Tetrahedron Vol. 34, pp. 2305–2314
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0040-4020/78/0801-2305/$02.00/0

THERMAL ADDITION OF DIBENZOYLACETYLENE TO CYCLOHEPTATRIENE AND THE PHOTO-REARRANGEMENT OF THE THERMAL ADDUCT

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(*Received in the UK* 30 *June* 1977; *Accepted for publication* 8 *January* 1978)

Abstract—The reaction of cycloheptatriene (CHT) with dibenzoylacetylene (DBA), in refluxing toluene gave a mixture of products consisting of 6,7-dibenzoyltricyclo[3.2.2.$0^{2,4}$]nona-6,8-diene 6 and 3,4-dibenzoylbicyclo[3.2.2]nona-2,6,8-triene 7. Neat heating of a mixture of CHT and DBA around 95–100° gave besides, 6 and 7, small amounts of two dimers of DBA. Photolysis of 6 in benzene solution gave a lactonic, rearrangement product. 25. The structures of the various products have been established and reasonable mechanisms for their formation have been suggested.

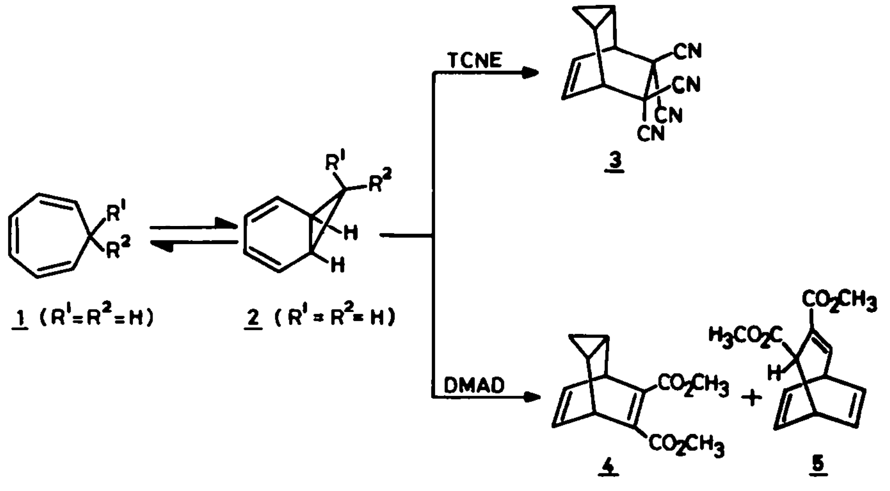
Several addition reactions of cycloheptatriene with olefinic substrates have been reported in the literature. The reaction of cycloheptatriene (CHT) with tetracyanoethylene (TCNE), for example, has been shown to give the 1:1-adduct 3.[1] The reaction of CHT with dimethyl acetylenedicarboxylate (DMAD), on the other hand, gave a mixture of products consisting of 4 and 5 (Scheme 1).[2,3] The formation of the 1:1-adducts 3 and 4 in these reactions has been rationalized in terms of the Diels–Alder additions of the respective dienophiles with the norcaradiene form 2, of the starting cycloheptatriene 1. It is known that the valence isomerization of 1 to give the norcaradiene 2 is a symmetry allowed, $[\pi^2s+\pi^2s+\pi^2s]$ type of reaction[4] and that the direction of the equilibrium between 1 and 2 is markedly influenced by the substituents (R^1 and R^2) present in 1. Thus, it has been observed that when π-acceptor substituents are present, the equilibrium is shifted in favour of the norcaradiene form 2, whereas π-donor substituents stabilize the cycloheptatriene form 1.[5] Goldstein and Gevirtz[3] have studied the addition reactions of DMAD with different substituted cycloheptatrienes and have shown that steric effects play a dominant role in dictating the stereochemical outcome of these addition reactions.

Apart from the Diels–Alder mode of addition, an "ene-type" of addition reaction has also been observed in the case of cycloheptatriene. Thus, the formation of the adduct 5 in the reaction of 1 with DMAD has been assumed to arise through this pathway.[2]

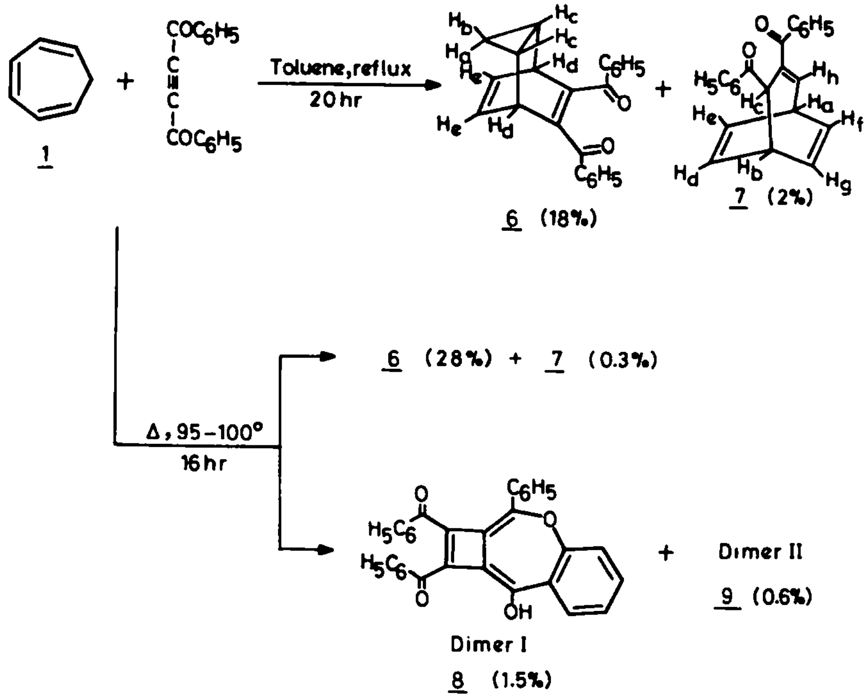
The object of the present investigation has been to examine the reaction of CHT with a dienophile like dibenzoylacetylene (DBA) with a view to studying the mode of addition in this case. In addition, we were interested in employing this reaction for the preparation of a suitably substituted *cis*-1,2-dibenzoylalkene system and to examine its photochemical rearrangements.

RESULTS AND DISCUSSION

Treatment of a mixture of CHT with DBA in refluxing toluene for 20 h resulted in the formation of a mixture of products consisting of 6,7-dibenzoyltricyclo[3.2.2.$0^{2,4}$]nona-6,8-diene 6 (18%) and 3,4-dibenzoylbicyclo[3.2.2]nona-2,6,8-triene 7 (2%) (Scheme 2). The structures of 6 and 7 were confirmed on the basis of analytical results and spectral information.



Scheme 1.



Scheme 2.

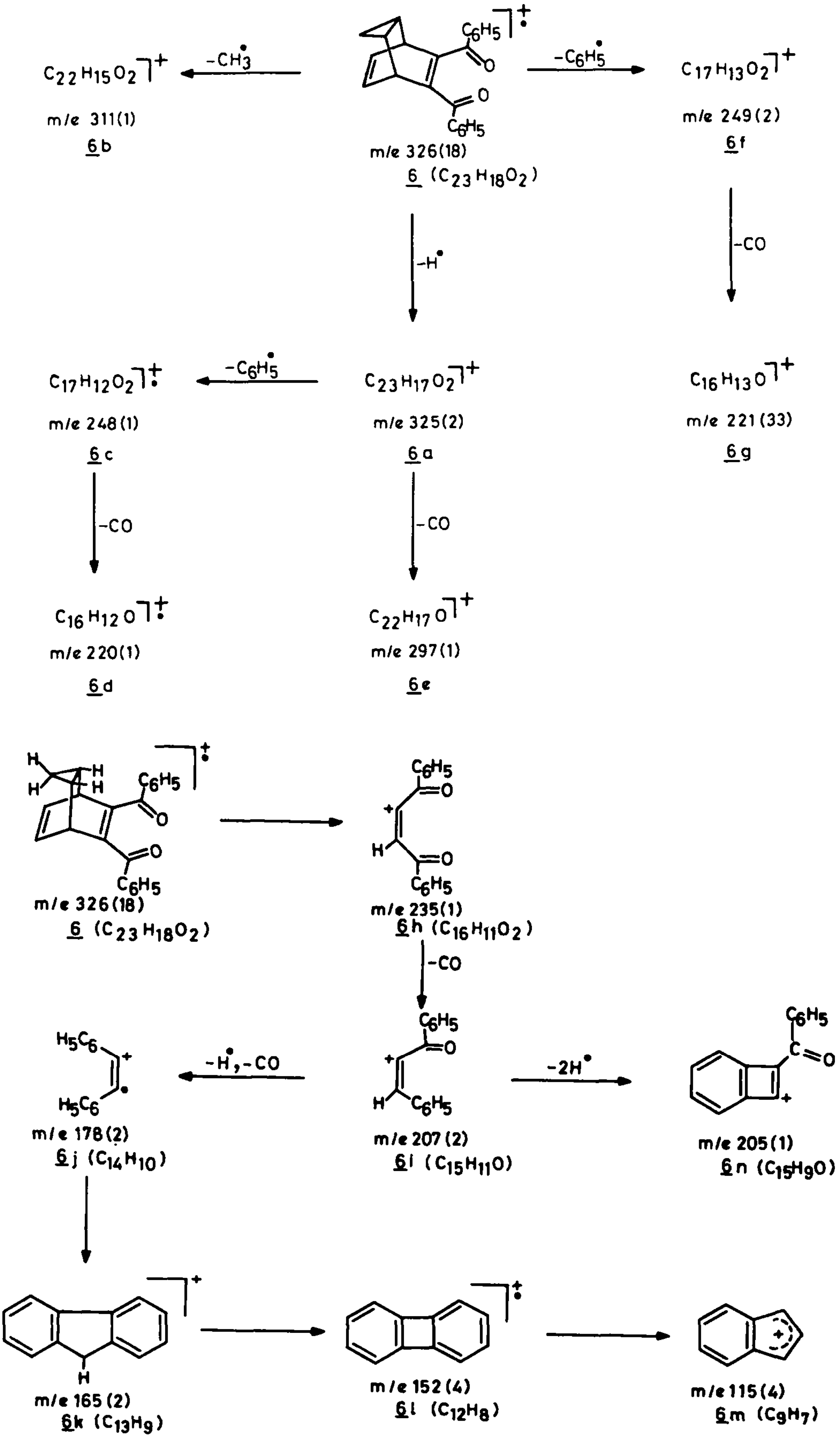
The IR spectrum of **6**, for example, showed a carbonyl absorption peak at 1645 cm^{-1}. The UV spectrum of **6** showed an absorption at 255 nm (ϵ, 13,500). Table 1 lists the UV and IR absorption data of a few 1,2-dibenzoyl-alkene systems which are reported in the literature.[6,7] Examination of this table reveals that the 1,2-dibenzoyl-alkenes are characterized by the presence of an absorption maximum in the range of 255–262 nm and that the spectral data of **6** are in agreement with its assigned structure.

The NMR spectrum of **6** for example, showed several multiplets at 0.72δ (1H), 0.88δ (1H), 1.68δ (2H), 4.30δ (2H), 6.27δ (2H) and 7.22δ (10H). Of these, the multiplet at 0.72δ has been assigned to the more shielded H_a proton of the cyclo-propane ring. Such shielding effects of the proton endo with respect to the double bond of **6** has been observed in analogous adducts of cycloheptatriene with different dienophiles.[1,3,8] The signals at 0.88δ and 1.68δ have been assigned to the H_b and H_c protons, respectively of the cyclopropane ring. The signals at 4.30δ and 6.27δ have been assigned to the bridgehead and olefinic protons, respectively, whereas the complex multiplet around 7.22δ has been attributed to the aromatic protons.

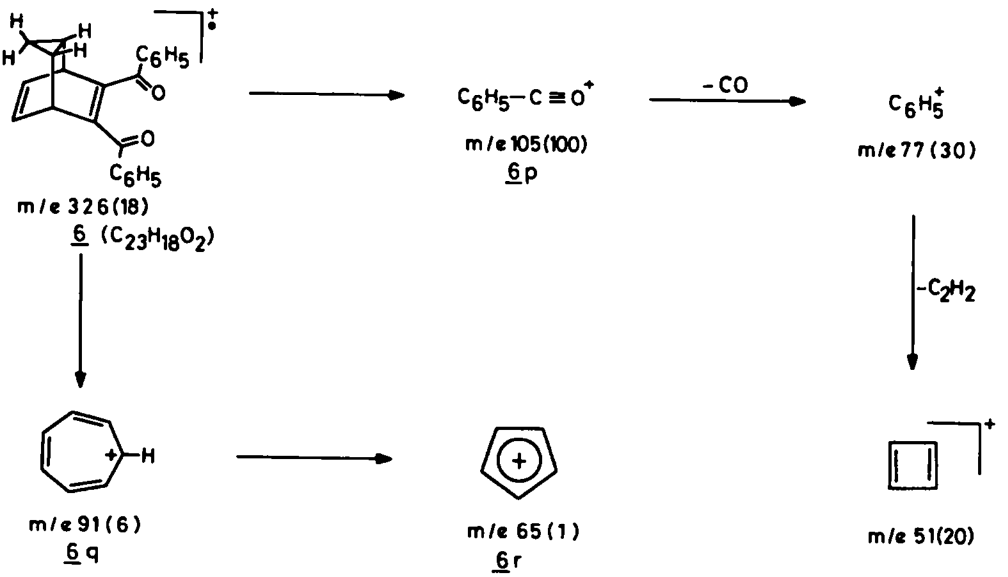
The mass spectrum of **6** revealed several interesting features. The molecular ion peak was observed at *m/e* 326 (18), whereas other prominent peaks were observed at 325 (2), 311 (1), 270 (7), 249 (2), 235 (1), 221 (33), 204 (2), 193 (2), 172 (2), 165 (2), 152 (1), 115 (4), 105 (100), 91 (6), 77 (30) and 51 (20), which can be assigned to some of

Table 1. UV and IR absorption characteristics of some 1,2-dibenzoyl-alkenes

Compound	UV absorptions λ_{max}^{EtOH} nm (ϵ)	IR absorptions $\nu_{C=O}$, cm^{-1}	$\nu_{C=C}$, cm^{-1}	Ref.
1 *cis*-1,2-Dibenzoylethylene	260 (18,100)	1650	1600,1580	6
2 2,3-Dibenzoylbicyclo-[2.2.1]hepta-2,5-diene	250 (16,200)	1635	1602,1575	7
3 2,3-Dibenzoylbicyclo-[2.2.2]octa-2,5-diene	256 (15,100)	1640	1605,1580	7
4 7-Oxa-2,3-dibenzoyl-bicyclo[2.2.1]hepta-2,5-diene	256 [13,000)	1645	1600,1580	7
5 1,4-Diphenyl-2,3-dibenzoyl-1,4-epoxynaphthalene	258 (14,000)	1657	1601,1581	7
6 9,10-Dihydro-11,12,-dibenzoyl-9,10-ethenoanthracene	262 (15,000)	1670	1620,1590	7
7 6,7-Dibenzoyltricyclo-[3.2.2.$0^{2,4}$]nona-6,8-diene **6**	255 (13,500)	1645	1595,1580	7
8 3,4-Dibenzoylbicyclo-[3.2.2]nona-2,6,8-triene **7**	250 (20,000)	1660 and 1680	1600,1585	7


-CH$_3^•$
$C_{22}H_{15}O_2$]+
m/e 311(1)
6b
m/e 326(18)
6 ($C_{23}H_{18}O_2$)
-$C_6H_5^•$
$C_{17}H_{13}O_2$]+
m/e 249(2)
6f
-CO
$C_{16}H_{13}O$]+
m/e 221(33)
6g
-H$^•$
$C_{23}H_{17}O_2$]+
m/e 325(2)
6a
-$C_6H_5^•$
$C_{17}H_{12}O_2$]+•
m/e 248(1)
6c
-CO
$C_{16}H_{12}O$]+•
m/e 220(1)
6d
-CO
$C_{22}H_{17}O$]+
m/e 297(1)
6e
m/e 326(18)
6 ($C_{23}H_{18}O_2$)
m/e 235(1)
6h ($C_{16}H_{11}O_2$)
-CO
-H$^•$, -CO
m/e 178(2)
6j ($C_{14}H_{10}$)
m/e 207(2)
6i ($C_{15}H_{11}O$)
-2H$^•$
m/e 205(1)
6n ($C_{15}H_9O$)
m/e 165(2)
6k ($C_{13}H_9$)
m/e 152(4)
6l ($C_{12}H_8$)
m/e 115(4)
6m (C_9H_7)

Scheme 3.



Scheme 3 (*Contd*).

the fragments shown in Scheme 3. The peak at *m/e* 325 has been assigned to the fragment **6a**, formed by the elimination of one hydrogen atom, whereas the peak at *m/e* 311 could be assigned to the fragment **6b**, formed through the loss of one methyl group. Similar loss of hydrogen atom and methyl groups have been observed in the mass spectra of several cycloheptatriene derivatives.[9,10] The peaks at *m/e* 248 and 220 were assigned to the fragments **6c** and **6d** respectively, arising through the fragmentation of **6a**. Elimination of a phenyl radical from **6** could lead to the fragment **6f** at *m/e* 249, which in turn can lose CO to give **6g** at *m/e* 211. The fragment **6g** may also be formed through an α-cleavage of **6**, with the elimination of a benzoyl group. Another mode of fragmentation of **6**, involves a retro-Diels-Alder reaction with hydrogen transfer, leading to fragments **6h** at *m/e* 235 and **6q** at *m/e* 91. The highest intensity peak at *m/e* 105 (100) has been assigned to the benzoyl fragment **6p**.

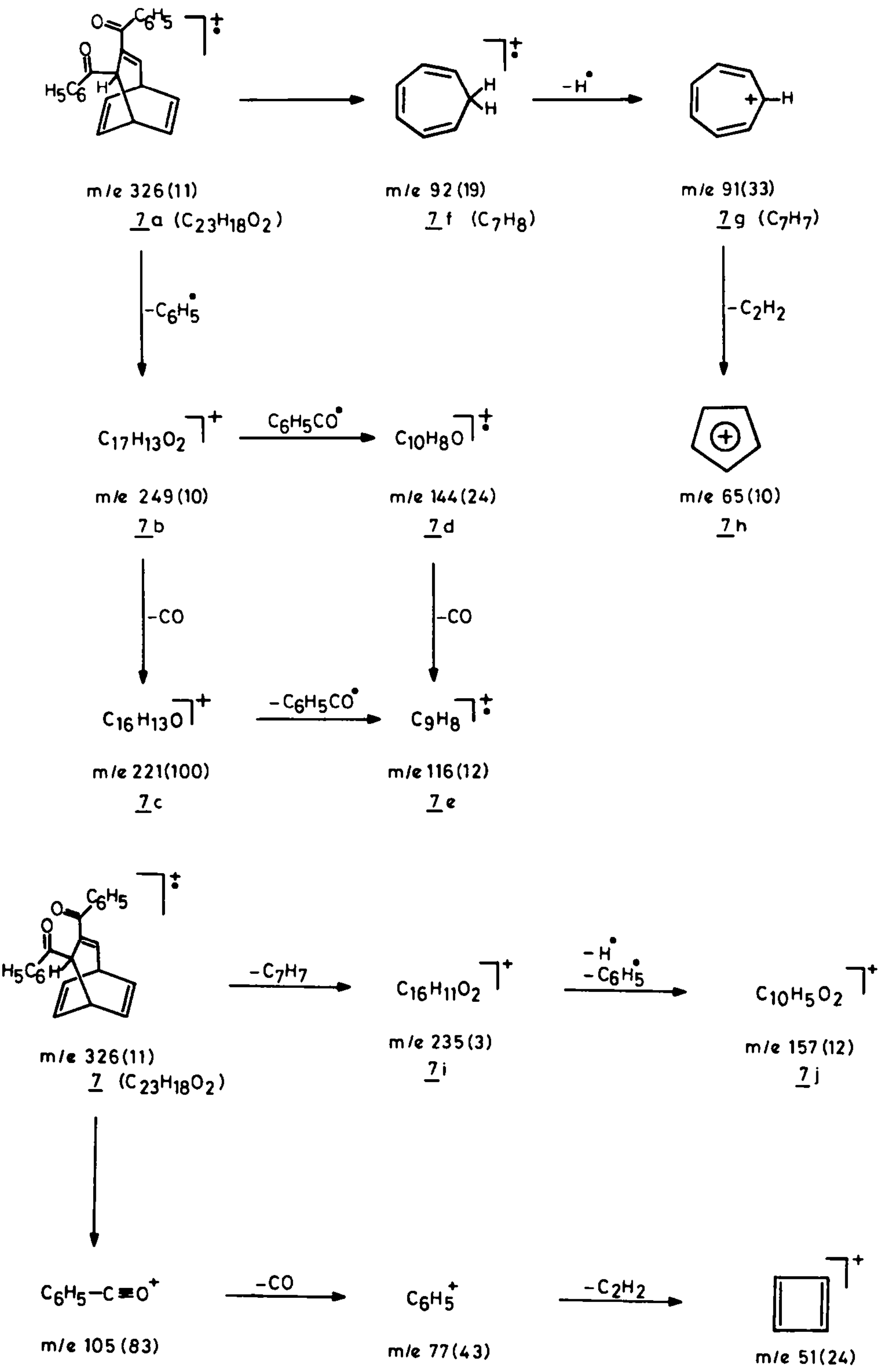
The structure of **7**, likewise, has been arrived at, on the basis of spectral evidences and analytical data. The IR spectrum of **7**, showed the presence of two carbonyl absorptions at 1680 and 1660 cm^{-1}, respectively. It has been observed that in most of the *cis*-1,2-dibenzoylalkenes that we have examined (Table 1), the α,β-unsaturated carbonyl absorptions occur around 1635–1660 cm^{-1}. On the basis of analogy, therefore, the band at 1660 cm^{-1} has been assigned to the α,β-unsaturated carbonyl group in **7**, whereas the absorption band at 1680 cm^{-1} could be assigned to the carbonyl group, attached to the sp^3 carbon atom.

Further confirmation of the structure of **7** was derived from its UV spectrum. The UV spectrum of **7** showed an absorption maximum at 250 nm, whereas, it has been observed that *cis*-1,2-dibenzoylalkenes, in general, are characterized by the presence of an absorption maximum around 255–262 nm (Table 1). It might be pointed out in this connection that the absorption maximum in 1,2-dibenzoylethane, however, has been observed around 244 nm.[6]

The NMR spectrum of **7** showed a complex multiplet around 3.63δ (2H), which may be assigned to the bridgehead protons H_a and H_b. The multiplet at 4.88δ (1H) may be assigned to the methine proton, H_c, attached to the carbon atom bearing the benzoyl group. The vinylic proton, H_d, appeared as a separate multiplet around 6.0δ, whereas H_e, H_f and H_g olefinic protons appeared as a complex multiplet around 6.66δ. The vinylic proton, H_h, appeared as a doublet, each one being further split into two separate doublets ($J_{H_a,H_h} = 8.5$ cps and $J_{H_c,H_h} = 2$ cps).

Further confirmation of the structure of **7** was derived from its mass spectrum. The mass spectrum of **7** showed a low intensity molecular ion peak at *m/e* 326 (11). The most prominent peak in the mass spectrum was observed at *m/e* 221 and this peak could be assigned to the fragment **7c**, formed by the loss of a benzoyl group from **7**. Other peaks were observed at *m/e* 249 (10), 235 (3), 208 (3), 204 (4), 195 (4), 190 (2), 180 (2), 170 (2), 164 (2), 157 (12), 144 (24), 130 (8), 126 (4), 116 (12), 114 (8), 105 (83), 92 (19), 91 (33), 77 (42), 65 (10), and 51 (24). Some of the fragmentation modes are shown in Scheme 4. Elimination of a phenyl group from **7**, for example, will lead to the formation of **7b** at *m/e* 249. Further loss of a benzoyl group from **7b**, will result in the fragment **7d**, at *m/e* 144. A similar loss of one benzoyl group from **7c** results in the formation of **7e** at *m/e* 116. A retro-addition mode of fragmentation has been observed due to the presence of the fragment **7i** at *m/e* 235. The peak at *m/e* 92 can be assigned to the fragment **7f**, formed through the fragmentation of **7a**, proceeding with hydrogen-transfer. Other peaks in the mass spectrum of **7**, can likewise be assigned to some of the fragments shown in Scheme 4.

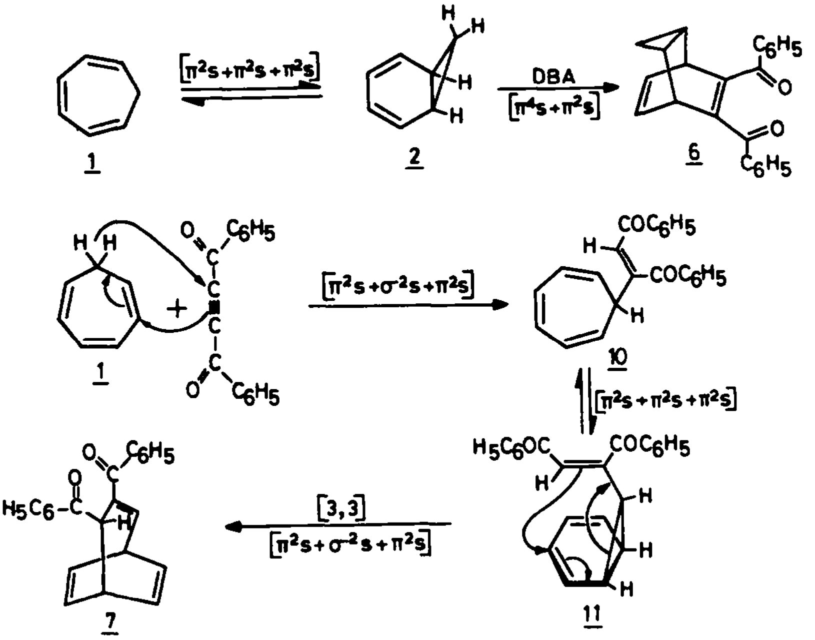
The formation of the adducts **6** and **7** in the reaction of cycloheptatriene with DBA has been rationalized in terms of the pathway shown in Scheme 5. In this scheme we assume that the adduct **6** is formed through the Diels–Alder reaction of the valence isomer **2**, of cycloheptatriene **1**. The formation of the adduct **7**, on the other hand, can be rationalized in terms of an initial "ene-reaction" between cycloheptatriene and DBA to give the intermediate **10**, which essentially involves a $[\pi^2s + \sigma^2s + \pi^2s]$ type of addition reaction. The adduct **10**, bearing a "π-acceptor" substituent will undergo facile valence isomerization to give the norcaradiene



Scheme 4.

derivative 11, which in turn can subsequently undergo a thermally allowed, [3, 3] sigmatropic shift to give the adduct 7 (Scheme 5).

When a mixture of DBA and excess of CHT was heated around 95–100° for 16 h, in the absence of any solvent, a 28% yield of 6 and 0.3% yield of 7 were obtained. In addition, small yields of two dimeric products of DBA, tentatively identified as 8 (1.5%) and 9 (0.6%) were also isolated from this reaction. Dimer I, identified as 8, melted at 206° and analysed for $C_{32}H_{20}O_4$. The IR spectrum of 8 showed an OH band at $3455\,cm^{-1}$ and carbonyl absorptions at 1670, 1655 and $1630\,cm^{-1}$, respectively. The NMR spectrum of 8 showed a singlet at 4.16δ (1H) assigned to the OH proton and multiplets



Scheme 5.

around 7.46δ (15H) and 8.26δ (4H), assigned to the aromatic protons. Further confirmation of the structure of 8, was derived from its mass spectrum. The mass spectrum of 8 showed a peak at m/e 468, assigned to the molecular ion peak.

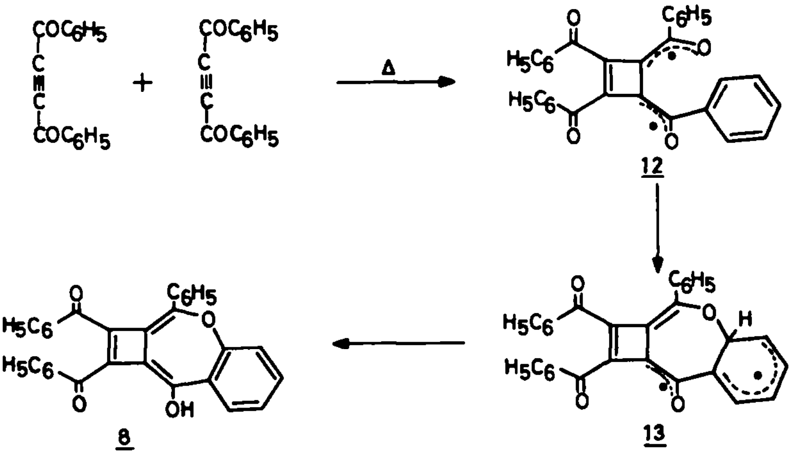
Quite recently Tsutsui et al.[11] have reported the formation of a dimer of DBA, on heating it around 150–200° in either decalin or chlorobenzene and have assigned the structure 8, for this product. They have rationalized the formation of 8, in terms of the pathway shown in Scheme 6.

The dimer II 9, m.p. 181°, analyzed for $C_{32}H_{20}O_4$. The mass spectrum of 9 showed a molecular ion peak at m/e 468 and was found to be quite similar to 8, as far as the fragmentation pattern was concerned. The exact structure of this dimer has yet to be established.

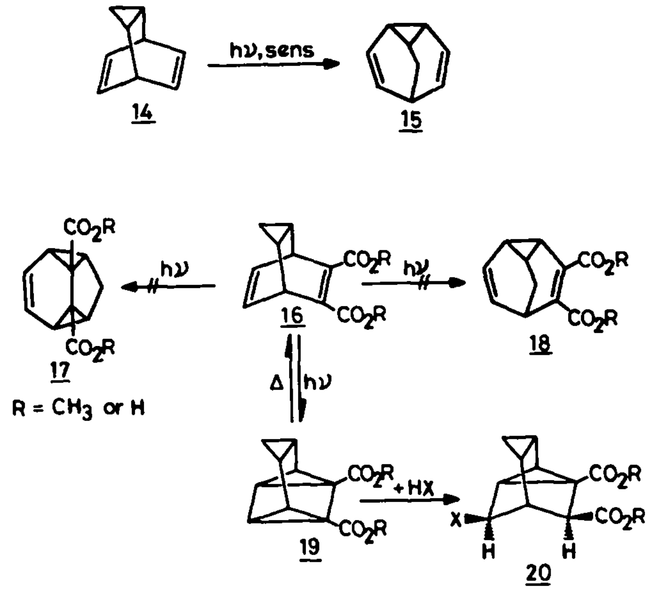
Photochemical transformations of 6,7-dibenzoyltricyclo-[3.2.2.0^{2,4}]nona-6,8-diene 6

The photochemical transformation of tricyclo[3.2.2.0^{2,4}]-nona-6,8-diene 14 has been reported to give rise to the dihydrosemibullvalene, 15, when the irradiation is carried out in the presence of a sensitizer like acetone (Scheme 7).[12] However, in the photolysis of tricyclo[3.2.2.0^{2,4}]nona-6,8-diene derivatives like 16, having substituents like carboxylic and ester groups, a [π^2s + π^2s] mode of addition, leading to the formation of the corresponding quadricyclane derivatives 19, has been observed. It has been shown that these quadricyclane derivatives are readily transformed to ring-opened products 20, in presence of protic solvents. It is interesting to note that in the photolysis of 16, none of the semibullvalene derivative, 18 could be obtained. Also, products like 17, resulting from a [σ^2s + π^2s] type of addition of 16, have not been observed, inspite of the stereochemically favourable exoarrangement of the three membered ring vis-à-vis the substituted double bond (Scheme 7).[13]

In view of our general interest in the photochemical transformations of cis-1,2-dibenzoylalkene systems, we have examined the photolysis of 6,7-dibenzoyltricyclo[3.2.2.0^{2,4}]-nona-6,8-diene 6. It might be



Scheme 6.

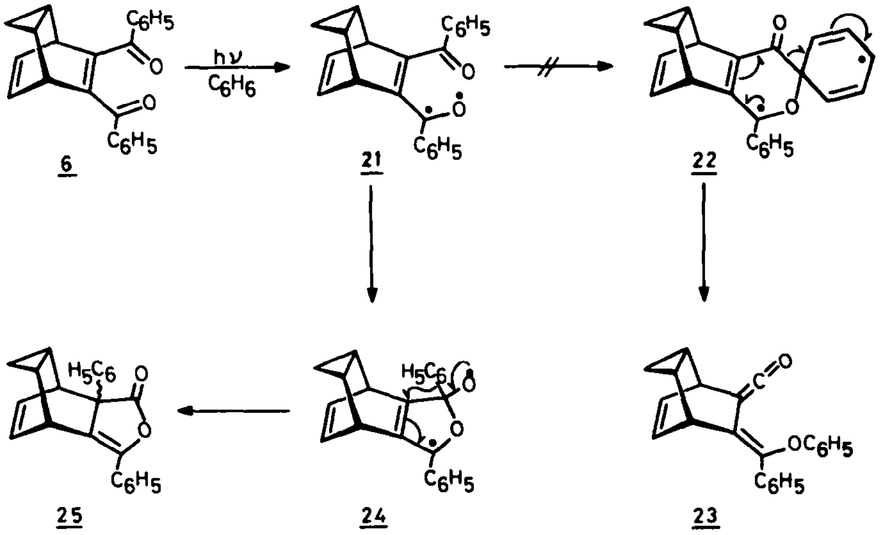


Scheme 7.

mentioned in this connection that the photolysis of dibenzoylethylenes has been studied by different group of workers, who have shown that these systems undergo interesting photorearrangements.[14–17] Thus, Zimmerman *et al.*[15,16] have shown that the photolysis of dibenzoylethylene in methanol, for example, gives rise to methyl 4-phenyl-4-phenoxy-3-butenoate. It has been suggested that this rearrangement proceeds through an initial n-π* excitation of the starting dibenzoylethylene, leading to the formation of the diradical intermediate which then rearranges to a ketene intermediate. Subsequent reaction of the ketene intermediate with methanol leads to the formation of the methyl ester.

In the present studies we have observed that the irradiation of a benzene solution of **6** for 2.5 h resulted in the formation of a 33% yield of a lactone, identified as **25** (Scheme 8). Analytical results have shown that the lactone **25** is isomeric with the starting dibenzoylalkene derivative **6**. The IR spectrum of **25**, showed a carbonyl band at 1770 cm^{-1}, characteristic of β,γ-unsaturated lactones. The UV spectrum of **25** (Fig. 1) showed several absorption maxima at 230 nm (ϵ, 5000), 242 nm (ϵ, 3500) and 260 nm (ϵ, 2500). It might be pointed out here that the UV spectrum of **25** shows remarkable similarity to the spectrum of 2,2,3,4-tetraphenylbut-3-enolide **26**, formed in the thermal rearrangement of cis-1,2-dibenzoylstilbene.[18]

The NMR spectrum of **25** showed the presence of two cyclopropyl methylene protons at 0.66δ (2H,m) and two cyclopropyl methine protons at 1.40δ (2H,m), respectively. In addition, the spectrum showed three complex multiplets at 3.85δ (2H), 5.82δ (2H) and 7.25δ (10H), which have been assigned to the bridgehead, vinylic and aromatic protons, respectively.



Scheme 8.

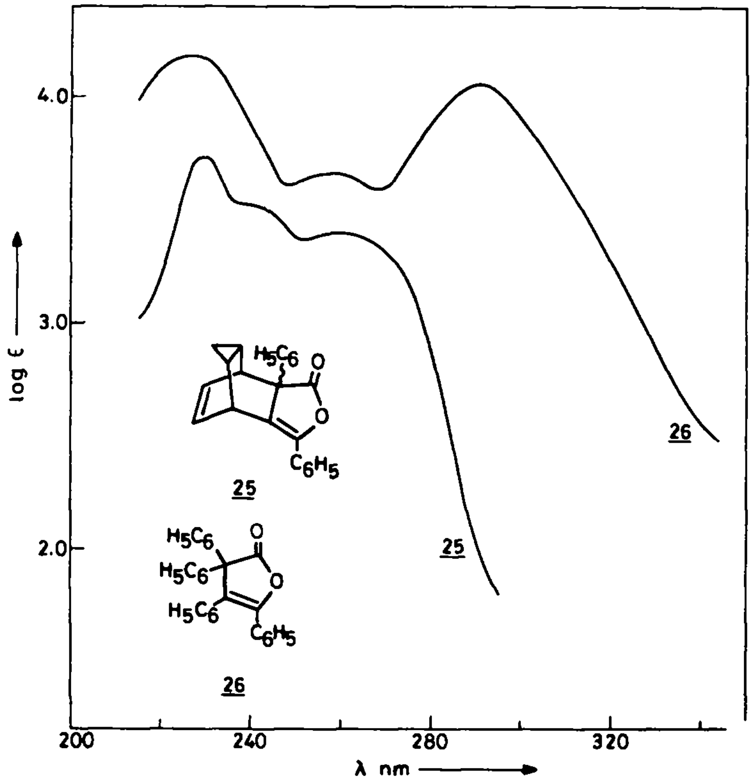
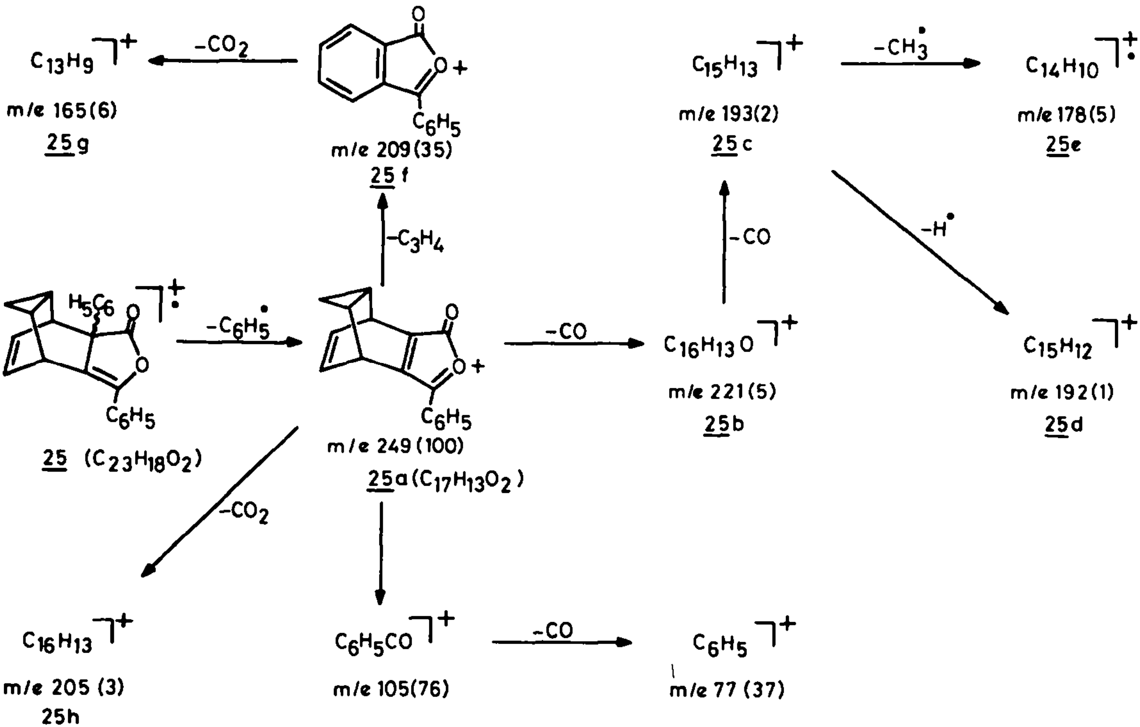


Fig. 1. Electronic spectra of **25** and **26**.

The mass spectrum of **25** did not show the molecular ion peak at *m/e* 326. However, the most intense peak in the spectrum was observed at *m/e* 249 (100). Other peaks in the spectrum were observed at *m/e* 234 (1), 232 (1), 231 (4), 221 (5), 209 (35), 205 (3), 204 (2), 203 (5), 202 (3), 193 (2), 192 (1), 191 (3), 190 (2), 189 (2), 178 (5), 165 (6), 153 (3), 152 (7), 143 (3), 127 (2), 115 (13), 105 (76), 94 (5), 91 (7), 77 (37), 65 (9) and 51 (7). Some of the probable fragmentation modes are shown in Scheme 9. The ready loss of a phenyl group from the molecular ion of **25**, to



Scheme 9.

give the stable fragment **25a**, at *m/e* 249 would perhaps explain for the absence of the molecular ion peak in the spectrum of **25**. The fragment **25a** can lose a CO fragment to give the ion **25b** at *m/e* 221, whereas the loss of a C_3H_4 fragment from **25a** will result in the fragment **25f** at *m/e* 209. The loss of CO_2 from **25a**, will lead to the fragment **25h** at *m/e* 205, whereas CO_2 loss from **25f** will give rise to the fragment **25g** at *m/e* 165. Other possible fragmentation modes are shown in Scheme 9.

The formation of the lactone **25** in the photolysis of **6** can be rationalized in terms of the pathway shown in Scheme 8. In this scheme we assume that the initial step in the reaction is a n-π^* excitation of one of the carbonyl groups present in **6** to give the diradical intermediate **21**, which subsequently interacts with the second carbonyl group to give the cyclic intermediate **24**. Rearrangement of **26**, involving a phenyl shift will lead to the lactone **25**. It might be pointed out here that ionic intermediates could also be involved in the transformation of **24** to **25**.

It is interesting to note that the photochemical transformation of a *cis*-1,2-dibenzoylalkene system like **6** results in the formation of the lactone **25** and not in a ketene derivative, **23**, arising through an alternative mode of rearrangement, as shown in Scheme 8. It might be mentioned in this connection that in the photolysis of dibenzoylethylene, for example, the photorearrangement proceeds through this alternative pathway leading to a ketene intermediate.[15,16] This difference in behaviour between **6** and dibenzoylethylene may be attributed to the difference in their structural features. The dibenzoylalkene **6**, for example, has a rigid *cis*-geometry and in this case a non-productive pathway like the *cis–trans* isomerization of the alkene double bond under photochemical conditions, will be prevented, as compared to the case of dibenzoylethylene. Further work concerning the photochemistry of different *cis*-1,2-dibenzoylalkenes having special structural features, is currently under progress.

EXPERIMENTAL

All melting points are uncorrected and were determined on a Mel-Temp. melting point apparatus. The IR spectra were recorded on Perkin–Elmer Model 521 Infrared Spectrometer. The electronic spectra were recorded on a Beckman DB Spectrophotometer. NMR traces were recorded on either a Varian A-60 or a 270 MHz NMR Spectrometer, using tetramethylsilane as internal standard. The mass spectra were recorded on a Varian Mat CH7 Mass Spectrometer at 70 eV.

Starting materials. Dibenzoylacetylene, m.p. 110–11° was prepared by a reported procedure.[19] Cycloheptatriene (Aldrich Chemical Co), b.p. 110°, was freshly distilled before use. Sodium-dried benzene was used for photolysis experiments. Petroleum ether used was the fraction b.p. 60–80°.

Reaction of cycloheptatriene with dibenzoylacetylene

(A) *In toluene.* A mixture of dibenzoylacetylene (2.3 g, 0.01 mol) and cycloheptatriene (2 g, 0.02 mol) was refluxed in toluene (50 ml) for 20 h. Removal of the solvent under vacuum gave a product which was chromatographed over alumina. Elution with a mixture (1:1) of petroleum ether and benzene gave 590 mg (18%) of 6,7-dibenzoyltricyclo[3.2.2.0^{2,4}]nona-6,8-diene **6** m.p. 133°, after recrystallization from a mixture (2:1) of petroleum ether and benzene. (Found: C, 84.84; H, 6.08; MW 326 (Mass spectrometry. $C_{23}H_{18}O_2$ requires: C, 84.66; H, 5.52%; MW 326.) IR spectrum (KBr)]sν_{max}: 3285 cm^{-1} (ν_{C-H}, cyclopropyl), 3060, 3005 and 2980 cm^{-1} (ν_{C-H}), 1645 cm^{-1} ($\nu_{C=O}$), 1595 and 1580 cm^{-1} ($\nu_{C=C}$), 1938 cm^{-1} (CH_2, wagging). UV spectrum (Ethanol) λ_{max}: 255 nm (ϵ, 13,500), 290 (6,300) and 350 (500).

Further elution of the column with benzene gave 70 mg (2%) of 3,4-dibenzoylbicyclo[3.2.2]nona-2,6,8-triene **7**, m.p. 156°, after recrystallization from a mixture (2:1) of petroleum ether and benzene. (Found: C, 84.66; H, 5.83; MW 326 (Mass spectrometry). $C_{23}H_{18}O_2$ requires: C, 84.66; H, 5.52%; MW 326.) IR spectrum (KBr) ν_{max}: 3220, 3150 and 3060 cm^{-1} (ν_{C-H}), 1680 and 1660 cm^{-1} ($\nu_{C=O}$), 1600 and 1585 cm^{-1} ($\nu_{C=C}$). UV spectrum (ethanol) λ_{max}: 250 nm (ϵ, 20,000), 274 (8700) and 320 (400).

(B) *In the absence of any solvent.* A mixture of 4.68 g (0.02 mol) of dibenzoylacetylene and excess (10 ml) of cycloheptatriene was heated in a sealed tube around 95–100° for 16 h. The reaction mixture was chromatographed over alumina. Elution with petroleum ether gave 1.8 g (28%) of **6**, m.p. 133° (m.m.p.), after recrystallization from a mixture (2:1) of petroleum ether and benzene.

Further elution of the column with a mixture (20:1) of petroleum ether and benzene gave 15 mg (0.3%) of **7**, m.p. 156° (m.m.p.), after recrystallization from a mixture (2:1) of petroleum ether and benzene.

Subsequent elution with a mixture (10:1) of petroleum ether and benzene gave 30 mg (0.6%) of the unidentified Dimer II **9**, m.p. 181°, after recrystallization from a mixture (1:1) of chloroform and petroleum ether (b.p. 60–80°). (Found: C, 81.53; H, 4.36; MW, 468 (Mass spectrometry). $C_{32}H_{20}O_4$ requires: C, 82.05; H, 4.27%; MW 468). IR spectrum (KBr) ν_{max}: 3205, 3185 and 3065 cm^{-1} (ν_{C-H}), 1655 cm^{-1} ($\nu_{C=O}$), 1638, 1630 and 1590 cm^{-1} ($\nu_{C=C}$). UV spectrum (Methanol) λ_{max}: 255 nm (ϵ, 40,000), 288 (18,200) and 328 (12,600). NMR spectrum ($CDCl_3$): 7.43δ (multiplet, 16H, aromatic) and 8.33δ (multiplet, 4H, aromatic).

Mass spectrum, *m/e* (rel. intensity): 468 (100), 451 (14), 392 (12), 391 (43), 363 (7), 313 (8) 305 (4), 276 (4), 234 (3), 229 (2), 105 (16), 92 (6), 91 (10), 78 (45) and 77 (18).

Continued elution of the column with the same solvent mixture gave 70 mg (1.5%) of the Dimer I **8**, m.p. 206°, after recrystallization from a mixture (1:1) of chloroform and petroleum ether. (Found: C, 81.72; H, 4.45; MW 468 (Mass spectrometry). $C_{32}H_{20}O_4$ requires: C, 82.05; H, 4.27%; MW 468). IR spectrum (KBr) ν_{max}: 3455 cm^{-1} (ν_{O-H}), 3195, 3055 and 2915 cm^{-1} (ν_{C-H}), 1670 and 1655 cm^{-1} ($\nu_{C=O}$), 1630 and 1590 cm^{-1} ($\nu_{C=C}$). UV spectrum (Methanol) λ_{max}: 254 nm (ϵ, 43,600), 287 (20,000) and 326 (14,000).

Photolysis of 6,7-dibenzoyltricyclo[3.2.2.0^{2,4}]*nona-6,8-diene* **6**. A solution of **6** (652 mg, 2 mmol) in benzene (210 ml) was irradiated for 2.5 h, using a 450W Hanovia medium pressure mercury lamp fitted with a Pyrex filter and under nitrogen atmosphere. The procedure was repeated five times to photolyse a total amount of 3.26 g (10 mmol) of **6**. Removal of the solvent from the combined photolyzed mixture gave a residue which was chromatographed over silica-gel. Elution of the column with a mixture (19:1) of petroleum ether and benzene gave 480 mg (33%) of white crystals of the lactone, **25**, m.p. 128°, after recrystallization from a mixture (8:1) of petroleum ether and benzene. (Found: C, 85.10; H, 5.41. $C_{23}H_{18}O_2$ requires: C, 84.66; H, 5.52%). IR spectrum (KBr) ν_{max}: 3045, 2980, 2970, 2905 and 2880 cm^{-1} (ν_{C-H}), 1770 cm^{-1} ($\nu_{C=O}$) and 1040 cm^{-1} (ν_{CH_2}, wagging). UV spectrum (Ethanol) λ_{max}: 230 nm (ϵ, 5000), 242 (3500) and 260 (2500). Further elution of the column with benzene gave 1.8 g (53%) of the starting material **6**, m.p. 133° (mixture m.p.), after recrystallization from a mixture (3:1) of petroleum ether and benzene.

Acknowledgements—The authors are grateful to Dr. K. Nagarajan of the CIBA-GEIGY Research Centre for the mass spectra and Mr. G. S. Hegde, Mr. S. K. Sinha and Mr. K. Rajagopalan of IIT Kanpur for microanalysis. One of the authors (VD) thanks the CSIR (India) for the award of a Senior Research Fellowship, while another (SL) thanks the authorities of IIT Kanpur for the award of a Research Assistantship.

REFERENCES

[1] G. H. Wahl, Jr., *J. Org. Chem.* **33**, 2158 (1968).
[2] M. J. Goldstein and A. H. Gevirtz, *Tetrahedron Letters* 4413 (1965).
[3] M. J. Goldstein and A. H. Gevirtz, *Tetrahedron Letters* 4417 (1965).

[4] R. B. Woodward and R. Hoffman, *The Conservation of Orbital Symmetry* Academic Press, New York (1970).

[5] For some of the references dealing with substituent effects in cycloheptatriene, see, [a]G. Maier, *Angew. Chem. Internat. Ed.* **6**, 402 (1967); [b]C. H. Bushweller, M. Sharpe and S. J. Weininger, *Tetrahedron Letters* 453 (1970); [c]H. Gunther, *Tetrahedron Letters* 5173 (1970); [d]R. Hoffmann, *Tetrahedron Letters* 2907 (1970); [e]E. Ciganek, *J. Am. Chem. Soc.* **93**, 2207 (1971).

[6] L. P. Kuhn, R. E. Lutz and C. R. Bauer, *J. Am. Chem. Soc.* **72**, 5058 (1950).

[7] S. Lahiri, Ph.D. Thesis, Indian Institute of Technology, Kanpur (1977).

[8] V. Rautenstrauch and F. Wingler, *Tetrahedron Letters* 4703 (1965).

[9] A. Venema, N. M. M. Nibbering and Th. J. De Boes, *Org. Mass Spectrom.* **6**, 675 (1972).

[10] A. Venema and N. M. M. Nibbering, *Org. Mass Spectrom.* **9**, 1234 (1974).

[11] M. Tsutsui, Y. C. Hsung, J. N. Francis and H. Kenji, *Chem. Lett.* 557 (1973).

[12] J. Daub and P. v. R. Schleyer, *Angew. Chem. Internat. Ed.* **7**, 468 (1968).

[13] H. Prinzbach, N. Eberbach and G. Philipposian, *Angew. Chem. Internat. Ed.* **7**, 887 (1968).

[14] G. W. Griffin and E. J. O'Connell, *J. Am. Chem. Soc.* **84**, 4148 (1962).

[15] H. E. Zimmerman, H. G. C. Durr, R. G. Lewis and S. Bram, *J. Am. Chem. Soc.* **84**, 4149 (1962).

[16] H. E. Zimmerman, H. G. C. Durr, R. S. Givens and R. G. Lewis, *J. Am. Chem. Soc.* **89**, 1863 (1967).

[17] A. Padwa, D. Gumrine and A. Shubber, *J. Am. Chem. Soc.* **88**, 3064 (1966).

[18a] N. Zinin, *Ber.* **5**, 1104 (1872); [b]D. R. Berger and R. K. Summerbell, *J. Org. Chem.* **24**, 1881 (1959); [c]S. Lahiri, V. Dabral and M. V. George, *Tetrahedron Letters* 2259 (1976).

[19] R. E. Lutz and N. R. Smithey, *J. Org. Chem.* **16**, 51 (1951).