Temperature Dependence in the Sensitized Photoreaction of 3,3-Dimethyloxepin-2(3*H*)-one and 2,2,7,7-Tetramethylcyclohepta-3,5-dien-1-one

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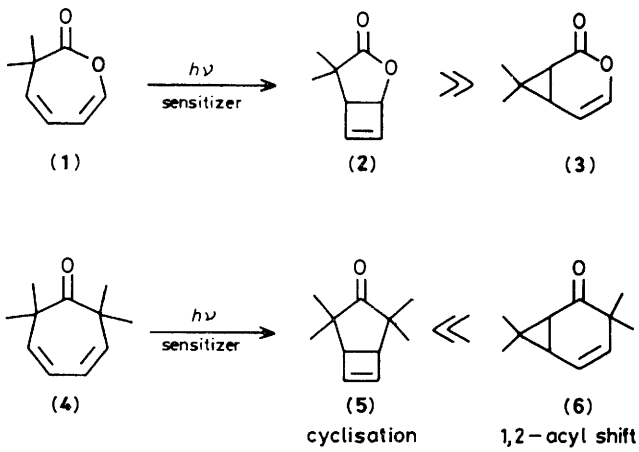
The triplet-sensitized photolysis of the title compounds (**1**) and (**4**) has been studied at various temperatures. 3,3-Dimethyloxepin-2(3*H*)-one (**1**) gave rise to the cycylisation product 4,4-dimethyl-2-oxabicyclo[3.2.0]hept-6-en-3-one (**2**) (major), and the 1,2-acyl shift product 7,7-dimethyl-3-oxabicyclo[4.1.0]hept-4-en-2-one (**3**) (minor, <5%), at room temperature. It was found that the (**3**) : (**2**) ratio depends upon the temperature applied for the photoreactions; the amount of (**3**) increased at higher temperatures (28% at 70 °C). The photoreaction of 2,2,7,7-tetramethylcyclohepta-3,5-dien-1-one (**4**) was also temperature dependent; an increasing amount of the cyclisation product 2,2,4,4-tetramethylbicyclo[3.2.0]hept-6-en-3-one (**5**), which is a hitherto unobserved product in the experiment run at room temperature, was produced at lower temperatures (34% at −60 °C). The results indicate that the thermodynamic activation parameters of each substrate in such systems play an important role in the preference of either of two competing photoprocesses, cyclisation or 1,2-acyl shift. A similar phenomenon was also observed in the photoreaction of 2,2,7-trimethyl-7-phenylcyclohepta-3,5-dien-1-one (**11**).

As part of a general study of the photochemical behaviour of 3-substituted oxepin-2(3*H*)-ones, we originally reported that triplet-sensitized photolysis of the 3,3-dimethyl derivative (**1**) at room temperature efficiently proceeded *via* a cyclisation to give 4,4-dimethyl-2-oxabicyclo[3.2.0]hept-6-en-3-one (**2**).[1] We have found, however, from re-examination of this photoreaction, that the 1,2-acyl shift (oxa-di-π-methane rearrangement) product, 7,7-dimethyl-3-oxabicyclo[4.1.0]hept-4-en-2-one (**3**) was also produced as a minor product (2.5—5% at room temperature). In contrast to the case of (**1**), 2,2,7,7-tetramethylcyclohepta-3,5-dien-1-one (**4**), a carbocyclic analogue of (**1**), had been shown to undergo exclusive 1,2-acyl shift to give only 3,3,7,7-tetramethylbicyclo[4.1.0]hept-4-en-2-one (**6**) on triplet-sensitized photolysis at room temperature.[2-4] Since the parent cyclohepta-3,5-dien-1-one produced only the cyclisation product,[5] the lack of formation of the cyclisation product 2,2,4,4-tetramethylbicyclo[3.2.0]hept-6-en-3-one (**5**) in the case of (**4**) was accounted for by the inhibition of cyclobutene ring closure due to severely increased steric interference of the methyl groups.[2] Schuster and his co-workers later found that the cyclobutene (**5**) was actually formed as one of four major products upon irradiation of (**4**) at 254 nm and, hence, (**5**) arose from the second singlet-excited state (S_2) of (**4**).[3] In the present paper, the sensitized photoreactions of both (**1**) and (**4**) at various temperatures are examined (Scheme 1). In disagreement with earlier work [2,3] the cyclisation of (**4**) leading to (**5**) is a possible photoprocess of the triplet excited state of (**4**); indeed, a considerable amount of (**5**) was produced upon sensitized photolysis at lower temperature. Also, the product distribution from (**1**) is greatly affected by reaction temperature, the amount of the 1,2-acyl shift product (**3**) increasing at higher temperature. Thus, both the triplet-photoreactions of (**1**) and (**4**) are temperature dependent, and the 1,2-acyl shift process has a higher energy barrier than the cyclisation process.†



Scheme 1.

Results and Discussion

A preparative-scale photoreaction of the oxepinone (**1**) at room temperature was carried out by irradiating an acetone (solvent and sensitizer) solution of (**1**) with a 500 W immersion-type high-pressure mercury lamp in an ordinary photoapparatus (see Experimental section). Two products were isolated by column chromatography (for the major product) and preparative gas–liquid partition chromatography (g.l.p.c.) (for the minor one). Elemental and spectroscopic analysis indicated that the major product was the cyclobutene γ-lactone derivative (**2**), while the minor one was the rearranged cyclopropano-δ-lactone derivative (**3**). The structure of (**3**) was confirmed by an alternative synthesis through the addition of 2-diazopropane to α-pyrone. Photoreactions at higher than room temperature were carried out in the following manner. A benzene solution of (**1**) and methyl 2-naphthyl ketone was placed in three Pyrex reaction tubes which were stoppered after flushing with nitrogen, set in a previously temperature-adjusted merry-go-round photoapparatus, and irradiated for 8 h with the same lamp as above. The conversion percentage and the ratio of products (**2**) and (**3**) were determined by g.l.p.c. analysis. As is clear from the results summarized in Table 1, the amount of the 1,2-acyl shift product (**3**) increased with a rise in reaction

† Several precedents for temperature-dependent triplet photoreactions have been reported: D. Gegiou, K. A. Muszkat, and E. Fischer, *J. Am. Chem. Soc.*, 1968, **90**, 3907; H. E. Zimmerman and W. R. Elser, *ibid.*, 1969, **91**, 887; P. J. Wagner and T. Nakahira, *ibid.*, 1973, **95**, 8474; N. Shimizu, M. Ishikawa, K. Ishikura, and S. Nishida, *ibid.*, 1974, **96**, 6456; R. O. Loutfy and P. de Mayo, *ibid.*, 1977, **99**, 3559; F. Barany, S. Wolff, and W. C. Agosta, *ibid.*, 1978, **100**, 1946; H. E. Zimmerman and R. T. Klun, *Tetrahedron*, 1978, **34** 1775.

Table 1. The value (**3**)/(**2**) at various temperatures obtained on irradiation of a solution of (**1**) (1.45×10^{-2}M) and methyl 2-naphthyl ketone (5.0×10^{-3}M) in anhydrous benzene[a]

Run	Temperature (° C)	Conversion[b] (%)	(**3**)/(**2**)[b,c]
1	70	100	0.39
2	60	96	0.27
3	50	78	0.20
4	40	80	0.13

[a] 8 h, with a 500 W high-pressure mercury lamp through Pyrex, under nitrogen. [b] Analysed by g.l.p.c. Average values of three experiments in each run. [c] No other product was detected.

Table 2. The value (**6**)/(**5**) at various temperatures obtained on irradiation of a solution of (**4**) (6.1×10^{-3}M) in anhydrous acetone

Run	Temperature (°C)	Conversion (%)	(**6**)/(**5**)[b,c]
1	−20	95	7.96
2	−40	96	4.15
3	−60	67	1.95
	[room temperature]	[70% yield]	[only (**6**)][d]

[a] 4 h, with a 100 W high-pressure mercury lamp through Pyrex, under nitrogen. [b] Analysed by g.l.p.c. Average values of three experiments in each run. [c] No other product was detected. [d] Preparative experiment by Paquette *et al.* (ref. 2).

temperature and reached *ca.* 28% yield in the photolysis at 70 °C.

The above finding indicates that a 1,2-acyl shift process by triplet sensitization would become favourable at higher temperatures in such a seven-membered dienone system and suggests that, in the case of the tetramethylcycloheptadienone (**4**), the cyclisation process leading to the cyclobutene derivative (**5**) would be observable in the triplet-sensitized photolysis under appropriate conditions. Thus, we examined the photolysis of (**4**) at below room temperature. Photoreactions were carried out in the following manner. Three Pyrex reaction tubes containing an acetone solution of (**4**) were stoppered after flushing with nitrogen and affixed to the exterior of the Pyrex immersion well. The whole photoapparatus was then placed in a cold methanol bath, previously cooled to a given temperature, and irradiated for 4 h with a 100 W high-pressure mercury lamp. The product distribution was analysed by g.l.p.c. The results are summarized in Table 2. Two products were isolated from a preparative-scale experiment, purified by preparative thin-layer chromatography (p.l.c.), and identified as the cyclobutene derivative (**5**) and the carene derivative (**6**) by comparison of the spectral properties with the reported ones.[2,3] As anticipated, the cyclobutene derivative (**5**) was apparently produced upon photolysis below room temperature. The yield increased on lowering the temperature, reaching about 34% [based on consumed (**4**)] at −60 °C. The results clearly indicate that the cyclisation of (**4**) to (**5**) does occur and that it competes with the 1,2-acyl shift leading to (**6**) in the reaction by triplet excitation, this being in disagreement with earlier findings.[2,3]

In both cases [compounds (**1**) and (**4**)] a plot of the logarithm of the ratio of the 1,2-acyl shift product [(**3**) or (**6**)] to the cyclisation product [(**2**) or (**5**)] against the reciprocal of the temperature results in a straight line. Apparent differences in the activation parameters between the two processes are estimated from the slope and intercept of the plot (Table 3). The results show that the 1,2-acyl shift process has a higher energy barrier than the cyclisation process, by *ca.* 7.7 for (**1**) and *ca.* 3.8 kcal mol^{-1} for (**4**), respectively. On the other hand, the entropy term is in favour of the 1,2-acyl shift. A higher energy barrier and a favourable entropy term for the 1,2-acyl shift are consistent with the previously postulated stepwise mechanism through the diradical intermediates (**7**) and (**8**) involving bond-breaking and -forming steps (Scheme 2). In the case of (**4**), the four methyl substituents adjacent to the ketonic function may stabilize greatly the diradical intermediate (**8**; X = CMe_2) facilitating the bond breaking in the precursory intermediate (**7**; X = CMe_2); the activation energy for the 1,2-acyl shift process may be significantly lower than that of the unsubstituted cycloheptadienone. In contrast, these substituents may destabilize enormously the (as yet undetected) twisted *cis-trans*-dienone intermediate (**10**), which had been proposed as the intermediate for the photochemical cyclisation of seven-membered diene systems.[2,3,6,7] As a result, the 1,2-acyl shift would become the exclusive photoprocess of the triplet excited state of the tetramethylcycloheptadienone (**4**) at room temperature; lowering the temperature would suppress the 1,2-acyl shift and allow production of the *cis-trans*-dienone (**10**), thus the cyclisation process would become observable.

Table 3. Activation parameter difference between the two processes

Substrate	ΔE_a (kcal mol^{-1})	$\Delta \log A$
(**1**)	7.7[a]	4.5[b]
(**4**)	3.8[c]	4.2[d]

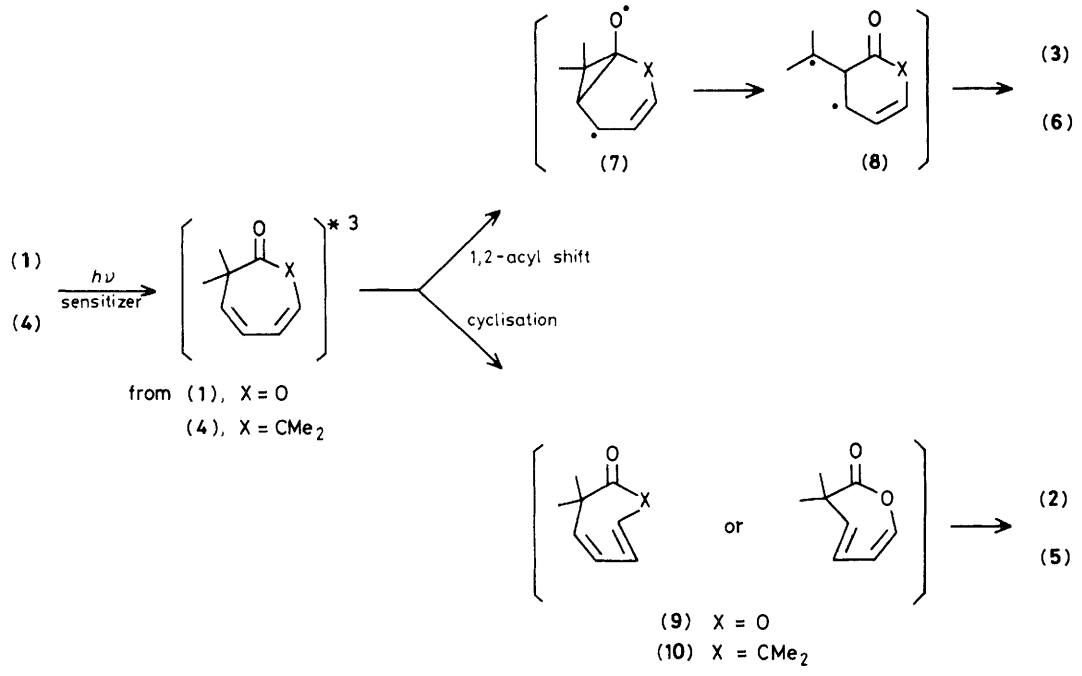
[a] [E_a for (**3**) (1,2-acyl shift)] − [E_a for (**2**) (cyclisation)]. [b] Log{[A for (**3**)]/[A for (**2**)]}. [c] [E_a for (**6**) (1,2-acyl shift)] − [E_a for (**5**) (cyclisation)]. [d] Log{[A for (**6**)]/[A for (**5**)]}.

In the case of (**1**) it is conceivable that the 1,2-acyl shift process of the lactonic carbonyl functionality would be thermodynamically less favourable than that of a ketonic group and that almost no effect would be expected for the formation of the *cis-trans*-dienone intermediate (**9**). Thus, the cyclisation to (**2**) is the most efficient pathway at room temperature.

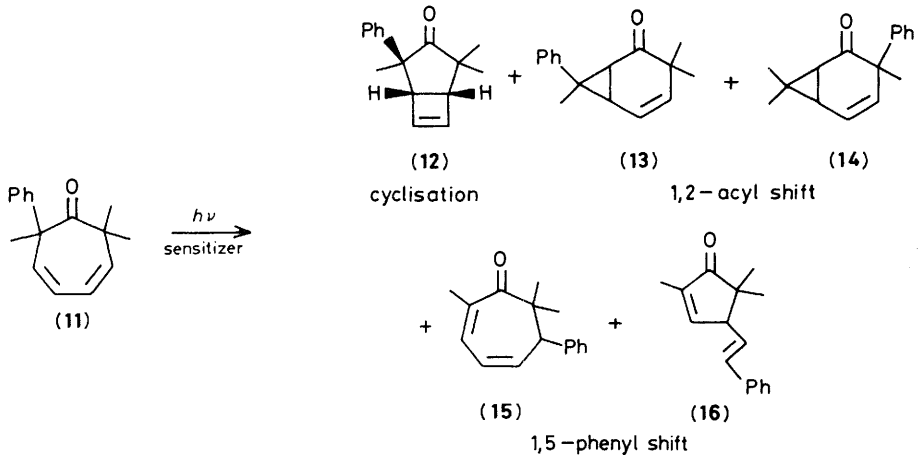
This interesting phenomenon was also observed in the sensitized photolysis of 2,2,7-trimethyl-7-phenylcyclohepta-3,5-dien-1-one (**11**). Ketone (**11**) was prepared by treating 2-phenylcyclohepta-2,4-dien-1-one with excess of potassium t-butoxide and methyl iodide. Photoreactions of (**11**) were carried out in anhydrous diethyl ether at 20 and −60 °C using methyl 2-naphthyl ketone as a sensitizer with a 500 W high-pressure mercury lamp through Pyrex. Since, in this case, prolonged irradiation [until complete consumption of (**11**)] resulted in an increase in the amount of polymeric material at the expense of primary photoproducts, the reactions were stopped at about 80% conversion. The products were isolated and purified by repeated p.l.c. The results are shown in Scheme 3 and Table 4.

The experiment run at 20 °C gave five products, one cyclisation, (**12**), two 1,2-acyl shift, (**13**) and (**14**), and two 1,5-phenyl shift products, (**15**) and (**16**),* respectively, and among them the 1,2-acyl shift products (**13**) and (**14**) were together the major photoproduct (53%). On the other hand, in the run at −60 °C the cyclised compound (**12**) was found to be the sole isolable product (34%). The structures of these products were

* 3-Phenylated oxepin-2(3*H*)-ones have been shown to undergo exclusively a 1,5-phenyl shift as the initial photoprocess on triplet-sensitized photolysis: N. Hoshi, H. Hagiwara, and H. Uda, *Chem. Lett.*, 1979, 1295, and references cited herein.



Scheme 2.



Scheme 3.

elucidated on the basis of their spectroscopic properties by comparison with those of each respective analogous compound (see Experimental section). Configuration of the phenyl group in (**12**) could be assigned to be *exo* from the very close chemical shift value of the vinyl protons in the ^{1}H n.m.r. spectrum at δ 6.21 to that of compound (**5**) at 6.25, no anisotropic effect due to the phenyl group being observed. The signals of C-7 in (**13**) and of C-3 in (**14**) in the ^{13}C n.m.r. spectra at δ_C 35.31 (C-3 43.74) and at 51.44 p.p.m. (C-7 30.33) were shifted markedly from those in the tetramethyl analogue (**6**), δ 43.31 for C-3 and 27.90 p.p.m. for C-7, due to phenyl substitution, thus indicating the position of the phenyl group at C-7 in (**13**) and at C-3 in (**14**) as formulated. However, the configuration of the phenyl group in (**13**) and (**14**) could not yet be determined, although each compound is a single isomer. Compound (**16**), which appears to be the secondary photoproduct, arose from the 1,5-phenyl shift product (**15**) through a photoinduced bond fission and recombination.

No reaction was observed on irradiation in the absence of methyl 2-naphthyl ketone. The indication is, therefore, that all of the observed photoproducts (**12**)—(**15**) certainly arose from the triplet excited state of (**11**). Thus, the ketone (**11**) undergoes, upon triplet sensitization, apparently three competing photoprocesses, *viz.* cyclisation, 1,2-acyl shift, and 1,5-phenyl shift, which are again temperature dependent. The 1,2-acyl shift is the thermodynamically most favourable photoprocess at 20 °C, while the cyclisation becomes the almost exclusive one at −60 °C.

From these results it can be concluded that, in such seven-membered 3,5-dien-1-one systems, both cyclisation and 1,2-acyl shift are possible and competitive photoprocesses of the triplet excited states. The preference for either of two photoprocesses at a given temperature may presumably be attributed to the thermodynamic activation parameters of each substrate.

Experimental

Liquids were normally purified, after chromatographic separation, by evaporative short-path distillation; oil-bath temperatures are recorded. I.r. spectra were obtained for

Table 4. The sensitized photolysis of (**11**) [a]

Run	Conditions: Temperature (°C)	Conditions: Reaction time (h)	Yield of products (%) [b]: Cyclisation (**12**)	1,2-Acyl shift (**13**)	1,2-Acyl shift (**14**)	1,5-Phenyl shift (**15**)	1,5-Phenyl shift (**16**)	Recovery (**11**)
1	20	2	6.4 (8)	8.5	33 (53)[c]	9.0	3.7 (16)[d]	20
2	−60	6	26 (34)	trace		0		24

[a] Photolyses were carried out in anhydrous diethyl ether using methyl 2-naphthyl ketone as a sensitizer with a 500 W high-pressure mercury lamp through Pyrex. [b] Isolated yields. Yields in parentheses are based on the consumed starting material. [c] Total yield [(**13**) + (**14**)]. [d] Total yield [(**15**) + (**16**)].

solutions in carbon tetrachloride with a Hitachi EPI-G2 or a Jasco A-3 spectrophotometer. U.v. spectra were run for solutions in ethanol on a Jasco UVIDEC-505 spectrophotometer. ^{1}H N.m.r. spectra were recorded with a Jeol PMX-60 or a PS-100 instrument, and ^{13}C n.m.r. spectra with a Jeol JNM-MH100 instrument, with tetramethylsilane as internal standard. Mass spectra were obtained on a Shimadzu LKB-9000 spectrometer. G.l.p.c. was carried out on a Jeol JGC-1100 gas chromatograph. Microanalyses were carried out in the microanalytical laboratory of this Institute. Light petroleum refers to the fraction boiling in the range 35—50 °C.

Irradiation of Dimethyloxepinone (**1**) *on a Preparative Scale.*—A solution of dimethyloxepinone (**1**)[8] (2 g) in anhydrous acetone (770 ml) under nitrogen was irradiated for 87 h with a Taika 500 W Pyrex-jacketed immersion-type high-pressure mercury lamp whilst being cooled in a running-water bath. After removal of the solvent, p.l.c. [developer hexane–ethyl acetate (10:4)] of the residue (2.25 g) on silica gel gave 4,4-dimethyl-2-oxabicyclo[3.2.0]hept-6-en-3-one (**2**) (200 mg) and a mixture of (**2**) and 7,7-dimethyl-3-oxabicyclo[4.1.0]hept-4-en-2-one (**3**) (12:1; 480 mg), along with the recovered oxepinone (**1**) (740 mg). Preparative g.l.p.c. (10% Carbowax 20M; 2 m; 170 °C) gave an additional crop of the cyclobutene-γ-lactone (**2**) (300 mg) and the cyclopropano-δ-lactone (**3**) (35 mg, 1.8%). *Compound* (**2**) had $\nu_{max.}$ 1 780 and 1 185 cm^{-1}; $\delta_H(CCl_4)$ 1.18 (6 H, s), 3.24 (1 H, d, *J* 3.5 Hz, 5-H), 5.07 (1 H, t, *J* 3.5 Hz, 1-H), 6.35 (1 H, d, *J* 2.7 Hz, 7-H), and 6.44 [1 H, dd, *J* 3.5 (allylic coupling with 1-H) and 2.7 Hz, 6-H] (Found: C, 69.4; H, 7.0. $C_8H_{10}O_2$ requires C, 69.5; H, 7.3%). *Compound* (**3**) had $\nu_{max.}$ 1 760, 1 652, 1 235, and 1 035 cm^{-1}; $\delta_H(CDCl_3)$ 1.04 (3 H, s), 1.28 (3 H, s), 1.73 (1 H, dd, *J* 7.5 and 4.5 Hz, 6-H), 1.88 (1 H, d, *J* 7.5 Hz, 1-H), 5.33 (1 H, dd, *J* 4.5 and 6.0 Hz, 5-H), and 6.35 (1 H, d, *J* 6.0 Hz, 4-H); $\delta_C(CDCl_3)$ 15.28 (q), 22.50 (s, C-7), 26.57 (q), 28.93 (d, C-6), 29.78 (d, C-1), 103.38 (d, C-5), 139.54 (d, C-4), and 166.23 p.p.m. (s, C-2) (Found: C, 69.4; H, 7.4. $C_8H_{10}O_2$ requires C, 69.5; H, 7.3%).

Alternative Synthesis of the Cyclopropano-δ-lactone (**3**).—To a solution of α-pyrone[9] (350 mg) in diethyl ether (40 ml) was added dropwise a freshly prepared ethereal solution of 2-diazopropane[10] (excess, 30 ml) at −60 °C.[11] The mixture was stirred at between −60 and 0 °C for 4 h, stored at 5 °C in a refrigerator overnight, and then stirred at room temperature for 80 min. After removal of the solvent under reduced pressure, the residue (550 mg) was dissolved in anhydrous acetone (280 ml) and the resulting solution was irradiated at −50 °C for 140 min with the same mercury lamp as in the preceding experiment, under nitrogen. The acetone was distilled off under reduced pressure, and the residue was dissolved in diethyl ether. Insoluble material was removed by filtration, and the filtrate was evaporated to dryness. P.l.c. of the residue (400 mg) on silica gel [developer light petroleum–diethyl ether (2:1)] gave the lactone (**3**) (91 mg, 18%), which was identical with the sample obtained in the preceding experiment (i.r., n.m.r., t.l.c., g.l.p.c.).

Photolysis Runs of Dimethyloxepinone (**1**) *at Elevated Temperatures.*—Results of the irradiation of (**1**) at 40, 50, 60, and 70 °C are tabulated in Table 1. Dimethyloxepinone (**1**) (340 mg; 1.45×10^{-2}M) and methyl 2-naphthyl ketone (145 mg; 5×10^{-3}M) were dissolved in anhydrous benzene (170 ml). In each run, the above solution was placed in three Pyrex reaction tubes (10 ml each). The Pyrex tubes were stoppered after flushing with nitrogen and set in a Riko RH400 10 W merry-go-round photoreactor fitted with the same mercury lamp as above, the water bath of which was previously adjusted to a given temperature, and photoreaction was carried out for 8 h. After removal of the solvent under reduced pressure, the residue from each reaction tube was analysed by g.l.p.c. on a 10% Carbowax 20M column (2 m; 160 °C), and the average values of the conversion percentage and of the product ratio were estimated.

Irradiation of Tetramethylcycloheptadienone (**4**) *on a Preparative Scale.*—A solution of the tetramethylcycloheptadienone (**4**) (328 mg) in anhydrous acetone (200 ml) was irradiated at −60 °C for 4 h with the same mercury lamp as above, under nitrogen. After removal of the solvent, p.l.c. of the residue on silica gel [developer hexane–ethyl acetate (19:1)] gave 2,2,4,4-tetramethylbicyclo[3.2.0]hept-6-en-3-one (**5**) (77 mg, 23%) and 3,3,7,7-tetramethylbicyclo[4.1.0]hept-4-en-2-one (**6**) (213 mg, 64%). The spectral data of both were in good agreement with the reported data.[2,3]

Photolysis Runs of Tetramethylcycloheptadienone (**4**) *at below Room Temperature.*—Results of the irradiation of compound (**4**) at −60, −40, and −20 °C are tabulated in Table 2. Compound (**4**) (100 mg; 6.1×10^{-3}M) was dissolved in anhydrous acetone (100 ml). In each run, the above solution was placed in three Pyrex reaction tubes (10 ml each). The Pyrex tubes were stoppered after flushing with nitrogen and affixed to the exterior of the Pyrex immersion well fitted with a Taika 100 W high-pressure mercury lamp. The whole photoapparatus was then placed in a circulating cold methanol bath, previously adjusted to a given temperature, and photoreaction was carried out for 4 h. After removal of the solvent under reduced pressure, the residue from each reaction tube was analysed by g.l.p.c. on a 20% Carbowax 20M column (3 m; 170 °C), and the average values of the conversion percentage and of the product ratio were estimated.

2,2,7-*Trimethyl*-7-*phenylcyclohepta*-3,5-*dien*-1-*one* (**11**).—A solution of 2-phenylcyclohepta-2,4-dien-1-one[12] (726 mg, 4 mmol) in t-butyl alcohol (10 ml) was added to a solution of potassium t-butoxide (4.48 g, 40 mmol) in t-butyl alcohol (20 ml) at room temperature under nitrogen, and the mixture was stirred for 15 min. A solution of methyl iodide (5.68 g, 40 mmol) in t-butyl alcohol (10 ml) was added very slowly. After being stirred at room temperature for 17 h, the reaction mixture was poured into water and the product was extracted with light petroleum (3 × 50 ml). The combined extracts were washed successively with water and brine, and evaporated to dryness. P.l.c. of the residue [silica gel; developer hexane–ethyl acetate (9:1)] gave the *trimethylphenylcycloheptadienone* (**11**) (685 mg, 77%), b.p. 90—100 °C at 0.1 mmHg; $\nu_{max.}$ 2 990, 2 950, 1 700, 1 500, 1 480, 1 450, 1 380, 1 030, 1 020, 700, and 690 cm^{-1}; $\lambda_{max.}$ 212 (ε 11 900), *ca.* 256 (sh, ε *ca.* 3 600), and *ca.* 296 nm (sh, ε *ca.* 500); $\delta_H(CCl_4)$ 1.20 (6 H, s), 1.50 (3 H, s), 5.32 (1 H, d, *J* 11 Hz, 3-H), 5.68 (1 H, d, *J* 10.5 Hz, 6-H), 5.77 (1 H, dd, *J* 11 and 5 Hz, 4-H), 6.27 (1 H, dd, *J* 10.5 and 5 Hz, 5-H), and 7.08 (5 H, s, Ph) (Found: C, 85.0; H, 7.9. $C_{16}H_{18}O$ requires C, 84.9; H, 8.0%).

Photolysis Runs of Trimethylphenylcycloheptadienone (**11**).—A solution of the dienone (**11**) (376 mg, 1.66 mmol) and methyl 2-naphthyl ketone (340 mg, 2 mmol) in anhydrous diethyl ether (400 ml) was irradiated at 20 °C for 2 h with a 500 W Pyrex-jacketed immersion-type high-pressure mercury lamp under nitrogen. After removal of the solvent, repeated p.l.c. of the residue (340 mg) [developer hexane–ethyl acetate (9:1) and (19:1, very lengthy development)] on silica gel gave, in order of their R_F values, the starting dienone (**11**) (75 mg, 20% recovery), 2,2,4-*trimethyl*-4-exo-*phenylbicyclo*[3.2.0]*hept*-6-*en*-3-*one* (**12**) (24 mg, 6.4%), 2,7,7-*trimethyl*-6-*phenylcyclohepta*-2,4-*dien*-1-*one* (**15**) (34 mg, 9%), 3,3,7-*trimethyl*-7-*phenylbicyclo*[4.1.0]*hept*-4-*en*-2-*one* (**13**) (32 mg, 8.5%), 3,7,7-*trimethyl*-3-*phenylbicyclo*[4.1.0]-*hept*-4-*en*-2-*one* (**14**) (125 mg, 33%), and 2,5,5-*trimethyl*-4-[(E)-*styryl*]*cyclopent*-2-*en*-1-*one* (**16**) (14 mg, 3.7%), respectively. Compound (**12**) had b.p. 65—75 °C at 0.45 mmHg; $\nu_{max.}$ 3 050, 2 970, 2 920, 1 740, and 700 cm^{-1}; $\delta_H(CCl_4)$ 0.66 (3 H, s), 1.04 (3 H, s), 1.30 (3 H, s), 3.04 (1 H, d, *J* 4 Hz, 1-H), 4.05 (1 H, d, *J* 4 Hz, 5-H), 6.21 (2 H, s), and 7.00—7.50 (5 H, m, Ph); $\delta_C(CDCl_3)$ 21.47 (Me), 24.93 (Me), 27.78 (Me), 47.99 (C-2), 49.68 (C-1 or -5), 53.14 (C-5 or -1), 54.48 (C-4), 126.13 (Arom.), 126.62 (Arom.), 128.82 (Arom.), 138.75 (C-6 or -7), 140.15 (C-7 or -6), 143.97 (Arom.), and 222.01 p.p.m. (C-3) (Found: C, 85.0; H, 7.6. $C_{16}H_{18}O$ requires C, 84.9; H, 8.0%). Compound (**15**) had $\nu_{max.}$ 3 030, 2 980, 2 940, 1 665, 1 600, 1 455, 720, and 700 cm^{-1}; $\lambda_{max.}$ 205.5 (ε 14 500), 244 (sh, ε 3 500), and 302 nm (ε 3 700); $\delta_H(CCl_4)$ 0.98 (3 H, s), 1.13 (3 H, s), 1.98 (3 H, s), 3.38 (1 H, d, *J* 5.8 Hz, 6-H), 5.88 (1 H, dd, *J* 11.8 and 6.8 Hz, 4-H), 6.06 (1 H, dd, *J* 11.8 and 5.8 Hz, 5-H), 6.33 (1 H, d, *J* 6.8 Hz, 3-H), and 6.90—7.30 (5 H, m, Ph) (Found: M^+, 226. $C_{16}H_{18}O$ requires *M*, 226). Compound (**13**) had b.p. 90—100 °C at 0.2 mmHg; $\nu_{max.}$ 3 030, 2 960, 1 700, 1 450, 1 330, 1 030, and 700 cm^{-1}; $\delta_H(C_6D_6)$ 0.85 (3 H, s), 0.88 (3 H, s), 0.94 (3 H, s), 1.73 (1 H, dd, *J* 7.5 and 3.5 Hz, 6-H), 1.93 (1 H, d, *J* 7.5 Hz, 1-H), 5.20 (1 H, d, *J* 10 Hz, 4-H), 5.42 (1 H, dd, *J* 10 and 3.5 Hz, 5-H), and 6.70—7.10 (5 H, m, Ph); $\delta_C(CDCl_3)$ 17.29 (Me), 22.81 (Me), 29.18 and 29.60 (Me and C-6), 34.64 (C-1), 35.31 (C-7), 43.74 (C-3), 121.16 (C-4 or -5), 126.55 (Arom.), 127.28 (Arom.), 128.56 (Arom.), 137.41 (C-5 or -4), 146.39 (Arom.), and 210.31 p.p.m. (C-2) (Found: M^+, 226. $C_{16}H_{18}O$ requires *M*, 226). Compound (**14**) had b.p. 100—110 °C at 0.25 mmHg; $\nu_{max.}$ 3 020, 2 950, 2 920, 1 700, 1 685, 1 495, 1 445, 1 325, 1 170, 1 025, 1 000, 720, and 700 cm^{-1}; $\delta_H(C_6D_6)$ 0.82 (3 H, s), 0.83 (3 H, s), 1.52 (3 H, s), 1.48 (1 H, dd, *J* 7.5 and 3.5 Hz, 6-H), 1.81 (1 H, d, *J* 7.5 Hz, 1-H), 5.74 (1 H, dd, *J* 10 and 3.5 Hz, 5-H), 5.81 (1 H, d, *J* 10 Hz, 4-H), and 6.90—7.60 (5 H, m, Ph); $\delta_C(CDCl_3)$ 16.62 (Me), 28.39 (Me), 30.33 [C-7 and (Me or C-6)], 31.36 (C-6 or Me), 37.55 (C-1), 51.44 (C-3), 122.85 (C-4 or -5), 126.55 (Arom.), 127.40 (Arom.), 127.95 (Arom.), 134.87 (C-5 or -4), 142.09 (Arom.), and 208.72 p.p.m. (C-2) (Found: M^+, 226. $C_{16}H_{18}O$ requires *M*, 226). Compound (**16**) had b.p. 90—100 °C at 0.15 mmHg; $\nu_{max.}$ 2 970, 2 930, 1 710, 1 450, 1 380, 975, and 695 cm^{-1}; $\lambda_{max.}$ 212 (sh, ε *ca.* 18 500), 218 (sh, ε *ca.* 16 100), 251 (ε 15 000), 285 (sh, ε *ca.* 4 300), and 293 nm (sh, ε *ca.* 2 700); $\delta_H(CCl_4)$ 0.96 (3 H, s), 1.15 (3 H, s), 1.82 (3 H, t, *J* 1.5 Hz, 2-Me), 3.21 (1 H, d of quint., *J* 8 and 1.5 Hz, 4-H), 5.98 (1 H, dd, *J* 16 and 8 Hz, C*H*=CH–Ph), 6.39 (1 H, d, *J* 16 Hz, CH=C*H*–Ph), 7.02 (1 H, quint., *J* 1.5 Hz, 3-H), and 7.10—7.40 (5 H, m, Ph) (Found: C, 84.7; H, 8.0. $C_{16}H_{18}O$ requires C, 84.9; H, 8.0%).

A solution of the dienone (**11**) (452 mg, 2 mmol) and methyl 2-naphthyl ketone (340 mg, 2 mmol) in anhydrous diethyl ether (400 ml) was irradiated at −60 °C for 6 h with the same photoapparatus. Work-up in the same manner as above gave, in addition to the recovery of (**11**) (110 mg, 24%), compound (**12**) (117 mg, 26%), and trace amounts of compounds (**13**) and (**14**) were detected.

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