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PHOTOCHEMISTRY OF ETHENOBENZOCYCLOHEPTENONES

A DI-π-METHANE REARRANGEMENT OF β,γ-UNSATURATED ARYL KETONES

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Abstract—Benzotropones **6** react with dienophiles **7** to give *endo*-adducts **8** as shown by PMR. Unlike similar ketones which usually undergo 1,3-acyl shifts or oxadi-π-methane rearrangements, these ethenobenzocycloheptenones **8**, on direct or sensitized irradiation, lead to the di-π-methane rearrangement products 1H-benzo[f]-cycloprop[cd]-indenones **9**. The structures of the latter were elucidated by the use of Eu(FOD)$_3$ and X-ray diffraction. Prolonged irradiation of tetrahydrofluorenone **19** a potential 1,3-acyl shift product of ethenobenzocycloheptenones, gave only dienyl aldehyde **21** in low conversion. These results suggest that the chemical pathway chosen in these reactions is dependent on geometrical and electronic factors.

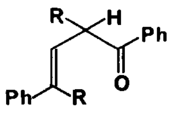
INTRODUCTION

The photochemistry of β,γ-unsaturated ketones has been the subject of a recent excellent and extensive review by Houk.[2] These compounds are capable of undergoing photochemical *cis–trans* isomerization about a double bond, 1,3-acyl shifts, di-π-methane (DPM) rearrangement or oxa-di-π-methane (ODPM) rearrangement.[2,3] In many cases photosensitized triplet reactions lead to ODMP products but exceptions are known.[4] Even among the few examples of β,γ-unsaturated ketones in which the ketone group is conjugated to an aromatic ring or a double bond, no definitive pattern in photochemical behavior has emerged: for example, direct irradiation of **1a** and **2** results in oxa-di-π-methane (ODMP) rearrangement,[5] while **1b** *trans–cis* isomerises,[6] **3a**, **3b** and **5** undergo a 1,3-acyl shift,[7-9] while **4** gives a di-π-rearrangement product.[10]

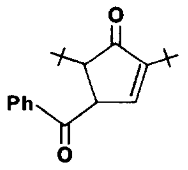
We report here our findings on the photolysis of ethenobenzocycloheptenones **8**, structurally very closely related to **3**, but which undergo di-π-methane (DPM) rearrangement to give 1H-benzo[f]cycloprop[cd]indenones **9** exclusively.

RESULTS

The ethenobridged benzocycloheptenones **8** were synthesized in fair yield (see Table 1) by Diels–Alder reaction of the benzotropones **6**[11] with the dieneophiles **7**, in refluxing toluene. Structural assignment to the cycloadducts **8** was facilitated by the use of benzotropone **6**,



1a R = Ph
1b R = H



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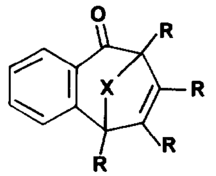
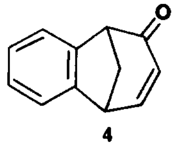


3a X = CMe$_2$; R = Me
3b X = ortho C$_6$H$_4$; R = H



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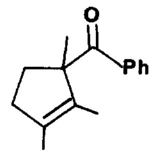

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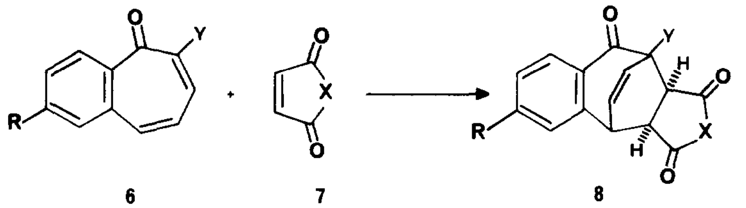
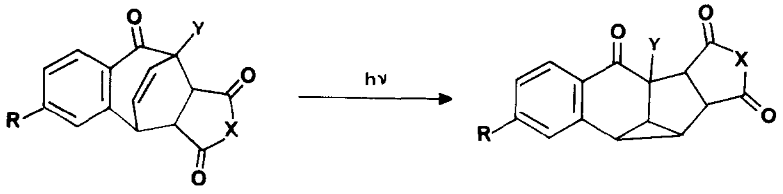
Table 1. Fields and spectra of the adducts **8**

	Y	R	X	Yield (%)	ν_{max} (ArCO)	H_a (δ, pattern)	λmax (EtOH)	ε
a	H	H	O	85	1670	3.8, s	336	138
b	H	H	NMe	66	1670	3.38, s	338	81
c	H	H	NPh	66	1669	3.8, s	340	88
d	H	MeO	O	72	1665	a	349	135
e	H	MeO	NMe	81	1658	3.82, s	b	b
f	Br	H	O	40	1692	3.4, m	340	95

a) signal obscured; b) spectrum unobtainable because of insolubility



6 **7** **8**



8 **9**

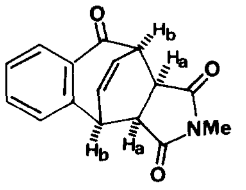
a R = H;	X = O;	y = H
b R = H;	X = NMe;	y = H
c R = H;	X = NPh;	y = H
d R = MeO:	X = 0;	y = H
e R = MeO;	X = NMe;	y = H
f R = H;	X = O;	y = Br

R = H, Y = H and N-methylmaleimide **7**, X = NMe as substrates. The resulting adduct displayed a Me singlet at 2.99δ, characteristic of the *endo*[12] configuration **8b** where the Me protons are not influenced by the shielding cone of the aromatic ring.[13,14] Furthermore, the ring junction protons (H_a) appeared as a singlet consistent with the dihedral angle of *ca.* 90° between H_a and H_b in the *endo*-configuration **8b**.[14,15] This assignment is in agreement with the work of Ebine *et al.*[16] who isolated the *endo*-adduct **10** from the reaction of maleic anhydride with 8-bromo-5H-benzocyclohepten-5-one **11**.

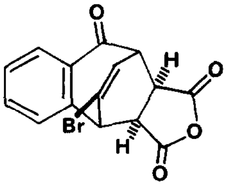
Direct or sensitized irradiation of the benzocycloheptenones **8** afforded benzo-[f]cycloprop[cd]indenones **9** in good yield as the only isolable products (Table 2); the results for adduct **8c** are typical. The 60 MHz NMR spectrum of the photoproduct showed, besides aromatic absorption only aliphatic protons (*viz.* 2.0–3.76δ).

This eliminates the 1,3-acyl shift product **12**; R = H, X = NPh, which would show vinylic absorption, and leaves for consideration the benzo[f]cycloprop[cd]indenone **9c** (DPM product) and the benzo[g]cycloprop[cd]indenone **13** (ODPM) product). The IR shift of the phenone CO stretching frequency from 1669 cm^{-1} to 1690 cm^{-1} in going from adduct **8c** to the photoproduct, though not conclusive, favors the DMP product **9c**.

The NMR spectrum, δ($CDCl_3$) 3.76 (H_d, broad dou-



8b



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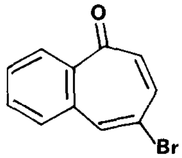

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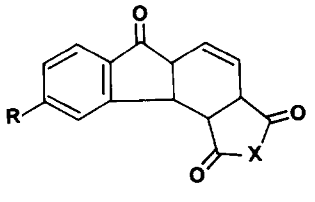
blet, J = 6.0 Hz) 3.03 (H_e and H_f, AB system) and 2.0–2.7 (H_gH_i and H_j, multiplet), is consistent with both **9c** and **13**. However, europium shift studies (Fig. 1), using Eu(FOD)$_3$, established the photoproduct as **9c**.



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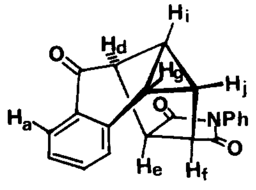

9c

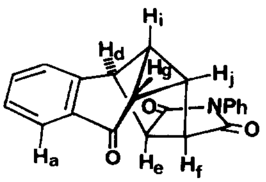

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Table 2. Di-π-methane rearrangement of **8** to **9**

	λ	Solvent	Time (hr)	Yield (%)	νmax (ArCO)
<u>a</u>	2537	Me_2CO	1	52	1690
<u>a</u>	a	EtOAc	1	90	
<u>a</u>	3500	EtOAc	1	93	
<u>b</u>	2537	Me_2CO	3	84	1680
<u>b</u>	a	EtOAc	3	61	
<u>c</u>	2537	Me_2CO	3	65	1690
<u>c</u>	2537	EtOAc	6	68	
<u>c</u>	a	EtOAc	5	50	
<u>d</u>	2537	Me_2CO	2.5	90	1680
<u>d</u>	3500	EtOAc	2	93	
<u>e</u>	a	EtOAc^b	2	63	1680
<u>f</u>	a	EtOAc	2	72	1705

a) Hanovia lamp, pyrex filter; b) suspension

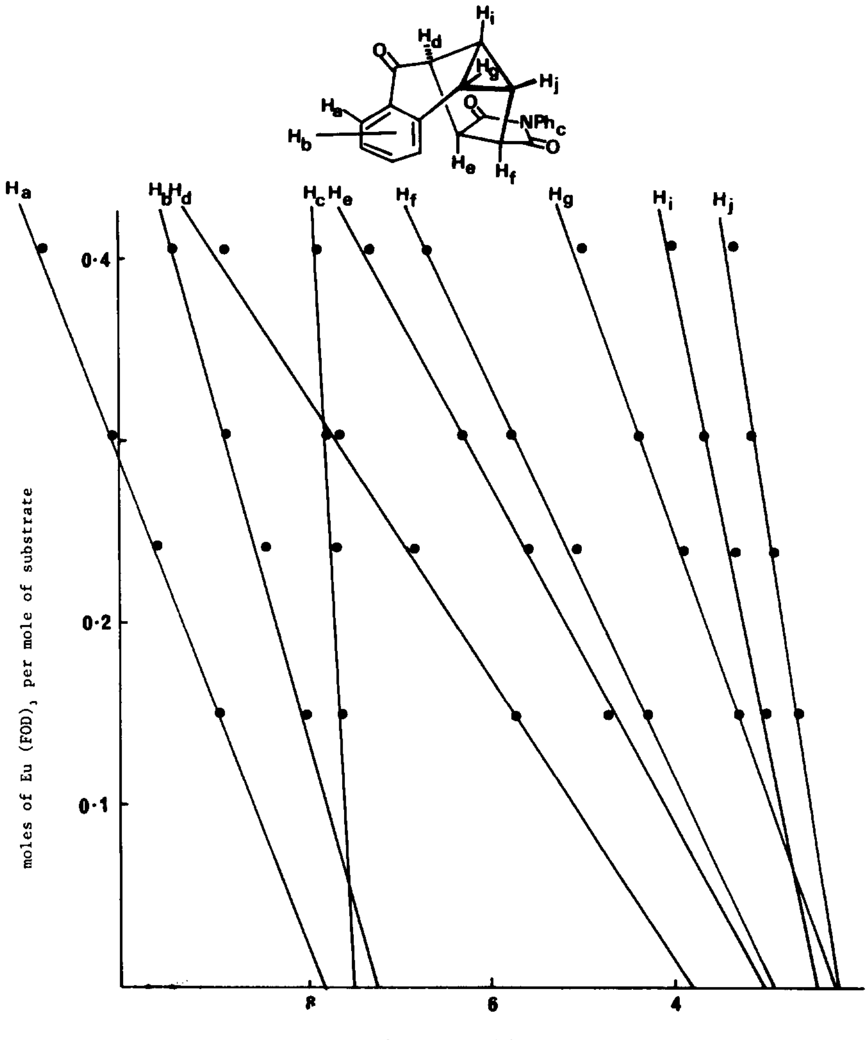


Fig. 1. Eu(FOD)$_3$ study on 2,2a,2b,7,7a,7b - hexahydro - 7 - oxo - N - phenyl - 1H - benzo[f]cycloprop[cd]indene - 1,2 - dicarboximide **9c**.

Table 3. 100 MHz data for photoproduct **9c** in the presence of 0.41 moles of Eu(FOD)$_3$ per mole of **9c**

Signal Position δ, ppm	Assignment	Signal description (coupling constants, Hz)	Relative Area
10.86	H_a	multiplet	1
9.40	H_b	multiplet	3
9.0	H_d	d, J_{di} = 6.0	1
7.5 - 8.1	H_c	multiplet	5
7.3	H_e	broad d, J_{ef} = 7.0, J_{de} <1.0	1
6.7	H_f	d, J_{ef} = 7.0	1
5.03	H_g	dd, J_{gj} = 8.5, J_{gi} = 5.5	1
4.04	H_i	multiplet J_{gi} = 5.5, J_{di} = 6.0 J_{ij} = 7.5	1
3.36	H_j	t, J_{gj} = 8.5, J_{ij} = 7.5	1

Table 4. Results of the direct irradiation of **8a** in deuteriobenzene in the presence of piperylene

Time min.	8a Moles x 10^{-4}	Piperylene Moles x 10^{-4}	% composition^b	
			8a	9a
13	1.4	0	68	32
13	1.4	3.0	71	29
13	1.4	6.0	88	12
32	1.4	0	33	67
32	1.4	14.0	52	48

a) Hanovia lamp, pyrex filter;

b) product ratios were determined by ^1H NMR

Figure 1 shows that the Eu(FOD)$_3$ is associated with the phenyl ketone rather than with the imide carbonyls, since H_a has a large, and the N-phenyl protons only a small, lanthanide induced shift (L.I.S.). The signal at 3.76δ assigned to H_d has the largest L.I.S. This can only be accommodated by the di-π-methane photoproduct **9c**, where H_d is the closest proton to the phenyl ketone. In the ODPM product **15**, H_d is on the other side of the ring to the phenyl ketone and consequently would only have a small L.I.S. The spectrum was fully resolved at a molar ratio of Eu(FOD)$_3$ to substrate of 0.41 and assignments were confirmed by double resonance experiments (Table 3).

Irradiation of H_d collapsed H_i (multiplet, J = 5.5, 6.0, 7.5 Hz) to a doublet of doublets (J = 5.5, 7.5 Hz) and sharpened the broad doublet due to H_e, while irradiation of H_i collapsed H_d (doublet J = 6.0 Hz) confirming J_{di} = 6.0 Hz. Irradiation of H_f collapsed H_e (broad doublet, J = 6.0 Hz) to a singlet and as expected had no effect on H_j where the H_fH_j dihedral angle is 90°. Irradiation of H_j collapsed H_g (doublet of doublets J = 5.5, 8.5 Hz) to a doublet (J = 5.5 Hz) giving the coupling constants J_{gi} = 5.5 Hz, J_{gj} = 8.5 Hz and J_{ij} = 7.5 Hz.

The structure of **9f** was confirmed by X-ray diffraction and is shown in Fig. 2. Atomic parameters for non-hydrogen atoms are given in Table 5, and bond lengths and angles in Tables 6 and 7. The errors in bond lengths (e.s.d. ~0.01Å) make discussion of distances and

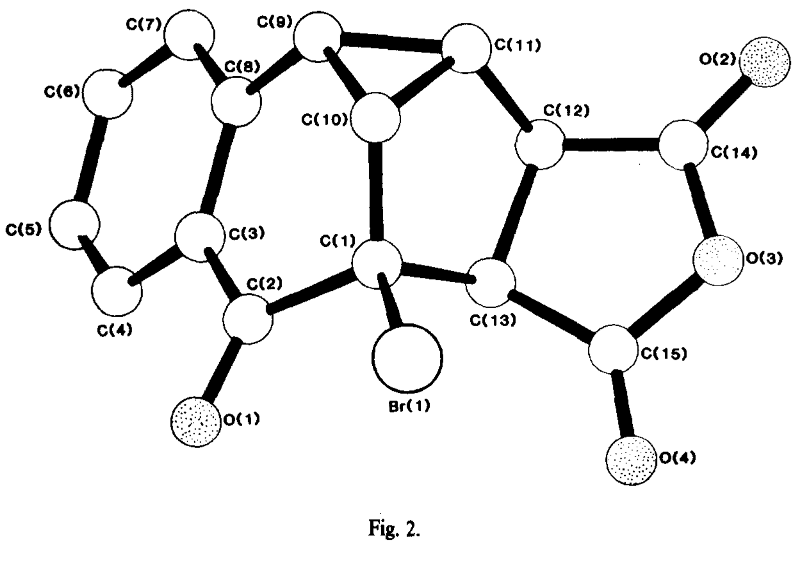


Fig. 2.

Table 5. Fractional atomic co-ordinates × 10,000 with E.S.D.S. in brackets

	X/A	Y/B	Z/C
C (1)	3207 (6)	2713 (6)	3723 (6)
C (2)	3767 (7)	1461 (7)	3315 (6)
C (3)	3321 (7)	0170 (7)	3675 (6)
C (4)	3301 (9)	-1004 (8)	3117 (10)
C (5)	2831 (10)	-2196 (9)	3358 (11)
C (6)	2470 (12)	-2270 (10)	4249 (12)
C (7)	2485 (11)	-1130 (12)	4833 (14)
C (8)	2945 (8)	0117 (7)	4596 (6)
C (9)	3042 (11)	1345 (11)	5261 (9)
C (10)	3385 (11)	2652 (10)	4883 (9)
C (11)	2011 (11)	2492 (11)	5010 (10)
C (12)	0854 (8)	2540 (9)	3963 (7)
C (13)	1580 (9)	2745 (9)	3130 (7)
C (14)	-0072 (8)	3745 (9)	3833 (7)
C (15)	0949 (8)	4058 (7)	2581 (7)
O (1)	4429 (6)	1515 (5)	2712 (5)
O (2)	-0870 (7)	4014 (7)	4273 (6)
O (3)	0122 (5)	4629 (5)	3102 (5)
O (4)	1074 (7)	4606 (7)	1824 (6)
Br (1)	4165 (1)	4263 (1)	3443 (1)
H (4A)	3382 (70)	-0993 (64)	2743 (66)
H (5A)	2957 (84)	-2770 (88)	3111 (69)
H (6A)	2453 (118)	-2893 (115)	4460 (98)
H (7A)	2423 (78)	-1024 (81)	5333 (72)
H (9A)	3347 (83)	1279 (80)	5584 (70)
H (10A)	3778 (81)	2936 (74)	5125 (68)
H (11A)	2099 (83)	2460 (77)	5550 (81)
H (12A)	0683 (71)	2158 (72)	3975 (60)
H (13A)	1450 (75)	2526 (74)	2828 (64)

angles presumptious but the shape and stereochemistry of the molecule are definitely established.

DISCUSSION

The photoproducts **9** could arise by a direct di-π-methane rearrangement (Scheme 1). However, since both 3,3-sigmatropic rearrangement and α-cleavage of nπ-excited states of ketones are well documented processes,[2,3,9,17] the possible intermediacy of the ketene **16** and/or the diradical **17**, ultimately leading to the same photoproduct **9** (Scheme 2), must be considered.

Thus, ketene **16** could either revert to diradical **17** and/or adduct **8** or cleave the other cyclopropyl bond to give a new diradical **18**, which in turn could go on to photoproduct **9** via the route shown. Thermal rearrangement of ketene **16** to the more stable diradical **17** (an allyl radical), rather than to the alternate diradical **18**, would be the more favored process. However, if diradical **17** preferred to recombine to give adduct **8** rather than fluorenone **12**, then drainage via **18** to the observed photoproduct **9** could result. The key experiment was therefore to determine by which pathway diradical **17** prefers to recombine.

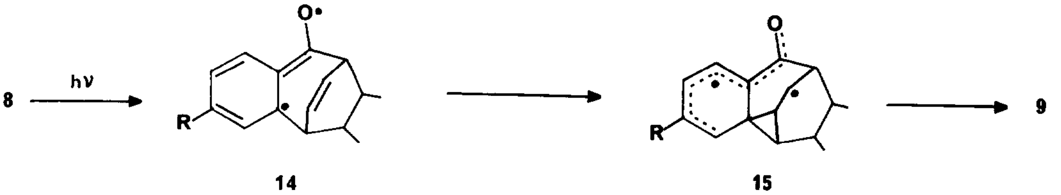
Irradiation of enone **19** to low conversion under conditions identical to those described for **8** resulted in the

Table 6. Bond angles (degrees) with E.S.D.S. in brackets

C (10)	-C (1)	-C (2)	114.0 (6)
C (13)	-C (1)	-C (2)	107.1 (6)
C (13)	-C (1)	-C (10)	104.0 (7)
Br(1)	-C (1)	-C (2)	107.7 (4)
Br(1)	-C (1)	-C (10)	110.5 (5)
Br(1)	-C (1)	-C (13)	113.6 (5)
C (3)	-C (2)	-C (1)	112.9 (6)
O (1)	-C (2)	-C (1)	123.6 (6)
O (1)	-C (2)	-C (3)	123.3 (7)
C (4)	-C (3)	-C (2)	120.1 (8)
C (8)	-C (3)	-C (2)	121.2 (6)
C (8)	-C (3)	-C (4)	118.7 (7)
C (5)	-C (4)	-C (3)	123.4 (10)
C (6)	-C (5)	-C (4)	118.6 (11)
C (7)	-C (6)	-C (5)	119.8 (11)
C (8)	-C (7)	-C (6)	122.9 (13)
C (7)	-C (8)	-C (3)	116.4 (9)
C (9)	-C (8)	-C (3)	120.3 (7)
C (9)	-C (8)	-C (7)	123.3 (10)
C (10)	-C (9)	C (8)	119.5 (9)
C (11)	-C (9)	-C (8)	126.6 (9)
C (11)	-C (9)	-C (10)	59.0 (7)
C (9)	-C (10)	-C (1)	115.6 (8)
C (11)	-C (10)	-C (1)	110.7 (9)
C (11)	-C (10)	-C (9)	61.2 (7)
C (10)	-C (11)	-C (9)	59.8 (6)
C (12)	-C (11)	-C (9)	119.5 (10)
C (12)	-C (11)	-C (10)	110.8 (10)
C (13)	-C (12)	-C (11)	105.3 (7)
C (14)	-C (12)	-C (11)	113.0 (7)
C (14)	-C (12)	-C (13)	104.5 (7)
C (12)	-C (13)	-C (1)	108.7 (7)
C (15)	-C (13)	-C (1)	116.7 (7)
C (15)	-C (13)	-C (12)	103.5 (6)
O (2)	-C (14)	-C (12)	129.4 (9)
O (3)	-C (14)	-C (12)	110.6 (6)
O (3)	-C (14)	-O (2)	120.0 (8)
O (3)	-C (15)	-C (13)	109.7 (7)
O (4)	-C (15)	-C (13)	130.3 (7)
O (4)	-C (15)	-O (3)	120.0 (7)
C (15)	-O (3)	-C (14)	110.9 (5)

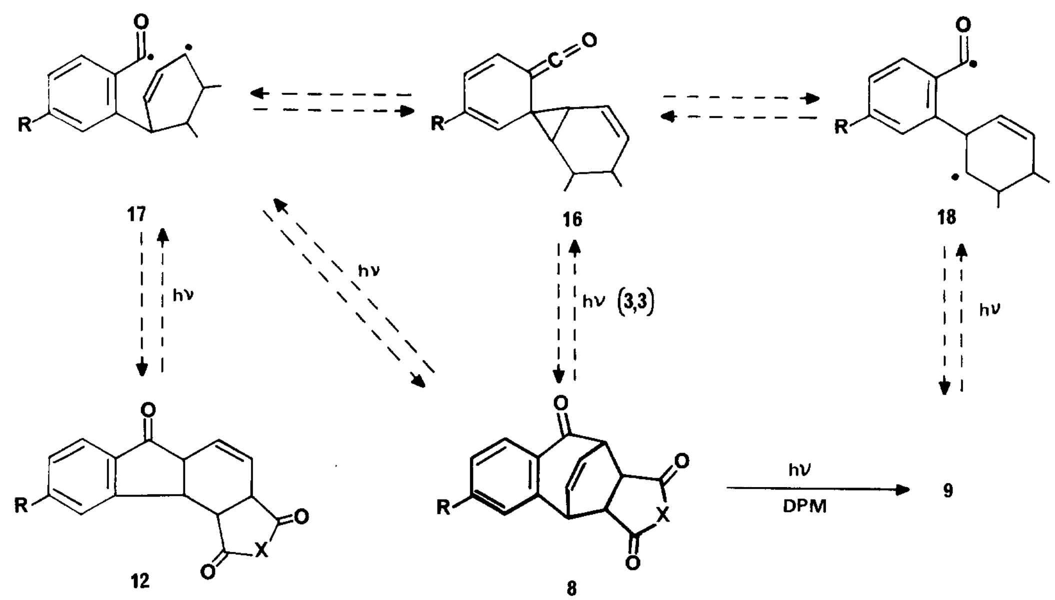
Table 7. Bond distances (Å) with E.S.D.S. in brackets

C .(1)	---C (2)	1.539 (9)
C (1)	---C (10)	1.488 (15)
C (1)	---C (13)	1.547 (10)
C (1)	---Br (1)	1.920 (6)
C (2)	---C (3)	1.490 (10)
C (2)	---O (1)	1.213 (9)
C (3)	---C (4)	1.376 (12)
C (3)	---C (8)	1.404 (12)
C (4)	---C (5)	1.353 (13)
C (5)	---C (6)	1.358 (17)
C (6)	---C (7)	1.367 (20)
C (7)	---C (8)	1.394 (13)
C (8)	---C (9)	1.486 (14)
C (9)	---C (10)	1.474 (14)
C (9)	---C (11)	1.495 (15)
C (10)	---C (11)	1.463 (15)
C (11)	---C (12)	1.464 (14)
C (12)	---C (13)	1.542 (12)
C (12)	---C (14)	1.489 (11)
C (13)	---C (15)	1.516 (11)
C (14)	---O (2)	1.181 (10)
C (14)	---O (3)	1.363 (11)
C (15)	---O (3)	1.381 (10)
C (15)	---O (4)	1.187 (11)



14 **15**

Scheme 1. Mechanism of the di-π-methane rearrangement of ethenobenzocycloheptenones **8**.



Scheme 2. Possible pathway to 1H-benzo[f]cycloprop[cd]indenones (9) via ketenes (16).

isolation in 25% yield of the aldehyde **21**. Formation of the latter demonstrates that the diradical **20** was generated and this prefers to recombine to give enone **19** or abstract a hydrogen to give aldehyde **21** rather than recombine to give the benzocycloheptenone **22**. By analogy, intermediacy of ketene **16** would dictate formation of cyclohexadienylbenzaldehyde (desmethyl **21**) or of fluorenone **12**. Since no product of this type was observed, we conclude that the photoproducts **9** are indeed formed by the expected DPM rearrangement.

Quenching experiments on **8a** with piperylene (Table 4) indicate that the rearrangement **8**→**9** is subject to triplet quenching. This and the fact that the photoproducts **9** are formed by direct as well as by sensitized irradiation indicate that a triplet is involved.

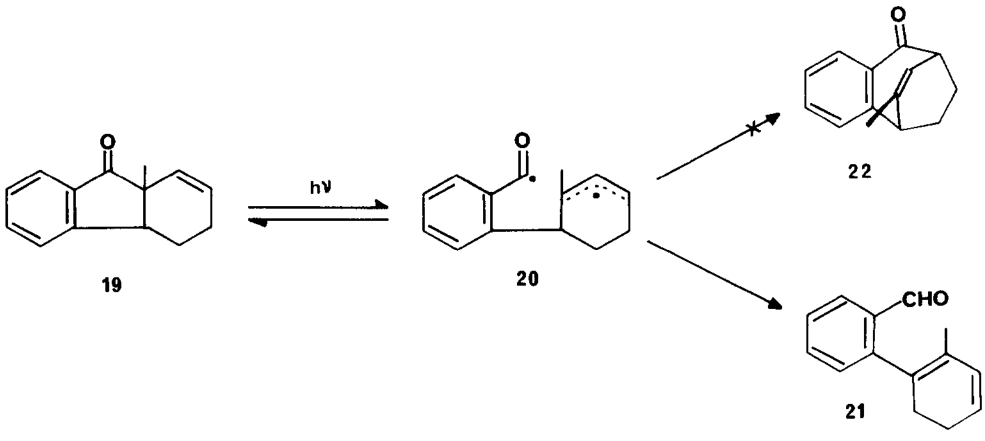
It is interesting that the two systems (**3** and **5**), related to **8**, do not undergo the DPM rearrangement. We believe that **3b** undergoes a 1,3-acyl shift because of the enhanced stability of diradical **23** (allylic and benzylic) over that of diradical **17**. This argument does not apply to the corresponding diradical **24** derived from **3a**. Here, a consideration of molecular models shows that the vinyl-vinyl bridged diradical **25**, a probable transient species along the DPM reaction coordinate, is very strained. Thus, a 1,3-acyl shift, via **24**, is probably an energetically more favorable process.

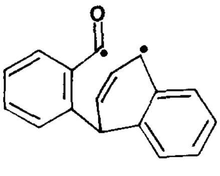
The fact that neither **8**, where both DPM and ODPM rearrangements are possible, nor **19**, where only ODPM rearrangement is possible, undergo ODPM rearrangements indicate the importance of a delocalized excited enone (e.g. **14**) as well as of geometric constraints for the chosen pathway. The rearrangement of **8** may reflect the difference in energy, on the reaction hypersurface, between the benzovinyl bridged structure **15**, where the electron on oxygen can be delocalized over 7 atoms, and the vinylcarbonyl bridged structure **26**, where no delocalization of the electrons is possible.

It is certainly remarkable that the di-π-methane reaction is preferred in the case of **8** in spite of the necessity of a benzyovinyl bridging which is often found to be less favorable in other systems.

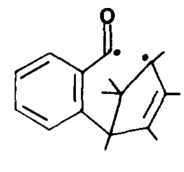
EXPERIMENTAL

5,8-endo-*Etheno-5,6,7,8-tetrahydro-N-methyl-9-oxo-benzocyclohepten-6,7-dicarboximide* (**8b**). A soln of 5H-benzocyclohepten-5-one[11] (3.2 g, 0.02M) and N-methyl maleimide

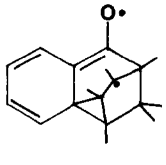




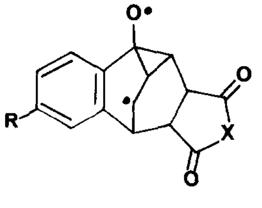
23



24



25



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(2.2 g, 0.02M) in toluene (10 ml) was refluxed overnight. Cooling afforded cream micro-crystals which were recrystallized from EtOAc to give colorless microcrystals (3.6 g, 66%) m.p. 219°. ν_{max} (nujol) 1670, 1700 and 1780 cm^{-1}; λ_{max} (EtOH) 260 (6,400), 293.5 (1700), 301 (sh), 338 (81); δ ($CDCl_3$) 8–8.3 and 7.2–7.62 (4H, m), 6.62 (2H, 2 × td J = 7 Hz, 7 Hz and 1.5 Hz) 4.2 (2H, td J = 7 Hz, 7 Hz and 1.5 Hz), 3.38 (2H, s), 2.99 (3H, s) (Found: C, 71.8; H, 5.0; N, 5.2. $C_{16}H_{13}NO_3$ Requires: C, 71.9; H, 4.9; N, 5.2%).

5,8 - endo - *Etheno* - 5,6,7,8 - *tetrahydro* - 9 - *oxo* - *benzocyclohepten* - 6,7 - *dicarboxylic anhydride* (**8a**, 85%), prepared in an analogous manner from maleic anhydride, colorless feathers m.p. 170° (from benzene) ν_{max} (nujol) 1860, 1780, 1670 and 1630 cm^{-1}; λ_{max} (EtOH) 257 (5800), 293 (1600), 336 (138), 349 (sh); δ ($CDCl_3$) 7.9–8.3 and 7.3–7.6 (4H, m), 6.79 and 6.28 (2H, 2xt J = 8 Hz, 8 Hz), 5.78 (1H, bd, J = 8 Hz), 5.82 (1H, bd, J = 8 Hz), 3.8 (2H, s). (Found: C, 71.1; H, 3.9; $C_{15}H_{10}O_4$ requires: C, 70.9; H, 4.0%).

5.8 - endo - 5,6,7,8 - *Tetrahydro* - 9 - *oxo* - *N* - *phenylbenzocyclohepten* - 6,7 - *dicarboximide* (**8c**, 66%), obtained similarly from N-phenylmaleimide, colorless needles m.p. 224–226° (from EtOAc); ν_{max} (nujol) 1772, 1702, 1669, 1600 cm^{-1}; λ_{max} (EtOH) 260 (6900), 294 (1800), 340 (88); δ (TFA) 8.05–8.55 (1H, m), 7.0–7.85 (8H, m), 6.88 (1H, t, J = 8 Hz and 8 Hz), 6.34 (1H, t, J = 8 Hz and 8 Hz), 4.17–4.63 (2H, m), 3.8 (2H, s). (Found: C, 76.4; H, 4.5; N, 4.3; $C_{21}H_{15}NO_3$ Requires: C, 76.6; H, 4.6; N, 4.25%).

5,8 - endo - *Etheno* - 5,6,7,8 - *tetrahydro* - 3 - *methoxy* - 9 - *oxobenzocycloheptene* - 6,7 - *dicarboxylic anhydride* (**8d**, 72%), was prepared similarly from 2-methoxy-5H-benzocycloheptene-5-one,[11] colorless needles, m.p. 208–209° (from toluene); ν_{max} (nujol) 1850, 1780, 1665, 1595 cm^{-1}; λ_{max} (EtOH) 231 (2500), 289 (2200), 349 (135); δ (d_6-acetone) 8.1 (1H, d J = 9 Hz), 6.7–7.3 (3H, m), 7.46 (1H, t J = 8 Hz and 8 Hz), 4.32 (1H, bd), 3.8–4.15 (6H, m). (Found: C, 67.4; H, 4.3; $C_{16}H_{12}O_5$ Requires: C, 67.7; H, 4.2%).

5,8 - endo - *Etheno* - 5,6,7,8 - *tetrahydro* - 3 - *methoxy* - *N* - *methyl* - 9 - *oxobenzocycloheptene* - 6,7 - *dicarboximide* (**8e**, 81%), similarly prepared, colorless microcrystals, m.p. 279–280° (from toluene); ν_{max} (nujol) 1770, 1680, 1658, 1580 cm^{-1}; λ_{max} (EtOH) 231 (2500); δ (TFA) 8.32 (1H, d, J = 9 Hz), 6.6–7.3 (3H, m), 6.35 (1H, t, J = 8 Hz and 8 Hz), 4.15–4.6; (2H, m), 4.08 (3H, s), 3.82 (2H, s), 3.12 (3H, s). (Found: C, 68.7; H, 5.05; N, 4.7; $C_{17}H_{15}NO_4$ Requires: C, 68.7; H, 5.05; N, 4.7%).

8 - *Bromo* - 5,8 - *exo* - *etheno* - 5,6,7,8 - *tetrahydro* - 9 - *oxobenzocycloheptene* - 6,7 - *dicarboxylic anhydride* (**8f**). A soln of 6 - bromo - 5H - benzocyclohepten - 5 - one[11a] (1 g; 0.0042 mol) and maleic anhydride (0.5 g; 0.0045 mol) in toluene (15 ml) was refluxed overnight. The soln was cooled to give colorless microcrystals (0.6 g; 40%) m,p. 136–137°; ν_{max} (nujol) 1860, 1777, 1692 cm^{-1}; λ_{max} 259 (6850), 295 (1750), 340 (95) (sh); δ ($CDCl_3$) 8.2 (1H, m), 7.3–7.7 (3H, m), 6–7 (2H, m), 4.3 (1H, bd), 3.7–4.1 (2H, m).

Photolyses. Solutions of the adducts **8** (1 g) in the appropriate solvent (150 ml) (Table 2) were degassed for 0.5 hr with N_2 and then irradiated in a Rayonet or Hanovia photochemical apparatus. The rearrangements were followed by tlc and on completion solvents was removed *in vacuo* and the residue triturated with ether to give the crystalline photoproducts **9** directly.

2,2a,2b,7,7a,7b - *Hexahydro* - 7 - *oxo* - 1H - *benzo[f]cycloprop[cd]indene* - 1,2 - *dicarboxylic anhydride* (**9a**, 93%), colorless microcrystals m.p. 169–170° (from benzene). ν_{max} (nujol) 1860, 1783, 1690, 1600 cm^{-1}; λ_{max} (EtOH) 255 (7400), 303 (1600), 349 (112); δ ($CDCl_3$) 7.2–8.1 (4H, m), 3.8 (1H, d, J = 6 Hz), 3.27 (2H, s), 2.2–2.94 (3H, m). (Found: C, 70.6; H, 4.0; $C_{15}H_{10}O_4$ Requires: C, 70.9; H, 3.9%).

2,2a,2b,7,7a,7b - *Hexahydro* - N - *methyl* - 7 - *oxo* - 1H – *benzo[f]cycloprop[cd]indene* - 1,2 - *dicarboximide* (**9b**, 84%), buff microcrystals m.p. 170–171° (from methanol). ν_{max} (nujol), 1775, 1695, 1680, 1600 cm^{-1}; λ_{max} (EtOH) 254 (6900), 298.5 (1500), 349 (57); δ ($CDCl_3$) 7.2–8.1 (4H, m), 3.7 (1H, d, J = 6 Hz), 3.1 and 2.97 (5H, s and AB system), 2.25–2.7 (3H, m). (Found: C, 71.7; H, 5.0; N, 5.3;; $C_{16}H_{13}NO_3$ Requires: C, 71.9; H, 4.9; N, 5.2%).

2,2a,2b,7,7a,7b - *Hexahydro* - 7 - *oxo* - N - *phenyl* - 1H - *benzo[f]cycloprop[cd]indene* - 1,2 - *dicarboximide* (**9c**, 68%); colorless flakes m.p. 196–198° (from ethyl acetate); ν_{max} (nujol) 1780, 1710, 1690, 1600 cm^{-1}; λ_{max} (EtOH) 251 (7900), 299 (1500), 349 (70); δ ($CDCl_3$) 7.8 (1H, m) 7.1–7.6 (8H, m), 3.76 (1H, bd, J = 6 Hz), 3.03 (2H, AB system), 2–2.7 (3H, m). (Found: C, 76.5; H, 4.6; N, 4.25; $C_{21}H_{15}NO_3$ Requires: C, 76.6; H, 4.6; N, 4.25%).

2,2a,2b,7,7a,7b - *Hexahydro* - 4 - *methoxy* - 7 - *oxo* - 1H - *benzo[f]cycloprop[cd]indene* - 1,2 - *dicarboxylic anhydride* (**9d**, 93%), colorless plates m.p. 195–197° (from ethyl acetate); ν_{max} (nujol) 1870, 1780, 1680, 1600 cm^{-1}; λ_{max} (EtOH) 236 (13000) (sh); 282 (13200), 349 (85); δ [$(CD_3)_2CO$/DMSO d_6] 7.75 (1H, d, J = 9 Hz), 7.28 (1H, d, J = 2 Hz), 7.0 (1H, dd, J = 9 Hz, 2 Hz), 5.98 (3H, s), 5.6 (1H, d, J = 6 Hz), 5.35 (2H, bs), 2.28–2.9 (3H, m). (Found: C, 67.45; H, 4.3; $C_{16}H_{12}O_5$ Requires: C, 67.6; H, 4.2%).

2,2a,2b,7,7a,7b - *Hexahydro* - 4 - *methoxy* - N - *methyl* - 9 - *oxo* - 1H - *benzo[f]cycloprop[cd]* - *indene* - 1,2 - *dicarboximide* (**9e**, 63%), buff prisms m.p. 181–182° (from EtOAc); ν_{max} (nujol) 1765, 1690, 1680, 1600 cm^{-1}; λ_{max} (EtOH) 235 (10400), 281 (10150), 349 (49) δ ($CDCl_3$) 7.76 (1H, d, J = 9 Hz), 6.76–7.0 (2H, m), 3.9 (3H, s), 3.56 (1H, d, J = 6 Hz), 3.0 and 2.7–3.1 (5H, s and AB system), 2.1–2.6 (3H, m). (Found: C, 68.7; H, 5.1; N, 4.7; $C_{17}H_{15}NO_4$ Requires: C, 68.7; H, 5.1; N, 4.7%).

7a - *Bromo* - 2,2a,2b,7,7a,7b - *hexahydro* - 7 - *oxo* - 1H - *benzo[f]cycloprop[cd]indene* - 1,2 - *dicarboxylic anhydride* (**9f**, 72%), buff microcrystals, m.p. 219–220° (from ethyl acetate); ν_{max} 1865, 1790, 1705 cm^{-1}; δ ($CDCl_3$–DMSOd_6) 7.28–7.85 (4H, m), 3.44 (2H, AB system), 2.7–3.1 (2H, m), 2.3–2.6 (1H, m); molecular ions. (Found 333.9661, Calc. for $^{12}C_{15}{}^{1}H_9{}^{16}O_5{}^{81}Br_1$ 333.9659; 331.9685 calc. for $^{12}C_{15}{}^{1}H_9{}^{16}O_5{}^{79}Br_1$ 331.9684).

Quenching studies. Solutions of **8a** (1.4×10^{-4} moles) in deuteriobenzene (0.4 ml) with and without added piperylene were irradiated, in NMR tubes, with a Hanovia lamp (pyrex filter). The composition of the photolysate was determined directly by ^1H NMR. These results are summarized in Table 4.

3,4,4a,9a - *Tetrahydro* - 9a - *methylfluoren* - 9 - *one* (19). To a soln of K (3 g, 0.66 g atom) in t-BuOH (65 ml) was added 2,3,4,4a-tetrahydrofluoren-9-one[18] (900 mg, 0.005 M) in t-BuOH (20 ml) followed by MeI (5 ml, 0.08 M) at 30–40°. After stirring for 10 min 2 M H_2SO_4 was added to bring the soln to pH 5. The soln was concentrated, extracted with ether and the organic phase washed with water, dried ($MgSO_4$) and evaporated to leave a brown oil (800 mg) which crystallized on standing. Recrystallization from light petroleum (b.p. 40–60°) at −30° afforded colorless microcrystals (600 mg, 62%) m.p. 52–53°; ν_{max} (nujol) 1707, 1607 cm^{-1};

δ (CCl_4) 7.1–7.9 (4H, m), 5.25–5.9 (2H, m), 3.0–3.3 (1H, m), 1.5–2.4 (4H, m), 1.31 (3H, s). (Found: C, 84.8; H, 7.1; $C_{14}H_{14}O$ Requires: C, 84.8; H, 7.1%).

Photolysis of 3,4,4a,9a - *tetrahydro* - 9a - *methylfluoren* - 9 - *one* (19). A soln of 3,4,4a,9a-tetrahydro-9a-methylfluoren-9-one (250 mg) in reagent acetone (100 ml) was degassed for 0.5 hr with N_2 and then irradiated with R.P.R. 2537A lamps. After 9 hr tlc (SiO_2:CH_2Cl_2) showed, besides starting material (R_f 0.5), the presence of a new product (R_f 0.65). Solvent was evaporated to leave a brown gum. The mixture was separated by preparative thick layer chromatography on silica with CH_2Cl_2 as solvent to give starting material (150 mg, 60%), and **21** (45 mg, 25%) as a tan gum. ν_{max} (liquid film) 2760, 1670, 1597 cm^{-1}; δ (CCl_4) 9.95 (1H, s), 7.85 (1H, bd), 7.0–7.7 (3H, m), 5.89 (2H, s), 2.34 (4H, s), 1.56 (3H, s).

X-Ray crystallography. Crystals of **9f** were examined by Weissenberg and precession photography and gave the following crystal data: $C_{15}H_9O_4Br$, Monoclinic, $P2_1/C, Z = 4$. Cell dimensions $a = 10.09(1)$, $b = 9.91(1)$, $c = 13.28(1)$Å; $\beta = 110.85(2)°$. $V = 1240.1$ Å^3, $F(000) = 664$, $\mu(\mathrm{Mo}K\alpha) = 32.27$ cm^{-1}. Crystal size 0.5 × 0.5 × 0.3 mm.

Intensity data were collected for layers *hkO*-11 in the range $5 < \theta < 25$ with Mo$K\bar{\alpha}$ radiation ($\lambda = 0.71069$Å). 1877 reflexions were collected of which 1559 had $I > 3\sigma(I)$. Lorentz, polarization, and absorption corrections were applied and the structure solved by normal heavy atom methods. Hydrogen atoms were introduced and the other atoms made anisotropic. The weighting scheme used was $w = (\sigma^2(F) + 0.014F^2)^{-1}$ and full matrix least squares was used throughout. Scattering factors were taken from *International Tables for X-ray Crystallography*[19] and all calculations were done on a CDC 7600 using the SHELX[20] programs. At the end of the refinement the conventional R-factor was 0.070.

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