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THERMAL AND ELECTRON-IMPACT TRANSFORMATIONS OF *cis*-1,2-DIBENZOYLALKENES

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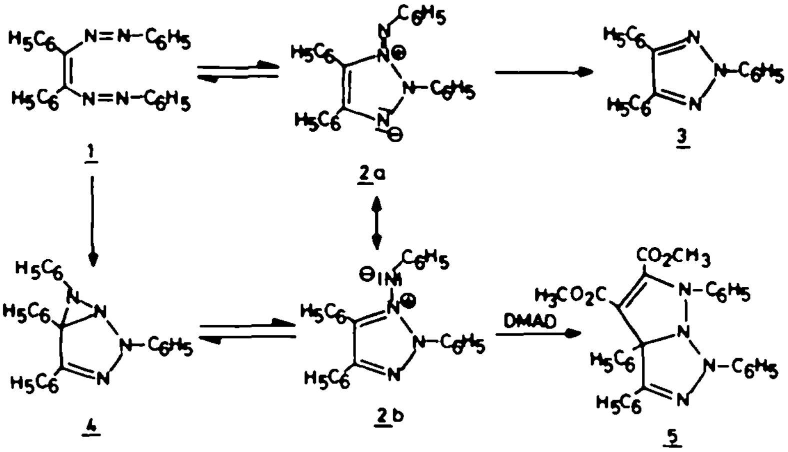
Abstract—Several *cis*-1,2-dibenzoylalkene derivatives have been prepared in yields ranging between 60–80%, through the Diels–Alder addition of the appropriate dienes to dibenzoylacetylene. These include, 2,3-dibenzoylbicyclo[2.2.1]hepta-2,5-diene (**10**), 2,3-dibenzoylbicyclo[2.2.2]octa-2,5-diene (**11**), 7-oxa-2,3-dibenzoylbicyclo[2.2.1]hepta-2,5-diene (**12**), 1,4-diphenyl-2,3-dibenzoyl-1,4-epoxynaphthalene (**13**) and 9,10-dihydro-11,12-dibenzoyl-9,10-ethenoanthracene (**15**), formed from cyclopentadiene, cyclohexa-1,3-diene, furan, 1,3-diphenylisobenzofuran and anthracene, respectively.

Thermolysis of 2,3-dibenzoylbicyclo[2.2.1]hepta-2,5-diene gave chiefly cyclopentadiene, arising through a retro-Diels–Alder mode of fragmentation. Similar retro-Diels–Alder fragmentations have been observed in the cases of 7-oxa-2,3-dibenzoylbicyclo[2.2.1]hepta-2,5-diene and 9,10-dihydro-11,12-dibenzoyl-9,10-ethenoanthracene. The thermoylsis of 1,4-diphenyl-2,3-dibenzoyl-1,4-epoxynaphthalene, however, gave a mixture of 1,3-diphenylisobenzofuran and 1,2-dibenzoylbenzene. The formation of 1,2-dibenzoylbenzene in this case has been shown to be through the air-oxidation of 1,3-diphenylisobenzofuran. Thermolysis of 2,3-dibenzoylbicyclo[2.2.2]octa-2,5-diene, on the other hand, gave a nearly quantitative yield of 1,2-dibenzoylbenzene, which did not undergo further transformation even on heating around 260° for several hours. In none of these cases, the expected pericyclic transformation, analogous to the conversion of *cis*-1,2-dibenzoylstilbene (**6**) to the isomeric 2,2,3,4-tetraphenylbut-3-enolide (**9**), has been observed under thermal conditions. Treatment of 9,10-dihydro-11,12-dibenzoyl-9,10-ethenoanthracene (**15**) with phosphorous pentasulphide resulted in the formation of a mixture of 12,14-diphenyl-9,10(3',4')furanoanthracene (**28**) and 12,14-diphenyl-9,10(3',4')thiophenoanthracene (**31**), arising through the postulated intermediates, 9,10-dihydro-11-benzoyl-12-thiobenzoyl-9,10-ethenoanthracene (**26**) and 9,10-dihydro-11,12-dithiobenzoyl-9,10-ethenoanthracene (**29**), respectively.

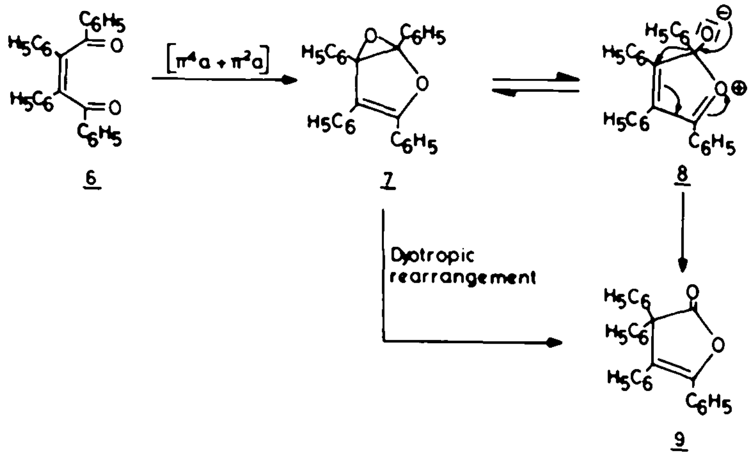
The electron-impact induced transformations of the *cis*-1,2-dibenzoylalkenes, **6**, **10**, **11**, **12**, **13** and **15** on the other hand, can be rationalized in terms of both retro-Diels–Alder type fragmentations and pericyclic transformations of the dibenzoylalkene components.

Recent studies have shown that heterotrienes, in general, can undergo pericyclic transformations leading to the formation of 5-membered heterocycles.[1] Thus, it has been observed that the thermolysis of a heterotriene like 1,2-bisphenylazostilbene (**1**) leads to the formation of 2,4,5-triphenyl-1,2,3-triazole (**3**) as the major product (Scheme 1).[2,3] The formation of the triazole **3** in this reaction has been rationalized in terms of the initial pericyclic reaction of **1** leading to the formation of the iminotriazolium intermediate **2**, which can subsequently lose phenylnitrene to give **3**. The cyclization of **1** to give the intermediate **2** is analogous to the pentadienyl anion cyclizations[4] and will be a symmetry allowed process.[5] An alternative mode of cyclization of **1** would involve a symmetry allowed $[\pi^4a + \pi^2a]$ type of addition leading to the bicyclic intermediate **4**, which can subsequently give rise to the triazole **3**, through the loss of phenylnitrene. An example of such a $[\pi^4a + \pi^2a]$ addition has been recently reported in the transformation of 1,2,4-benzoxadiazines to benzoxazoles.[6] The intermediacy of an iminotriazolium species like **2** in the transformation of **1** to **3** has been proved by trapping experiments, leading to the formation of 1,3-dipolar cycloadducts like **5**.

Numerous examples of reactions are reported in the



Scheme 1.



Scheme 2.

literature which can be classified under the pericyclic transformation of heterotrienes, analogous to the transformation of **1** shown in Scheme 1. However, a careful survey of the literature has revealed that there are only very few reported examples of such pericyclic transformations of heterotrienes having oxygen as hetero atoms. The best known example of such a reaction, however, is the reported transformation of *cis*-1,2-dibenzoylstilbene (**6**) to give 2,2,3,4-tetraphenylbut-3-enolide (**9**), observed by Zinin[7] in 1872. The transformation of **6** to the lactone **9** may be rationalized in terms of the intermediate **7**, formed through a $[\pi^4a + \pi^2a]$ type of addition or the zwitterionic intermediate **8**, which can subsequently rearrange to **9** (Scheme 2). The bicyclic intermediate **7** can also directly rearrange to the lactone **9** through a dyotropic transformation.[8] A similar transformation has been observed in the thermal conversion of 1,2,4-triphenylbut-2-ene-1,4-dione to 2,2,4-triphenylbut-3-enolide.[9]

The object of the present investigation has been to examine the possible pericyclic transformations of certain selected examples of *cis*-1,2-dibenzoylalkene derivatives, under both thermal and electron-impact conditions.

RESULTS AND DISCUSSION

Synthesis of cis-*1,2-dibenzoylalkenes*

A convenient method of preparing *cis*-1,2-dibenzoylalkenes would be through the Diels–Alder addition of suitable dienes to dibenzoylacetylene.[10] In our present studies, we have examined the reactions of a few dienes and trienes like cyclopentadiene, cyclohexa-1,3-diene, furan, 1,3-diphenylisobenzofuran and anthracene with dibenzoylacetylene (DBA), with a view to preparing some *cis*-1,2-dibenzoylalkene derivatives.

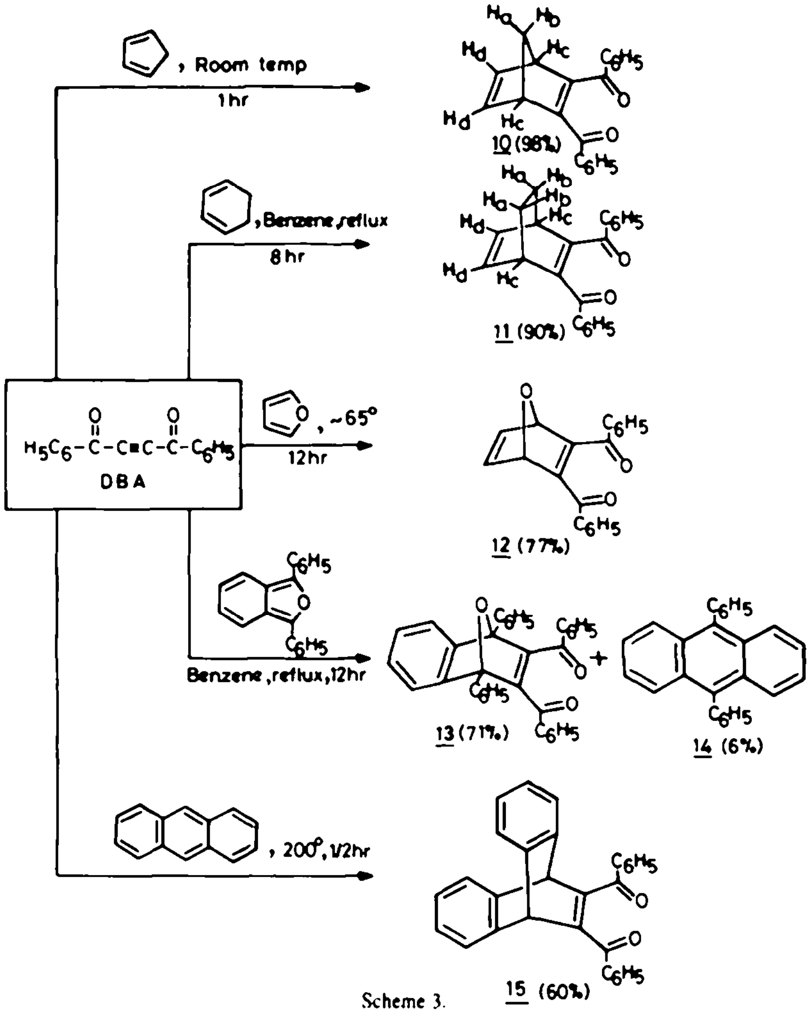
Earlier workers[11-13] have reported the reaction of cyclopentadiene with DBA to give 2,3,-dibenzoylbicyclo[2.2.1]hepta2,5-diene (**10**). In the present studies we have observed that **10** is formed in a nearly quantitative yield when DBA is treated with excess of cyclopentadiene at room temperature (Scheme 3). The NMR spectrum of **10** is of interest in that it showed two pairs of doublets (AB type of quartet), around 2.32δ and 2.65δ, assigned to H_a and H_b protons, respectively (J_{H_a,H_b} = 8 c/s). The doublet around 2.32δ due to H_a proton was further split into a triplet, whereas, the one around 2.65δ due to H_b proton was split into a multiplet. Such a splitting pattern would be expected in view of the fact that H_a proton will be split only by the H_c protons to give the observed triplets (J_{H_a,H_c} = 1.5 c/s), whereas, the H_b proton will be split both by H_c and H_d protons, respectively. Similar splitting patterns have been observed in the NMR spectra of certain bicycloheptene derivatives.[14] The two bridgehead protons (H_c) appeared as a multiplet around 4.27δ whereas, the second multiplet around 7.27δ has been assigned to the vinylic protons (H_d). The aromatic protons appeared as a complex multiplet around 7.5δ (10 H).

Treatment of a mixture of cyclohexa-1,3-diene and DBA in refluxing benzene for 8 hr gave a 90% yield of 2,3-dibenzoylbicyclo[2.2.2]octa-2,5-diene (**11**). The structure of **11** was confirmed on the basis of analytical data and spectral evidences. The NMR spectrum of **11** showed an AB type of quartet and the signals at 1.65δ and 1.76δ have been assigned to H_a and H_b protons, respectively (J_{H_a,H_b} = 9.5 c/s). The multiplet around 4.32δ has been assigned to the bridgehead protons (H_c), whereas the vinylic protons (H_d) appeared as a multiplet centered around 6.75δ. The aromatic protons appeared as a multiplet around 7.45δ (10 H).

Neat heating of a mixture of DBA with excess of furan gave a 77% yield of 7-oxa-2,3-dibenzoylbicyclo[2.2.1]hepta-2,5-diene (**12**), identified through analytical data and spectral evidences. The NMR spectrum of **12** showed the bridgehead protons around 6.03δ (2 H), whereas the vinylic and aromatic protons appeared as a multiplet centered around 7.5δ (12 H).

The reaction of 1,3-diphenylisobenzofuran with DBA in refluxing benzene gave a 71% yield of 1,4-diphenyl-2,3-dibenzoyl-1,4-epoxynaphthalene (**13**). In addition, a 6% yield of 9,10-diphenylanthracene (**14**) was also isolated from this reaction. The exact mode of formation of **14** in this reaction is not very clear.

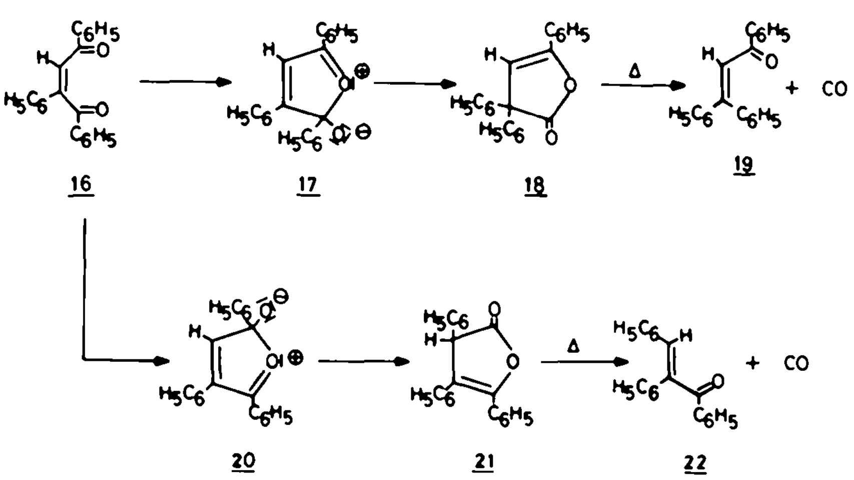
It has been reported earlier[15,16] that the reaction of anthracene with DBA gives rise to 9,10-dihydro-11,12-dibenzoyl-9,10-ethenoanthracene (**15**). We have obtained **15** in a 60% yield by the neat heating of anthracene with DBA around 200° for 30 min. Scheme 3 summarises the results of our studies concerning the preparation of different *cis*-1,2-dibenzoylalkenes. The structures of these products have been established on the basis of analytical results and spectral data.



Scheme 3.

Thermal transformations of cis-*1,2-dibenzoylalkenes*

It has been reported earlier[7] that on thermolysis, a diketoalkene like *cis*-1,2-dibenzoylstilbene (**6**) is quantitatively converted to the lactone **9** at a temperature around 250° (Scheme 2). At higher temperatures, the lactone **9** itself undergoes decarbonylation to give 1,2,3,3-tetraphenylprop-2-ene-1-one, perhaps through a symmetry allowed, linear cheletropic reaction.[5,17] It is interesting to note that the thermal transformation of a related 1,2-dibenzoylalkene like 1,2,4-triphenylbut-2-ene-1,4-dione (**16**) leads to the formation of 2,2,4-triphenylbut-3-enolide (**18**), and not the isomeric 2,3,4-triphenylbut-3-enolide (**21**). The structure of **18** was further confirmed through its conversion to the enone **19**, on pyrolysis (Scheme 4). The preferential formation of the lactone **18** in the transformation of **16** may be rational-



Scheme 4.

Table 1.

Compound	Refluxing solvent	Temp. °C and time	Product	Yield (%)
cis-1,2-Dibenzoylstilbene (6)	Nitrobenzene	214°; 20 hr	2,2,3,4-Tetraphenylbut-3-enolide (9)	96%
2,3-Dibenzoylbicyclo[2.2.1]hepta-2,5-diene (10)	Neat	160°; 4 hr	Cyclopentadiene	63%
2,3-Dibenzoylbicyclo[2.2.2]octa-2,5-diene (11)	Neat	160°; 2 hr	1,2-Dibenzoylbenzene (23)	99%
7-Oxa-2,3-dibenzoylbicyclo[2.2.1]hepta-2,5-diene (12)	Dioxan	100°; 4 hr	Dibenzoylacetylene	91%
1,4-Diphenyl-2,3-dibenzoyl-1,4-epoxynaphthalene (13)	Diphenyl ether	210°; 12 hr	1,3-Diphenylisobenzofuran + 1,2-Dibenzoylbenzene (23)	2%
9,10-Dihydro-11,12-dibenzoyl-9,10-ethenoanthracene (15)	Neat	260°; 2 hr	Anthracene	83%

ized in terms of the greater stability of the zwitterionic intermediate 17, when compared to the corresponding intermediate 20, in the alternative route which will lead to the lactone 21 (Scheme 4).

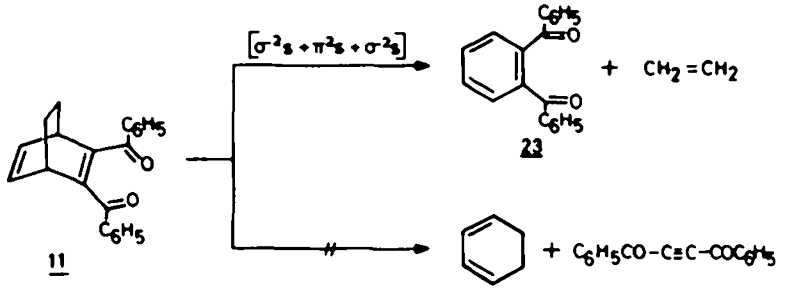
In the present studies we have examined the thermolysis of several 1,2-dibenzoylalkenes like **10**, **11**, **12**, **13** and **15** with a view to finding out whether these substrates will undergo the pericyclic reactions leading to the formation of the corresponding lactones. Table 1 summarizes the results of our studies. The thermolysis of *cis*-1,2-dibenzoylstilbene (**6**) itself was repeated in refluxing nitrobenzene (214°). It was observed that a nearly quantitative yield of the lactone **9** is formed on heating **6**, for about 16 hr. The thermolysis of 2,3-dibenzoylbicyclo[2.2.1]hepta-2,5-diene (**10**) around 160°, on the other hand, resulted in the formation of a 30% yield of cyclopentadiene, arising through a retro-Diels–Alder reaction. When the thermolysis of **10** was carried out around 200° in air, a small yield of benzoic acid was also obtained. The formation of benzoic acid may be through the air-oxidation of **10**, or some of its degradation products.[11] Similar retro-Diels–Alder reactions have been observed in the thermolysis of 7-oxa-2,3-dibenzoylbicyclo[2.2.1]hepta-2,5-diene (**12**) and 9,10-dihydro-11,12-dibenzoyl-9,10-ethenoanthracene (**15**).

The thermolysis of 1,4-diphenyl-2,3-dibenzoyl-1,4-epoxynaphthalene (**13**), by refluxing in diphenyl ether gave a mixture of products consisting of 1,3-diphenylisobenzofuran (2%) and 1,2-dibenzoylbenzene (**23**) (42%). The formation of **23** in this reaction is assumed to be through the air-oxidation of 1,3-diphenylisobenzofuran.[18,19] In a separate experiment we have shown that by refluxing 1,3-diphenylisobenzofuran alone in diphenyl ether for 18 hr, a 73% yield of **23** is formed.

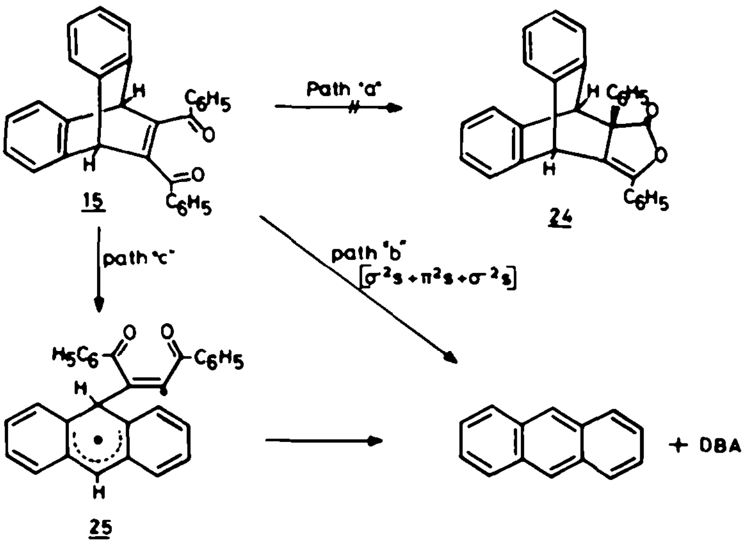
The thermolysis of 2,3-dibenzoylbicyclo[2.2.2]octa-2,5-diene (**11**) is of interest in that, it gives rise to a nearly quantitative yield of 1,2-dibenzoylbenzene (**23**). It is apparent that the loss of ethylene through a symmetry allowed $[\sigma^2s + \pi^2s + \sigma^2s]$ process is more favoured than a simple retro-Diels–Alder fragmentation leading to the formation of 1,3-cyclohexadiene (Scheme 5).

Our studies involving the thermal transformations of *cis*-1,2-dibenzoylalkenes like **10**, **12**, **13** and **15** clearly indicate that in these cases the retro-Diels–Alder mode of fragmentation is preferred over the pericyclic transformation. Thus, in the thermal decomposition of **15**, it appears that the energetically favourable pathway is the formation of anthracene and not path "a" leading to the formation of the lactone **24** (Scheme 6). However, it is not very clear whether the retro-Diels–Alder reaction leading to the formation of anthracene is proceeding through a symmetry allowed, $[\sigma^2s + \pi^2s + \sigma^2s]$ mode (path "b") or through a multistep pathway, involving the diradical intermediate **25** (path "c").

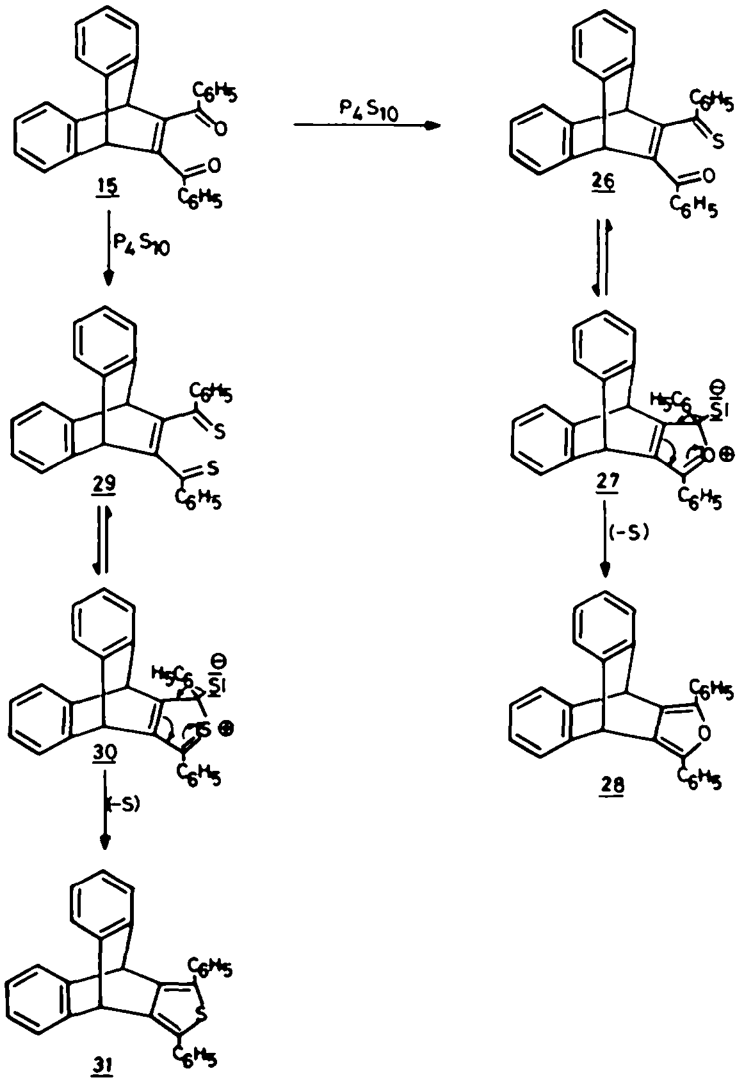
We reasoned that the pericyclic transformation of a heterotriene like **15**, proceeding through path "a", may be more favoured if the hetero atoms are changed from O to S, as in the case of 9,10-dithio-11,12-dibenzoyl-9,10-ethenoanthracene (**29**). With this view in mind, we have examined the reaction of **15** with phosphorous pentasulphide. Treatment of **15** with phosphorous pentasulphide in refluxing xylene for 1 hr gave a mixture of 12,14-diphenyl-9,10(3′,4′)-furanoanthracene (**28**) and 12,14-



Scheme 5.



Scheme 6.



Scheme 7.

diphenyl-9,10(3′,4′)thiophenoanthracene (**31**), from which 25% yield of pure **28** could be isolated through adduct formation with maleic anhydride (Scheme 7).

The structure of **28** was confirmed on the basis of analytical results and spectral data. The mass spectrum of **28**, for example, showed a molecular ion peak at *m/e* 396 (100). Other peaks in the spectrum were observed at *m/e* 319 (3), 318 (4), 317 (3), 292 (9), 291 (35), 290 (13), 289 (34), 288 (5), 287 (9), 188 (7), 178 (7), 159 (4), 145 (3), 144 (2), 105 (62), 77 (80) and 51 (8). Some of these fragmentation modes are shown in Scheme 8.

The mass spectrum of the mixture consisting of **28** and **31**, on the other hand, showed prominent peaks at *m/e* 412 (100) and *m/e* 396 (51), corresponding to their molecular ions. Our attempts to isolate a pure sample of **31** from this mixture have been unsuccessful.

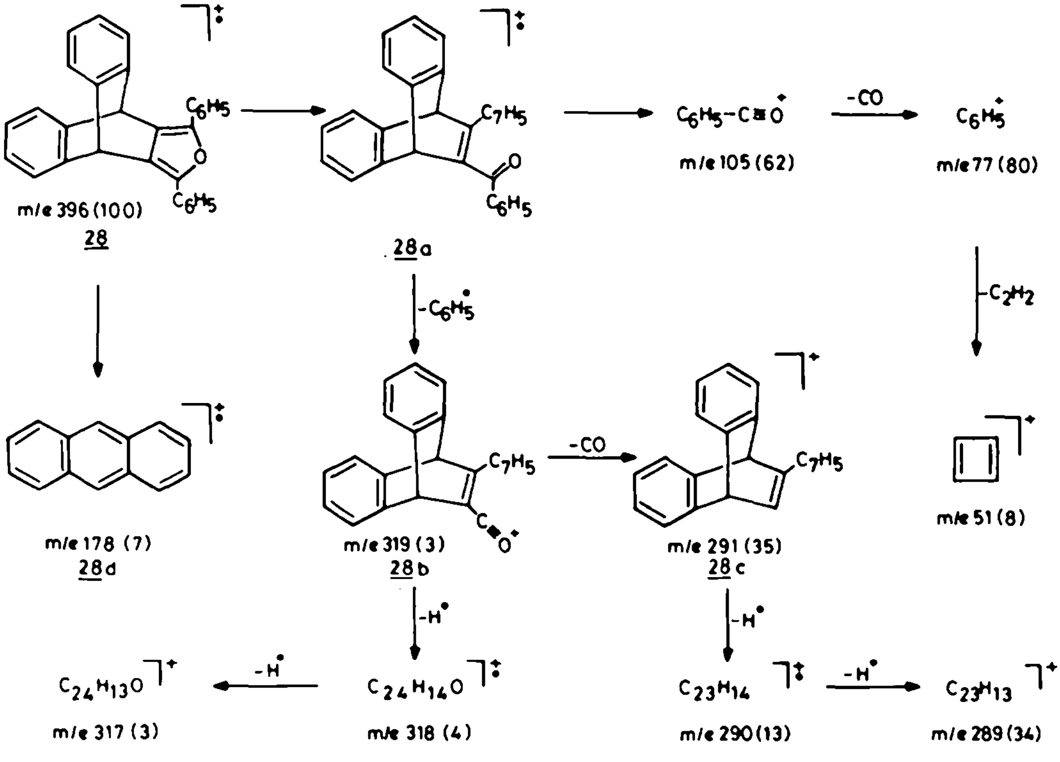
The formation of the products **28** and **31** in the reaction of **15** with P_4S_{10} is rationalized in terms of the pericyclic transformations of the monothioderivative, **26** and the dithioderivative **29**, as shown in Scheme 7.

Electron-impact transformation of cis-*1,2-dibenzoylalkenes*

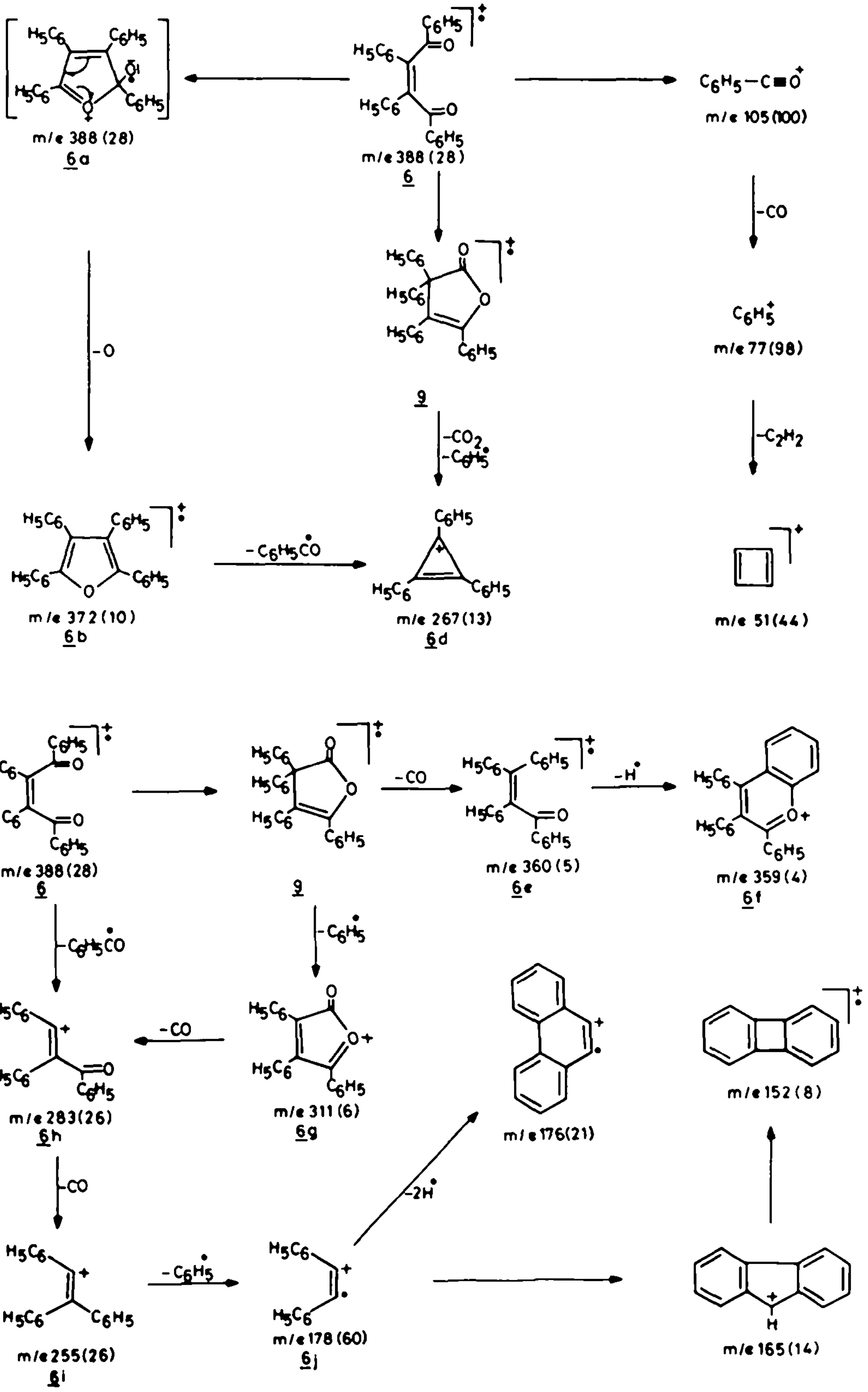
In contrast to the numerous studies on the mass spectral fragmentations of saturated aliphatic ketones, only scant attention has been paid to the study of unsaturated ketones.[20–26] Djerassi *et al.*[21] for example, have studied the mass spectral fragmentations of several aryl and alkyl substituted Δ^2-cyclohexenones and related bicyclic ketones and have shown that decarbonylations, followed by known skeletal rearrangements are occurring in these systems.[27,28] No detailed study has so far been made on the mass spectral fragmentations of 1,4-dicarbonylalkenes of related systems. In the present investigation we have examined the mass spectral fragmentations of a few representative *cis*-1,2-dibenzoylalkenes with a view to studying the mode of cleavage in these systems and also to compare their electron-induced and thermal modes of transformations.

The mass spectrum of *cis*-1,2-dibenzoylstilbene (**6**), for example, showed the molecular ion peak at *m/e* 388 (28). Other peaks were observed at *m/e* 283 (26), 255 (26), 178 (60), 105 (100) and 77 (98) which could be assigned to some of the fragments shown in Scheme 9. The peak at *m/e* 372 could be assigned to the fragment **6b**, formed through the loss of oxygen from the intermediate **6a**. Further loss of a benzoyl fragment from **6b** could lead to the formation of the fragment **6d** at *m/e* 267. Another mode of fragmentation that had been observed was the loss of a benzoyl group by α-cleavage, from the starting compound to give a fragment **6h** at *m/e* 283. The peak at *m/e* 360 could be assigned to the fragment **6e**, formed through the loss of CO from the intermediate lactone **9**, which in turn, could be formed through the pericyclic transformation of the starting diketone.

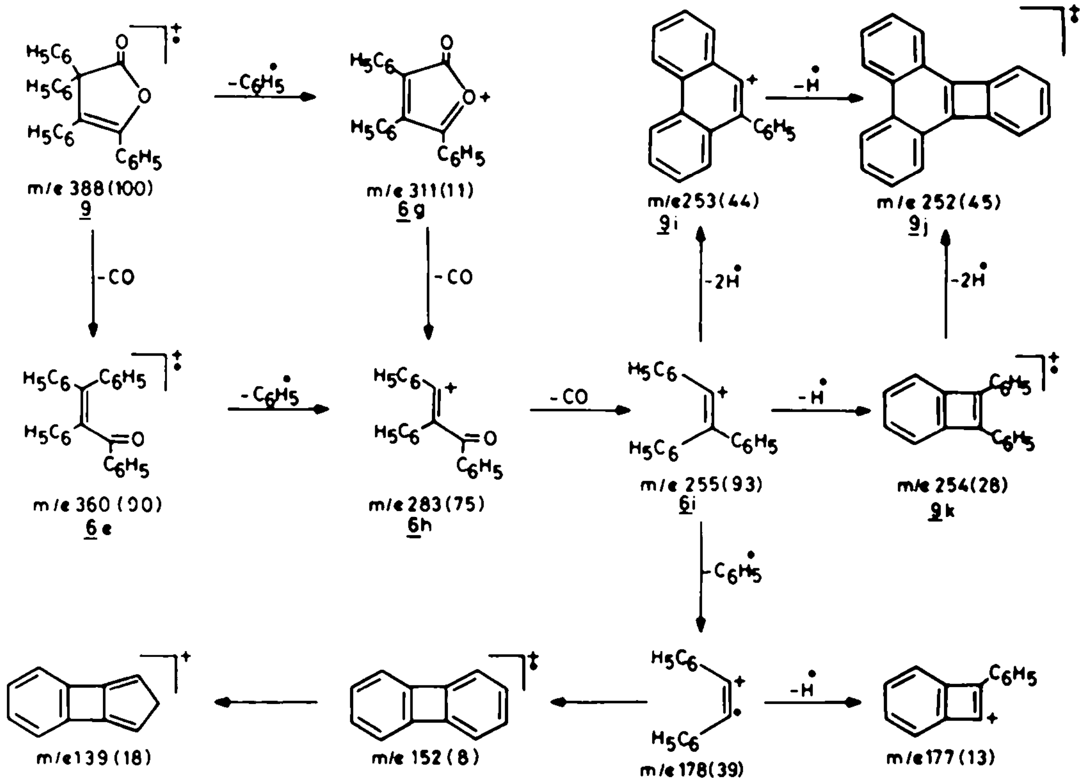
With a view to assessing whether at least some of the fragments observed in the mass spectrum of **6** arose through the lactone intermediate **9**, the mass spectrum of 2,2,3,4-tetraphenylbut-3-enolide (**9**) was examined separately. The mass spectrum of **9** showed the molecular ion peak at *m/e* 388 (100). Other peaks were observed at *m/e* 360 (91), 359 (65), 344 (11), 311 (11), 283 (76), 267 (17), 265 (15), 255 (93), 253 (45), 252 (45), 239 (21), 227 (6), 209 (3), 178 (39), 163 (20), 151 (32), 152 (33), 139 (18), 130 (10), 126 (21), 105 (90), 77 (86), 55 (42) and 51 (69), which could be assigned to some of the fragments shown in Scheme 10. It is interesting to note that several peaks in the mass spectrum of **6** correspond to the fragments observed in the mass spectrum of the lactone **9**, indicating thereby that **6** undergoes at least partial transformation to **9** under electron impact, similar to the observed thermal mode of transformation of **6**.



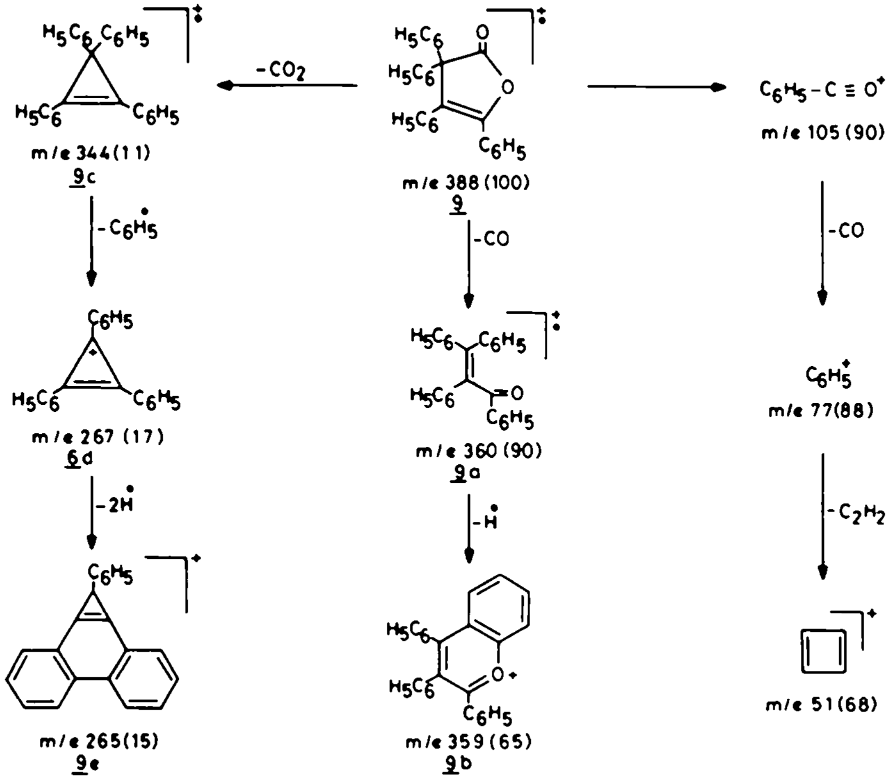
Scheme 8.


m/e 388 (28)
6a
m/e 388 (28)
6
$C_6H_5-C\equiv\overset{+}{O}$
m/e 105 (100)
-CO
$C_6H_5^+$
m/e 77 (98)
$-C_2H_2$
m/e 51 (44)
-O
9
$-CO_2$, $-\dot{C}_6H_5$
$-C_6H_5\dot{C}O$
m/e 372 (10)
6b
m/e 267 (13)
6d
m/e 388 (28)
6
9
-CO
m/e 360 (5)
6e
$-\dot{H}$
m/e 359 (4)
6f
$-C_6H_5\dot{C}O$
$-\dot{C}_6H_5$
-CO
m/e 283 (26)
6h
m/e 311 (6)
6g
m/e 176 (21)
m/e 152 (8)
-CO
$-\dot{C}_6H_5$
$-2\dot{H}$
m/e 255 (26)
6i
m/e 178 (60)
6j
m/e 165 (14)

Scheme 9.



Scheme 9. (*Contd*).



Scheme 10.

Examination of the mass spectra of the *cis*-1,2-dibenzoylalkenes, **10**, **11**, **12**, **13** and **15** reveals that certain characteristic and common modes of fragmentation are observed in all these cases. Table 2 lists some of the most prominent peaks observed in the mass spectra of these *cis*-1,2-dibenzoylalkenes. It is evident from Table 2 that all these adducts show prominent molecular ion peaks (*a*), except in the cases of the 1,4-epoxy derivatives, **12** and **13**.

A characteristic mode of fragmentation of the *cis*-1,2-dibenzoylalkene derivatives involves the loss of CO from their molecular ions (*a*). It is reasonable to assume that the starting *cis*-1,2-dibenzoylalkenes undergo a pericyclic transformation to give the corresponding 3-butenolides (*b*), under electron impact, which subsequently lose CO by a cheletropic fragmentation pathway to give the fragment *c*, as shown in Scheme 11. An alternative pathway for the formation of the fragment *c* would be through the direct loss of CO from the molecular ions (*a*). It might be pointed out in this connection that similar rearrangements of the starting *cis*-1,2-dibenzoylalkenes have not been observed under thermal conditions, except in the case of *cis*-1,2-dibenzoylstilbene (**6**), which readily rearranges to the corresponding butenolide, **9**.[7]

It is also apparent that other fragmentation modes like the loss of phenyl and benzoyl groups from the molecular ions (*a*) are also prominent in the case of most of the *cis*-1,2-dibenzoylalkenes that we have examined (Scheme 11).

Another pathway for the fragmentation of *cis*-1,2-dibenzoylalkenes is through the retro-Diels–Alder reaction, as shown in Scheme 12. As is evident from Scheme 12, the adducts **10**, **12**, **13** and **15**, give rise to the appropriate diene fragments (*j*) in relatively high abundance. In some cases where there is a possibility for the retro-Diels–Alder reaction to proceed with hydrogen migration, as in **10** and **12**, such fragmentation modes have also been observed (Scheme 12). Similar examples of retro-Diels–Alder reactions with hydrogen transfer has been reported in the literature.[29–31]

It is interesting to note that the retro-Diels–Alder mode of fragmentation of the *cis*-1,2-dibenzoylalkenes is observed both under thermal and electron-impact conditions, unlike the pericyclic mode of transformation. Table 3 lists the different fragments formed from the *cis*-1,2-dibenzoylalkenes, **10**, **11**, **12**, **13** and **15** and their yields or relative intensities, as the case may be, for comparison purposes.

An intersting mode of fragmentation has been observed in the case of both the 1,4-epoxy derivatives, **12** and **13** under electron impact. The molecular ions of these substances (*a*) lose an O atom to give the fragment *i*, as shown in Scheme 12. Similar loss of O atoms have been observed in the mass spectral fragmentations of both 1,4-dihydro-1,4-epoxynaphthalene[32] and dibenzo-1,4-dioxin.[33]

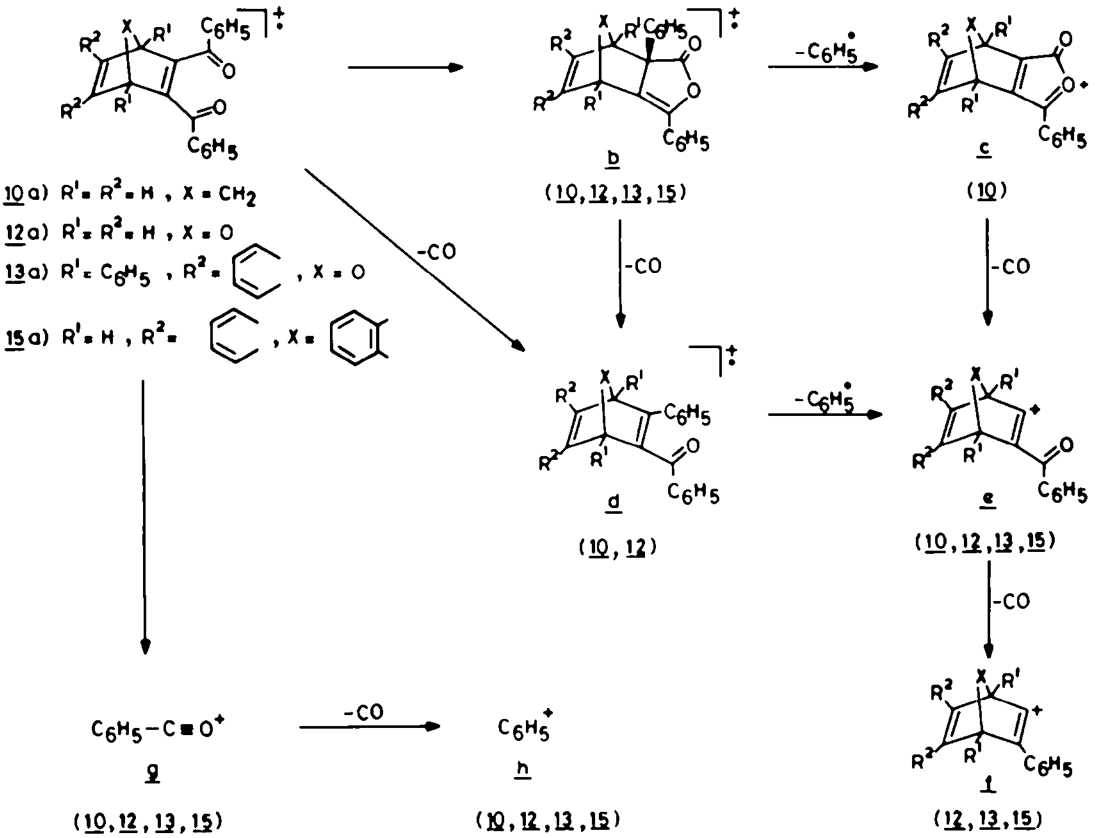
The mass spectrum of 2,3-dibenzoylbicyclo[2.2.2]octa-2,5-diene (**11**) is of interest in that it showed a prominent peak at *m/e* 286 which is attributed to the fragment **11i**, the molecular ion peak of 1,2-dibenzoylbenzene (**23**) (Scheme 12). It appears that under electron impact, **11** undergoes ready fragmentation with the loss of ethylene to give 1,2-dibenzoylbenzene (**23**).

It may be pointed out in this connection that a similar loss of ethylene fragment was also observed in the thermal transformation of **11**. The most prominent peak in the spectrum of **11** was observed at *m/e* 209 (100), which might arise through the loss of a phenyl radical from **23** to give **11** as shown in Scheme 13. The fragment at *m/e* 258 could be rationalized in terms of **11c**, formed by the loss of CO from the lactone intermediate, **11b**, which in turn is formed from **23** (Scheme 13).

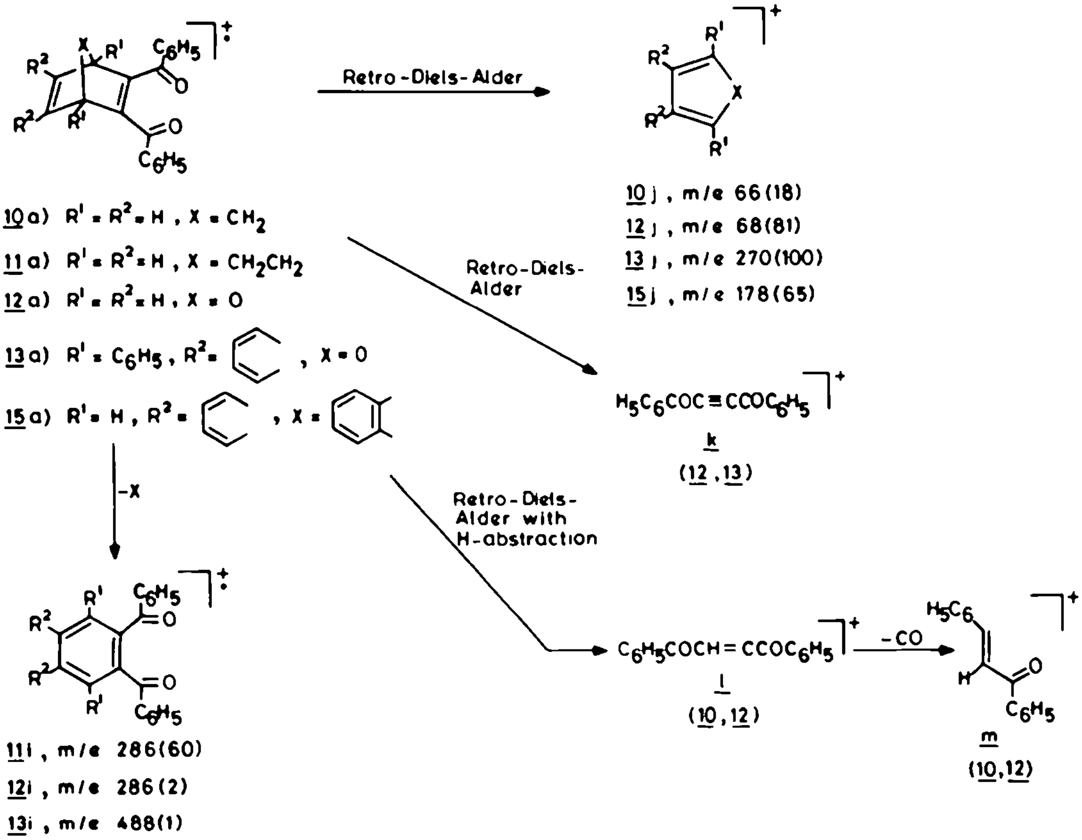
We have examined the mass spectrum of 1,2-dibenzoylbenzene (**23**) also to ascertain whether the frag-

Table 2.

1	2	3	4	5
Compound	Molecular ion peak m/e (Intensity)	Fragments as per Scheme 11 m/e (Intensity)	Fragments as per Scheme 12 m/e (Intensity)	Other fragments m/e (Intensity)
10	10a, 300 (100)	10c, 223 (4); 10d, 272 (5); 10e, 195 (21); 10g, 105 (38); 10h, 77 (34)	10j, 66 (18); 10l, 235 (12); 10m, 207 (4)	271 (4); 195 (21); 178 (3); 165 (10); 152 (8); 129 (3); 115 (3)
11	11a, 314 (67)		11i, 286 (60)	286 (60); 258 (1); 257 (2); 209 (100); 181 (7); 180 (2); 153 (5); 152 (10); 105 (40); 77 (25)
12	12a, 302 (15)	12d, 274 (6); 12e, 197 (13); 12f, 169 (2); 12g, 105 (100); 12h, 77 (65);	12i, 286 (2); 12j, 68 (8); 12k, 234 (87); 12l, 235 (26); 12m, 207 (3)	273 (16); 209 (2); 207 (3); 206 (11); 205 (11); 199 (4); 179 (9); 178 (34); 177 (4); 176 (5); 165 (1); 152 (4); 130 (7); 129 (3); 76 (5); 42 (7); 40 (11)
13	13a, 504 (5)	13e, 399 (9); 13g, 105 (35); 13h, 77 (15)	13i, 488 (1); 13j, 270 (100); 13k, 234 (15)	383 (1); 382 (4); 269 (4); 241 (3); 239 (5); 193 (3); 178 (5); 165 (5); 129 (15)
15	15a, 412 (83)	15e, 307 (27); 15f, 279 (13); 15g, 105 (100); 15h, 77 (21)	15j, 178 (65)	202 (14)

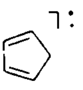
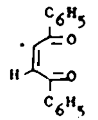
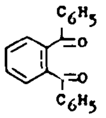
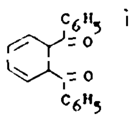
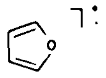
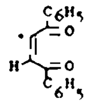
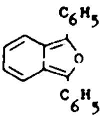
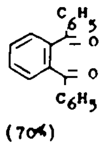
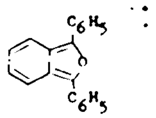
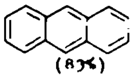
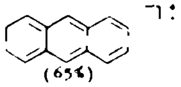


Scheme 11.



Scheme 12.

Table 3

Adduct	Thermal Retro-Diels-Alder Reaction Products: Diene (%)	Thermal Retro-Diels-Alder Reaction Products: Dienophile (%)	Mass spectral Retro-Diels-Alder Reaction fragments: Diene (Intensity %)	Mass spectral Retro-Diels-Alder Reaction fragments: Dienophile (Intensity %)	Mass spectral Retro-Diels-Alder Reaction with H transfer: Diene (Intensity %)	Mass spectral Retro-Diels-Alder Reaction with H transfer: Dienophile (Intensity %)
1	2	3	4	5	6	7
2,3-Dibenzoylbicyclo[2.2.1]hepta-2,5-diene (**10**)	 (62.5%)		 (18%)			 (12%)
2,3-Dibenzoylbicyclo[2.2.2]octa-2,5-diene (**11**)	 (99%)		 (60%)			
7-Oxa-2,3-dibenzoylbicyclo[2.2.1]hepta-2,5-diene (**12**)		DBA (91%)	 (81%)	DBA (87%)		 (26%)
1,4-Diphenyl-2,3-dibenzoyl-1,4-epoxynaphthalene (**13**)	 (2%) and  (70%)		 (100%)	DBA (15%)	-	-
9,10-Dihydro-11,12-dibenzoyl-9,10-ethenoanthracene (**15**)	 (83%)		 (65%)		-	-

mentation modes of **11** correspond to some of the fragments due to **23**. It was interesting to note that the mass spectrum of **23** showed several peaks at *m/e* 286 (32), 258 (3), 209 (100), 193 (3), 181 (6), 165 (4), 152 (30), 105 (37), 77 (37) and 51 (15), corresponding to some of the peaks observed in the spectrum of **11**.

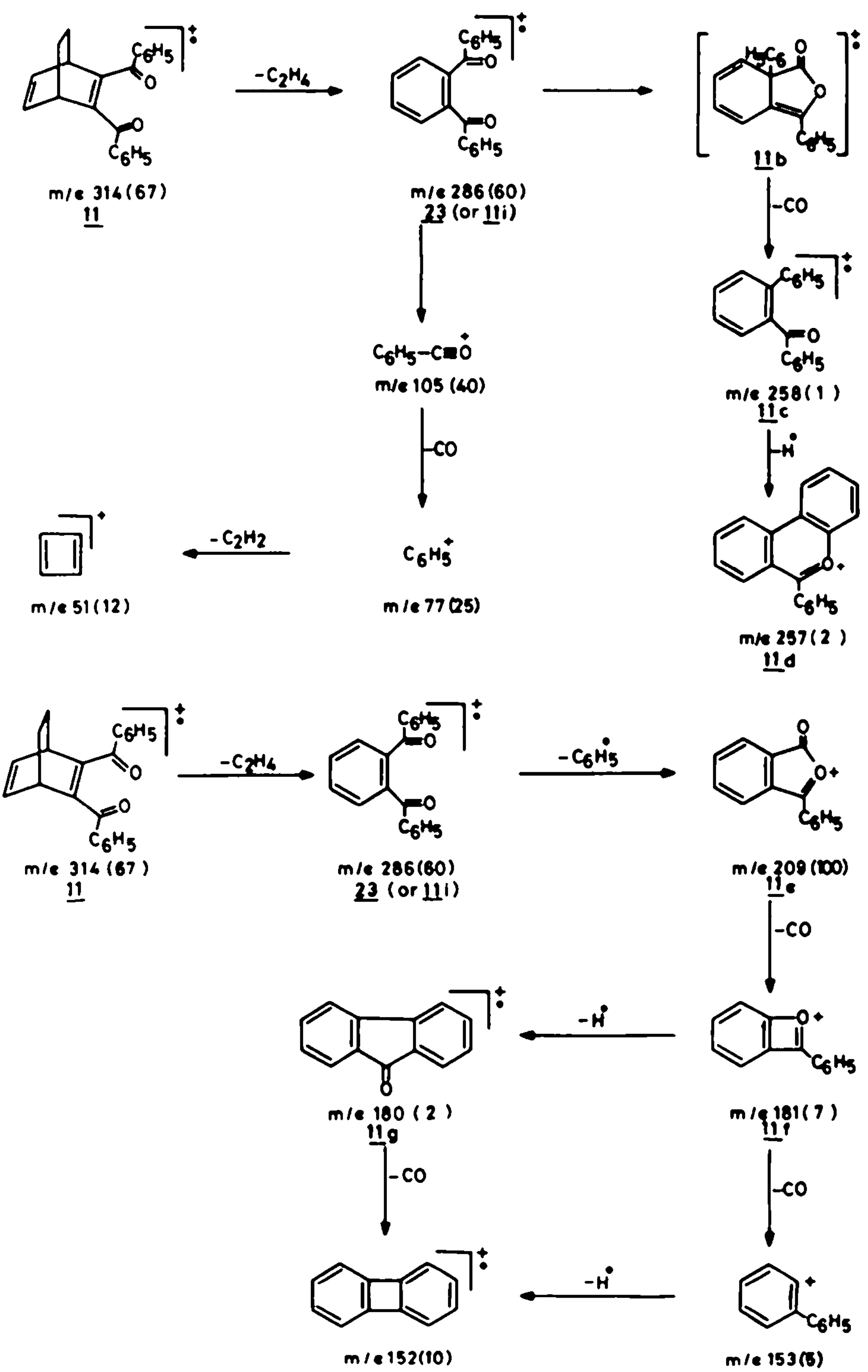
The mass spectra of all the *cis*-1,2-dibenzoylalkenes that we have examined show several peaks due to the different fragments from the diene components of these adducts and some of these fragments are listed in Table 3. It might be mentioned in this connection that most of these peaks can be rationalized in terms of the known fragmentation modes of the different diene components, and also in terms of some of the secondary fragments derived from the different fragments shown in Schemes 11 and 12.

EXPERIMENTAL

All m.ps are uncorrected and were determined on a Mel-Temp, m.p. apparatus. The IR spectra were recorded on Perkin-Elmer Model 137 or 521 Infrared Spectrometers. The electronic spectra were recorded on a Beckman DB spectrophotometer. NMR traces were recorded on Varian A-60 or XL-100 NMR spectrometers using TMS as internal standard. The mass spectra were recorded on a Hitachi RMU-6E Single Focussing Mass Spectrometer or a Varian Mat CH7 Mass Spectrometer at 70 eV.

Starting materials. Dibenzoylacetylene, m.p. 110–111°, was prepared by a reported procedure involving the bromination of *trans*-dibenzoylethylene,[14] followed by dehydrobromination of the dibromo derivative.[15] *trans*-Dibenzoylethylene itself was prepared by a reported procedure.[16] Cyclopentadiene, b.p. 41°, was freshly distilled before use and was obtained by the depolymerization of the "Technical Grade" dicyclopentadiene. 1,3-Cyclohexadiene,[17] b.p. 79–80° and 1,3-diphenylisobenzofuran,[18] m.p. 130°, were prepared by reported procedures. *cis*-Dibenzoylstilbene, m.p. 216–17°, was prepared by the perbenzoic acid oxidation of tetraphenylfuran.[19] Petroleum ether used was of b.p. 60–80°.

Reaction of cyclopentadiene with dibenzoylacetylene. A mixture of cyclopentadiene (1.5 g, 0.02 mol) and dibenzoylacetylene (2.3 g, 0.01 mol) was refluxed in benzene (30 ml) for 3 hr. Removal of the solvent under vacuum and recrystallization of the residue from a mixture (2 : 1) of petroleum ether and benzene gave 2.9 g (98%) of **10**, m.p. 144° (lit.[11] m.p. 142–43°). (Found: C, 84.25; H, 5.46; Mol. wt., 300 (Mass spect). $C_{21}H_{16}O_2$ requires: C, 84.0; H, 5.33; Mol. wt., 300). IR spectrum (KBr)ν_{max}: 3060, 3005 and 2983 cm^{-1} (ν_{C-H}, aromatic and olefinic), 2940 and 2875 cm^{-1} (ν_{CH_2}, asymmetric and symmetric), 1635 cm^{-1} ($\nu_{C=O}$), 1602 and 1575 cm^{-1} ($\nu_{C=C}$). UV spectrum (ethanol) λ_{max}: 258 nm (ε, 16,200), 292 (6600) and 349 (650).



Scheme 13.

In a repeat run, 3.2 g (0.014 mol) of DBA was mixed with excess (15 ml) of cyclopentadiene and left at room temp. for 30 min. The reaction was exothermic and work-up of the mixture by removal of the unchanged cyclopentadiene under vacuum and fractional crystallization of the product from a mixture (1:1) of petroleum ether and benzene gave 3.95 g (99%) of **10**, m.p. 144° (m.m.p.).

Reaction of 1,3-*cyclohexadiene with dibenzoylacetylene.* A mixture of DBA (2.3 g, 0.01 mol) and 1,3-cyclohexadiene (2 g, 0.025 mol) in benzene (30 ml) was refluxed for 8 hr. Removal of the solvent under vacuum gave a product which was recrystallized from a mixture (2:1) of petroleum ether and benzene to give 2.8 g (90%) of **11**, m.p. 153°. (Found: C, 84.35; H, 5.62; Mol. wt., 314 (Mass spect.). $C_{22}H_{18}O_2$ requires: C, 84.07; H, 5.73; Mol. wt., 314). IR spectrum (KBr) ν_{max}: 3080 and 3005 cm^{-1} (ν_{C-H}), 2935 and 2865 cm^{-1} (ν_{CH_2}, asymmetric and symmetric, 1640 cm^{-1} ($\nu_{C=O}$), 1605 and 1580 cm^{-1} ($\nu_{C=C}$). UV spectrum (ethanol) λ_{max}: 256 nm (ϵ, 15,100), 287 (7500) and 345 (400).

Reaction of furan with dibenzoylacetylene. A mixture of DBA (0.6 g, 2.5 mmol) and furan (0.2 g, 2.5 mmol) was heated in a sealed tube around 50° for 9 hr. Removal of the unchanged furan gave a product which was chromatographed over silica-gel. Elution with a mixture (1:1) of petroleum ether and benzene gave 0.1 g (17%) of unchanged DBA, m.p. 111° (m.m.p.).

Further elution of the column with a mixture (1:2) of petroleum ether and benzene gave 0.3 g (46%) of **12**, m.p. 122–23°, after recrystallization from a mixture (1:1) of petroleum ether and benzene. (Found: C, 79.9; H, 4.48; Mol. wt., 302). (Mass spect). $C_{20}H_{14}O_3$ requires: C, 79.9; H, 4.66; Mol. wt., 302). IR spectrum (KBr) ν_{max}: 3265, 3105, 3055 and 3030 cm^{-1} (ν_{C-H}), 1645 cm^{-1} ($\nu_{C=O}$), 1600 and 1580 cm^{-1} ($\nu_{C=C}$). UV spectrum (EtOH) λ_{max}: 256 nm (ϵ, 13,000), 292 (5900) and 344 (500).

In a repeat run a mixture of 2 g (8.5 mmol) of DBA and excess (10 ml) of freshly distilled furan was heated in a sealed tube around 60–65° for 12 hr. Work-up of the mixture as in the earlier case gave 2 g (77%) of **12**, m.p. 122–23° (m.m.p.).

Reaction 1,3-*diphenylisobenzofuran with dibenzoylacetylene.* A mixture of DBA (2.34 g, 0.01 mol) and 1,3-diphenylisobenzofuran (2.7 g, 0.01 mol) in benzene (50 ml) was refluxed for 8 hr. Removal of the solvent under vacuum gave a product which was treated with a small amount of hot EtOH. The solvent-insoluble portion was recrystallized from a mixture (2:1) of petroleum ether and cyclohexane to give 200 mg (6%) of a product, m.p. 250°, identified as 9,10-diphenylanthracene (lit.[40] m.p. 249–50°). (Found: C, 94.40; H, 5.51; Mol. wt., 330 (Mass spect.). $C_{26}H_{18}$ requires: C, 94.54; H, 5.45; Mol. wt., 330). IR spectrum (KBr) ν_{max}: 3065 and 3030 cm^{-1} (ν_{C-H}), 1597 cm^{-1} ($\nu_{C=C}$). UV spectrum (Cyclohexane) λ_{max}: 221 nm (ϵ, 24,000), 261 (114,800) and 375 (13,200). NMR spectrum ($CDCl_3$): 7.6δ (aromatic protons). Mass spectrum, *m/e* (rel. intensity): 330 (100), 329 (12), 328 (10), 327 (9), 253 (14), 252 (25), 163 (4), 162 (3), 156 (4), 150 (4), 138 (2), 137 (2), 126 (2) and 77 (22).

Concentration of the alcohol-soluble portion and fractional crystallization from EtOH gave 3.6 g (71%) of **13**, m.p. 157°. (Found: C, 85.90; H, 4.35; Mol. wt., 504 (Mass spect.). $C_{36}H_{24}O_3$ requires: C, 85.70; H, 4.76; Mol. wt., 504). IR spectrum (KBr) ν_{max}: 3055 and 3025 cm^{-1} (ν_{C-H}), 1657 cm^{-1} ($\nu_{C=O}$), 1601, 1581 and 1500 cm^{-1} ($\nu_{C=C}$). UV spectrum (EtOH) λ_{max}: 258 nm (ϵ, 14,000), 284 (5500) and 348 (250). NMR spectrum ($CDCl_3$): 7.5δ (multiplet, aromatic).

Reaction of anthracene with dibenzoylacetylene. Heating a mixture of DBA (2.34 g, 0.01 mol) and anthracene (1.78 g, 0.01 mol) around 200° in a sealed tube for 30 min and work-up of the mixture by fractional crystallization from xylene gave 2.5 g (60%) of **15**, m.p. 212° (lit.[15] m.p. 212–215.5°). IR spectrum (KBr) ν_{max}: 3225 cm^{-1} (ν_{C-H}), 1670 cm^{-1} ($\nu_{C=O}$), 1620 and 1590 cm^{-1} ($\nu_{C=O}$). UV spectrum (MeOH) λ_{max}: 262 nm (ϵ, 15,000), 295 (5600) and 345 (1400). NMR spectrum ($CDCl_3$): 5.66δ (singlet, 2 H, bridgehead) and 7.25δ (multiplet, 14 H, aromatic).

Thermolysis of cis-*dibenzoylstilbene* (**6**). A sample of **6** (60 mg, 0.15 mmol) was heated around 260° for 30 min. The mixture was fractionally crystallized from EtOH to give 55 mg (92%) of **9**, m.p. 137–38° (m. m.p.).

In a repeat run, 200 mg (0.51 mmol) of **6** was refluxed in 30 ml of nitrobenzene for 20 hr. Removal of the solvent under vacuum and work-up of the mixture as in the earlier case gave 125 mg (96%) of **9**, m.p. 138° (m. m.p.).

Thermolysis of 2,3-*dibenzoylbicyclo*[2.2.1]*hepta*-2,5-*diene* (**10**). A 500 mg (1.67 mmol) sample of **10** was heated around 160° in a sealed tube under vacuum for 4 hr. After cooling, the sealed tube was broken and the clear liquid that was collected in the upper portion of the tube was removed to give 33 mg (30%, 63% on the basis of reacted starting material) of cyclopentadiene, identified through a comparison of its IR spectrum and glc retention time, with those of an authentic sample.

The dark residual mass left in the tube was fractionally crystallized from a mixture (2:1) of petroleum ether and benzene to give 200 mg (40%) of the unchanged starting material, m.p. 144° (m. m.p.). No other product could be isolated from this run.

In a repeat run, 190 mg (0.63 mmol) of **10** was heated around 200° in an open tube for 2 hr. Colourless droplets of cyclopentadiene were collected in the cooler parts of the tube. On continued heating for 12 hr, a small amount (15 mg, 19%) of benzoic acid, m.p. 121° (m. m.p.) was isolated from the cooler parts of the tube. Work-up of the residual brown mass in the reaction tube did not give rise to any isolable product.

Thermolysis of 2,3-*dibenzoylbicyclo*[2.2.2]*octa*-2,5-*diene* (**11**). A sample of **11** (0.4 g, 1.2 mmol) was heated in a sealed tube around 160° for 2 hr. The product mixture was crystallized from a mixture (1:2) of acetone and EtOH to give 0.36 g (99%) of **23**, m.p. 150° (m. m.p.).

Attempted thermolysis of 1,2-*dibenzoylbenzene* (**23**). A sample of **23** (150 mg, 0.52 mmol) was heated in a sealed tube around 250° for 6 hr. Work-up of the mixture in the usual manner and crystallization of the product from a mixture (1:1) of petroleum ether and benzene gave 145 mg (97%) of the unchanged starting material, m.p. 149–50° (m. m.p.).

Thermolysis of 7-*oxa*-2,3-*dibenzoylbicyclo*[2.2.1]*hepta*-2,5-*diene* (**12**). A soln of **12** (100 mg, 0.32 mmol) in dioxan (20 ml) was refluxed for 4 hr. Removal of the solvent under vacuum gave a solid mass which was treated with water and then was extracted with chloroform. Work-up of the chloroform extract in the usual manner gave 70 mg (90%) of dibenzoylacetylene, m.p. 110° (m. m.p.), after recrystallization from cyclohexane.

Thermolysis of 1,4-*diphenyl*-2,3-*dibenzoyl*-1,4-*expoxynaphthalene* (**13**). A soln of **13** (250 mg, 0.5 mmol) in diphenyl ether (20 ml) was refluxed for 12 hr. Removal of the solvent under vacuum gave a product mixture which was chromatographed over silica-gel.

Elution of the column with a mixture (10:1) of petroleum ether and benzene gave 2 mg (2%, 2.5% on the basis of the reacted starting material) of 1,3-diphenylisobenzofuran, m.p. 130° (m. m.p.).

Further elution of the column with a mixture (5:1) of petroleum ether and benzene gave 100 mg (40%) of the starting material, m.p. 156–57° (m. m.p.).

Subsequent elution with 1:1 mixture of petroleum ether and benzene gave 60 mg (42%, 71% on the basis of the reacted starting material) of **23**, m.p. 149–50° (m. m.p.).

Thermolysis of 1,3-*diphenylisobenzofuran.* A soln of 1,3-diphenylisobenzofuran (54 mg, 0.2 mmol) in diphenylether (15 ml) was refluxed for 18 hr.. Removal of the solvent under vacuum gave a product which was fractionally crystallized from a mixture (1:1) of petroleum ether and benzene to give 42 mg (73%) of **23**, m.p. 149–50° (m. m.p.).

Thermolysis of 9,10-*dihydro*-11,12-*debenzoyl*-9,10-*ethenoanthracene* (**15**). A sample of **15** (200 mg, 0.5 mmol) was thermolyzed around 260° for 2 hr in a sealed tube. The thermolyzed product was chromatographed over alumina. Elution with petroleum ether gave 50 mg (58%, 83% on the basis of the reacted starting material) of anthracene, m.p. 215° (m. m.p.).

Further elution of the column with a mixture (20:1) of petroleum ether and benzene gave 60 mg (30%) of the unchanged starting material, m.p. 212° (m. m.p.).

Reaction of 9,10-*dihydro*-11,12-*dibenzoyl*-9,10-*ethenoanthracene with phosphorous pentasulphide.* A mixture of 9,10-dihydro-11,12-dibenzoyl-9,10-ethenoanthracene (1.03 g, 2.5 mmol) and P_4S_{10} (1.11 g, 5 mmol) was refluxed in *o*-oxylene (50 ml) for 1 hr. Removal of the solvent under vacuum gave a product which was treated with a 5% NaOHaq and subsequently extracted with CH_2Cl_2. Removal of the solvent from the CH_2Cl_2-extract gave a product which was chromatographed over neutral alumina.

Elution with petroleum ether gave 0.8 g of a mixture of products consisting of **28** and **31**, m.p. 215–220°.

The mixture consisting of **28** and **31** (0.8 g) was treated with 0.2 g (2 mmol) of maleic anhydride in dry benzene (20 ml) and the soln was allowed to stand at room temp. for 3 hr. Removal of the solvent under reduced pressure gave a product-mixture which was recrystallized from cyclohexane. The recrystallized product appeared to be a mixture of two crystalline products. The colourless crystals from this mixture were hand-separated and were subsequently chromatographed over alumina. Elution of the column with petroleum ether gave 0.2 g (20%) of **28**, m.p. 217–18°, after recrystallization from a mixture (1:2) of petroleum ether and benzene. (Found: C, 90.63; H, 5.18; Mol. wt., 396 (Mass spect.). $C_{30}H_{20}O$ requires: C, 90.91; H, 5.05; Mol. wt., 396)

IR spectrum (KBr) ν_{max}: 3020, 3000 and 2980 cm^{-1} (ν_{C-H}), 1602 and 1490 cm^{-1} ($\nu_{C=C}$). UV spectrum (cyclohexane) λ_{max}: 250 nm (ϵ, 15,050) and 312 (20,900). NMR spectrum ($CDCl_3$): 5.65δ (singlet, 2 H, bridgehead) and 7.37δ (multiplet, 14 H, aromatic).

Removal of the colourless crystals of maleic anhydride adduct, left behind 0.45 g (44.5%) of a crystalline material which appeared to be a 1:1 mixture of 12,14-diphenyl-9,10(3',4')furanoanthracene and 12,14-diphenyl-9,10(3',4')-thiophenoanthracene, m.p. 226–228°. (Found: C, 89.05; H, 5.07. $C_{60}H_{40}OS$ requires: C, 89.11; H, 4.95%). IR spectrum (KBr) ν_{max}: 3030, 3005 and 2985 cm^{-1} (ν_{C-H}), 1605, 1580 and 1494 cm^{-1} ($\nu_{C=C}$). UV spectrum (cyclohexane) λ_{max}: 250 nm (ϵ, 20, 410) and 324 (31,090). NMR spectrum ($CDCl_3$): 5.53δ (singlet, 2 H, bridgehead protons of thiophenoanthracene), 5.63δ (singlet, 2 H, bridgehead protons of furanoanthracene) and 7.37δ (multiplet, 36 H, aromatic). Mass spectrum: *m/e* 412 (100), 396 (51), 379 (21), 376 (51), 335 (10), 334 (10), 302 (11), 292 (7), 291 (36), 290 (10), 289 (26), 287 (7), 263 (4), 189 (9), 188 (4), 178 (7), 167 (6), 121 (48), 105 (35) and 77 (7).

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