178-99-4; **9g**, 74397-22-1; **9h**, 74397-23-2; *cis*-**10**, 74397-24-3; *trans*-**10**, 74397-25-4; *cis*-**11**, 74397-26-5; *trans*-**11**, 74397-27-6; **12**, 68965-57-1; **13**, 74397-28-7; **14**, 34945-05-6; *cis*-**15**, 74397-29-8; *trans*-**15**, 74397-30-1; *cis*-**16**, 74397-31-2; *trans*-**16**, 74397-32-3; **17**, 57917-95-0; **18**, 13505-34-5; *cis*-1,2-dimethylcyclohexanol, 19879-11-9; *trans*-1,2-dimethylcyclohexanol, 19879-12-0; *cis*-4-*tert*-butyl-1-methylcyclohexanol, 16980-56-6; *trans*-4-*tert*-butyl-1-methylcyclohexanol, 16980-55-5.

Photochemical Transformations of *cis*-1,2-Dibenzoylalkenes[1]

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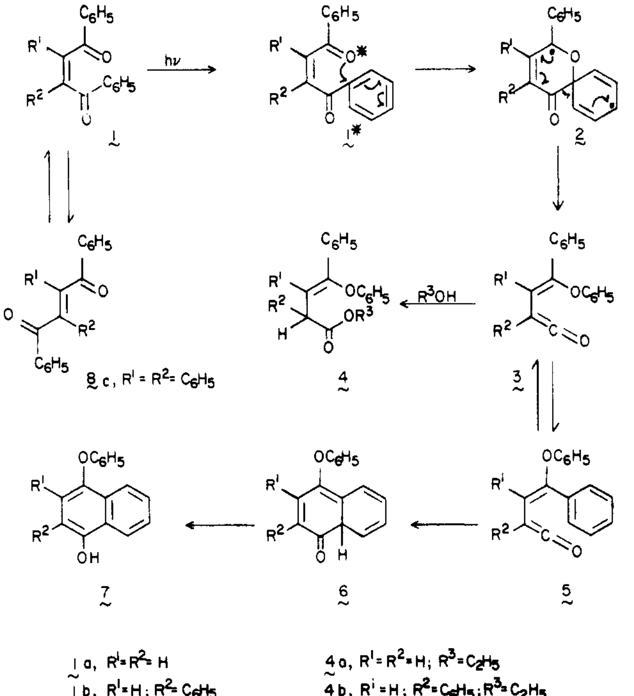
Photorearrangements of *cis*-1,2-dibenzoylalkenes such as 2,3-dibenzoylbicyclo[2.2.2]octa-2,5-diene (**9**), 2,3-dibenzoylbicyclo[2.2.2]oct-2-ene (**21**), 2,3-dibenzoylbicyclo[2.2.1]hept-2-ene (**28**), and 2,3-dibenzoylbicyclo[2.2.1]hepta-2,5-diene (**35**) are reported. Irradiation of **9** in methanol gives a mixture of isomeric esters **13** (69%) and **14** (1%), whereas in benzene a mixture of carboxylic acids **10** (26%) and **11** (6%) and lactone **12** (23%) is formed. Similar rearrangements have been observed in the case of **21** and **28**. Irradiation of **35** in benzene, however, gives mostly the quadricyclane **36**. Laser flash-photolysis studies have shown that diradical intermediates such as **18** and **19** may be involved in the transformation of **9** to the different products. Similar diradical intermediates have been postulated in the rearrangements of **21** and **28**.

Introduction

It has been shown by Griffin and O'Connell[3] and also by Zimmerman and co-workers[4,5] that dibenzoylethylenes (**1**) undergo an interesting photorearrangement in protic solvents, leading to the formation of the corresponding esters (**4**) (Scheme I). Thus, it has been observed that the photolysis of dibenzoylethylene (**1a**) in ethanol leads to the formation of 4-phenyl-4-phenoxy-3-butenoate (**4a**). Similar transformations have been observed in the case of both dibenzoylstyrene (**1b**) and dibenzoylstilbene (**1c**), leading to the formation of the corresponding esters **4b** and **4c**, respectively. In a recent investigation, Padwa et al.[6] have shown that the photolysis of *trans*-dibenzoylstilbene (**8c**) gives rise to different products, depending on the nature of the solvent employed. Thus, the photolysis of **8c** in benzene, for example, gives a mixture of products consisting of *cis*-dibenzoylstilbene (**1c**) and 1-hydroxy-2,3-diphenyl-4-phenoxynaphthalene (**7**), whereas 2,3,4-triphenyl-4-phenoxy-3-butenoic acid (**4d**) is formed in aqueous dioxane. Similarly, Sugiyama and Kashima[7] have observed that the photolysis of dibenzoylethylene (**1a**) in acidic methanol results in the formation of a mixture of products consisting of methyl 4-phenyl-4-phenoxy-3-butenoate, 1,2-dibenzoyl-1-methoxyethane, and 2,5-diphenylfuran. Also, it might be pointed out in this connection that tetrabenzoylethylene is reported to undergo photochemical transformation to an isomeric lactone.[8]

Scheme I



1a, $R^1 = R^2 = H$
1b, $R^1 = H$; $R^2 = C_6H_5$
1c, $R^1 = R^2 = C_6H_5$

4a, $R^1 = R^2 = H$; $R^3 = C_2H_5$
4b, $R^1 = H$; $R^2 = C_6H_5$; $R^3 = C_2H_5$
4c, $R^1 = R^2 = C_6H_5$; $R^3 = CH_3$
4d, $R^1 = R^2 = R^3 = H$

Zimmerman and co-workers[4,5] have suggested that the phototransformations of dibenzoylethylenes (**1**) to the corresponding esters (**4**) can be rationalized in terms of the pathway shown in Scheme I. On the basis of detailed quenching studies they have also suggested that the pho-

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[1] Document No. NDRL-2042 from the Notre Dame Radiation Laboratory.

[2] (a) Indian Institute of Technology; (b) University of Notre Dame.

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

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

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

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

[7] N. Sugiyama and C. Kashima, *Bull. Chem. Soc. Jpn.*, **43**, 1875 (1970).

[8] H. Schmid, M. Hochweber, and H. van Halban, *Helv. Chim. Acta*, **30**, 1135 (1947).

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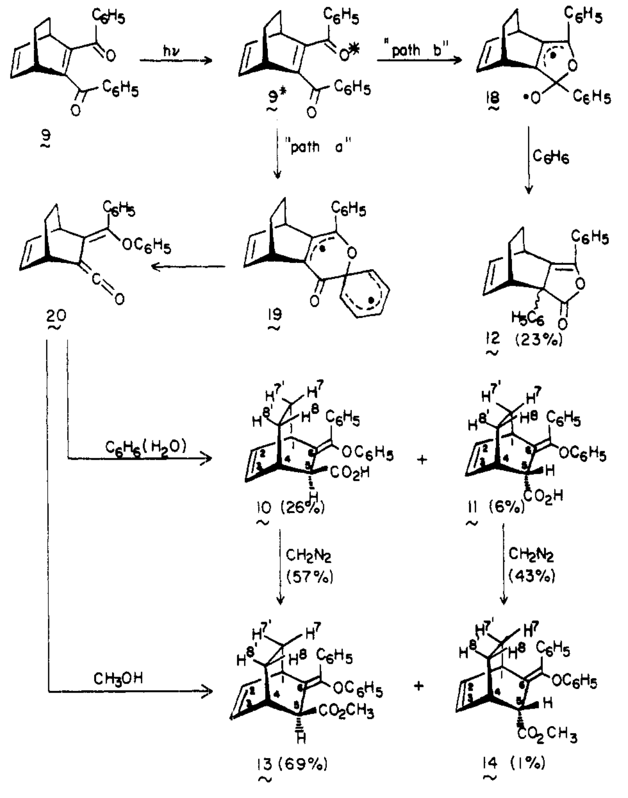
Scheme II



totransformations of dibenzoylethylenes proceed mostly through the excited singlet state.[5,9]

It has been generally observed that in the photoreaction of dibenzoylalkene systems, a major photochemical pathway involves the cis–trans isomerization of the alkene double bond.[6,7,10] Further, the cis–trans isomerization proceeds with higher efficiency than the photorearrangement, as in the case of dibenzoylethylenes.[4-6] The object of the present investigation has been to study the photochemical transformations of a few *cis*-dibenzoylalkenes, having rigid structural features, wherein the cis–trans isomerization pathway is prevented. The *cis*-dibenzoylalkenes that we have examined include, 2,3-dibenzoylbicyclo[2.2.2]octa-2,5-diene (**9**), 2,3-dibenzoylbicyclo[2.2.2]oct-2-ene (**21**), 2,3-dibenzoylbicyclo[2.2.1]hept-2-ene (**28**), and 2,3-dibenzoylbicyclo[2.2.1]hepta-2,5-diene (**35**).

Results and Discussion

1. Preparative Photochemistry and Product Identification. Irradiation of a benzene solution of **9** (3.5 h) gave a mixture of 6-(phenoxyphenylmethylene)bicyclo[2.2.2]oct-2-ene-5-*exo*-carboxylic acid (**10**, 26%), 6-(phenoxyphenylmethylene)bicyclo[2.2.2]oct-2-ene-5-*endo*-carboxylic acid (**11**, 6%), and a lactone **12** (23%), isomeric with the starting material (Scheme II). The structures of these products have been established on the basis of elemental analysis and spectral data.

The NMR spectrum of **10** showed two multiplets centered around δ 1.53 (2 H) and 1.88 (2 H), respectively, due to the methylene protons. The multiplets centered around δ 2.95 (1 H) and 3.58 (1 H), respectively, have been assigned to the two bridgehead protons, whereas the doublet at δ 3.28 (1 H) has been assigned to the endo proton, H-5 ($J_{4,5}$ = 2.5 Hz). Further splitting of this doublet due to long-range coupling between H-5 and H-8′ protons ($J_{5,8'}$ = 1 Hz) confirmed the endo assignment for the H-5 proton in **10**. It may be pointed out here that the splitting pattern that has been observed for the H-5 proton doublet and the values for the coupling constant are in agreement with the reported values for similar systems.[11,12] The multiplet centered around δ 6.35 (2 H) has been assigned to the two ortho protons of the phenoxy group in **10**. Such a high-field shift of the ortho protons in an aromatic ring attached to an oxygen atom has been reported in the literature.[13] In addition, the spectrum of **10** showed two complex multiplets centered around δ 6.81 (4 H) and 7.29 (7 H), respectively, which have been assigned to the carboxylic, vinylic, and aromatic protons. It has been observed that one of the protons in the multiplet at δ 6.81 could be exchanged with D_2O, indicating thereby that the carboxylic proton is partially responsible for this signal.

Further proof of the structure of **10** was derived from its mass spectrum. The mass spectrum of **10** showed a molecular ion peak at m/e 332 (26). The fragmentation modes of **10** were in agreement with the assigned structure.

Additional support for the structure of **10** was derived through its conversion to the corresponding methyl ester. Treatment of **10** with diazomethane gave a 57% yield of methyl 6-(phenoxyphenylmethylene)bicyclo[2.2.2]oct-2-ene-5-*exo*-carboxylate (**13**). The NMR spectrum of **13** showed a sharp singlet at δ 3.45 (3 H), characteristic of an ester methoxy group and in agreement with the assigned structure.

The NMR spectrum of the isomeric acid **11**, obtained from the photolysis of **9**, showed striking similarity to that of the exo acid **10**. The four methylene protons in **11** appeared as an AB quartet with signals at δ 1.41 (2 H) and 1.69 (2 H), respectively (J = 10 Hz). The bridgehead protons appeared as two sets of multiplets centered around δ 3.0 (1 H) and 3.62 (1 H), respectively. The exo proton in **11** appeared as a clean doublet at δ 3.45 (1 H, $J_{4,5}$ = 2.5 Hz). It is pertinent to observe that this doublet has not been further split into multiplets, in contrast to the case of the isomeric acid **10**. A downfield shift of the H-5 proton in **11**, as compared to its exo isomer **10**, is in agreement with the reported observation concerning the chemical shifts of endo protons in similar systems.[14] The ortho protons of the phenoxy group appeared as a triplet at δ 6.30 (2 H), each being further split into doublets ($J_{\text{ortho,meta}}$ = 6, $J_{\text{ortho,para}}$ = 2 Hz). The olefinic protons and the other aromatic protons appeared as two sets of multiplets around δ 6.86 (3 H) and 7.30 (7 H), respectively. The broad signal centered around δ 9.95 (1 H), which disappeared on shaking with D_2O, has been assigned to the carboxylic acid proton.

The mass spectrum of **11** showed a molecular ion peak at m/e 332. The fragmentation pattern has been found to be quite similar to that of the isomeric acid **10**, as would be expected from their structural similarities.

On treatment with diazomethane, the endo acid **11** gave a 43% yield of methyl 6-(phenoxyphenylmethylene)bicyclo[2.2.2]oct-2-ene-5-*endo*-carboxylate (**14**), which showed a characteristic singlet at δ 3.38 (3 H) in its NMR spectrum due to the ester methoxy protons.

Of the two possible structures **12** and **15** for the lactonic product obtained from the photolysis of **9** (Scheme III),

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[9] H. E. Zimmerman and V. J. Hull, *J. Am. Chem. Soc.*, **92**, 6515 (1970).

[10] G. Cauzzo, U. Mazzucato, and A. Foffani, *Bull. Soc. Chim. Belg.*, **71**, 838 (1962); *Chem. Abstr.*, **58**, 9784 (1963).

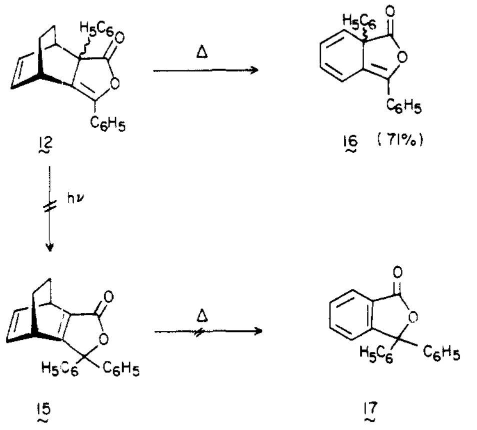
[11] D. B. Roll, B. J. Nist, and A. C. Huitric, *Tetrahedron*, **20**, 2851 (1964).

[12] K. Tori, Y. Takano, and K. Kitahonoki, *Chem. Ber.*, **97**, 2798 (1964).

[13] S. Castellano, C. Sun, and R. Kostelnik, *Tetrahedron Lett.*, 5205 (1967).

[14] R. R. Fraser and S. O'Farrell, *Tetrahedron Lett.*, 1143 (1962).

Scheme III



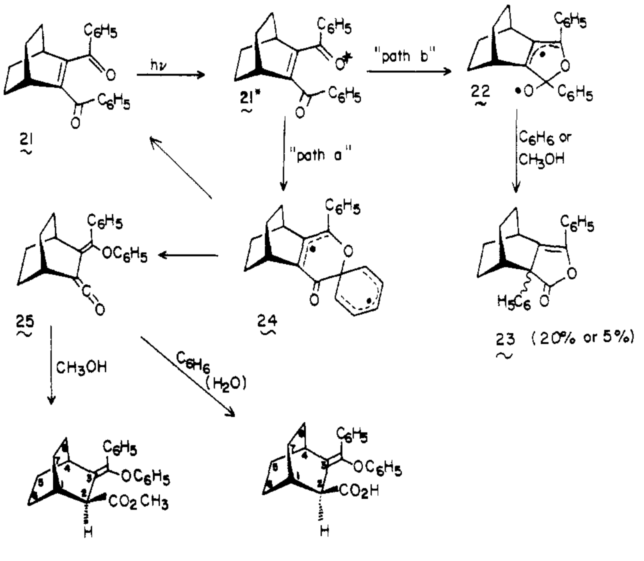
structure 12 has been arrived at on the basis of spectral information and chemical evidences. The IR spectrum of 12, for example, showed a strong carbonyl peak at 1771 cm^{-1}, indicating the presence of a β,γ-butenolide. The UV spectrum of 12 showed three absorption maxima at 224, 240, and 260 nm and was similar to the spectrum of an analogous lactone, 2,2,3,4-tetraphenyl-3-butenolide, formed from the thermal rearrangement of *cis*-1,2-dibenzoylstilbene (**1c**).[15] The NMR spectrum of 12 showed several signals at δ 1.25 (4 H, m, CH_2), 3.98 (2 H, m, bridgehead), 6.21 (2 H, m, vinylic), and 7.35 (10 H, m, aromatic), in agreement with the assigned structure.

Further confirmation of the structure 12 for the lactonic product was derived through its thermal decomposition studies. It has been recently shown that the thermal decomposition of a *cis*-1,2-dibenzoylalkene system, such as **9**, proceeds through the loss of elements of ethylene, leading to the formation of *o*-dibenzoylbenzene.[16] We reasoned that similar pathways will be followed in the thermal decompositions of **12** and **15** to give the corresponding products, **16** and **17**, respectively. Heating of **12** in the absence of any solvent at ca. 140–145 °C for 0.75 h, for example, gave a 71% yield of a product, identified as the lactone **16** (Scheme III). The structure of **16** has been arrived at on the basis of analytical results and spectral data (see Experimental Section).

The formation of products such as 10–12 in the photolysis of **9** can be rationalized in terms of the pathway shown in Scheme II. In this scheme, we assume that the initial step in the reaction is the excitation of **9**, which following intersystem crossing presumably leads to the triplet state **9***. Subsequent interaction of the carbonyl site in **9*** with the π system of an adjacent aromatic ring leads to the diradical intermediate **19** (path a), which in turn is transformed to the ketene derivative **20** through pathways similar to the transformations of dibenzoylethylenes.[4-6] The ketene intermediate **20** can subsequently react with the moisture present in the system to give a mixture of carboxylic acids **10** and **11**.

Further support for the involvement of the ketene intermediate **20** is obtained through the isolation of a mixture of the two isomeric methyl esters **13** (69%) and **14** (1%), when the photolysis of **9** was carried out in methanol. The same esters (**13** and **14**) were obtained on treatment of acids **10** and **11**, respectively, with diazomethane (Scheme II).

Scheme IV



An alternative mode of transformation of **9*** is through path b shown in Scheme II. As per this route, **9*** can interact with the π system of the adjacent carbonyl group to give the diradical intermediate **18**, which can subsequently rearrange to the lactone **12**. The fact that **12** is observed in the phototransformation of a rigid *cis*-dibenzoylalkene system such as **9** would indicate that this is a feasible pathway for the transformation of dibenzoylethylenes in which the cis–trans isomerization mode is prevented. It may be mentioned in this connection that a similar photorearrangement of a *cis*-1,2-dibenzoylalkene derivative leading to the corresponding lactonic product has been observed in the case of 6,7-dibenzoyltricyclo[3.2.2.0^{2,3}]nona-6,8-diene.[17]

In continuation, we have examined the photolysis of 2,3-dibenzoylbicyclo[2.2.2]oct-2-ene (**21**) to study its phototransformations. Photolysis of **21** in benzene (3 h) gave a mixture of lactone **23** (20%) and 3-(phenoxyphenylmethylene)bicyclo[2.2.2]octane-2-carboxylic acid (**27**, 7%). Photolysis of **21** in methanol, however, gave a complex mixture of products. In one run with a Hanovia medium-pressure lamp (450 W), a 5% yield of lactone **23** was obtained, whereas irradiation of **21** using an RPR (3500 Å) lamp source gave a 20% yield of methyl 3-(phenoxyphenylmethylene)bicyclo[2.2.2]octane-2-carboxylate (**26**) (Scheme IV). The formation of products such as **23**, **26**, and **27** from **21** can be understood in terms of the biradical intermediates **22** and **24**, shown in Scheme IV.

To study the effect of minor structural variations on the photorearrangements of *cis*-1,2-dibenzoylalkenes analogous to **9** and **21**, we have examined the photolysis of both 2,3-dibenzoylbicyclo[2.2.1]hept-2-ene (**28**) and 2,3-dibenzoylbicyclo[2.2.1]hepta-2,5-diene (**35**). Irradiation of **28** in benzene gave a 15% yield of 3-(phenoxyphenylmethylene)bicyclo[2.2.1]heptane-2-*exo*-carboxylic acid (**34**), whereas in methanol, a 41% yield of methyl 3-(phenoxyphenylmethylene)bicyclo[2.2.1]heptane-2-*exo*-carboxylate (**33**) is formed (Scheme V). The structures of both **33** and **34** have been arrived at on the basis of analytical results and spectral information (see Experimental Section).

The formation of products such as **33** and **34** in the photolysis of **28** can be rationalized in terms of the ketene

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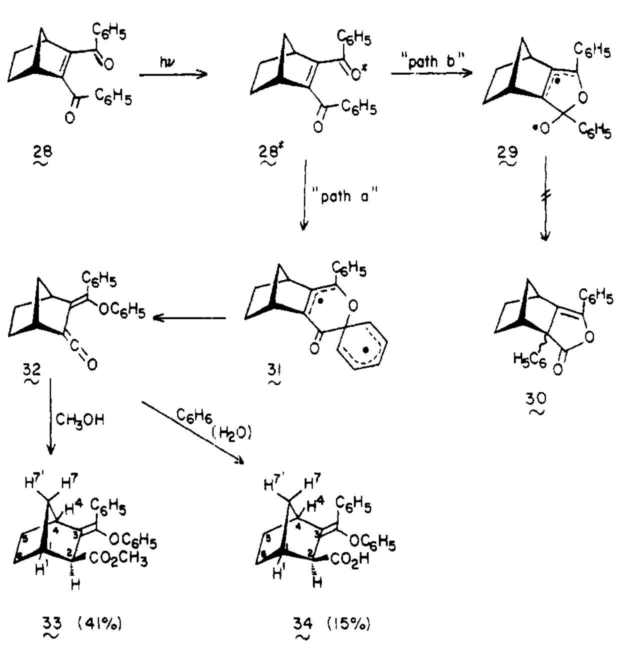
[15] (a) N. Zinin, *Ber.*, **5**, 1104 (1872); (b) D. R. Berger and R. K. Summerbell, *J. Org. Chem.*, **24**, 1881 (1959); (c) S. Lahiri, V. Dabral, and M. V. George, *Tetrahedron Lett.*, 2259 (1976).

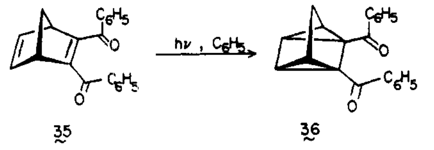
[16] S. Lahiri, V. Dabral, M. P. Mahajan, and M. V. George, *Tetrahedron*, **33**, 3247 (1977).

[17] S. Lahiri, V. Dabral, and M. V. George, *Tetrahedron*, **34**, 2305 (1979).

Scheme V



Scheme VI



intermediate **32**, shown in Scheme V. It is pertinent to observe that none of the lactonic product **30** has been isolated in these reactions. It is not clear whether steric considerations are involved in directing the course of the photoreaction of **28** through the diradical intermediate **31** in any preferential manner.

In contrast to the phototransformations of **9**, **21**, and **28**, photolysis of **35** gave mostly 2,3-dibenzoylquadricyclo[2.2.1.0^{2,6}.0^{3,5}]heptane (**36**, 90%) (Scheme VI). The NMR spectrum of **36** showed the cyclopropyl protons at δ 2.58 (4 H) and the methylene protons at δ 2.90 (2 H); the aromatic protons appeared as a multiplet around δ 7.30 (10 H). The mass spectrum of **36** showed the molecular ion peak at m/e 300 (36) and the fragmentation patterns were in agreement with the assigned structure. It is known that the mass-spectral fragmentations of norbornadiene and quadricyclane exhibit remarkable similarity in the range of 20–70 eV.[18] In the present studies, we find that the mass-spectral fragmentations of **36** are very similar to those of the starting norbornadiene derivative **35**, indicating, thereby, that common fragments are involved in both these cases.

The formation of **36** as the major product in the phototransformation of **35** would suggest that the predominant reaction in this case is a [$_\pi2 + {}_\pi2$] type of cycloaddition, which may be taking place either through a concerted or stepwise process, characteristic of other norbornadiene derivatives.[19-25]

Table I

substrate	method	Φ[a]	mass balance,[b] %	λ_{exc}, nm
9	UV	0.6		254
21	GC	0.04	35	350
21	UV	0.06		350
28	GC	~0.02	80	350
35	UV	0.17		254

[a] Errors are typically 20%. [b] Based on the main product of reaction.

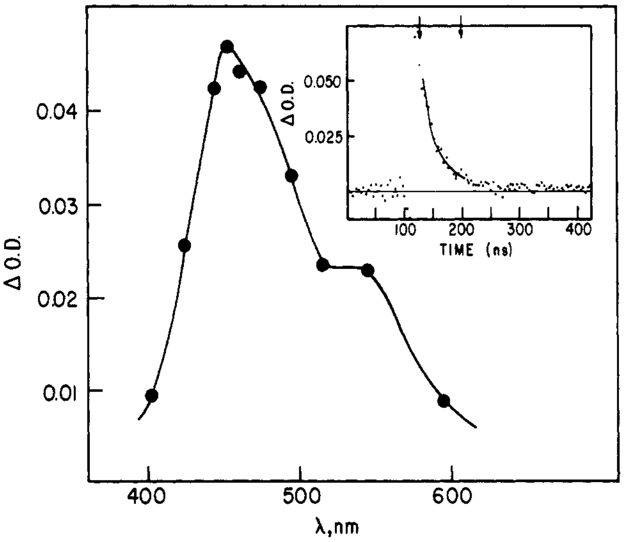


Figure 1. Transient spectrum of the species produced upon laser excitation of **9** in methanol and (insert) typical decay trace.

2. **Quantum-Yield Studies.** The quantum yields for the consumption of the parent molecules were examined by either gas chromatography or monitoring the progress of the reaction by UV spectrophotometry. Table I shows a summary of the results. In our UV experiments, where monitoring as a function of time was easier, we observe linear plots of consumption vs. time during at least 30% of the reaction.

In the case of **21**, we find at least two additional products produced in low yields. The total mass balance, taking these into account is in the neighborhood of 50%; it is clear that other (higher molecular weight) products are also formed. Some of these clearly result from further photolysis of rather photosensitive primary reaction products.

In the case of **21** and **28**, we have observed that air saturation of the solution results in a decrease of the quantum yields, typically by 20–30%. Di-*tert*-butyl nitroxide also has a small effect, while addition of 2,5-dimethyl-2,4-hexadiene results in a slight enhancement of the rate of consumption of the parent molecule and a substantial change in product distribution, with significant yields of new products. While these aspects were not pursued any further, they can perhaps be taken as examples of the reactivity of the biradicals (**24** and **31**) or the ketenes (**25** and **32**) toward conjugated dienes.

Phenanthrene triplet sensitization of the reaction of **28** leads to the same products (although the analysis is considerably more difficult) as the direct irradiation. Both GC and UV techniques suggest that within the relatively large analytical error limits the quantum yields and product distribution of the direct and sensitized processes are about equal.

3. **Laser Flash-Photolysis Studies.** The samples were excited with pulses (337.1 nm, 8 ns, 3 mJ) from a nitrogen laser. Unless otherwise indicated, the experiments were

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(18) Z. Dolejsek, V. Hanus, and H. Prinzbach, *Angew. Chem., Int. Ed. Engl.*, **1**, 598 (1962).

(19) S. J. Cristol and R. L. Snell, *J. Am. Chem. Soc.*, **80**, 1950 (1958).

(20) R. Hoffman, E. Heilbronner, and G. Gleiter, *J. Am. Chem. Soc.*, **92**, 706 (1970).

(21) H. G. Dauben and R. L. Cargill, *Tetrahedron*, **15**, 197 (1961).

(22) W. L. Dilling, *Chem. Rev.*, **66**, 373 (1966).

(23) A. A. Gorman and J. B. Sheridan, *Tetrahedron Lett.*, 2569 (1969).

(24) G. Kaupp and H. Prinzbach, *Helv. Chim. Acta*, **52**, 956 (1969).

(25) H. M. Frey, *J. Chem. Soc.*, 365 (1964).

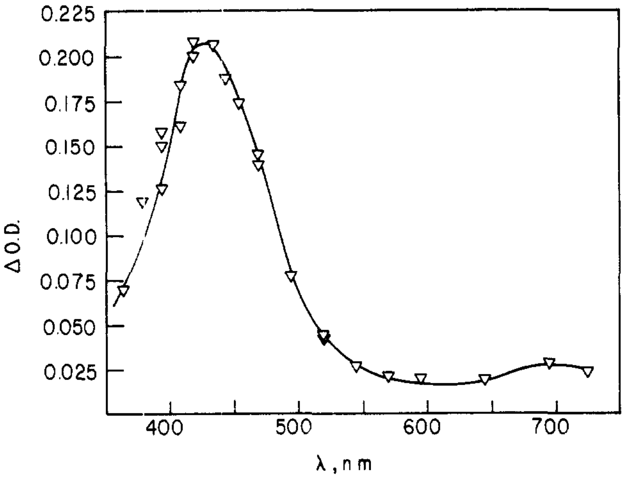
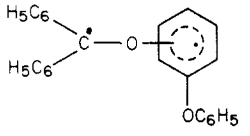


Figure 2. Transient spectrum observed upon irradiation of **21**.

carried out under oxygen-free conditions. The transient absorptions produced were monitored with a detection system having nanosecond response. Further details can be found in the Experimental Section.

3.1. 2,3-Dibenzoylbicyclo[2.2.2]octa-2,5-diene (9). Examination of samples of **9** in methanol in concentrations of around 10^{-2} M leads to relatively weak transient absorptions, the spectrum of which is illustrated in Figure 1. The decay of this transient follows clean first-order kinetics (see insert in Figure 1) and has a lifetime of 40 ns. This transient can in principle be assigned to an excited state of **9** or to species **19** or **20** in Scheme II. The lifetime measured seems too long to correspond to the excited singlet state. The ketene **20** would probably be expected to be longer lived; the same is true of **19**. For example, **37**, which has rather similar structure, has a



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lifetime of 13 µs.[26] We therefore believe that the transient of Figure 1 should be tentatively assigned to the triplet state of **9**, i.e., **9***. We assume that this transient is responsible for the chemistry observed. Unfortunately, the weak signals and short lifetime observed tend to limit the usefulness of laser photolysis in this particular system, and our conclusion is, to some extent, based on an analogy with the cases of **21** and **28** (see below).

The final quantum yields of reaction will be determined by the quantum yield of intersystem crossing, i.e., the efficiency with which **9*** is generated, and by the partition of the triplet states between reaction paths a and b, as well as by the possible reversibility of the reactions leading to biradicals **19** and **18**. It should be noted that the conversion of either **19** or **18** back to **9** can be expected to be an important pathway, since both are thermodynamically favored. Back reactions of this type are common in biradical chemistry.

3.2. 2,3-Dibenzoylbicyclo[2.2.2]oct-2-ene (21). Laser excitation of solutions of **21** in methanol led to intense transient signals with λ_{max} ~440 nm and a lifetime (monitored at 430 nm) of 16 ± 2 µs. This transient decays into a new species of rather similar spectrum, with λ_{max} ~410 nm; the lifetime of this species is long enough to be beyond the resolution of our instrument and we could only establish that it must exceed 50 µs. In several cases we observed that the first two or three points in our decay trace did not fit well with the rest of the data, suggesting the involvement of an even shorter-lived transient, which unfortunately we could not characterize in detail. Figure 2 shows the spectrum of the short-lived transient mentioned before, while Figure 3 shows a first-order kinetic plot for its decay and a typical decay trace. The yield of transient produced (monitored at 440 nm) changed linearly with the excitation dose, indicating a monophotonic process; a 14-fold change in excitation dose was achieved by using suitable neutral density filters. Experiments in benzene revealed the presence of a transient, which from its spectral properties seems to correspond to the short-lived one in methanol and which has a lifetime of 3.8 µs.

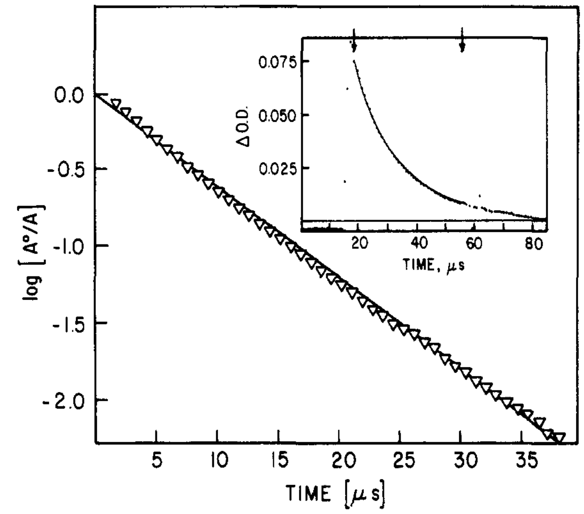

Figure 3. First-order plot for the decay of the transient produced on excitation of **21** and (insert) typical decay trace.

We believe that the main transients observed cannot be attributed to the triplet state of **21** (**21***). Our attempts to quench this transient with triplet quenchers, e.g., 1-methylnaphthalene, were unsuccessful. While it could be claimed that the triplet energy of **21*** is likely to be lower than that of the naphthalene triplet, other experiments confirm the same observation. For example, di-*tert*-butyl peroxide, which in high concentration quenches even low-energy triplets (e.g., anthracene),[27] does not affect the lifetime of the 16-µs transient even in concentrations as high as 3 M. While the lifetime of the transient is insensitive to the addition of peroxide, its yield is indeed affected. For example, a 3 M concentration will decrease the transient absorbance by roughly a factor of two. The same effect was also observed in benzene.

Oxygen and di-*tert*-butyl nitroxide do quench the 16-µs transient; however, this result should not be taken as sufficient evidence for a triplet-state assignment, since the reactivity of triplet-derived biradicals toward paramagnetic reagents is now well-established.[28,29]

In conclusion, we are confident that the 16-µs transient is not the triplet state of **21**, even if we have evidence (vide infra) that the reaction proceeds from the triplet manifold. In fact, it seems likely that the short-lived precursor observed (see above), but which we could not characterize in detail, could be the excited triplet state.

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[26] R. D. Small, Jr., and J. C. Scaiano, *J. Phys. Chem.*, **82**, 2064 (1978).

[27] G. Wubbels and J. C. Scaiano, *J. Am. Chem. Soc.*, in press.

[28] R. D. Small, Jr., and J. C. Scaiano, *J. Am. Chem. Soc.*, **100**, 4512, (1978); R. A. Cadwell, D. Creed *J. Am. Chem. Soc.*, **99**, 8360 (1977).

[29] M. V. Encinas and J. C. Scaiano, *J. Photochem.*, **11**, 241 (1979).

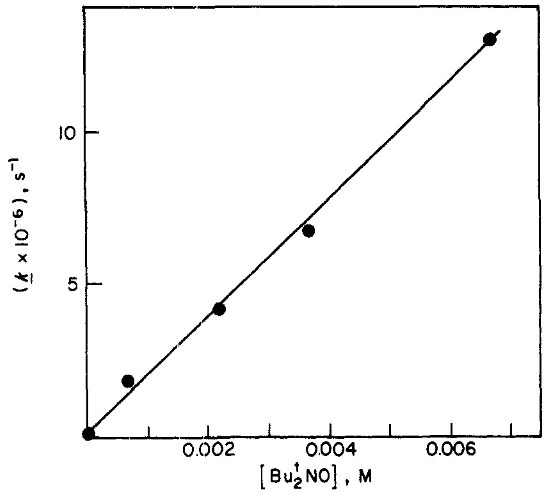

Figure 4. Effect of di-*tert*-butyl nitroxide on the rate of decay of the transient from 21.

We believe that the transient observed is a biradical, though it is difficult to decide whether the species should be assigned to 22 or 24. This biradical interacts with oxygen and di-*tert*-butyl nitroxide; the rate constants for these processes in methanol are 5.7 × 10^8 and 1.8 × 10^9 M^{-1} s^{-1}, respectively. Figure 4 shows a representative plot for di-*tert*-butyl nitroxide. These rates are entirely consistent with those observed for other triplet-derived biradicals.[28-30]

The long-lived transient should probably be assigned to 25 since on the lactonic reaction path there seems to be no need to postulate another transient. If, as suggested by the transient studies, the two species observed are on the same reaction pathway, then the biradical should be assigned to 24, though it is evident that this assignment is only tentative.

We have also carried out some triplet-sensitization experiments. Phenanthrene is a very convenient sensitizer for flash experiments using the nitrogen laser, because one of the absorption bands coincides almost exactly with the laser line (337.1 nm). The triplet state of phenanthrene is efficiently quenched by 21, with a rate constant of ~10^9 M^{-1} s^{-1}. The quenching process leads to formation of the same transients as in the direct-irradiation experiments. In addition, other processes of less importance also seem to lead to some transient absorption in the region of interest. The nature of these reactions was not pursued any further. Quantum-yield studies also lead to the conclusion that the reaction can be sensitized with phenanthrene.

An important question to which we refer here is that of the relation between the flash photolysis and quantum yield data. The transient signals observed in the photochemistry of 21 are quite intense and clearly cannot be attributed to species generated with a quantum yield as low as the ones observed for product formation. If one were to make such an assignment, the transient would need to have an extinction coefficient on the order of 10^5 M^{-1} cm^{-1}, an unreasonable value for the intermediates in Scheme IV. We therefore believe that the transients involved in the reaction are produced with quantum yields considerably higher than those of the products. It seems reasonable to assume that if 24 is produced with higher quantum yields than those of the final products, then its main reaction must be the regeneration of 21. This type of behavior is not uncommon in biradical chemistry,[28-30] as is the change in the yields of products in modes that do not resemble conventional quenching of the reaction intermediates.

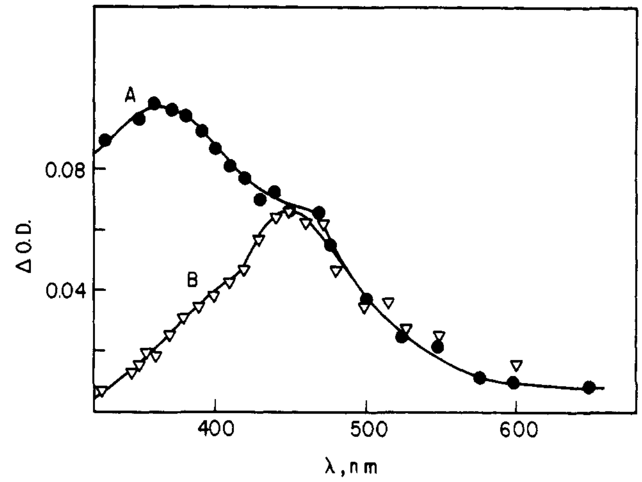

Figure 5. Transient spectra obtained upon excitation of 28: (A) short-lived transient; (B) long-lived transient.

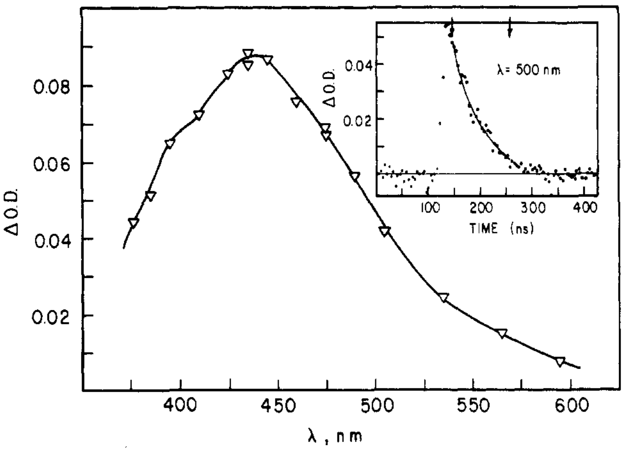

Figure 6. Transient spectrum observed upon excitation of 35 and (insert) typical decay trace.

3.3. 2,3-Dibenzoylbicyclo[2.2.1]hept-2-ene (28). In the case of 28 we carried out a series of experiments closely resembling those performed in the case of 21. On the whole, we found this system to be quite complicated. The transient spectra (Figure 5) are less intense than those observed for 21 and the short- and long-lived transients overlap extensively in the visible region of the spectrum. It is possible that some underlying absorptions due to as yet noncharacterized species make the visible region of the spectrum even more complicated. Most of our kinetic measurements were carried out at 322 nm, this wavelength being chosen largely because of the availability of an interference filter that prevented the scattered (337 nm) light from reaching the monochromator and detector.

We find that the short-lived species lives 3 μs and it interacts with O_2 with k = 7 × 10^8 M^{-1} s^{-1}, with di-*tert*-butyl nitroxide with k = 1.7 × 10^9 M^{-1} s^{-1}, and with a typical triplet quencher, 2,5-dimethyl-2,4-hexadiene, with k = 7 × 10^7 M^{-1} s^{-1}. Di-*tert*-butyl peroxide has some effect on the lifetime, but it also seems to participate in other reactions leading to significant transient absorptions and the results are rather complex. 1-Methylnaphthalene has very little effect on the kinetics, but there is some indication that the triplet state may be formed, though rather inefficiently. In a way, the weaker signals detected in this system make the work with quenchers and sensitizers simpler.

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(30) R. D. Small, Jr., and J. C. Scaiano, *Chem. Phys. Lett.*, 48, 354 (1977).

In the phenanthrene-sensitization experiments, we find that **28** quenches phenanthrene triplets with $k_q \simeq 2.4 \times 10^9$ M^{-1} s^{-1} and leads to transient phenomena similar to those observed in the direct irradiations. As in the case of **21**, we find that other minor processes also seem to participate in the sensitized reaction.

3.4. 2,3-Dibenzoylbicyclo[2.2.1]hepta-2,5-diene (35). The transient phenomena observed in the case of **35** bear surprising similarity to our experiments in the case of **9** (see Figure 6), perhaps as a reminder that transient phenomena do not necessarily reflect fully the chemical changes. The lifetime of the transient, which, because of its kinetic and spectroscopic resemblance to **9**, we tentatively assign to the triplet state of **35**, has a value of 54 ns in methanol.

Experimental Section

All melting points are uncorrected and were determined on a Mel-Temp melting-point apparatus. The IR spectra were recorded on either Perkin-Elmer Model 137 or Model 521 infrared spectrometers. The electronic spectra were recorded on either Beckman DB or Cary 219 spectrophotometers. NMR traces were recorded on either Varian A-60 or HL-100 NMR spectrometers, using tetramethylsilane as internal standard. The mass spectra were recorded on a Varian Mat CH7 mass spectrometer at 70 eV. Irradiations were carried out in a Srinivasan–Griffin Rayonet photochemical reactor (3500 Å), using either a Hanovia 450-W medium-pressure mercury lamp in a quartz-jacketed immersion well or a low-pressure mercury arc (254 nm).

Starting Materials. 2,3-Dibenzoylbicyclo[2.2.2]octa-2,5-diene (**9**),[16] mp 153 °C, 2,3-dibenzoylbicyclo[2.2.2]oct-2-ene (**21**),[31] mp 145 °C, 2,3-dibenzoylbicyclo[2.2.1]hept-2-ene (**28**),[31,32] mp 134–135 °C, and 2,3-dibenzoylbicyclo[2.2.1]hepta-2,5-diene (**35**),[31] mp 143–144 °C, were prepared by reported procedures. Solvents for photolysis studies were purified and distilled before use, whereas Aldrich Gold-Label solvents were used for laser studies. Petroleum ether used was the fraction with bp 60–80 °C.

Photolysis of 2,3-Dibenzoylbicyclo[2.2.2]octa-2,5-diene (9). A solution of **9** (575 mg, 2.46 mmol) in benzene (210 mL) was photolyzed for 3.5 h under a 450-W Hanovia medium-pressure mercury lamp provided with a Pyrex filter. The photolysis was repeated several times to photolyze in all 2.3 g (10 mmol) of **9**. Removal of the solvent from the photolyzed mixture gave a residual solid, which was chromatographed over silica gel. Elution of the column with petroleum ether gave 100 mg of biphenyl, mp 69–70 °C (mixture melting point).[33]

Further elution with a mixture (50:1) of petroleum ether and benzene gave 350 mg (23%) of the lactone **12**, mp 139–140 °C, after recrystallization from a mixture (5:1) of petroleum ether and benzene: IR ν_{max} (KBr) 3045, 2955, 2945 (CH), 2925, 2865 (CH_2, asymmetric and symmetric), 1771 (C=O), 1666 and 1596 (C=C) cm^{-1}; UV λ_{max} (ethanol) 224 nm (ϵ 5500), 240 (4400), 260 (2500); mass spectrum, *m/e* (relative intensity) 314 (M^+, 1), 270 ($M^+ - CO_2$, 3), 257 (1), 237 ($M^+ - C_6H_5$, 34), 209 ($M^+ - C_2H_4$, $M^+ - C_6H_5$, 100), 181 (1), 180 (2), 179 (1), 178 (1), 166 (2), 165 (4), 153 (9), 152 (16), 140 (1), 105 ($C_6H_5CO^+$, 11), 94 (2), 93 (2), 77 ($C_6H_5^+$, 26), 65 (8), 57 (5), 55 (3), 51 (4).

Anal. Calcd for $C_{22}H_{18}O_2$: C, 84.07; H, 5.73. Found: C, 84.35; H, 5.65.

Further elution of the column with a mixture (20:1) of petroleum ether and benzene gave 800 mg (35%) of unchanged starting material (**9**), mp 153 °C (mixture melting point), after recrystallization from a mixture (2:1) of petroleum ether and benzene.

Continued elution of the column with a mixture (1:1) of petroleum ether and benzene gave 400 mg (26%) of 6-(phenoxyphenylmethylene)bicyclo[2.2.2]oct-2-ene-5-*exo*-carboxylic acid (**10**), mp 293 °C, after recrystallization from a mixture (2:1) of petroleum ether and benzene: IR ν_{max} (KBr) 3035, 2935, 2895 (CH), 2945, 2845 (CH_2, asymmetric and symmetric), 1710 (C=O), 1650, 1600 and 1590 (C=C) cm^{-1}; UV λ_{max} (ethanol) 229 nm (ϵ 12 000), 260 (14 500); mass spectrum, *m/e* (relative intensity) 332 (M^+, 26), 314 (1), 304 (4), 287 (3), 259 (100), 239 (9), 238 (6), 216 (3), 215 (2), 211 (6), 210 (9), 209 (3), 194 (2), 193 (4), 183 (8), 182 (6), 181 (3), 178 (4), 166 (5), 165 (10), 153 (5), 152 (6), 139 (2), 133 (4), 131 (5), 115 (11), 105 (22), 104 (13), 94 (4), 91 (7), 78 (6), 77 (22), 65 (5), 62 (3), 51 (10).

Anal. Calcd for $C_{22}H_{20}O_3$: C, 79.50; H, 6.02. Found: C, 79.71; H, 5.63.

Subsequent elution of the column with a mixture (1:2) of petroleum ether and benzene gave 100 mg (6%) of 6-(phenoxyphenylmethylene)bicyclo[2.2.2]oct-ene-5-*endo*-carboxylic acid (**11**), mp 269 °C, after recrystallization from a mixture (2:1) of petroleum ether and benzene: IR ν_{max} (KBr) 3045, 2977, 2915, 2885 (CH), 2935, 2835 (CH_2, asymmetric and symmetric), 1715 (C=O), 1668, 1600 and 1590 (C=C) cm^{-1}; UV λ_{max} (ethanol) 226 nm (ϵ 13 200), 260 (11 000).

Anal. Calcd for $C_{22}H_{20}O_3$: C, 79.50; H, 6.02. Found: C, 79.45; H, 6.10.

Esterification of 6-(Phenoxyphenylmethylene)bicyclo[2.2.2]oct-2-ene-5-*exo*-carboxylic Acid (10). Diazomethane was passed through an ice-cold solution of **10** (99 mg, 0.3 mmol) in ether (25 mL) until the mixture became distinctly yellow in color. The mixture was kept at 0 °C for 3 h and later the solvent was removed under vacuum to give a residual solid. Recrystallization of this product from a mixture (9:1) of petroleum ether and benzene gave 60 mg (57%) of methyl 6-(phenoxyphenylmethylene)bicyclo[2.2.2]oct-2-ene-5-*exo*-carboxylate (**13**): mp 131 °C; IR ν_{max} (KBr) 3080 (CH), 1750 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.51 (2 H, m, CH_2), 1.88 (2 H, m, CH_2), 2.92 (1 H, m, bridgehead proton), 3.31 (1 H, m, tertiary endo proton attached to the carbon atom bearing the CO_2CH_3 group), 3.43 (3 H, s, OCH_3), 3.58 (1 H, m, bridgehead proton), 6.80 (12 H, complex multiplet, vinylic and aromatic protons).

Anal. Calcd for $C_{23}H_{22}O_3$: C, 79.76; 6.41. Found: C, 80.05; H, 6.36.

Esterification of 6-(Phenoxyphenylmethylene)bicyclo[2.2.2]oct-2-ene-5-*endo*-carboxylic Acid (11). Diazomethane was passed through a solution of **11** (66 mg, 0.2 mmol) in ether (20 mL), until the solution became yellow in color. The reaction mixture was kept at 0 °C for 3 h. Removal of the solvent under vacuum and recrystallization of the residue from a mixture (9:1) of petroleum ether and benzene gave 30 mg (43%) of methyl 6-(phenoxyphenylmethylene)bicyclo[2.2.2]oct-2-ene-5-*endo*-carboxylate (**14**): mp 125 °C; IR ν_{max} (KBr) 3100 (CH), 1760 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.39 (2 H, m, CH_2), 1.63 (2 H, m, CH_2), 2.92 (1 H, m, bridgehead proton), 3.88 (3 H, s, OCH_3), 3.47 (1 H, d, tertiary exo proton at C-5), 3.62 (1 H, m, bridgehead proton), 6.83 (12 H, m, armoatic and vinylic protons).

Photolysis of 9 in Methanol. A solution of **9** (250 mg, 0.75 mmol) in absolute methanol (160 mL) was photolyzed under an RPR (3500 Å) light source for 5 h. In several repeat runs, a total of 750 mg of **9** was photolyzed and the combined mixture was worked up by chromatographing it over neutral alumina. Elution with petroleum ether gave 300 mg (69%) of **13**, mp 130 °C (mixture melting point), after recrystallization from a mixture (9:1) of petroleum ether and benzene.

Further elution of the column with petroleum ether gave 5 mg (1%) of **14**, mp 125 °C (mixture melting point), after recrystallization from a mixture (9:1) of petroleum ether and benzene.

Subsequent elution with a mixture (10:1) of petroleum ether and benzene gave 350 mg (47%) of the unchanged starting material (**9**), mp 153 °C (mixture melting point).

Thermolysis of Lactone 12. A sample of **12** (100 mg, 0.32 mmol) was heated at ca. 140–145 °C in a sealed tube for 0.75 h. The thermolyzed mixture was recrystallized from a mixture (1:3) of chloroform and petroleum ether to give 65 mg (71%) of lactone **16**: mp 158 °C; IR ν_{max} (KBr) 3100, 3000, 2900 (CH), 1770 (C=O), 1490 (C=C) cm^{-1}; UV λ_{max} (cyclohexane) 235 nm (ϵ 8700), 246 (8700), 266 (5500), 325 (1100); ^{1}H NMR ($CDCl_3$) δ 6.92 (4 H, m, vinylic), 7.45 (10 H, m, aromatic); mass spectrum, *m/e* (relative intensity), 257 (2), 211 (3), 210 (33), 209 ($M^+ - C_6H_5$, 100), 208 (3), 181 (2), 180 (3), 165 (3), 163 (1), 154 (2), 153 (20), 152 (37), 151 (11), 150 (2), 126 (2), 125 (1), 106 (1), 105 (9), 104 (2), 94 (1),

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(31) D. M. Chipman, S. M. S. Shauhan, and M. V. George, in press.

(32) (a) G. Dupont and J. Germain, *Bull. Soc. Chim. Fr.*, 526 (1947); *Chem. Abstr.*, **42**, 545 (1948); (b) G. Dupont and J. Germain, *C. R. Hebd. Seances Acad. Sci.*, **233**, 743 (1946); *Chem. Abstr.*, **41**, 2420 (1947).

(33) The source of biphenyl remains unclear, even though its formation in complex photochemical systems of this type is not unprecedented: Y. Ito, T. Matsuura, H. Yokoya *J. Am. Chem. Soc.*, **101**, 4010 (1979).

93 (2), 78 (2), 77 (9), 76 (5), 75 (2), 74 (1), 65 (4), 63 (2), 62 (1), 57 (1), 55 (1), 51 (6).

Anal. Calcd for $C_{20}H_{14}O_2$: C, 83.98; H, 4.96. Found: C, 84.28; H, 4.83.

Photolysis of 2,3-Dibenzoylbicyclo[2.2.2]oct-2-ene (21) in Benzene. A solution of **21** (1.1 g, 3.7 mmol) in dry benzene (500 mL) was photolyzed for 3 h under a 450-W Hanovia medium-pressure mercury lamp provided with a Pyrex filter. The photolysis was repeated again with an additional quantity (1.1 g, 3.7 mmol) of **21** and the combined photolysates were worked up by removal of the solvent under vacuum to give a residual solid. Chromatography of this product mixture over silica gel and elution with a mixture (5:1) of petroleum ether and benzene gave 440 mg (20%) of a product, mp 206 °C after recrystallization from a mixture (1:1) of petroleum ether and benzene, identified as the lactone **23**: IR ν_{max} (KBr) 3000, 2950, 2898, 1750 (C=O), 1668, 1660 cm^{-1}; UV λ_{max} (methanol) 236 nm (ϵ 21 300), 242 (10 000, sh), 280 (7100), 290 (6500); ^{1}H NMR (CDCl$_3$) δ 1.38–1.66 (4 H, m, CH$_2$), 1.86 (4 H, m, CH$_2$), 2.90 (1 H, d, bridgehead), 3.40 (1 H, d, bridgehead), 6.81–7.90 (10 H, m, aromatic); mass spectrum, *m/e* (relative intensity) 316 (M$^+$, 14), 288 (1), 240 (5), 239 (23), 222 (1), 221 (1), 212 (1), 211 (11), 209 (3), 194 (3), 193 (2), 182 (2), 166 (1), 165 (6) 156 (1), 154 (1), 153 (1), 152 (1), 115 (3), 105 (44), 43 (1), 32 (22), 28 (100).

Anal. Calcd for $C_{22}H_{20}O_2$: C, 83.52; H, 6.37. Found: C, 82.72; H, 6.69.

Further elution of the column with a mixture (1:1) of petroleum ether and benzene gave 160 mg (7%) of 3-(phenoxyphenylmethylene)bicyclo[2.2.2]octane-2-carboxylic acid (**27**), mp 218 °C, after recrystallization from benzene: IR ν_{max} (KBr) 3550–3250 (OH, br), 2980, 2900, 1715 (C=O), 1660 cm^{-1}; UV λ_{max} (methanol) 222 nm (ϵ 12 000), 260 (12 200); mass spectrum, *m/e* (relative intensity) 334 (M$^+$, 50), 315 (1), 290 (4), 289 (18), 241 (9), 240 (43), 239 (9), 213 (50), 212 (19), 211 (10), 197 (5), 196 (10), 195 (12), 185 (9), 184 (30), 183 (19), 168 (19), 167 (25), 166 (18), 165 (24), 155 (19), 154 (10), 153 (23), 152 (30), 135 (14), 129 (16), 128 (20), 117 (12), 115 (37), 105 (77), 77 (100), 65 (23), 57 (12), 55 (22), 51 (45).

Anal. Calcd for $C_{22}H_{22}O_3$: C, 79.05; H, 6.58. Found: C, 78.42; H, 6.12.

Photolysis of 21 in Methanol. A solution of **21** (316 mg, 1 mmol) in methanol (100 mL) was photolyzed for 8 h under an RPR (3500 Å) light source. The experiment was repeated several times to photolyze, in all, 1.58 g (5 mmol) of **21**. Removal of the solvent under vacuum gave a residual solid, which was chromatographed over silica gel. Elution with a mixture (9:1) of petroleum ether and benzene gave 350 mg (20%) of methyl 3-(phenoxyphenylmethylene)bicyclo[2.2.2]octane-2-carboxylate (**26**), mp 144 °C, after recrystallization from a mixture of petroleum ether and benzene: IR ν_{max} (KBr) 3000, 2990, 2981, 1780, 1630, 1590 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.65 (8 H, m, H-5, H-6, H-7, H-8), 2.00 (1 H, m, bridgehead), 2.65 (1 H, m, bridgehead), 3.40 (3 H, s, OCH$_3$), 3.40 (1 H, dd, $J_{1,2}$ = 3.50, $J_{2,7}$ = 1.0 Hz), 6.75–7.25 (10 H, m, aromatic); mass spectrum, *m/e* (relative intensity) 348 (M$^+$, 2), 304 (2), 303 (9), 257 (6), 256 (99), 255 (100), 228 (8), 227 (52), 211 (20), 199 (5), 162 (5), 134 (8), 133 (12), 106 (6), 105 (26), 78 (11), 77 (40), 65 (9), 51 (9).

Anal. Calcd for $C_{23}H_{24}O_3$: C, 79.28; H, 6.94. Found: C, 78.50; H, 6.76.

Further elution of the column with a mixture (2:1) of petroleum ether and benzene gave 0.78 g (51%) of unchanged starting material (**21**), mp 144–145 °C (mixture melting point).

In a repeat run, 1.58 g (5 mmol) of **21** was photolyzed, in several lots, in methanol with a 450-W Hanovia medium-pressure mercury lamp provided with a Pyrex filter. The reaction mixture, after removal of the solvent under vacuum, was chromatographed over silica gel. Elution of the column with a mixture (4:1) of petroleum ether and benzene gave 75 mg (5%) of lactone, **23**, mp 206 °C (mixture melting point).

Further elution of the column with different solvents gave a complex mixture of products from which no definite compound could be isolated.

Photolysis of 2,3-Dibenzoylbicyclo[2.2.1]hept-2-ene (28) in Benzene. A solution of **28** (1.0 g, 3.3 mmol) in dry benzene (450 mL) was photolyzed for 3 h under a 450-W Hanovia medium-pressure mercury lamp provided with a Pyrex filter. The photolysis was repeated a few times to photolyze in all 3.02 g (10 mmol) of **28**. Removal of the solvent under vacuum from the combined photolysates gave a residual solid, which was chromatographed over silica gel. Elution of the column with a mixture (4:1) of petroleum ether and benzene gave 850 mg (28%) of unchanged starting material, mp 134–135 °C (mixture melting point).

Continued elution of the column with a mixture (1:1) of petroleum ether and benzene gave 480 mg (15%) of 3-(phenoxyphenylmethylene)bicyclo[2.2.1]heptane-1-*exo*-carboxylic acid (**34**), mp 190 °C, after recrystallization from benzene: IR ν_{max} (KBr) 3550–3250 (OH, br), 3140, 3000, 2950, 1715 (C=O), 1650, 1600, 1500 cm^{-1}; UV λ_{max} (methanol) 229 nm (ϵ 11 400), 260 (13 500); ^{1}H NMR (CDCl$_3$) δ 1.40–1.78 (5 H, m, H-5, H-6, and H-7′ or H-7), 1.90 (1 H, m, H-7 or H-7′), 2.66 (1 H, m, H-1 or H-4), 3.16 (1 H, m, H-4 or H-1), 3.50 (1 H, dd, J = 3.8 Hz, H^2), 6.68–7.34 (10 H, m, aromatic); mass spectrum, *m/e* (relative intensity) 320 (M$^+$, 4), 275 (2), 247 (2), 227 (4), 226 (19), 200 (7), 199 (47), 198 (7), 171 (23), 170 (10), 167 (4), 166 (6), 165 (8), 153 (12), 152 (12), 151 (3), 141 (11), 128 (8), 115 (15), 105 (80), 94 (10), 77 (100), 51 (8).

Anal. Calcd for $C_{20}H_{20}O_3$: C, 78.75; H, 6.25. Found: C, 78.91; H, 6.41.

Photolysis of 28 in Methanol. A solution of **28** (300 mg, 1 mmol) in methanol (100 mL) was photolyzed for 8 h under an RPR (3500 Å) light source and the photolysis was repeated several times to photolyze, in all, 1.5 g (5 mmol) of **28**. Removal of the solvent under vacuum gave a residual solid, which was chromatographed over silica gel.

Elution of the column with a mixture (9:1) of petroleum ether and benzene gave 680 mg (41%) of methyl 3-(phenoxyphenylmethylene)bicyclo[2.2.1]heptane-2-*exo*-caroboxylate (**33**), mp 100 °C, after recrystallization from benzene: IR ν_{max} (KBr) 3040, 2980, 2950, 1720 (C=O), 1605, 1502 cm^{-1}; UV λ_{max} (methanol) 233 nm (ϵ 12 600), 260 (19 300), 274 (9100); ^{1}H NMR (CDCl$_3$) δ 1.38–1.71 (5 H, m, H-5, H-6, and H-7 or H-7′), 1.80 (1 H, m, H-7′ or H-7), 2.58 (1 H, m, H-1 or H-4), 3.05 (1 H, m, H-4 or H-1), 3.15 (3 H, s, OCH$_3$), 3.42 (1 H, dd, J = 4.00 Hz, H-2), 6.65–7.25 (10 H, m, aromatic); mass spectrum, *m/e* (relative intensity) 334 (M$^+$, 25), 302 (2), 275 (8), 247 (5), 243 (100), 185 (36), 181 (8), 165 (8), 153 (12), 152 (11), 141 (7), 128 (6), 115 (16), 105 (41), 77 (53), 65 (17), 59 (14), 51 (14), 43 (4), 41 (8).

Anal. Calcd for $C_{22}H_{22}O_3$: C, 79.42; H, 6.58. Found: C, 79.25; H, 6.35.

Further elution of the column with a mixture (4:1) of petroleum ether and benzene gave 170 mg (11%) of unchanged starting material (**28**), mp 134–135 °C (mixture melting point).

Photolysis of 2,3-Dibenzoylbicyclo[2.2.1]hepta-2,5-diene (35). A solution of **35** (500 mg, 1.67 mmol) in benzene (160 mL) was irradiated under an RPR (3500 Å) light source for 2 h. The solvent was removed under vacuum and the residue was recrystallized from a mixture (2:1) of petroleum ether and benzene to give 450 mg (90%) of white needle-shaped crystals of 2,3-dibenzoylquadricyclo[2.2.1.0^{2,6}.0^{3,5}]heptane (**36**): mp 151–152 °C; IR ν_{max} (KBr) 3065 (CH), 2935 and 2865 (CH$_2$, asymmetric and symmetric), 1660 (C=O) cm^{-1}; UV λ_{max} (ethanol) 243 nm (ϵ 24 550), 280 (4400); mass spectrum, *m/e* (relative intensity) 300 (M$^+$, 36), 235 (8), 223 (M$^+$ – C$_6$H$_5$, 4), 207 (5), 195 (M$^+$ – COC$_6$H$_5$, 26), 178 (3), 167 (11), 166 (3), 165 (9), 152 (4), 115 (4), 105 (C$_6$H$_5$CO$^+$, 100), 77 (C$_6$H$_5$$^+$, 67), 66 (45), 51 (42).

Anal. Calcd for $C_{21}H_{16}O_2$: C, 84.00; H, 5.33. Found: C, 83.83; H, 5.70.

Quantum Yields. Quantum yields were determined by UV spectrophotometry or gas chromatography, in which case we used a Beckman GC-5 instrument equipped with flame-ionization detectors and Apiezon L or SE-30 Silicone-oil columns.

The photofragmentation of valerophenone was used as an actinometer, taking the quantum yield of acetophenone formation as 0.30 in benzene.[34] In experiments at 254 nm, it was necessary to use methanol as solvent for the actinometer solution and in this case we assumed Φ (acetophenone) = 0.85.

Laser Photolysis. Our instrument makes use of a Molectron UV-400 nitrogen laser for excitation. The system is fully interphased with a PDP 11/55 multiuser computer which controls the

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(34) P. J. Wagner, P. A. Kelso, A. E. Kemppainen, J. M. McGrath, H. N. Schott, and R. G. Zepp, *J. Am. Chem. Soc.*, 94, 7506 (1972).

experiment, averages signals, and processes the data. The instrument allows the monitoring of transient phenomena in the 10-ns–100-μs time range. Further details have been given elsewhere.[35,36]

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Registry No. 9, 66933-94-6; **10**, 73367-64-3; **11**, 73395-35-4; **12**, 73367-65-4; **13**, 73464-65-0; **14**, 73367-66-5; **16**, 73367-67-6; **21**, 73367-68-7; **23**, 73395-62-7; **26**, 73367-69-8; **27**, 73367-70-1; **28**, 56585-39-8; **33**, 73367-71-2; **34**, 73367-72-3; **35**, 1096-50-0; **36**, 73367-73-4; biphenyl, 92-52-4.

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(35) M. V. Encinas and J. C. Scaiano, *J. Am. Chem. Soc.*, 101, 2146 (1979).

(36) L. K. Patterson and J. C. Scaiano, to be published.

Photochemical Pathways for the Interconversion of Nootkatane and Spirovetivane Sesquiterpenes[1]

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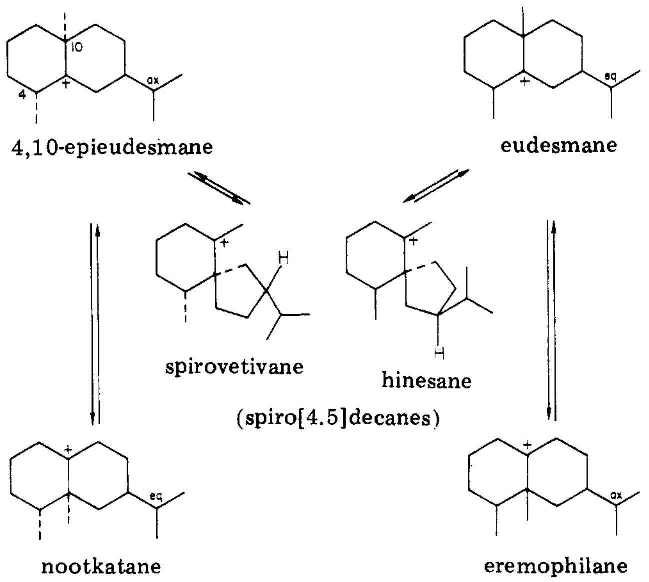
Tricyclodecenones **2a** and **2b**, prepared by irradiation of the corresponding cross-conjugated dienones in anhydrous dioxane at 254 nm, were converted into the spiro dienones **4a** and **4b**, respectively, on irradiation in aqueous acetic acid with ultraviolet light of wavelengths >300 nm. Irradiation of tricyclodecenone **11** for 30 min under similar conditions gave anhydro-β-rotunol (**12**), the bicyclic trienone **13**, and 3,4-dehydronootkatone (**10b**) in 46, 37, and 12% yields, respectively. However, monitoring of the course of the reaction by GLC indicated that **12** and **13** were formed in an initial ratio of 7:3 and that **13** and also **10b** were produced by further rearrangement of **12**. This was shown to proceed via the intermediate bicyclohexenone derivatives **16**. An independent stereospecific synthesis of the bicyclic trienone **13** from (−)-2-carone was developed. Tricyclodecenone **17**, derived from **13**, gave a mixture of **10b**, **12**, and **13**, in 20, 40, and 15% yields, respectively, when irradiated under the same conditions described for **13**. The tricyclodecenone derivative **19**, which was prepared by irradiation of 3,4-dehydro-α-vetivone (**18**) in dioxane at 254 nm, was converted exclusively into (±)-dehydro-β-vetivone (**20**) on irradiation in aqueous acetic acid with >300-nm light. Likewise, **20** was photochemically convertible into **18** via bicyclohexenones **21**. Catalytic reduction of **20** gave a 3:1 mixture of (±)-β-vetivone (**22a**) and (±)-10-epi-β-vetivone (**22b**) in low yield. Lithium–ammonia reduction of **20** gave a 3:7 mixture of **22a** and **22b** in good yield. The mechanisms of the various photochemical transformations are discussed.

Introduction

The generally accepted biogenetic pathways for interconversions of eudesmane, eremophilane (nootkatane), and spiro[4.5]decane sesquiterpenes involve Wagner–Meerwein rearrangements of appropriate carbonium ion intermediates.[2] As shown in Scheme I, methyl or methylene migrations in a eudesmane cation can yield the eremophilane or hinesane skeletons, and the corresponding rearrangements in a 4,10-epieudesmane cation can lead to the nootkatane or spirovetivane ring systems. Several examples of thermal in vitro 1,2-methyl migrations are known,[3-5] and one report of a biogenetic-like 1,2-methylene migration has appeared in the literature.[8]

Scheme I



It is well-known that cross-conjugated cyclohexadienones having a eudesmane skeleton are converted into guaiane derivatives on irradiation in protic solvents.[9,10] Consid-

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(2) For a recent review, see: Marshall, J. A.; Brady, S. F.; Andersen, N. H. *Fortschr. Chem. Org. Naturst.* **1974**, *31*, 283.

(3) (a) For a recent review, see: Coates, R. M. *Fortschr. Chem. Org. Naturst.* **1976**, *33*, 73. (b) Huffman, J. W. *J. Org. Chem.* **1972**, *37*, 2736. (c) Hochstetler, A. R. *Ibid.* **1974**, *39*, 1400.

(4) (a) Kitagawa, I.; Yamazoe, Y.; Shibuya, H.; Takeda, R.; Takeno, H.; Yosioka, I. *Chem. Pharm. Bull.* **1974**, *22*, 2662. (b) Kitagawa, I., Shibuya, H.; Takeno, H.; Nishino, T.; Yosioka, T. *Ibid.* **1976**, *24*, 56.

(5) Miller, C. A.; Pinder, A. R. *J. Chem. Soc., Chem. Commun.* **1977**, 230.

(6) (a) Caine, D.; Graham, S. L. *Tetrahedron Lett.* **1976**, 2521. (b) Caine, D.; Graham, S. L.; Vora, T. T. *J. Org. Chem.*, following paper in this issue.

(7) (a) Buchi, G.; Greuter, F.; Tokoroyama, T. *J. Org. Chem.* **1962**, *27*, 827. (b) Streith, J.; Pasnelle, P.; Ourisson, G. *Bull. Soc. Chim. Fr.* **1963**, 518. (c) Ourisson, G., *Proc. Chem. Soc., London* **1964**, 274.

(8) Hikino, H.; Aota, K.; Kuwano, D.; Takemoto, T. *Tetrahedron* **1971**, *27*, 4831. (b) We thank Professor Hikino for providing us with copies of the IR and NMR spectra of anhydro-β-rotunol.

(9) For reviews, see: (a) Kropp, P. J. *Org. Photo. Chem.* **1967**, *1*, 1. (b) Schaffner, K. *Adv. Photochem.* **1966**, *4*, 81. (c) Schaffner, K. "Organic Reactions in Steroid Chemistry"; Fried, J., Edwards, J. A., Eds., Van Nostrand-Reinhold: New York, 1972; Vol. II, pp 330–338.

0022-3263/80/1945-3790$01.00/0