurred, but this could possibly have resulted from competitive direct capture of light by the aldehyde.



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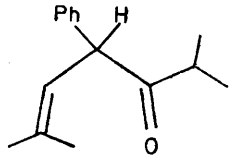
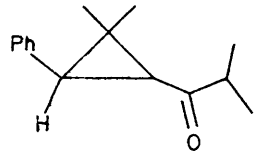


(13)



(14)

Since direct irradiation of methyl ketone (1) results in

[2] (*a*) L. P. Tenney, D. W. Boykin, jun., and R. E. Lutz, *J. Amer. Chem. Soc.*, 1966, **88**, 1835; (*b*) N. C. Yang and Do-Minh Thap, *Tetrahedron Letters*, 1966, 3671; (*c*) E. F. Kiefer and D. A. Carlson, *ibid.*, 1967, 1617.

[3] E. Baggiolini, H. P. Hamlow, and K. Schaffner, *J. Amer. Chem. Soc.*, 1970, **92**, 4906.

[4] (*a*) M. Julia and M. Baillarge, *Bull. Soc. chim. France*, 1966, 734; (*b*) H. E. Zimmerman and A. C. Pratt, *J. Amer. Chem. Soc.*, 1970, **92**, 6259.

[5] H. C. Brown and C. P. Garg, *J. Amer. Chem. Soc.*, 1961, **83**, 2952.

[6] R. T. Arnold and S. Searles, jun., *J. Amer. Chem. Soc.*, 1949, **71**, 1150.

[7] H. E. Zimmerman and P. S. Mariano, *J. Amer. Chem. Soc.*, 1969, **91**, 1718.

[8] P. Sabatier and M. Murat, *Ann. Chim.* (*France*), 1915, **4**, 296; K. v. Auwers, *Ber.*, 1929, **62**, 693.

[9] H. E. Zimmerman and A. C. Pratt, unpublished work.

formation of photoketone (3) and the latter is not observed during sensitised irradiations, it appears that ketone (3) is derived from a singlet excited state of (1). A similar result has been reported by Dauben and co-workers [1c] for the singlet excited state allylic rearrangement of the closely-related ketone (12) to (13). These 1,3-acyl migrations may be explained in terms of the ketonic α-cleavage mechanism [route (i)]. Competitive loss of carbon monoxide from the intermediate acyl radical would account for the ultimate formation of decarbonylation products in both cases. Alternatively, a concerted, symmetry-allowed 1,3-acyl migration [10] may be in competition with a less efficient α-cleavage reaction. These results for ketones (1) and (12) are in accord with those previously found for cyclic systems.[1a, d] Since Pyrex filtered light was used it seems likely that an $n \longrightarrow \pi^*$ excited state is responsible for the 1,3-acyl migration, particularly since it has been recently demonstrated that phenyl substitution on the carbon–carbon double bond is not essential for the success of the reaction in acyclic systems.[11]

Acetophenone-sensitised irradiation of ketone (12) was reported by Dauben *et al.*[1c] to result in 1,2-acyl migration to yield the cyclopropyl ketone (14) as sole product in 93% yield. This is in marked contrast to the present report where the corresponding cyclopropyl ketone (8) could not be detected. This difference in behaviour observed for the ketones (1) and (12) on acetophenone-sensitised irradiation is difficult to rationalise. Presumably in the case of ketone (1) a $\pi \longrightarrow \pi^*$ excited state associated with the diphenylethylene chromophore results from triplet sensitisation. Formation of cyclopropyl ketone (8) may be prevented by preferred geometrical isomerisation. Such isomerisation has been previously observed for a βγ-unsaturated ketone.[1e]

EXPERIMENTAL

Irradiations were conducted using a water-cooled immersion well with Pyrex filtered light from a 100 W medium pressure mercury vapour lamp. Photolysis solutions were purged with nitrogen for 30 min before irradiation and a slow stream was maintained during the irradiation. Solvents used in the irradiations were of analytical reagent quality. N.m.r. spectra were recorded in carbon tetrachloride as solvent with tetramethylsilane as internal standard. I.r. spectra are reported for liquid films unless otherwise indicated. Preparative thin layer chromatography (p.l.c.) was effected on Merck silica gel GF_{254}.

2,2-Dimethyl-4,4-diphenylbut-3-enal (2).—This aldehyde was synthesised as previously described.[4]

3,3-Dimethyl-5,5-diphenylpent-4-en-2-one (1).—The aldehyde (2) (6·0 g) in dry ether (50 ml) was slowly added to methylmagnesium iodide [from methyl iodide (4·5 g), magnesium (0·75 g), and ether (20 ml)]. The mixture was refluxed for 60 min and cooled to room temperature. Saturated aqueous ammonium chloride solution (100 ml) was added and the mixture extracted with ether. The extract was washed with water and dried ($MgSO_4$). Evaporation yielded an oil which was distilled to give *3,3-dimethyl-5,5-diphenylpent-4-en-2-ol* (4·9 g, 77%), b.p. 152° at 0·5 mmHg, $\nu_{max.}$ 3375 cm^{-1}, δ 0·78 (s) and 0·87 (s) (CMe_2), 1·10 (d, *J* 6 Hz, MeCO), 2·62br (s, exchangeable with D_2O, OH), 3·45 (q, *J* 6 Hz, OCH), 6·05 (s, C:CH), and 7·10 p.p.m. (m, aromatic) (Found: C, 85·95; H, 8·05. $C_{19}H_{22}O$ requires C, 85·7; H, 8·25%).

The carbinol (4·5 g) in ether (80 ml) was oxidised by dropwise addition, with stirring, of a solution of sodium dichromate dihydrate (4·2 g) and concentrated sulphuric acid (16 ml) in water (85 ml) while maintaining the temperature below 25°. Stirring was continued for a further 60 min. Extraction with ether followed by washing with water and 5% sodium hydrogen carbonate solution, drying, and concentration gave an oil which was distilled under reduced pressure to give *3,3-dimethyl-5,5-diphenylpent-4-en-2-one* (1) (3·9 g, 87%), b.p. 140° at 0·2 mmHg, $\nu_{max.}$ 1706 cm^{-1}, δ 1·12 (s, CMe_2), 1·90 (s, $CO{\cdot}CH_3$), 6·06 (s, C:CH), and 7·20 p.p.m. (m, aromatic) (Found: C, 86·0; H, 7·25. $C_{19}H_{20}O$ requires C, 86·35; H, 7·55%).

Direct Irradiation of 3,3-Dimethyl-5,5-diphenylpent-4-en-2-one (1).—A solution of methyl ketone (1) (1·012 g) in benzene (270 ml) was irradiated for 3 h. Removal of the solvent under reduced pressure gave a pale yellow oil. P.l.c. [three developments with 35% petroleum (b.p. 40—60°) in benzene] separated the material into three bands.

The material recovered from the fastest-moving band (160 mg) by chloroform extraction showed no carbonyl absorption in the i.r. spectrum, and the n.m.r. spectrum suggested that it contained a number of components.

The second band yielded an oil (282 mg) which was distilled to give *5-methyl-3,3-diphenylhex-4-en-2-one* (3), b.p. 138° at 0·2 mmHg, $\nu_{max.}$ 1708 cm^{-1}, δ 1·24 (d, *J* 1·5 Hz) and 1·87 (d, *J* 1·5 Hz) (C:CMe_2), 2·01 (s, $CO{\cdot}CH_3$), 6·17 (m, C:CH), and 7·25 p.p.m. (m, aromatic) (Found: C, 86·0; H, 7·25. $C_{19}H_{20}O$ requires C, 86·35; H, 7·55%).

The slowest-moving band contained only starting material (310 mg).

Similar results were obtained using propan-2-ol as solvent.

Acetophenone Sensitised Irradiation of 3,3-Dimethyl-5,5-diphenylpent-4-en-2-one (1).—A solution of methyl ketone (1) (500 mg) in benzene (200 ml) containing freshly distilled acetophenone (80 ml) was irradiated for 97 h. Benzene was distilled off and the acetophenone removed under reduced pressure (0·1 mmHg; bath temperature 45°). The resulting viscous oil was investigated spectroscopically and by t.l.c. Some starting material remained. No evidence for the presence of either photoketone (3) or the cyclopropyl ketone (8) could be obtained. The oil contained a complex product mixture.

Catalytic Hydrogenation of 5-Methyl-3,3-diphenylhex-4-en-2-one (3).—Photoketone (3) (165 mg) was dissolved in ethanol (20 ml) and hydrogenated in the presence of palladium black (Johnson Matthey & Co.) (50 mg). Uptake of hydrogen was complete after 2 h. Following filtration and removal of solvent, the residual oil was purified by short path distillation (0·05 mmHg; bath temperature 180°). The resulting oil was identical with a sample of authentic 5-methyl-3,3-diphenylhexan-2-one (4) (see below) as judged by t.l.c., and i.r. and n.m.r. spectroscopy.

5-Methyl-3,3-diphenylhexan-2-one (4).—4-Methyl-2,2-diphenylpent-4-enoic acid (5) was prepared by the literature method,[6] m.p. 121° (lit.,[6] 120·5—121·5°), δ 1·30br (s,

[10] R. B. Woodward and R. Hoffmann, 'The Conservation of Orbital Symmetry,' Verlag Chemie, Aschaffenburg, Germany, 1970, p. 96.

[11] (*a*) J. M. Conia and M. Bortolussi, *Bull. Soc. chim. France*, 1972, 3402; (*b*) P. S. Engel and M. A. Schexnayder, *J. Amer. Chem. Soc.*, 1972, **94**, 9252.

C:CMe), 3·15br (s, C:C·CH_2), 4·57br (s) and 4·67br (s) (C:CH_2), 7·22 (m, aromatic), and 12·30 p.p.m. (s, exchangeable with D_2O, CO_2H).

Hydrogenation of the acid (5) (3·5 g) in ethanol (20 ml) over palladium black (150 mg) gave *4-methyl-2,2-diphenylpentanoic acid* (6) (2·8 g, 79%), m.p. 124—125° (from benzene), $\nu_{max.}$ (Nujol) 2660br and 1690 cm^{-1}, δ 0·65 (d, *J* 6·5 Hz, CMe_2), 1·30 (m, CH), 2·32 (d, CH_2), and 7·23 p.p.m. (m, aromatic) (Found: C, 80·8; H, 7·65. $C_{18}H_{20}O_2$ requires C, 80·6; H, 7·45%).

Anhydrous cadmium chloride (5·0 g) was added to methylmagnesium iodide [prepared from magnesium (1·08 g) and methyl iodide (8·0 g) in ether (100 ml)]. The mixture was refluxed for 2 h and then ether (70 ml) was distilled off. Benzene (50 ml) was added and further distillate (35 ml) collected. A further portion of benzene (50 ml) was added and the mixture cooled to room temperature. A solution of 4-methyl-2,2-diphenylpentanoyl chloride (7) [from the acid (6) (1·35 g) and thionyl chloride (10 ml)] in benzene (25 ml) was added slowly with stirring and the mixture was then refluxed for 2 h. Water (50 ml) was added to the cooled mixture and the organic phase was separated, washed with water and 10% sodium carbonate solution and dried. Removal of the solvent gave a pale yellow oil (1·02 g). The n.m.r. spectrum showed it to be predominantly the required methyl ketone. It was purified by p.l.c. Elution with 5% ether in petroleum (b.p. 40—60°) gave *5-methyl-3,3-diphenylhexan-2-one* (4) (820 mg, 61%) which was distilled under reduced pressure, b.p. 135° at 0·2 mmHg, $\nu_{max.}$ 1705 cm^{-1}, δ 0·60 (d, *J* 6·5 Hz, CMe_2), 1·27 (m, CH), 1·93 (s, CH_3·CO), 2·20 (d, *J* 5·0 Hz, CH_2), and 7·27 p.p.m. (m, aromatic) (Found: C, 85·8; H, 8·5. $C_{19}H_{22}O$ requires C, 85·7; H, 8·25%).

2,2-Dimethyl-3,3-diphenylcyclopropyl Methyl Ketone (8).—Using the method described for 4-methyl-2,2-diphenylpentanoic acid (6) (see above), 2,2-dimethyl-3,3-diphenylcyclopropanecarboxylic acid (9) [7,4b] (1·2 g) was converted into the ketone (8). The crude product (950 mg) was purified by p.l.c. Elution with 5% ether in petroleum (b.p. 40—60°) gave the *cyclopropyl ketone* (8) (720 mg, 60%) which was distilled under reduced pressure, b.p. 146° at 0·3 mmHg, δ 1·08 (s) and 1·40 (s) (CMe_2), 2·32 (s, CH_3·CO), 2·52 (s, cyclopropyl H), and 7·20 p.p.m. (m, aromatic) (Found: C, 88·6: H, 7·85. $C_{19}H_{20}O$ requires C, 86·35; H, 7·55%).

Direct Irradiation of 2,2-Dimethyl-4,4-diphenylbut-3-enal (2).—A solution of aldehyde (2) (1·00 g) in benzene was irradiated for 2 h. Removal of the solvent gave a pale yellow oil. The n.m.r. spectrum showed that all the aldehyde had been consumed. P.l.c. [repeated development with petroleum (b.p. 40—60°)] gave two bands. The less polar band yielded an oil (722 mg) which was identified as 3-methyl-1,1-diphenylbut-1-ene (10) by comparison with an authentic specimen (see below). The more polar band yielded another oil (87 mg) which was shown to be 3-methyl-1,1-diphenylbut-2-ene (11) by comparison with an authentic specimen (see below).

3-Methyl-1,1-diphenylbut-1-ene [8] (10).—Reaction of ethyl isovalerate with excess of phenylmagnesium bromide in ether, followed by dehydration of the resulting carbinol with hydrochloric acid in glacial acetic acid yielded olefin (10).

3-Methyl-1,1-diphenylbut-2-ene [9] (11).—Reaction of isopropylidenetriphenylphosphorane in hexane [4b] with diphenylacetaldehyde [12] yielded olefin (11).

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[3/1191 *Received*, 8*th June*, 1973]

[12] H. E. Zimmerman and K. G. Hancock, *J. Amer. Chem. Soc.*, 1968 **90**, 3749.