Influence of a Proximate 1,3-Diene upon the Photoreactivity of Some αβ-Unsaturated Ketones

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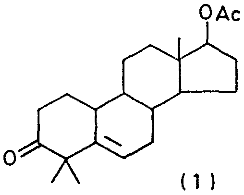
Bicyclo[3.3.1]nona-3,7-dien-2-ones (7)—(10) and the bicyclo[3.3.1]nona-3,6-dien-2-one (11) were synthesised and irradiated. Ketones (7), (10), and (11) were photostable and (8) and (9) only underwent equilibration by geometrical photoisomerisation. This 'free rotor' effect by the diene system dissipates energy and prevents other photorearrangements.

THE efficiency of photorearrangements of αβ- and βγ-unsaturated ketones depends upon the availability of competing modes of energy dissipation. Typically cyclic βγ-unsaturated ketones undergo 1,3-photorearrangement from the excited singlet state but 1,2-photorearrangement from the triplet state,[1-4] but acyclic βγ-unsaturated ketones simply undergo geometrical photoisomerisation.[2,3] This difference in behaviour has been attributed[3] to the 'free rotor' effect as a mode of energy dissipation, which is only available to acyclic ketones. When the olefinic system is constrained as in cyclic ketones, a 'free rotor' effect is inoperative and formation of cyclopropyl ketones by 1,2-acyl shift becomes important.

Thus triplet photosensitisation of the constrained ketone (1) gives[5] (2), but acyclic (3)[6] or flexible germacrone[7] (4) only give (5) or (6) respectively by geometrical photoisomerisation from the triplet state. Efficient 1,2-photorearrangement from the triplet state is possible only in the absence of a 'free rotor' mechanism of energy dissipation.

Recently, we have shown that both bicyclo[3.3.1]-nona-3,7-dien(e)-2,6-diones[8] and -2-ones[9] undergo competitive 1,2- and 1,3-photorearrangement from the triplet state. Here we report the study of the photochemistry of ketones (7)—(11) in which the combination of structural features affords a number of possible modes of photorearrangement. In addition to the possibility of 1,2-, 1,3-, or effective 1,5-rearrangement which have precedent,[8] the proximate diene system now affords a competitive energy dissipation by geometrical isomerisation. The quenching of ketone triplet states by dienes as an intermolecular process,[10] and the photorearrangement of constrained cyclic dienes, for example (12),[11] are established, but it was of interest to establish whether other modes of photorearrangement might compete with energy dissipation by a 'free rotor' effect in ketones (7)—(11) having unconstrained diene chromophores.



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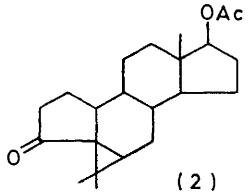

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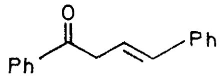

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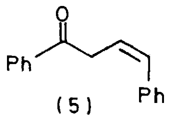

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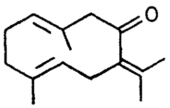

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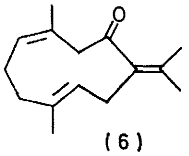

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Ketones (7)—(11) were synthesised in a routine manner either by reaction of the appropriate dione[12] with methylmagnesium iodide and dehydration of the intermediate keto-alcohol under acid conditions, or by reaction with a Wittig reagent. Ketone (11) could only be prepared by Wittig reaction as under acid conditions dehydration of the tertiary alcohol gave only (7). A

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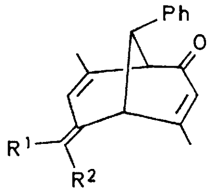
possible photoproduct of ketone (7) is the ketone (13). As keto-alcohol (14) was available[9] it was used to *afford* (13) by dehydration. Details of other products obtained in this dehydration are described[9] elsewhere.

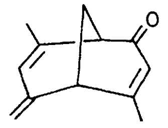
TABLE 1

N.m.r. data for 6-methylene- and 6-ethylidene-bicyclo[3.3.1]nona-3,7-dien-2-ones in $CDCl_3$

	Hydrogens (τ, multiplicity, J/Hz)						Methyls		
Compound	1-H	5-H	9-H	3-H	7-H	6-H	C-4	C-8	Ethylidene
(7)	6·78, m	6·63, m	6·47, t, $J_{1,9}$, $J_{5,9}$ 2·4	4·40, m	4·07, m	5·06, s 4·92, s	8·08, d, J 1·5	8·10, m	
(10)	6·98, t, $J_{1,9}$ 3·7	7·19, t, $J_{5,9}$ 3	7·66 and 7·96, ABq, $J_{1,9}$, $J_{5,9}$ 3, J_{AB} 12	4·40, m	4·16, m	5·14, s 5·01, s	8·00, d, J 1·5	8·18, m	
(8)	6·79, d, $J_{1,9}$ 2·6	6·79, d, $J_{5,9}$ 2·6	6·54, t, $J_{1,9}$, $J_{5,9}$ 2·6	4·39, m	3·81, m	4·42, q, J 7·2	8·09, d	8·09	8·19, d, J 7·2
(9)	6·82, m	6·27, m	6·60, t, $J_{1,9}$, $J_{5,9}$ 2·4	4·32, m	4·16, m	4·45, q, J 7·2	8·06, d, J 1·4	8·13, m	8·05, d, J 7·2



(7) $R^1 = R^2 = H$
(8) $R^1 = Me, R^2 = H$
(9) $R^1 = H\ R^2 = Me$



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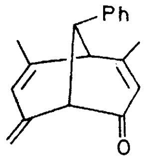

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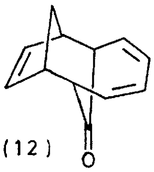

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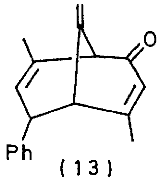

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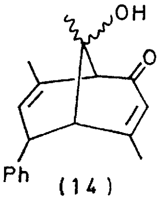

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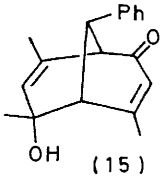

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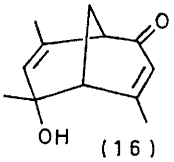

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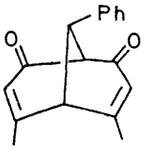

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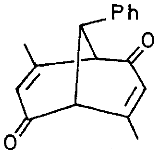

(18)

Structures of ketones (7), (10), and (11) are defined by their method of preparation and their spectra are entirely consistent with the assigned structures. The gross structural features of (8) and (9) are similarly defined and the distinction between them is made on the following basis. In Table 1, the n.m.r. spectral data are recorded for (7)—(10). Assignments of structure to (8) and (9) are based on the respective chemical shifts of resonances associated with 5- and 7-H. Decoupling experiments established that in one isomer 7-H resonated at τ 3·81 and in the other isomer at 4·16. Comparison with other dienes[13] suggests that the former isomer is (8) and the latter isomer is (9). This assignment is substantiated by the relative position of the 5-H resonance at τ 6·79 in (8) and at 6·27 in (9).

The stereochemistry of the hydroxy and phenyl groups in keto-alcohol (14) will be defined[9] elsewhere. Although ketone (13) undergoes further acid catalysed rearrangements it is formed as the initial product from (14). N.m.r. spectra are consistent with the assigned structure (13) and hence the phenyl group occupies the *endo*-position.

In addition to the i.r. and n.m.r. spectra described in the Experimental section, which permit structures to be defined, the u.v. spectra tabulated in Table 2 are of some interest. In ketones (7)—(11) enhancement of the $n \longrightarrow \pi^*$ transition probability indicates extensive interaction between the chromophores of the diene and the αβ-unsaturated ketone. The close similarity between the spectra of (7)—(10) suggests little twisting by adverse

TABLE 2

U.v. spectral maxima of bicyclo[3.3.1]nonadienones

Compound	Maxima (nm)	$\epsilon_{max.}$	Solvent
(7)	229	36,600	EtOH
	348	1016	
(7)	230	27,600	n-Hexane
	279sh	4830	
	320	337	
	333	575	
	347	808	
	364	741	
	382	323	
(8)	232	31,750	EtOH
	293	3540	
	348	1725	
(9)	230	29,100	EtOH
	293	2760	
	349	1390	
(10)	223	30,700	EtOH
	350	944	
	229	21,600	n-Hexane
	268sh	3630	
	309	243	
	319	356	
	333	549	
	348	875	
	364	603	
	381	270	
(11)	227	8990	EtOH
	299	910	
	349	198	
(13)	244	7860	EtOH
	340	387	

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steric interactions in (8) or (9). The spectrum of (11) shows substantially less interaction than that of (7). The magnitude of interaction of a $\beta\gamma$-double bond with a carbonyl group is related to the ionisation potential of the highest occupied orbital of the olefin. In (7) this will be characteristic of a diene system but in (11) because of the relative bonding of diene and carbonyl, this interaction is not possible and reduced interaction is expected. The magnitude of interaction in (13) is also substantially less than that in (7), which again accords with the higher ionisation potential of the $\beta\gamma$-double bond in (13) relative to that in (7).

Irradiation of ketone (7) in benzene, ether, or acetone leads to the quantitative recovery of unchanged starting material. Similarly, no photoproduct is obtained either by direct or acetone sensitised excitation of (10) or (11). Rearrangement by 1,3-acyl shift would give (13) from (7). This possible product was not observed as a result of irradiation of (7). However, irradiation of (13) showed that the reverse 1,3-acyl shift [(13) $\longrightarrow$ (7)] readily occurred.

A number of explanations could account for the absence of the rearrangement product (13) on irradiation of (7). Hancock and Grider [3] have established that the major factor controlling the position of a photostationary equilibration by 1,3-acyl shift of two $\beta\gamma$-unsaturated ketones is not the quantum efficiency of rearrangement, but rather the absorptivity of the ketone. If absorptivity were important in determining the position of equilibrium between (7) and (13) then (13) should be the major product.

The absence of (13) either on direct or sensitised excitation of (7) suggests a low quantum efficiency of rearrangement (7) $\longrightarrow$ (13). The best explanation is the interaction of a new energy dissipating process from excited (7). The 'free rotor' effect requiring geometrical isomerisation of the diene provides such a mechanism.

Confirmation of this mechanism is afforded by irradiation of (8) or (9). Both give a photostationary equilibrium (1 : 1) with n-π^* excitation. Only geometrical isomerisation is observed and again no photorearrangement by 1,3-acyl shift occurs. Hence, it is concluded that no products of photorearrangement are obtained from ketones (7)—(10) because of the intervention of the energy dissipating geometrical isomerisation.

In the absence of absolute rate studies comparison with other ketones incorporating a diene system must be tentative. In the case of (7) it is likely that intersystem crossing of the $\alpha\beta$-unsaturated ketone is efficient and geometrical isomerisation is possible from the triplet state. In contrast, those ketones having constrained dienes [11,14,15] show a different photochemical behaviour.

EXPERIMENTAL

I.r. spectra were measured for chloroform solutions with a Unicam SP 200 spectrophotometer. N.m.r. spectra were measured for deuteriochloroform solutions with a Varian HA 100 spectrometer. U.v. spectra were measured for solutions in ethanol or n-hexane with a Unicam SP 800 spectrophotometer. Mass spectra were measured with an A.E.I. M.S.12 spectrometer. Photochemical reactions were conducted, unless otherwise stated, by irradiation through Pyrex under nitrogen with a 125 W medium pressure lamp.

4,8-*Dimethyl*-6-*methylene*-9-*phenylbicyclo*[3.3.1]*nona*-3,7-*dien*-2-*one* (7).—Ketone [9] (15) (16 g) and toluene-*p*-sulphonic acid (4 g) were heated under reflux in benzene (1200 ml) for 2 h. Work-up gave a yellow solid (15 g) and recrystallisation from ethyl acetate–light petroleum (b.p. 60—80°) gave the *ketone* (7), m.p. 81—82° (Found: C, 86·2; H, 7·3. $C_{18}H_{18}O$ requires C, 86·4; H, 7·3%); $\nu_{max.}$ 1660 cm^{-1}; M^+ 250; τ 2·8—3·0 (5H, m, 9-Ph), 4·07 (1H, m, 7-H), 4·40 (1H, m, 3-H), 4·92 and 5·06 (2H, 6-CH_2), 6·47 (1H, t, J 2·4 Hz, 9-H), 6·63 (1H, m, 5-H), 6·78 (1H, m, 1-H), and 8·08—8·10 (6H, 4- and 8-CH_3). Preparation of ketone (7) was also achieved by Wittig reaction with an ylide prepared from methyltriphenylphosphonium iodide.

4,8-*Dimethyl*-6-*methylenebicyclo*[3.3.1]*nona*-3,7-*dien*-2-*one* (10).—Ketone [9] (16) (100 mg) and toluene-*p*-sulphonic acid (30 mg) were heated under reflux in benzene for 2 h. The cooled solution was washed with water, dried, and the solvent removed under reduced pressure to give a yellow residue which on recrystallisation from light petroleum (b.p. 60—80°) gave the *ketone* (10) (90 mg), m.p. 54—55° (Found: C, 82·8; H, 8·0. $C_{12}H_{14}O$ requires C, 82·7; H, 8·1%); $\nu_{max.}$ 1660 cm^{-1}; M^+ 174; τ 4·16 (1H, m, 7-H), 4·40 (1H, m, 3-H), 5·01 (1H, s, 6-CH_2), 5·14 (1H, s, 6-CH_2), 6·98 (1H, t, J 3 Hz, 1-H), 7·19 (1H, t, J 3 Hz, 5-H), 7·75 (2H, t, J 3 Hz, 9-H), 8·00 (3H, d, J 1·5 Hz, 4-CH_3), and 8·18 (3H, m, 8-CH_3).

4,6-*Dimethyl*-8-*methylene*-9-*phenylbicyclo*[3.3.1]*nona*-3,6-*dien*-2-*one* (11).—To methyltriphenylphosphonium iodide (0·6 g) in tetrahydrofuran butyl-lithium (0·15 g) in hexane was added with vigorous stirring, and then dione (17) (0·35 g) in tetrahydrofuran was added. The mixture was heated under reflux for 15 h, the solvent removed under reduced pressure and the residue taken up in ether. Preparative t.l.c. of the concentrated extract afforded a pale yellow crystalline solid. Recrystallisation from ethyl acetate–light petroleum (b.p. 60—80°) gave the *ketone* (11), m.p. 110—112°; $\nu_{max.}$ 1660 cm^{-1}; m/e 250 (M^+), 235, and 207; τ 2·8—3·0 (5H, m, 9-Ph), 4·05 (1H, m, 7-H), 4·30 (1H, m, 3-H), 4·82 (1H, s, 8-CH_2), 5·04 (1H, s, 8-CH_2), 6·28 (1H, m, 1-H), 6·42 (1H, t, $J_{1,9}$ 2·6, $J_{5.9}$ 2·6 Hz, 9-H), 6·99 (1H, d, $J_{5,9}$ 2·6 Hz, 5-H), 7·95 (3H, s, 6-CH_3), and 8·04 (3H, d, J 1·5 Hz, 4-CH_3).

cis- (9) *and* trans-6-*Ethylidene*-4,8-*dimethyl*-9-*phenylbicyclo*[3.3.1]*nona*-3,7-*dien*-2-*one* (8).—4,8-Dimethyl-9-phenylbicyclo[3.3.1]nona-3,7-diene-2,6-dione [8] (18) (2·5 g) on treatment with ethylmagnesium bromide [from magnesium (1 g)] gave a crude product (2·92 g), which with toluene-*p*-sulphonic acid (0·3 g) was heated under reflux in benzene (250 ml) for 2 h. Work-up and preparative t.l.c. over silica gel afforded a mixture of the olefins (8) and (9) (0·8 g). Further preparative t.l.c. afforded by elution with ether (1%) in light petroleum the crystalline trans-*olefin* (8) (0·30 g), m.p. 103—106°, $\nu_{max.}$ 1660 cm^{-1}; $\lambda_{max.}$ 230

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[14] L. A. Paquette, R. F. Eizember, and O. Cox, *J. Amer. Chem. Soc.*, 1968, **90**, 5153.

[15] D. I. Schuster, B. R. Schnolick, and F.-T. H. Lee, *J. Amer. Chem. Soc.*, 1968, **90**, 1300.

(ε 29,100), 293 (2760), and 349 nm (1390); M^+ 264, and the non-crystalline *cis*-isomer (9) (0·45 g), $\nu_{max.}$ 1660 cm^{-1}; $\lambda_{max.}$ 232 (ε 31,750), 293 (3540), and 348 nm (1725); M^+ 264. On standing, (9) readily polymerised.

4,8-*Dimethyl*-9-*methylene*-6-*phenylbicyclo*[3.3.1]*nona*-3,7-*dien*-2-*one* (13).—Ketone [9] (14) (52 mg) was heated under reflux with toluene-*p*-sulphonic acid (12 mg) in benzene (15 ml) for 18 h. Work-up and preparative t.l.c. over silica gel afforded as a yellow oil, the *ketone* (13), $\nu_{max.}$ 1670, 1630, and 920 cm^{-1}; *m*/*e* 250 (M^+), 235 ($M - CH_3$), and 207 ($M - CH_3CO$); τ 2·7—3·0 (5H, m, 6-Ph), 4·23 (1H, m, 3-H), 4·48 (1H, m, $J_{6,7}$ 2 Hz, 7-H), 5·22 (1H, s, 9-CH_2), 5·31 (1H, s, 9-CH_2), 6·04 (1H, m, $J_{5,6}$ 7 Hz, 6-H), 6·69 (1H, s, 1-H), 6·73 (1H, d, $J_{5,6}$ 7 Hz, 5-H), 8·16 (3H, q, J 1·5 and 2·4 Hz), and 8·98 (3H, d, J 1·5 Hz).

Irradiation of Ketones (7)—(11).—Ketone (7) was irradiated in benzene for 5 days. Removal of the solvent afforded unchanged (7) quantitatively. Similarly, ketone (7) was recovered unchanged after irradiation in ether or in acetone. Ketone (10) was recovered unchanged after irradiation in benzene, ether, or acetone. Ketone (11) was recovered unchanged after irradiation in benzene. Under similar conditions ketones (8) and (9) were readily photoequilibrated. Further examination of this photoequilibrium using a merry-go-round apparatus with a 450 W mercury lamp and Pyrex tubes established that equilibration of (8) (50 mg) in benzene (10 ml) proceeded at an undiminished rate in the presence of 2M-*trans*-piperylene. Similarly, photoequilibration of (9) (50 mg) in benzene (10 ml) was not quenched by added piperylene. Starting with either (8) or (9) and in the presence or absence of piperylene a photostationary equilibrium was established containing *ca.* 50% (8) (determined by n.m.r.).

Irradiation of Ketone (13).—Ketone (13) (60 mg) in benzene (250 ml) was irradiated for 75 min. Removal of the solvent under reduced pressure gave quantitatively ketone (7) [identical by spectroscopic (i.r. and n.m.r.) and chromatographic (t.l.c.) comparison with an authentic sample].

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