Mechanism of Photorearrangement of Bicyclo[3.3.1]nona-3,7-diene-2,6-diones

By **Choi-nang Lam** and **John M. Mellor**, *Department of Chemistry, The University, Southampton SO9 5NH

Irradiation of some 9-arylbicyclo[3.3.1]nona-3,7-diene-2,6-diones gives triasteranediones by successive 1,2-acyl migrations and 6-arylbicyclo[3.3.1]nona-3,7-diene-2,9-diones by 1,3-rearrangement. Emission, photosensitisation, and quenching studies show that both photorearrangements are triplet-derived, and these results are contrasted with other studies of βγ-unsaturated ketones.

WE have reported[1] the synthesis of triasteranedione (1) by photorearrangement of bicyclo[3.3.1]nona-3,7-diene-2,6-dione (2a). In this study it was established that irradiation of 4,8-dimethyl-9-phenylbicyclo[3.3.1]nona-3,7-diene-2,6-dione (3a) gave not only the triasteranedione (4a) by successive 1,2-acyl shifts but also the products of 1,3-rearrangement, (5a) and (6a). Although exceptions are now known,[2] βγ-unsaturated ketones typically undergo 1,3-rearrangement from the lowest excited singlet state[3] but 1,2-rearrangement from a triplet state populated by photosensitisation.[4] Although other explanations[5] of this divergent behaviour have

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[1] P. A. Knott and J. M. Mellor, *J.C.S. Perkin I*, 1972, 1030.

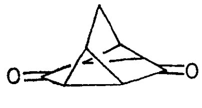
[2] J. R. Williams and H. Ziffer, *Tetrahedron*, 1968, **24**, 6725; J. Gloor, K. Schaffner, and O. Jeger, *Helv. Chim. Acta*, 1971, **54**, 1864, D. A. Plank and J. C. Floyd, *Tetrahedron Letters*, 1971, 4811; H. Sato, K. Nakanishi, J. Hayashi, and Y. Nakadaira, *Tetrahedron*, 1973, **29**, 275.

[3] R. S. Givens, W. F. Oettle, R. L. Coffin, and R. G. Carlson, *J. Amer. Chem. Soc.*, 1971, **93**, 3957.

[4] P. S. Engel and M. A. Schexnayder, *J. Amer. Chem. Soc.*, 1972, **94**, 9252.

[5] D. I. Schuster, G. R. Underwood, and T. P. Knudsen, *J. Amer. Chem. Soc.*, 1973, **93**, 4304.

been given, an analysis[6] suggests that $n\pi^*$ states will preferentially give products of 1,3-rearrangement but $\pi\pi^*$ states will give products of 1,2-rearrangement. The observed preference of βγ-unsaturated ketones for 1,2-rearrangement from the triplet state is explained by the $\pi\pi^*$ character of the lowest excited triplet state. In the light of this analysis it was of considerable interest to establish further details concerning the mechanism of photorearrangement of bicyclo[3.3.1]nona-3,7-diene-2,6-diones. We present results which establish that both 1,2- and 1,3-rearrangements are triplet-derived and contrast these results with studies of other βγ-unsaturated ketones.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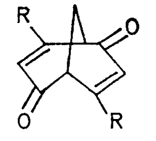
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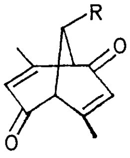
b; R = Me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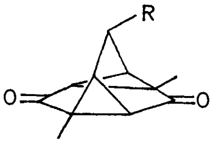
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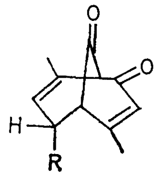
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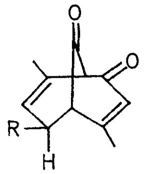
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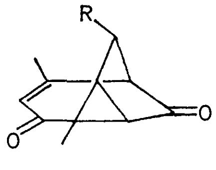
(7)

a; R = Ph
b; R = p-MeO·C_6H_4
c; R = m-O_2N·C_6H_4
d; R = p-ClC_6H_4
e; R = p-BrC_6H_4

RESULTS

Product Studies.—The dienediones (3a—e) were prepared[7] and irradiated in solution in benzene. Major products of reaction of (3a) have been characterized earlier.[1] Careful chromatography of reaction products of (3d) led to isolation of (4d), (5d), and (6d), analogous to products already described from (3a), and to a novel tricyclic dione (7d), identified by spectral and elemental analysis. I.r. and u.v. spectra established the tricyclic nature of (7d) but further definition required n.m.r. analysis. Observation in the spectrum of (7d) of a quartet at τ 5·72 associated with the benzylic proton enabled structure (8) to be rejected and defines the tricyclic dione as (7d), (9), or (10). A distinction between these structures is best made by the observation that the tricyclic dione is readily photoisomerized to the tetracyclic dione (4d). The structure of (4d) is established by the observation of two methyl resonances at τ 8·79 and 8·81 (further separated on addition of a shift reagent) and of a triplet associated with the benzylic proton. Only rearrangement by a 1,2-acyl shift from (7d) or (10) can lead to this tetracyclic dione. Neither 1,2-alkyl nor 1,2-acyl rearrangement from (9) can give (4d), and therefore the tricyclic dione must be one of the epimers (7d) and (10). We prefer structure (7d) on the basis of the observed coupling constants ($J_{1,9}$ 4·4, $J_{6,9}$ 8·4 Hz). This product study shows that the dione (3d) gives the epimeric diones (5d) and (6d) by 1,3-rearrangement, a single tricyclic dione (7d), and a single tetracyclic dione (4d). Irradiation of the diones (3b, c and e) gives product mixtures of a similar nature (see Table 1). The dione (3a) was irradiated in acetone, in methanol, and in acetic acid; products were analysed by n.m.r. and are shown in Table 1. Oxygen affected neither the nature nor the rate of formation of products.

TABLE 1

Products of irradiation of bicyclo[3.3.1]nona-3,7-diene-2,6-diones

Compound irradiated	Time (h)	Solvent	Products (%)				
			(3)	(4)	(5)	(6)	(7)
(3a)	3	PhH	70	5	7	10	8
(3a)	10	PhH	46	15	8	21	10
(3a)	35	PhH	18	29	12	27	14
(3a)	3	AcOH	54	9	7	16	14
(3a)	10	AcOH	23	26	13	21	17
(3a)	35	AcOH		58	6	24	12
(3a)	3	MeOH	59	7	5	16	12
(3a)	10	MeOH	34	20	9	21	15
(3a)	35	MeOH		50	16	24	10
(3a)	3	Me_2CO	69	4	4	15	7
(3a)	10	Me_2CO	46	18	7	16	13
(3a)	35	Me_2CO	24	34	12	18	12
(3a)	1	PhH	77	4	4	8	7
(3a)	25	PhH		45	12	29	14
(3b)	1	PhH	75	4	5	7	9
(3b)	25	PhH		51	7	28	14
(3c)	1	PhH	82	4	4	5	5
(3c)	25	PhH	45	14	10	6	25
(3d)	1	PhH	71	4	7	9	8
(3d)	25	PhH		54	10	25	11
(3e)	1	PhH	67	12	5	9	7
(3e)	25	PhH		*ca.* 80	*ca.* 20		

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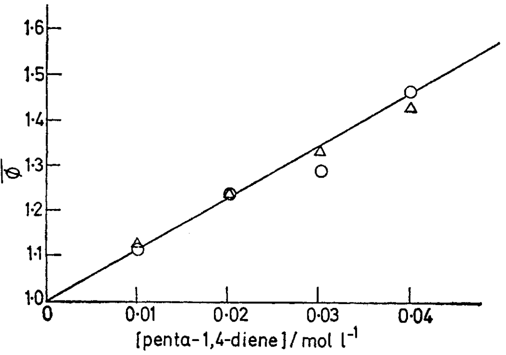
[6] K. N. Houk, D. J. Northington, and R. E. Duke, *J. Amer. Chem. Soc.*, 1972, **94**, 6233.

[7] P. A. Knott and J. M. Mellor, *J. Chem. Soc.* (*C*), 1971, 670.

Formation of all products was completely quenched by 0·5M-penta-1,4-diene. Stern–Volmer plots showed that at lower concentrations of the diene a similar quenching efficiency was observed with products of 1,2- and of 1,3-rearrangement (see Figure).



Quenching of photolysis of the dienedione (3a) (0·005M) in benzene by *trans*-penta-1,4-diene: ○ products of 1,3-rearrangement; △ products of 1,2-rearrangement

TABLE 2

N.m.r. data for bicyclo[3.3.1]nona-3,7-diene-2,6-diones in $CDCl_3$ (τ values; J in Hz)

Compound	1-H and 5-H	3-H	7-H	9-H	4-Me	8-Me
(3a)	6·56 (d, $J_{1,9}$ 3)	4·42 (m)	4·27 (m)	5·88 (t, $J_{1,9}$ and $J_{5,9}$ 3)	8·06 (d, J 2)	7·92 (d, J, 2)
(3b)	6·64 (d, $J_{1,9}$ 2·4)	4·47 (m)	4·34 (m)	6·01 (t, $J_{1,9}$ and $J_{5,9}$ 2·4)	8·12 (d, J, 1·5)	7·98 (d, J, 1·4)
(3c)	6·47 (d, $J_{1,9}$ 2·6)	4·35 (m)	4·21 (m)	5·75 (t, $J_{1,9}$ and $J_{5,9}$ 2·6)	7·97 (d, J, 1·4)	7·86 (d, J, 1·5)
(3d)	6·57 (m)	4·40 (m)	4·26 (m)	5·91 (t, $J_{1,9}$ and $J_{5,9}$ 2·2)	8·04 (d, J, 1·4)	7·91 (d, J, 1·4)
(3e)	6·64 (m)	4·47 (m)	4·33 (m)	6·00 (t, $J_{1,9}$ and $J_{5,9}$ 2·4)	8·12 (d, J, 1·4)	7·97 (d, J, 1·4)

Emission Studies.—The emission spectrum of (3a) in ether–isopentane at 77 K was recorded. Phosphorescent emission at 485 nm was observed (τ_p *ca.* 3·4 ms). Similarly the dione (2b) emitted at 479 nm (τ_p *ca.* 5·5 ms), and related αβ-unsaturated diones showed similar emission.

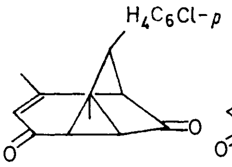
DISCUSSION

Only minor differences are observed in the photorearrangement of the ketones (3a—e). Even with the ketone (3e) a heavy atom effect affects neither products nor rate substantially. We have already noted the reversible photorearrangement of (3a), (5a), and (6a) and suggested that the tetracyclic dione (4a) is produced by successive 1,2-rearrangements *via* a tricyclic intermediate. As a result of this present study we can not only confirm the nature of the photorearrangements but comment upon the excited states involved.

Analysis of the products of rearrangement of (3d) shows that in the early part of the irradiation the products of 1,3-rearrangement (5d) and (6d) are formed in preference to the tricyclic (7d) or tetracyclic product (4d). Further irradiation leads to a decrease in the bicyclic diones with formation of tricyclic and tetracyclic products. As irradiation of (5d) or (6d) leads to photoequilibration *via* (3d) these results indicate that the tricyclic dione (7d) might be formed from one or more of the diones (3d), (5d), and (6d). Irradiation of (7d) gives only the tetracyclic product (4d). By 1,2-rearrangement (7d) can only be formed from (3d) or (5d). A distinction between these two possibilities is difficult as the product analysis (Table 1) fails to distinguish between them. Earlier precedents[2] suggest that formation of (7d) occurs by oxa-di-π-methane rearrangement.

The nature of the excited state responsible for product formation is clearly established by the following results. The formation of products of both 1,2- and 1,3-rearrangement is quenched by penta-1,4-diene. The unlikely possibility that this is due to the quenching of an excited singlet state is eliminated by the observation that irradiation of a dilute solution of (3a) in acetone gives products of both 1,2- and 1,3-rearrangement in a similar ratio to that obtained by direct excitation. It is concluded that all photoproducts are triplet-derived. Linear Stern–Volmer plots were obtained, showing an equal quenching of products of 1,2- and of 1,3-rearrangement.

The absence of singlet products from (3a—e) is not unexpected. Reaction from the singlet competes unfavourably with intersystem crossing, which may be expected to be efficient for an αβ-unsaturated ketone. Other examples of ketones having the dual characteristics of αβ- and βγ-unsaturation failing to react from the singlet state are known. Direct irradiation of (11) gave only (12) and (13) from a triplet state and (14) was recovered unchanged after irradiation. We attribute the absence of singlet products from (11) and (14) to rapid intersystem crossing typical of an αβ-unsaturated ketone.



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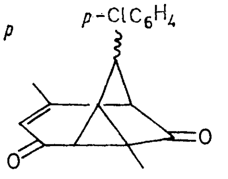

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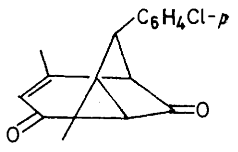

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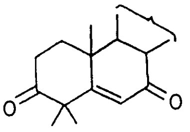

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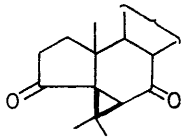

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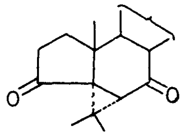

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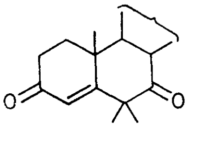

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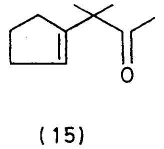

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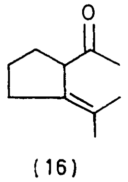

(16)

The observation of products of both 1,2- and 1,3-rearrangement from a triplet state has a recent precedent.[4] Although direct irradiation of ketone (15) gives only the expected product of 1,3-rearrangement (16), reaction by population of a triplet state of the ketone (15) gives products of both 1,2- and 1,3-rearrangement. Our study shows clearly that 1,3-rearrangement proceeds from the triplet and not from the singlet state. It is not conclusively established whether 1,2-rearrangement takes place from triplet (3a—e) or from triplet (6a—e). However the linearity of the Stern–Volmer plot leads us to favour rearrangement of triplet (3a—e).

These results can be contrasted with earlier rationalisations of the observed photoreactivity of $\beta\gamma$-unsaturated ketones. Schuster *et al.*[5] suggested that different spin density distributions in the excited singlet and triplet states lead to differing initial bonding interactions and hence to different products. However owing to the enhanced rate of intersystem crossing we observe here 1,3-rearrangements from the triplet state. Houk *et al.*[6] concluded that reaction from the triplet proceeded from a $\pi\pi^*$ state and the differing photochemistry might be explained by the differences in bonding interactions between an $n\pi^*$ state and a $\pi\pi^*$ state. In (3a—e) the nature of the triplet state is not known but the emission spectrum, the lifetime, and the slope of the Stern–Volmer plot with (3a) suggest an $n\pi^*$ triplet.

TABLE 3

N.m.r. data for photoproducts of bicyclo[3.3.1]nona-3,7-diene-2,6-diones in $CDCl_3$ (τ values; J in Hz)

Compound Triasteranediones	1-H and 5-H	9-H	Methyls
(4a)	7·68 (m)	6·17 (s)	8·72 (s), 8·69 (s)
(4b)	7·73 (m)		8·75 (s), 8·73 (s)
(4c)	7·69 (m)	6·04 (s)	8·76 (s), 8·72 (s)
(4d)	7·78 (m)	6·27 (s)	8·81 (s), 8·79 (s)
(4e)	7·76 (m)	6·27 (s)	8·80 (s), 8·78 (s)

Tricyclo[4.2.1.0^{2,8}]non-4-ene-3,7-diones

	1-H	4-H	6-H	8-H	9-H	Methyls
(7a)						8·50 (s), 8·28 (d, J 1·5)
(7b)						85·1 (s), 8·28 (d, J 1·5)
(7c)	7·73 (t)	4·21 (m)	6·60 (d)		5·57 (q)	8·51 (s), 8·28 (d, J 1·5)
(7d)	7·44 (t)	4·19 (m)	6·70 (d)	7·73 (d)	5·72 (q)	8·56 (s), 8·32 (d, J 1·5)
(7e)	7·42 (t)		6·71 (d)		5·72 (q)	8·57 (s), 8·33 (d, J 1·5)
Bicyclo[3.3.1]nona-3,7-diene-2,9-diones						
(5a)	6·50 (s)	3·89 (m)	6·26 (d)	5·7 (m)	4·41 (m)	8·88 (d, J 1·3), 8·09 (q, J 2·6 and 1·5)
(6a)	6·46 (s)	3·99 (m)	6·95 (s)	6·07 (m)	4·60 (m)	7·81 (d, J 1·4), 8·14 (t, J 1·5)
(5b)						8·85 (d, J 1·4)
(6b)						7·84 (d, J 1·5)
(5c)						8·90 (d, 1·4)
(6c)						7·82 (d, J 1·4)
(5d)	6·56 (s)	3·96 (m)	6·69 (d)	5·84 (m)	4·53 (m)	8·91 (d, J 1·4), 8·17 (q, J 2·6 and 1·4)
(6d)	6·52 (s)	4·0 (m)	7·07 (s)	6·13 (m)	4·58 (m)	7·88 (d, J 1·4), 8·20 (t, J 1·5)
(5e)	6·59 (s)	3·98 (m)	6·73 (d)	5·91 (m)	4·54 (m)	8·86 (d, J 1·5), 8·15 (q)
(6e)	6·48 (s)		7·02 (s)	6·07 (m)		7·81 (d, 1·5), 8·17 (t, J 1·5)

EXPERIMENTAL

For general details, see ref. 1.

9-*Aryl*-4,8-*dimethylbicyclo*[3.3.1]*nona*-3,7-*diene*-2,6-*diones* (3b—e).—The diones were prepared by the method [7] used for preparation of 4,8-dimethyl-9-phenylbicyclo[3.3.1]nona-3,7-diene-2,6-dione (3a). Dehydration of intermediate triones from condensation of the appropriate aldehydes with acetylacetone gave 9-(p-*methoxyphenyl*)-4,8-*dimethylbicyclo*[3.3.1]*nona*-3,7-*diene*-2,6-*dione* (3b), m.p. 126°, $\nu_{max.}$ 1660 and 1636 cm^{-1}, $\lambda_{max.}$ 228, (ε 20,700), 269sh (3120), and 344 nm (913), M^+ 282; 4,8-*dimethyl*-9-(m-*nitrophenyl*)*bicyclo*[3.3.1]*nona*-3,7-*diene*-2,6-*dione* (3c), m.p. 170—171°, $\nu_{max.}$ 1660 and 1630 cm^{-1}; $\lambda_{max.}$ 240 (ε 22,500), 264sh (11,060) and 345 nm (1038), M^+ 297; 9-(p-*chlorophenyl*)-4,8-*dimethylbicyclo*[3.3.1]*nona*-3,7-*diene*-2,6-*dione* (3d), m.p. 150—151°, $\nu_{max.}$ 1660 and 1635 cm^{-1}; $\lambda_{max.}$ 223 (25,200), 272sh (1980), and 346 nm (875), M^+ 288 and 286; 9-(p-*bromophenyl*)-4,8-*dimethylbicyclo*[3.3.1]*nona*-3,7-*diene*-2,6-*dione* (3e), m.p. 159—161°, $\nu_{max.}$ 1665 and 1635 cm^{-1}, $\lambda_{max.}$ 229 (25,800), 271sh (2095), and 346 nm (856), M^+ 332 and 330. N.m.r. data for these diones are given in Table 2.

Irradiation of 9-*Aryl*-4,8-*dimethylbicyclo*[3.3.1]*nona*-3,7-*diene*-2,6-*diones*.— 9-(*p*-Chlorophenyl)-4,8-dimethylbicyclo[3.3.1]nona-3,7-diene-2,6-dione (3d) (2·86 g) in benzene (300 ml) was irradiated for 7 h. Removal of the solvent under reduced pressure and chromatography of the residue over silica gel (200 g) afforded three fractions. Elution with ether–benzene (5 : 95) gave a crystalline solid (330 mg), shown by t.l.c. to be a mixture. Preparative t.l.c. of this fraction afforded 6-endo-(p-*chlorophenyl*)-4,8-*dimethylbicyclo*[3.3.1]*nona*-3,7-*diene*-2,9-*dione* (5d), m.p. 169—170° [from chloroform–light petroleum (b.p. 60—80°)] (Found: C, 71·3; H, 5·05. $C_{17}H_{15}ClO_2$ requires C, 71·2; H, 5·3%), $\nu_{max.}$ 1725, 1665, and 1625 cm^{-1}, $\lambda_{max.}$ 222 (ε 25,600) and 330 nm (281), M^+ 286 and 288; and 6-exo-(p-*chlorophenyl*)-4,8-*dimethylbicyclo*[3.3.1]*nona*-3,7-*diene*-2,9-*dione* (6d), m.p. 161—162° [from chloroform–light petroleum (b.p. 60—80°)] (Found: C, 71·1; H, 5·2. $C_{17}H_{15}ClO_2$ requires C, 71·2; H, 5·3%), $\nu_{max.}$ 1720, 1665, 1630, and 1600 cm^{-1}, $\lambda_{max.}$ 224 (ε 31,900) and 330 nm (253), M^+ 286 and 288. Elution with ether–benzene (5 : 95) then gave unchanged dione (3d) (1·95 g). Elution with ether–benzene (8 : 92) gave 9-(p-*chlorophenyl*)-2,5-*dimethyltricyclo*[4.2.1.0^{2,8}]*non*-4-*ene*-3,7-*dione* (7d) (60 mg), m.p. 140—142° [from chloroform–light petroleum (b.p. 60—80°)] (Found: C, 71·0; H, 5·15. $C_{17}H_{15}ClO_2$ requires C, 71·2; H, 5·3%), $\nu_{max.}$ 1720, 1680, 1650, and 1630 cm^{-1}; $\lambda_{max.}$ 254sh (ε 6300), 295 (983), and

370 nm (383), M^+ 286 and 288. Elution with ether–benzene (10 : 90) gave a mixture (400 mg) of the ketone (7d) and a further product. Attempted chromatographic separation of these components was unsuccessful. Irradiation of this mixture led to loss of the ketone (7d) and afforded crystalline 9-(p-*chlorophenyl*)-2,6-*dimethyltetracyclo*-[3.3.1.0^{2,8}.0^{4,6}]*nonane*-3,7-*dione* (4d), m.p. 163—164° [from chloroform–light petroleum (b.p. 60—80°)] (Found: C, 71·2; H, 5·3. $C_{17}H_{15}ClO_2$ requires C, 71·2; H, 5·3%), $\nu_{max.}$ 1680 cm^{-1}, $\lambda_{max.}$ 221 (22,650), 225 (18,240), 254 (280), 260 (348), 267 (414), and 275 nm (352), M^+ 286 and 288. The n.m.r. spectrum of (4d) was recorded in [^{2}H]chloroform (see Table 3) and also in benzene, where resonances were observed at τ 6·13 (1H, t, $J_{1,9}$ and $J_{5,9}$ 2·5 Hz, 9-H), 8·08 (2H, d, $J_{4,5}$ and $J_{1,8}$ 8 Hz, 4-H and 8-H), 8·57 (2H, q, $J_{1,9}$ and $J_{5,9}$ 2·5, $J_{1,8}$ and $J_{4,5}$ 8 Hz, 1-H and 5-H), and 9·05 (6H, s).

In a similar manner the diones (3b, c, and e) were separately irradiated and the major products of each photolysis characterized by their n.m.r. spectra (see Table 3).

Quenching of the photoreaction of the ketone (3a) with penta-1,4-diene was examined in a ' merry-go-round '. Each tube contained (3a) (120 mg) in benzene (10 ml) with the appropriate quantity of *trans*-penta-1,4-diene. After irradiation products were analysed by n.m.r. The measured slope was 11·5 l mol^{-1} for both 1,2- and 1,3-rearrangement.

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