Tetrahedron Vol. 37, No. 19, pp 3245 to 3261, 1981
Printed in Great Britain.

0040-4020/81/193245-17$02.00/0

PHOTOCHEMICAL AND THERMAL REARRANGEMENTS OF A BENZOYLNAPHTHOBARRELENE-LIKE SYSTEM[1]

MARTIN DEMUTH, WALTER AMREIN,† CHRISTOPHER O. BENDER,‡ SILVIA E. BRASLAVSKY, ULRICH BURGER,† MANAPURATHU V. GEORGE,§ DIETER LEMMER and KURT SCHAFFNER*
Max-Planck-Institut fur Strahlenchemie, D-4330 Mülheim a.d. Ruhr, West Germany

(*Received in USA April* 1981)

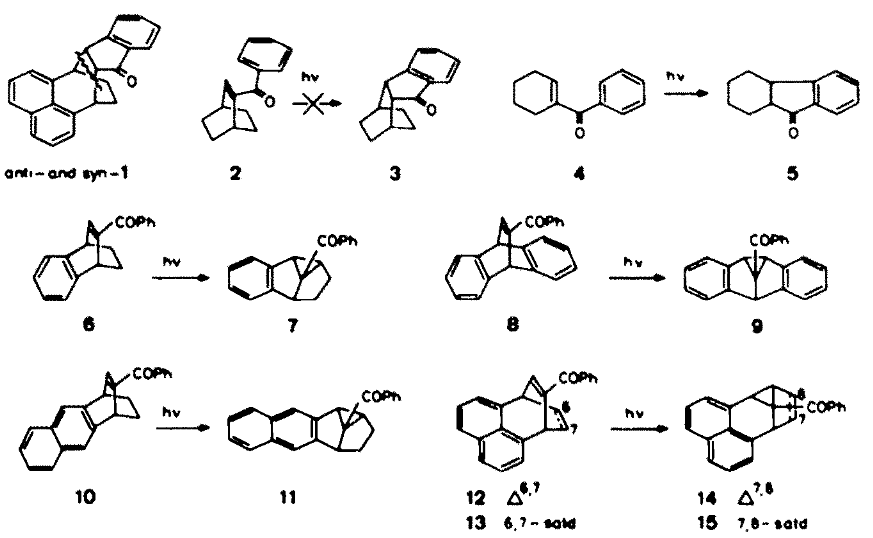
Abstract—8-Benzoyl-9-deuterionaphtho[*de*-2.3.4]bicyclo[3.2.2]nona-2,6,8-triene (**12a**) rearranges in a photochemical di-π-methane-type process to the 1-benzoylnaphtho[*de*-2.3.4]tricyclo[4.3.0.0^{2,9}]nona-3,7-dienes **14a–c**. The dihydro derivate **13a** and the hydroxyphenylmethyl analogs **21a** and **22a** undergo similarly regioselective rearrangements to **15a** + **c**, **23a–c**, and **24a**, respectively. At 298 K the primary photoreaction directly occurs from the $S_1(n, \pi^*)$ and $T_2(n, \pi^*)$ states, and it proceeds from $T_1(\pi, \pi^*)$ and from $S_2(\pi, \pi^*)$ either directly or via T_2. At lower temperature on direct irradiation, $S_1 \rightarrow T$ intersystem crossing and triplet reaction compete with reaction from the singlet. The rearrangement **12a** → **14a–c** proceeds along three reaction paths evolving from the two primary photochemical processes of naphthyl–vinyl and vinyl–vinyl bonding in β-position to the CO (**12** → **25** + **29**). Two ground-state triplet diradical intermediates such as **25** and **27** have been shown to intervene consecutively—for the first time in di-π-methane photochemistry. Each has been characterized by ESR and IR, and the second one additionally by fluorescence and fluorescence excitation, and by laser flash photolysis.

The failure of products **14a–c** to interconvert photochemically is ascribed to efficient energy dissipation through thermally reversible photocleavage of the 3-membered ring.

Compounds **12** and **14** thermally interconvert in the dark which constitutes the first example of a ground-state counterpart of a di-π-methane photorearrangement. The thermal reaction includes a path with highly regioselective (and possibly concerted) product formation competing with a stepwise process causing positional scrambling. The sequence **12** → **14** (photochemically; $\Phi = 1.0$ at 366 nm and 298 K) and an electrophile-catalyzed reversal **14** → **12** in the dark is a model of a chemical light energy storage cycle which can be conducted without loss of reactants.

A few years ago we reported on the intramolecular energy transfer in diastereoisomers such as *syn*- and *anti*-**1**[2] (Scheme 1). In a first synthetic approach to the parent indanone **3**,[2a,3] compound **2** resisted all attempts to photocyclization analogous to the facile photo-Nazarov transformation **4**–**5**.[4] It slowly decomposed instead to an ill-defined product mixture,[5,7] whereas the aro homologs **6**, **8**,[8] **10**, **12** and **13** underwent smooth photoconversions to **7**, **9**, **11**, **14**, and **15**, respectively.[7] These transformations phenomenologically belong to the di-π-methane-type rearrangements described also for other structurally related compounds (i.e. the barrelenes,[9] aro-[10] and diarobarrelenes,[9e,10c,11] triptycene,[12] and benzobicyclo[2.2.2]octadienes[13]).

In an impressively systematic and thorough study,[15] Zimmerman has amply demonstrated the generality of the di-π-methane photorearrangement, and has elucidated a large array of mechanistic features controlling the reaction. *Inter alia*, barrelene-type compounds were



Scheme 1.

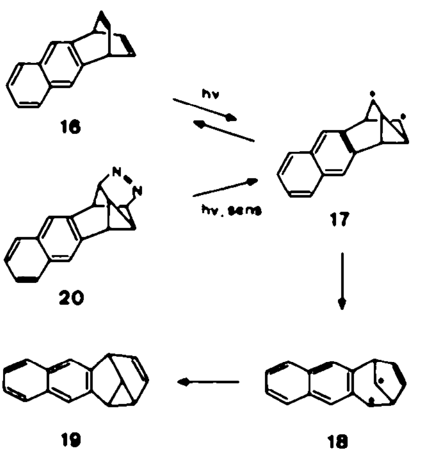
---

†Département de Chimie Organique, Université de Genève, Switzerland.

‡On sabbatical leave at Geneva, 1975–1976, from the University of Lethbridge, Alberta.

§On leave at Mülheim a.d. Ruhr, 1980, from the Indian Institute of Technology, Kanpur.

found to rearrange preferentially via their triplet excited states, and intricate details of the reaction path were elaborated by the use of deuterium labels and by the independent generation of cyclopropyldicarbinyl diradicals proposed as possible intermediates. For example, 1,2-naphthobarrelene was shown to rearrange by both initial α-naphthyl–vinyl and vinyl–vinyl bonding, and the 2,3-isomer only by the latter bridging process.[10d] The resulting reaction path is illustrated for the 2,3-isomer **16** ($\Phi_{rearr} = 0.46$) in Scheme 2. The diradical structures **17** and **18** are, *a priori*, approximations of species on the reaction hypersurface and need not necessarily be at energy minima. However, the photosensitized decomposition of the azo compound **20** gave a *ca.* 1:6 mixture of **16** and **19**.[9e] The triplet diradical **17** may therefore reasonably approximate a primary intermediate photochemically derived from **16**.

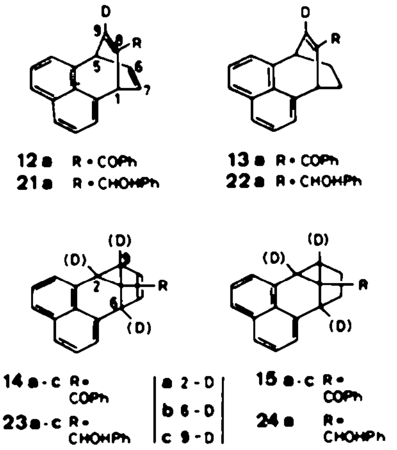


Scheme 2. Photochemical reaction path **16** → **19** with hypothetical diradical intermediates, in accord with results of deuterium labelling experiments,[10d] and photosensitized decomposition of azo compound **20** to triplet diradical **17**.[9e]

We now report, in particular detail, on the benzoylnaphthobarrelene-like system **12**. Evidence will be presented for the nature of the reactive excited states, for the reaction paths followed in the di-π-methane photorearrangement to **14**, and—for the first time in di-π-methane photochemistry—for the involvement of two discrete consecutive intermediates. It will be shown, moreover, that **12** and **14** interconvert thermally in the dark, with the forward reaction, **12** → **14**, constituting the first example of a ground-state di-π-methane rearrangement. The detailed elucidation of the skeletal transformation required that most studies were performed with compound **12a** (Scheme 3), in which the two labels, COPh and D, served as tracers of the different reaction paths. Compounds **13a**, **21a** and **22a** were starting materials for supplementary photochemical work to be discussed.

SYNTHESES AND PRODUCT STRUCTURE PROOFS

The preparation of **12a** and **13a** followed the procedure previously described for the non-labelled compounds.[7a] Base-catalyzed H/D exchange with 1-phenylprop-2-yn-1-one[16] and addition to cyclohepta[*de*]naphthalene ("pleiadiene")[17] afforded **12a**. Selective hydrogenation of the double bond of this product (**12a**) and its photoisomers **14a–c** with tris(triphenylphosphine)rhodium chloride quantitatively gave **13a** and **15a–c**, respectively. Reduction of **12a** and **13a** with sodium borohydride gave **21a** and **22a**, both as mixtures of diastereoisomeric carbinols, which were directly used for photochemical experiments. For some additional irradiations, the mixture of **21a** was separated by thick-layer chromatography into (1*R**)- and (1*S**)-**21a**. Prior to NMR analysis, the resulting products **23a–c** and **24a** were first oxidized to **14a–c** and **15a**, respectively, with pyridinium chlorochromate. The former, **14a–c**, was then hydrogenated to **15a–c**.



Scheme 3.

The positions and the degree of deuterium labelling were determined by the integration differences in the ^{1}H-NMR spectra of the labelled and non-labelled compounds. The signals of the protons at C(1), C(5), C(6) and C(7) in **12** were sufficiently separated at 100 MHz to allow for assignments by extensive decoupling, and for accurate integration. Only the C(9) signal overlapped with aromatic resonances. It was localized by INDOR technique. Quantitative information was obtained in this case by proton-decoupled ^{2}H-NMR at 373 K, at which temperature line broadening was minimal. A direct analysis of deuteriation at C(2), C(6) and C(9) of **14a–c** was impaired by the superimposition of the C(2) and C(9) signals. These samples were therefore converted into **15a–c** where at 270 MHz the signals of all alicyclic protons were again satisfactorily separated for the purposes of integration and assignment by decoupling. Furthermore, ^{2}H-NMR of **14a–c** confirmed that deuterium was exclusively attached at C(2), C(6), and C(9).

THE PHOTOREARRANGEMENT OF THE 8-BENZOYL-NAPHTHOBICYCLONONATRIENE 12

The reaction paths. On direct and on sensitized irradiations, **12a** gave isotopomers of a single product, **14a–c**. Reaction conditions, quantum yields and deuterium distribution in the products are given in Table 1. The deuterium distributions varied only insignificantly in all runs at room temperature (runs 1, 3–5, 7, 9–11), which included irradiation in different solvents (t-butyl alcohol, benzene), direct excitation at different wavelengths (313–436 nm), and triplet sensitization with donor energies in the range E_T 61.9–68.6 kcal/mol. The only notable difference appeared in run 2 at 77 K.

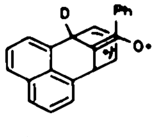
The rearrangement of **12a** was highly regioselective giving exclusively the C(1) benzoyl substituted products **14a–c**. This selectivity demands, in the formulation of any mechanism, that either the 4,5 or 5,6 single bond of the

Table 1. Quantum yields of product formation and deuterium distribution in the products 14 and 23.

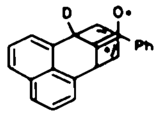
Run no	Compound	Excitation wavelength, nm	Temperature, K	Sensitizer (E_T, kcal/mol)	Proposed initial 12* and 21* states populated[a]	Φ[b]	% Deuterium[c] C(2)-% 14a	C(6)-% 14b	C(7)-% 14c
1	12a[d]	313	298	-	S_2 (π,π^*)	0.52	58	33	9
2	12a[e]	366	77	-	S_1 (n,π^*)	n.d.	72	10	18
3	12a[f]	366	298	-	S_1 (n,π^*)	0.90	54	32	14
4	12a[d]	366	298	-	S_1 (n,π^*)	1.02	58	32	10
5	12a[d]	405	298	-	T_2 (n,π^*)	0.48	64	28	8
6	12a[d]	436	278	-	T_1 (π,π^*)	0.001	n.d.	n.d.	n.d.
7	12a[d]	436	298	-	T_1 (π,π^*)	0.011	60	30	10
8	12a[d]	436	348	-	T_1 (π,π^*)	0.016	n.d.	n.d.	n.d.
9	12a[d]	366	298	benzophenone (68.6)	T_2 (n,π^*)	0.57[g]	61	31	8
10	12a[d]	366	298	thioxanthone (65.5)	T_2 (n,π^*)	0.54[g]	57	33	10
11	12a[d]	366	298	phenanthrene (61.9)	T_1 (π,π^*)	< 0.05	64	29	7
							% 23a	% 23b	% 23c
12	21a[d]	366	298	benzophenone (68.6)	T_1 (n,π^*)	0.029	39	39	22

[a] For state notations see ref 19. [b] Actinometry in runs 1-4 and 9-12 as desribed in ref 18. For runs 5-8, λ^{exc} was isolated by line filters and ferrioxalate actinometry was employed. Product analysis of all runs by GLC at several conversions. Φ's given are extrapolated to zero conversion and maximum sensitization rates; experimental error < 5% (runs 5-8 and 11: < 30%). [c] Experimental error < 5%. [d] $7\cdot10^{-3}$ M in benzene. [e] $7\cdot10^{-3}$ M in ether-isopentane-ethanol 5:5:2. [f] $7\cdot10^{-3}$ M in t-butyl alcohol. [g] Corrected for 10% direct absorption.

starting compound be broken and that in either case both C(8) and C(9) be involved in the formation of two new single bonds in the product. In the most plausible *stepwise* formation which adopts the general diradical di-π-methane mechanism (Scheme 2), the *major* route for **12** is initial naphthyl–vinyl bonding to **25** (Scheme 4; evidence for the diradical nature of **25** and the other intermediates will be discussed in a subsequent chapter). The subsequent transformation of this species can only furnish **14a** + **14b** and no **14c**. Furthermore, one might argue that a stepwise sequence alone from **25** via **27** should give the final products with equal probability if one assumes symmetric conditions for the ring closures of **27** to **14a** and **14b** (i.e. neglecting an isotope effect owing to the asymmetric deuterium substitution, which appears reasonable in any event). This stipulation is not met for **12a** → **14a** + **14b**, however. The 2:1 predominance of **14a** over **14b** can be ascribed, *a priori*, to either of three alternative mechanisms, or to a combination thereof. An overall concerted σ^2a (or s) + π^2a + $\pi^{10}s$ (or a) process[20] could specifically lead to **14a**. It would involve the 4,5-single bond and the Δ^8 and naphtho π systems. Any similarly concerted photochemical mechanism en route to **14b** is forbidden by orbital symmetry. There is still another specific path to **14a** which might compete with the fully stepwise route. The electrophilic nature of the α-keto radical in **25** could provide a driving force for a direct conversion **25** → **14a** by displacing C(4) at C(5) in a cyclopropane cleavage concomitant with regiospecific cyclization (an S_H2i reaction). Finally, the (*E*)- and (*Z*)-conformers contributing to the benzoylcarbinyl radical moiety of **27**, might exert regioselection in the cyclization even if the fully stepwise path should exclusively be followed.

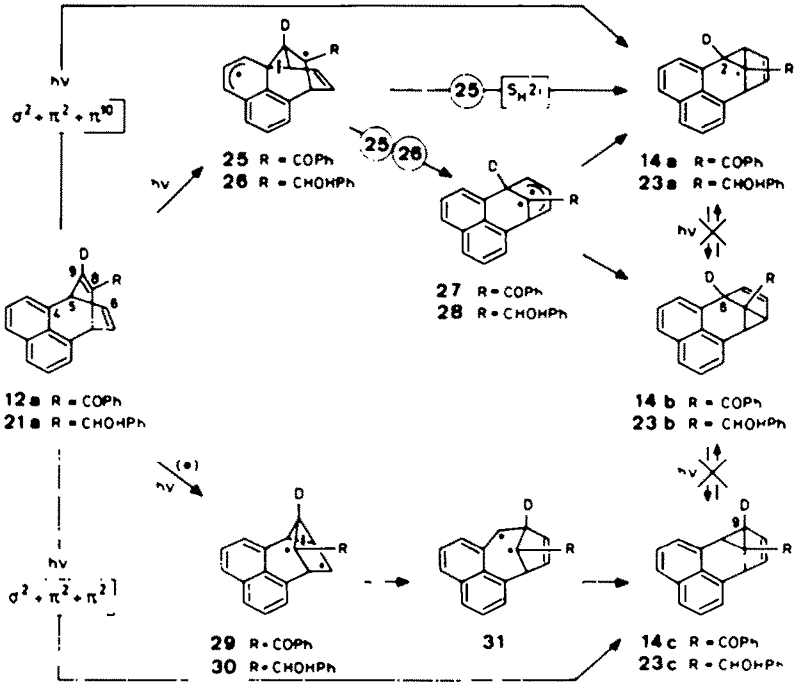


(*E*)-27



(*Z*)-27

The validity of either the S_H2i and *E*/*Z* regioselection hypotheses was explored by resorting to compound **21a**. With the reduction of the keto group the electrophilicity at C(8) of **26** is diminished, and *E*/*Z* isomerism in **28** is avoided. In either case the product ratio should approach unity more closely for **23a**/**23b** than for **14a**/**14b**.

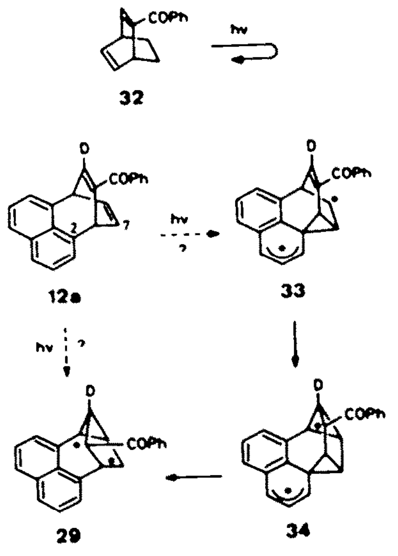


Scheme 4. Photorearrangement of **12a** and **21a** to **14a–c** and **23a–c**, respectively, and possible stepwise and symmetry-allowed concerted reaction paths (*see Scheme 5 for further discussion of step **12a** → **29**).

A sensitized irradiation of **21a** afforded in 40% yield products **23a–c**. The other products were shown by NMR not to be regioisomers of **23**. Products **23a** and **23b** were now formed indeed in equal amounts (Table 1: run 12). This supports the proposal that the involvement of intermediates such as **28** is mandatory for **21a** → **23a,b**, and **27** for at least part of the reaction **12a** → **14a,b**. A low temperature IR study, discussed below, will show that neither the concerted nor the S_H2i mechanisms can be important at 77 K, and regioselective reaction of (*E*)- and (*Z*)-**27** must predominate.

The *minor* route to products **14c** and **23c** may again be attributed to a photochemically allowed concerted mechanism, in this case involving the 5,6-single bond and the Δ^6 and $\Delta^8\pi$ systems[20]. Any stepwise alternative must proceed via **31** rather than **27**/**28**, and it must therefore include an eventual 6,9-bonding step. The most economic path is initiated by direct vinyl–vinyl bonding **12**,**21** → **29**,**30**. Another route to **14c** and **23c** would originate from naphthyl bonding to C(8), followed by a 6(5 → 9) vinyl shift and cleavage of the initially formed bond. Although our experiments do not directly differentiate between these routes, the latter one is rendered unlikely, at least for the carbinol **21a**, by the results given below in Scheme 8. The failure of the dihydrocarbinol **22a** to give any **24c** precludes naphthyl bonding to C(8) in this particular case where no other route to **24c** is available. Consequently, one should not expect it for **21a** → **23c** either.

Another result may serve to elaborate the transformation **12a** → **29** still further. If vinyl–vinyl bonding were a direct primary process, the diene **32** (Scheme 5) could be expected to react in an analogous fashion. However, it remained photochemically inert under several conditions, such as irradiations at 254, 300 and > 340 nm, and triplet sensitization with acetophenone and acetone (E_T of **32** was 69.5 kcal/mol by phosphorescence). This negative finding suggests either that structural differences in the two compounds, **12** and **32**, favor the thermal reversal of the photochemical bridging in **32** and the forward reaction of **29**, or that the latter is not the primary photoproduct. In the first case, extensive delocalization of both radical centres in the subsequent intermediate may be responsible for the further rearrangement of **29**. A similar stabilization would not be available in the primary product of **32**. For the second case, a hypothetical alternative is considered in the sequence **12a** → **33** → **34** → **29**, where naphthyl–vinyl



Scheme 5. The photorearrangement of **12a** to **14c** and the photostability of **32**: possible alternative (**12a** → **33**) to the initial vinyl–vinyl bridging **12a** → **29**.

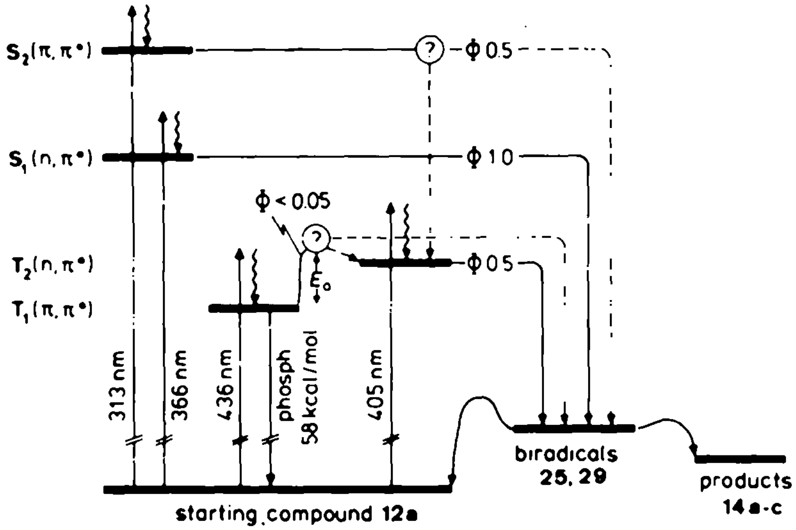


Fig. 1. State and reaction diagram for the di-π-methane rearrangement 12 → 14a–c. Branching broken arrows (--) designate processes not discriminated by experiment.[19]

bridging, now between C(2) and C(7), would again initiate the reaction.

The high regioselectivity of the rearrangement of **12** with respect to the benzoyl group is characteristic of the directing effects by electron-withdrawing substituents in related barrelenes. Thus, similar bridgings have been reported to predominate when carbomethoxy[10a,11] and cyano groups[10f,i,11a] are at the potential carbinyl carbon (e.g., corresponding to C(8) in **25** and **29**, and to C(1) in **27** and **31**).

The nature of the reactive excited states of **12**. The dependence of the rearrangement quantum yield of **12** on excitation wavelength and sensitizer triplet energy at room temperature (Table 1) indicates that reaction can occur directly from *at least* the lowest singlet and one upper triplet excited state as shown in Fig. 1. A straightforward assignment of the excited singlet states of **12** is possible from its UV absorption properties. Thus, the benzoyl $S_1(n,\pi^*)$ and an $S_2(\pi,\pi^*)$ state are populated on direct irradiation with wavelengths of 366 and 313 nm, respectively.[19]

An immediate ordering of the triplet state energies is less secure, but it is predictable on the basis of considering the naphthalene and aryl ketone partial chromophores of **12** as separate entities. Their lowest triplet energies are around 60 and 70 kcal/mol, respectively. The low energy of T_1 and its naphthalene nature were confirmed by the phosphorescence spectrum of **12** in ether–isopentane–ethanol 5:5:2 glass at 77 K, characterized by a 0–0 transition of E_T 58.2 kcal/mol and an exponential decay with a lifetime of τ_p 1.56 s. The spectral position and shape (see Fig. 7A and 8B) were essentially identical with those of the dihydro derivative **13** (E_T 59.2 kcal/mol; Fig. 8B), the carbinol **21** (E_T 58.9 kcal/mol), and with that of the parent naphthalene 2,3-dihydrophenalene (**35**; E_T 59.2 kcal/mol, τ_p 2.38 s[2a]). The phosphorescence spectrum of the alternate parent chromophore, the benzoylbicyclooctene **2**, showed a much higher E_T value of 69 kcal/mol, and a typical carbonyl lifetime of τ_p 5.4 ms and n,π^* vibrational structure with four bands separated by 1607, 1627, and 1541 cm^{-1}. The spectrum of the corresponding bicyclooctadiene, **32**, was practically identical.

Laser flash measurements in benzene showed that sensitizer triplets of $E_T \geq 62$ kcal/mol, including those used in runs 9–11 of Table 1, were quenched by **12** at

Table 2. Rate constants of the quenching of various sensitizer triplets by **12**[a]

Exp. no[b]	Donor (E_T, kcal/mol)	λ_{obs}, nm	τ_D (exp), s	[**12**], M[c]	k_q, mol^{-1} s^{-1}[d]
1	$8.8 \cdot 10^{-2}$ M Benzophenone (68.6)	535	$1.2 \cdot 10^{-6}$	$(3\text{–}16) \cdot 10^{-4}$	$4.0 \cdot 10^{9}$
2	$1.5 \cdot 10^{-3}$ M Thioxanthone (65.5)	650	$3.0 \cdot 10^{-7}$	$(0.5\text{–}7) \cdot 10^{-3}$	$4.2 \cdot 10^{9}$
3	$1.3 \cdot 10^{-4}$ M Michler ketone (∿62)	500	$2.2 \cdot 10^{-7}$	$(0.5\text{–}7) \cdot 10^{-3}$	$6.0 \cdot 10^{9}$
4	$5.4 \cdot 10^{-2}$ M Phenanthrene (61.9)	420	$1.0 \cdot 10^{-6}$	$(0.5\text{–}1) \cdot 10^{-3}$	$3.0 \cdot 10^{9}$
5	$6.2 \cdot 10^{-3}$ M Chrysene (56.6)	560	$2.0 \cdot 10^{-7}$	$(0.5\text{–}5) \cdot 10^{-3}$	$9.0 \cdot 10^{8}$
6	$6.0 \cdot 10^{-3}$ M 1-Acetylnaphthalene (56.4)	500	$5.0 \cdot 10^{-7}$	$(4\text{–}8) \cdot 10^{-3}$	$7.0 \cdot 10^{8}$
7	$6.0 \cdot 10^{-3}$ M Benzil (53.4)	470	$1.0 \cdot 10^{-6}$	$(1\text{–}5) \cdot 10^{-3}$	$1.2 \cdot 10^{8}$
8	$6.2 \cdot 10^{-3}$ M Pyrene (48.2)	420	$7.0 \cdot 10^{-7}$	$(1\text{–}5) \cdot 10^{-3}$	$\sim 5 \cdot 10^{7}$

[a] Laser flash excitation at 353 nm; benzene solutions. [b] Numbers correspond to those in Figure 2. [c] Range of quencher concentrations used for the determination of the Stern-Volmer slopes. [d] Calculated from the Stern-Volmer slopes = $k_q \cdot \tau_D$.

similar rates close to diffusion control (Table 2: expts 1–4). The values sharply fell off with lower sensitizer energies (expts 5–8). A Herkstroeter–Hammond plot[21] of these rate constants vs. sensitizer energy (Fig. 2) indicates an E_T of *ca.* 59 kcal/mol for the lowest-lying reactive triplet of **12**, which identifies it as the phosphorescent state, $T_1(\pi, \pi^*)$. Yet, the quantum yields obtained with benzophenone and thioxanthone on one hand and with phenanthrene on the other are distinctly different. And so are the yields of the irradiations with 405 and 436 nm ($\epsilon^{405} = 1.098$ and $\epsilon^{436} = 0.824$, in benzene), wavelengths with which evidently two different forbidden $S_0 \rightarrow T$ transitions of **12** are directly effected (runs 5–8). The yields with the former higher-energy sensitizers (Table 1: runs 9 and 10) coincide with those of the direct irradiations at 313 and 405 nm (runs 1 and 5), whereas the yield with the latter (run 11) falls into the category of the 436 nm irradiations (runs 6–8). We should stress the point here that the quantum yields were obtained on extrapolation to zero conversion and high quencher concentration. In other words, they are limiting values at maximum sensitization rates. The results therefore place the T_2 state in the range of *ca.* $60 \leq E_T \leq 63$ kcal/mol, assuming that the energy transfer in all these sensitizations, shown to occur at encounter rates (Table 2: expts 1, 2 and 4), is exothermic by ≥ 2 kcal/mol. The energy of T_2 of **12** (of presumed n, π^* configuration) is thus markedly lower than that of $T(n, \pi^*)$ of **2** and **32**. This is possibly a consequence of additional orbital delocalization throughout the extensively unsaturated naphthobarrelene-like system of **12**.

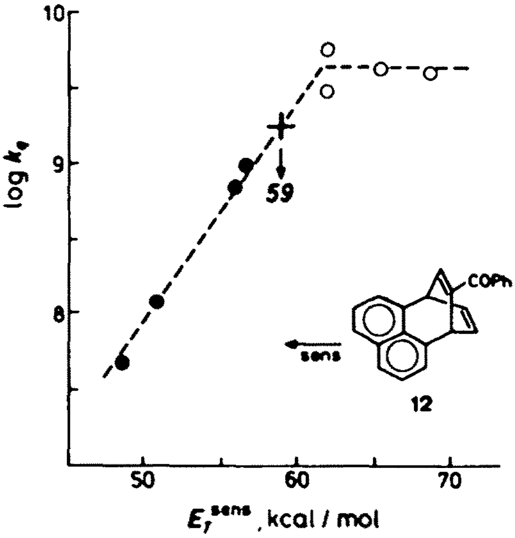


Fig. 2. Herkstroeter–Hammond plot of rate constants of the quenching of various sensitizer triplets by **12** vs. the triplet energy of the sensitizers. Determination of the energy of the lowest-lying reactive triplet state of **12**. For more details see Table 2.

The quantum yields obtained from the $T_1(\pi, \pi^*)$ state of **12** on direct irradiation increase with temperature (E_a *ca.* 8 kcal/mol) (Table 1: runs 6–8). The unity yield upon singlet $n \rightarrow \pi^*$ excitation at 298 K (run 4) and the significantly lower yields on the direct $S_0 \rightarrow T$ excitations at the same temperature (runs 5 and 7) preclude then any $S_1 \rightarrow T$ intersystem crossing prior to reaction, whereas intersystem crossing with unity quantum yield and endothermic internal conversion to T_2 remain alternatives to direct reactions from $S_2(\pi, \pi^*)$ and $T_1(\pi, \pi^*)$, respectively. The present data do not unambiguously differentiate between these options. It should be noted, however, that Φ of the sensitized rearrangement of **21** (run 12), where reaction must directly occur from a $T(\pi, \pi^*)$ state, was of the same order of magnitude as the Φ values measured upon initial population of the $T_1(\pi, \pi^*)$ state of **12** (runs 6–8 and 11).

A temperature dependence of the rearrangement efficiency of **12** is also found for the S_1 state. On cooling, $S_1 \rightarrow T$ intersystem crossing starts increasingly to compete with reaction from S_1, and phosphorescence from T_1 reaches a quantum yield of Φ_p 0.42 ± 10% at 77 K in 2-methyltetrahydrofuran. This value is beyond the maximum yield which could be attributed to the *ca.* 25% nonreactive conformer frozen out at 77 K (see below). Possibly some of the rearrangement to **14** observed at this temperature is also a T_2 process, with internal conversion[19] $T_2 \rightarrow T_1$ being relatively inefficient at room temperature ($\Phi_{ic} \leq 0.5$).

Triplet ground-state diradicals as intermediates in the rearrangement **12** → **14**. Having established the reactive excited states to the extent shown in Fig. 1, we turned our attention to search for the reaction intermediates tentatively proposed in Scheme 4; the variable-temperature flash photolytic, ESR, IR and emission techniques were employed. When compound **12** was subjected to laser flash photolysis at λ^{exc} 353 nm in the temperature range 88–200 K in ether-isopentane-ethanol 5:5:2, a transient absorption with maxima at 380 and 430 nm was recorded (Figs. 3B and 3C). The decay followed first order kinetics identical at both wavelengths. The lifetime ($\tau = k_d^{-1}$) varied from 50 μs at 88 K to 15 ns at 173 K in ether–isopentene–ethanol, from 1 μs at 173 K to 15 ns at 200 K in methylcyclohexane, from 50 ns at 169 K to 15 ns at 208 K in i-propyl alcohol, and it was 1 μs at 223 K in glycerol triacetate. Activation energies were calculated from Arrhenius plots (log k_d vs T^{-1}) of data obtained in ether–isopentane–ethanol at 105–150 K and in i-propyl alcohol and methylcyclohexane at 166–200 K. All E_a values were around 3 ± 0.5 kcal/mol, which corresponds in magnitude to the activation energies for the viscosity change with temperature[22] for each solvent.

The transient was identified as the T_1 state of **12** by comparison with the parent naphthalene **35**. At low temperature, both compounds exhibited phosphorescences of identical spectral shape and energy (see above), and gave comparable flash photolytic results. The transient absorption obtained from **35** (Fig. 3A) was invariant from 77 to 297 K in ether–isopentane–ethanol. The lifetime ranged from τ 1 ms at 113 K to 2 μs at 297 K, with E_a 4 ± 0.5 kcal/mol at 105–150 K, and it was quenched by oxygen at 260 K with k_q $2 \cdot 10^9\ M^{-1}\ s^{-1}$, typical for diffusion controlled triplet quenching.[23]

At temperatures ≥ 210 K in the flash experiments, the spectrum of triplet **12** disappeared. In its place, a single sharp band due to a new transient grew in at 380 nm (Fig. 3E), with τ 20 ± 4 ns in benzene, i-propyl alcohol and glycerol triacetate, and < 15 ns in methylcyclohexane (all at room temp). In benzene, the lifetime was temperature independent from 278 to 363 K, and the species was not quenched by oxygen. This is in accord with the measured lifetime, with an assumed $k_q \sim 10^9\ M^{-1}\ s^{-1}$ and $[O_2] = 2 \cdot 10^{-3}$ M, and with the lack of oxygen quenching of the rearrangement **12** → **14** in benzene at room temperature.

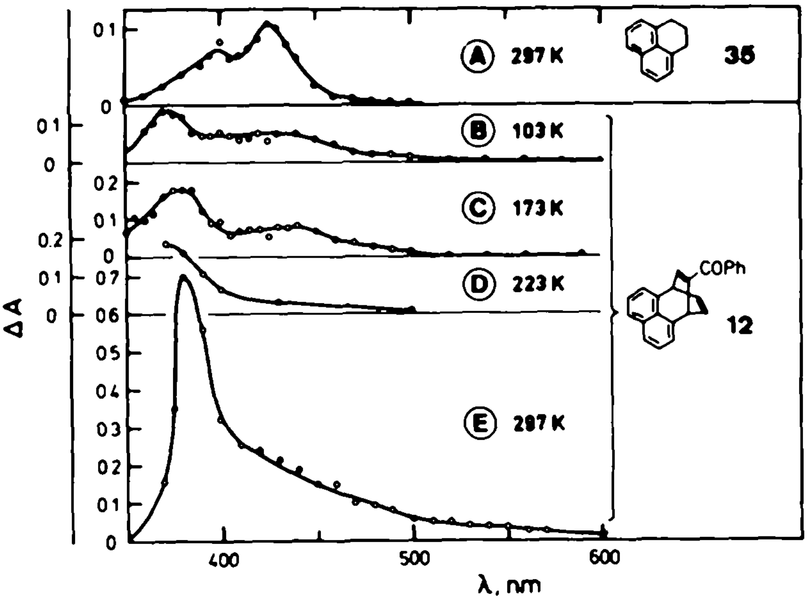


Fig. 3. Transient spectra obtained on laser flash photolysis of 2,3-dihydrophenalene (35) and the benzoylnaphthobicyclononatriene 12. Solvents: ether–isopentane–ethanol 5:5:2 (A and B), methylcyclohexane (C and D), benzene (E); concentrations: $1.1 \cdot 10^{-2}$ M 35 (A), $3 \cdot 10^{-3}$ M 12 (B–D), $1.1 \cdot 10^{-2}$ M 12 (E); λ^{exc}: 265 nm (A and B), 353 nm (B–E).

The conditions of its generation—$n \rightarrow \pi^*$ excitation with 353 nm—and quenching studies rule out an excited state for this second transient. A Stern–Volmer slope of $k_q \cdot \tau = 1.1\ M^{-1}$ was obtained for the quenching of product formation at concentrations up to 3 M 1,3-cyclohexadiene at λ^{exc} 366 nm in benzene. The rate constant $k_q = 5 \cdot 10^7\ M^{-1}\ s^{-1}$ is far too small for triplet quenching, considering the exothermicity by *ca.* 6 kcal/mol of such a process. Rather, chemical quenching of a ground state intermediate by the diene appears a reasonable possibility.[24] Moreover, the extinction coefficient at 380 nm in benzene at ambient temperature was $\epsilon_{max} \leq 2500\ M^{-1}\ cm^{-1}$. Values for ϵ of T→T transitions are significantly greater for, e.g., benzophenone and naphthalene.[25]

More detailed evidence of the number, sequence and nature of the reaction intermediates came forth from the ESR, IR and emission spectroscopy. In these experiments, the irradiations of 12 were carried out in 2-methyltetrahydrofuran[26] matrixes with > 340 nm light at 77 K. Control runs with 313 nm always gave the same results. Continuous irradiation gave two overlapping ESR spectra. A transient spectrum showed a strong half-field ($\Delta m = 2$) transition at 1764 G and a zero-field XYZ pattern ($\Delta m = 1$) with $D' = 800$ G ($D = 0.075\ cm^{-1}$) and $E' = 66$ G ($E = 0.0065\ cm^{-1}$). In addition, a partially line-resolved signal dominated at 3244 G ($= H_0$). Unlike this latter signal, the former component disappeared when irradiation was discontinued. The parameters of this short-lived spectrum have all the characteristics of an

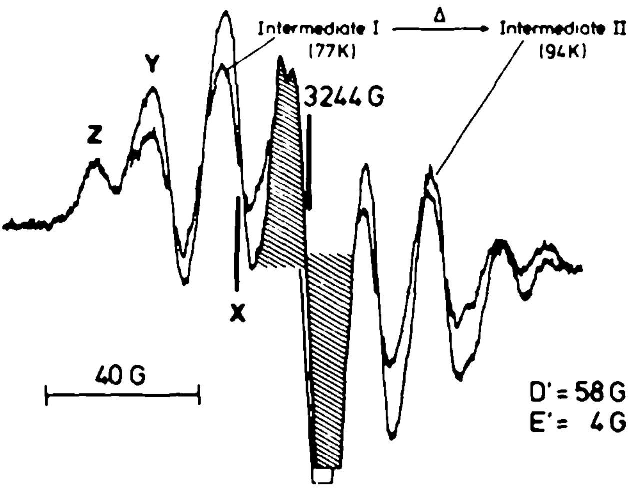


Fig. 4. Long-lived components of the ESR spectrum, recorded in the dark after irradiation of 12 at > 340 nm in 2-methyltetrahydrofuran matrix at 77 K (intermediate I; spectrum with smaller amplitudes) and after subsequent warming to 94 K and re-cooling to 77 K (intermediate II; spectrum with larger amplitudes). The shaded portion corresponds to radical by-products.

electronically excited and randomly oriented aromatic triplet state.[27] It can be attributed[28] to the naphthalene T_1 state of **12** which had already been detected by phosphorescence and by flash photolysis in the 88–200 K range.

The long-lived ESR signal persisted at 77 K in the dark for at least two hours without any detectable decrease in intensity. It could be resolved into the spectrum given in Fig. 4 (intermediate I). The zero-field parameters are $D' = 58$ G ($D = 0.0054$ cm^{-1}) and $E' = 4$ G (0.0004 cm^{-1}). A $\Delta m = 2$ transition could not be identified with certainty even under high gain and modulation adjustment, and in particular it could not be discriminated from a possible impurity signal of the solvent. When this sample was warmed from 77 to 94 K without any further irradiation, a marked increase in amplitude and a concomitant slight expansion of the spectrum was observed. The expansion was found to be a temperature effect, and it reversed when the sample was re-cooled to 77 K (Fig. 4: intermediate II). The change in amplitude, however, was not reversible. It lasted without decrease for two hours at 77 K, but had a significantly shorter lifetime of a few minutes at 94 K. It rapidly disappeared when the sample was warmed to about 100 K. We conclude that at 94 K the 77 K intermediate I irreversibly changes to intermediate II. Both have practically identical ESR parameters, but intermediate II has larger amplitudes.

The spectra of the two longer-lived intermediates I and II have all the characteristics of randomly oriented ground-state triplet diradicals.[29,30] The lack of a half-field signal is in accord with the small zero-field parameters, characteristic of a weak interaction between the radical centers.

We assign these diradical spectra to intermediates in the rearrangement **12** → **14**. No ESR signal was found on irradiation of **14** at either 313 and > 340 nm in 2-methyltetrahydrofuran at 77 K. In view of the lack of quantitative information from ESR, a kinetic correlation, in terms of relative amounts formed as a function of irradiation time, of the transient spectrum intensity with the formation of final product was now desirable. The Y line of the intermediate I signal (Fig. 4) was chosen in view of its large amplitude, symmetric shape, and independence from the zero-field monoradical absorption. Its amplitude reached maximum intensity after an irradiation of about 35 min at 313 nm and about 15 min at > 340 nm. Since the signal intensity did not decrease in the dark within two hours, a comparison with product formation was meaningful. The amount of **14** formed was measured by glc after the ESR samples were warmed to room temperature. Normalizing maximum product formation and ESR signal saturation to 100% enabled the relative increases in product formation and ESR signal intensity with progressing irradiation to be compared (Fig. 5). The close fit of the two curves for both excitation wavelengths is compatible with, and indeed suggestive of the role of intermediate I, and consequently also of II, as diradical precursors of **14**.

The possibility that these diradicals are intermediates leading to another product (rather than to **14**) can be discarded. For a line width of 12 G (Y line), a minimum steady-state concentration of *ca.* 10^{-5} M is required for detection of any ESR signal with our equipment. Yet no products other than **12** and **14** were found by glc, under conditions where a product concentration $\geq 5 \cdot 10^{-7}$ M could have been detected.[31]

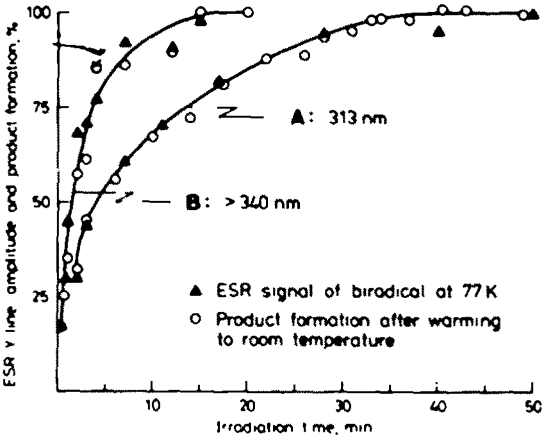


Fig. 5. Comparison of the ESR signal intensity of the long-lived intermediate I and the formation of product **14** as a function of irradiation time. (A) Excitation at 313 nm; (B) excitation at > 340 nm; (▲) amplitude of ESR Y line; (○) product **14** formation after the ESR sample was warmed to room temperature. Maxima of ESR intensity and product formation taken as 100%. Note that the diagram is not normalized for light intensities of the two excitation wavelengths.

An IR investigation was also carried out under the conditions employed in the ESR study. It showed, on one hand, that new frequencies consecutively appeared upon irradiation for 30 min at 77 K (1634 and 1648–1655 cm^{-1} for intermediate I) and subsequent warming in the dark to 92 K (1660 cm^{-1} for intermediate II). Only at higher temperatures (≥ 182 K) did the CO band due to **14** (1665 cm^{-1}) grow in (Fig. 6).

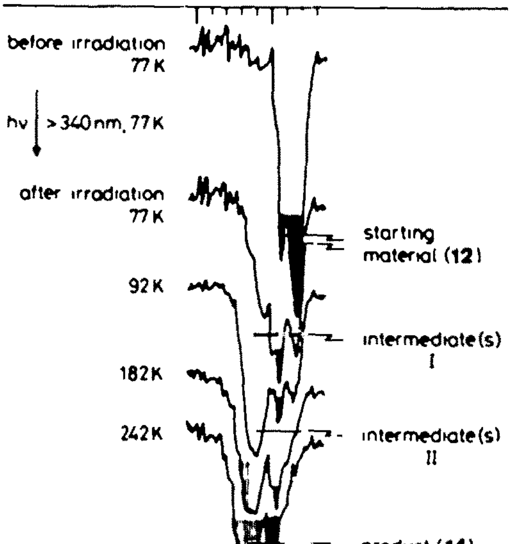


Fig. 6. IR spectra recorded at 77 K before irradiation of **12** and after irradiation of **12** ($\lambda^{exc} > 340$ nm, 30 min) during warming up from 77 to 242 K. Solvent 2-methyltetrahydrofuran. Note that the band shapes of **12** (dark portions) and **14** (shaded) at 242 K are the same as those of the respective reference samples at this temperature. Only one frozen-out rotamer of **12** remained at 77–182 K after irradiation, and the buildup of **14** began to show at 182 K.

Thus the IR results, in unison with the ESR data, suggest the involvement of a three-step sequence. This sequence can be accommodated by the stepwise mechanism proposed in Scheme 4. The ESR and IR spectra of intermediate I were observable only below 92–94 K, i.e. they may well arise from the primary metastable photoproduct **25**. Consequently, the ESR and IR spectra of II, both succeeding I above 77 K, should be due to the secondary diradical **27**, which ultimately leads to **14a** + **b**. Of course, a minor and not identified contribution by **29** and **31** (and perhaps **33** and **34**; Scheme 5) to the ESR and IR spectra is possible. Judging from the product composition resulting from **12a** at 77 K (Table 1: run 2), this reaction should be about one fifth of the total.

The observed D value of 0.0054 cm^{-1} is considerably smaller than any of the D values reported previously for triplet diradicals. Its assignment to the extensively delocalized major diradicals **25** and **27** is acceptable, however, in light of the spread of D from 0.01–0.03 cm^{-1} for only partly delocalized diradicals[32] to 0.08 cm^{-1} for the localized 1,3-cyclopenta diyl.[33] The IR frequencies of I and II are suggested to be those due to the α-keto (oxallyl) radical groups, although we are not aware of appropriate reference data.

The IR results disclose two further points of interest. Neither after irradiation at 77 K nor after warming of the photolysate to 92 K could product **14** be detected in a significant amount. Yet, the final product (= **14a**) should already have appeared either concomitant with intermediate I (i.e., **25**) or with intermediate II (**27**), to the extent that the concerted (**12a** → **14a**) and S_H2i mechanisms (**25** → **14a**), respectively, were operating. Evidently, at least at 77 K, these routes could not be of importance.[34] Rather, the uneven **14a**/**14b** distribution must be determined predominantly by regioselective cyclization of (E)- and (Z)-**27**.

Another striking fact is that of the two rotamers of **12** which are frozen out at 77 K,[35] the major component (ν_{CO} = 1633 cm^{-1}) photoreacted preferentially while the minor component (ν_{CO} = 1644 cm^{-1}) remained largely unchanged. This accounts for the observation that *ca.* 30% of **12** is recovered after exhaustive irradiation at 77 K. The remarkable influence of excited-state geometry, as reflected by the ground-state conformation, on the photoreactivity of **12** at 77 K could not be observed at room temperature, with unity Φ_{366} for product formation (Table 1: run 4). The effect which is currently under further investigation, obviously is associated with benzoyl conformation. The naphthalene-like T_1 of both conformers were indistinguishable by phosphorescence. After exhaustive irradiation at 77 K, the initial phosphorescence of **12** (Fig. 7A) was merely reduced to about 25% (7B), and the fluorescence shown in Fig. 7C had built up instead. The intensity of the fluorescence slowly increased in the dark at 77 K over a period of 12 hr. The maximum intensity was reached after warming to 115 K for 10 min and re-cooling to 77 K (Fig. 7D), with the residual phosphorescence of **12** remaining unaltered. No further change occurred when the sample was kept overnight at 77 K. The fluorescence nature of this new emission is evident from the mirror-image relationship of excitation and emission spectra (Fig. 7E). The fluorescence shown in this last spectrum was obtained by computer-aided abstraction of the 25% residual phosphorescence from **12** in spectrum 7C.

The temperature dependent behaviour of this new fluorescence source approximates that noted for the ESR and IR spectra of intermediate II (= **27**) rather than that of I (= **25**). Apparently intermediate I does not noticeably emit, unless a weak emission at around 400 nm in Fig. 7C is attributable to this species. It must have been partially converted to intermediate II already during irradiation and emission measurement at 77 K. Its transformation into II was then completed during the temporary warming process.

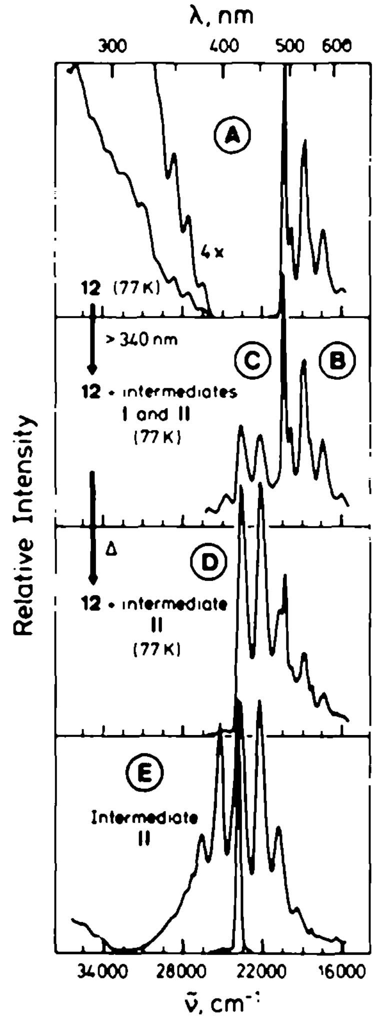


Fig. 7. Emission at 77 K in 2-methyltetrahydrofuran: (A) phosphorescence and phosphorescence excitation of **12**; (B) residual phosphorescence of **12** and (C) fluorescence of intermediate II (plus possibly some emission from intermediate I at around 25000 cm^{-1}) immediately after exhaustive irradiation at 77 K, and (D) after reaching maximum intensity(i.e., after warming to 115 K and re-cooling to 77 K); (E) fluorescence and fluorescence excitation of intermediate II after computer-aided substraction of phosphorescence in (C). All spectra corrected; λ^{em} 491 (A) and 450 nm (E); λ^{exc} 355 nm (A–E).

The spectral position of the fluorescence excitation spectrum in Fig. 7E is comparable to that of the transient spectrum obtained by flash photolysis above 210 K (Fig. 3E). Taking into account that the two spectra were recorded under very different conditions, both may well have intermediate II (**27**) as a common origin.

THE PHOTOREARRANGEMENT OF THE 8-BENZOYLNAPHTHOBICYCLONONADIENE 13

Compound **13a** cleanly rearranged at room temperature to 88% **15a** and 12% **15c** when subjected to

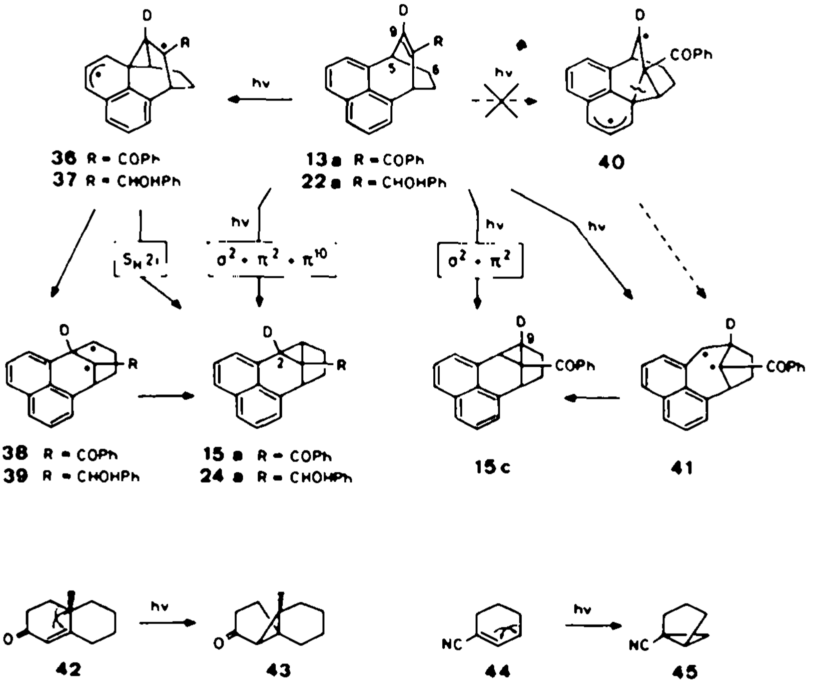
Table 3. Quantum yields of product formation and deuterium distribution in the products **15** and **24**[a]

Run no	Compound	Excitation wavelength, nm	Sensitizer (E_T, kcal/mol)	Proposed initial **13*** and **22*** states populated[b]	Φ[c,d]	% Deuterium[d] C(2)= % **15a**	C(9)= % **15c**
1	**13a**	366	-	$S_1(n,\pi^*)$	0.51	88	12
2	**13a**	366	benzophenone (68.6)	$T_2(n,\pi^*)$	0.31		
3	**13a**	366	Michler ketone (∼ 62)	$T_1(\pi,\pi^*)$	0.05		
4	**13a**	313	-	$S_2(\pi,\pi^*)$	0.18		
						% **24a**	% **24c**
5	**22a**	313	-	$S_1(\pi,\pi^*)$	n.d.	100	0

[a] All runs $7\cdot10^{-3}$ M in benzene at room temperature. [b] For state notations see footnote 19. [c] Actinometry as described in ref 18. Φ's given are extrapolated to zero conversion; experimental error ± 5%. [d] Experimental error ± 2.5%.

direct and triplet-sensitized irradiation (Scheme 6).[1e] The results are summarized in Table 3. The quantum yields of product formation were generally smaller here than for **12**→**14**, but they followed the same trend in terms of relative magnitudes. One may therefore conclude that **13a** has a similar excited state-dependent photoreactivity. In principle then, the state and reaction diagram of Fig. 1 can be adapted to the system **13**→**15** without any qualitative change. An E_T value of 58.6 kcal/mol and a lifetime of τ_p 2.05 s at 77 K by phosphorescence (see Fig. 8B) as well as a fall-off in quantum yield at a sensitizer energy of 62 kcal/mol (run 3) characterize the lowest-lying reactive excited state again as the naphthalene-like T_1 state.

On the basis of the results obtained swith **12a**→**14a–c** (Scheme 4), the formation of only **15a** was to be expected, either in a concerted manner $(\sigma^2+\pi^2+\pi^{10})$,[20] or in one including a direct S_H2i-type or a two-step (via **38**) transformation of the naphthyl-vinyl bridged primary photoproduct **36**. In order to rationalize the rearrangement to the unexpected byproduct **15c**, one might first resort to the alternative naphthyl–vinyl bridging (→**40**) which would then first undergo a 1,2-shift of the methylene group C(6) from C(5) to C(9), followed by reversion of

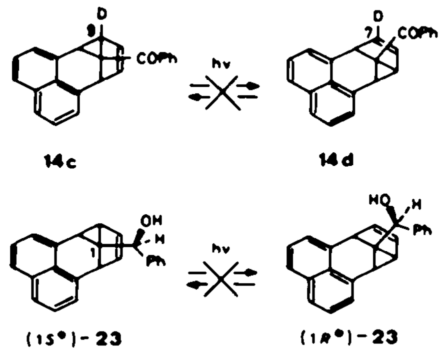


Scheme 6. The photorearrangement of **13a** and **22a** to **15a**+c and **24a**, respectively, and possible stepwise and symmetry-allowed concerted reaction paths.

the primary photochemical bonding (→**41**). However, the carbinol **22a** afforded exclusively product **24a**, which can again arise via any of the three routes, including intermediates **37** and **39**, given in Scheme 6. This result renders the formation of **15c** via **40** unlikely as both ketone **13a** and carbinol **22a** should bridge to **40** with similar probability. There remains then the concerted mechanism $(\sigma^2+\pi^2)^{20}$ or the stepwise alternative with a direct 1,2-shift to **41** and subsequent ring closure. We are not aware of any close precedence for this photoreaction. The nearest analogies can be seen in the rearrangements of conjugated cyclohexenones (e.g. **42**→**43**)[36] and of 1-cyanocyclohexene (**44**→**45**).[37]

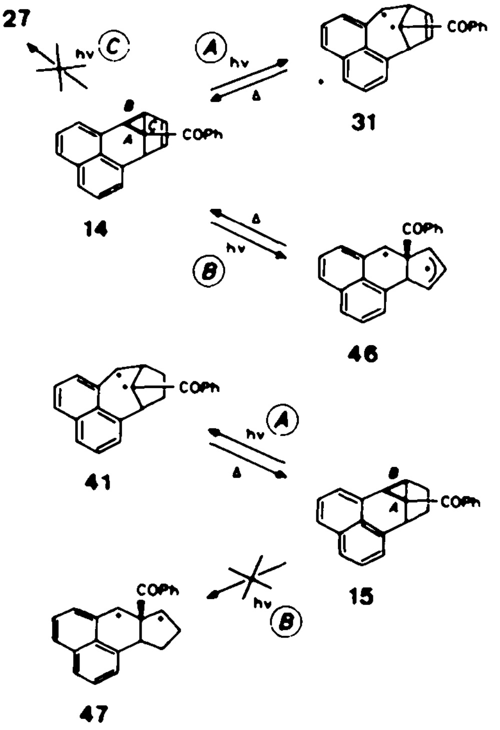
THE PHOTOCHEMICAL STABILITY OF THE PHOTOPRODUCTS 14a–c

Since the ratio of the components in the mixtures **14a–c** and **23a–c** did not change with progressing conversion of **12a** and **21a**, the isotopic isomers evidently were not interconvertible under the conditions of formation. The photostability of the products was further confirmed in the following control experiments (Scheme 7). In separate direct and sensitized irradiations of **14a–c**, no change of the initial deuterium labels was seen by NMR. In particular, no exchange of the C(9) position of **14c** with C(7) (**14d**) was observed, although the appearance of an olefinic deuterium should have readily been detected by ^{2}H NMR. Similarly, prolonged sensitization of diastereoisomerically pure (1*R**)-**23** did not afford any (1*S**) isomer and *vice versa*, which would have been recognized by the different chemical shift of the carbinol ^{1}H NMR signal (a singlet at δ 5.34 vs 5.29).



Scheme 7.

It is interesting to consider the possible cause for the failure of the components of **14a–c** and **23a–c** to interconvert. Equilibration of **14a** and **14b** on one hand, and **14c** and **14d** on the other, could have been anticipated *a priori* to be a facile photochemical process (path *C* in Scheme 8). Efficient competition by another, thermally fully reversible photoreaction might in fact represent an



Scheme 8. Thermally reversible photocleavage as possible mechanism for the dissipation of excitation energy in **14** and **15**.

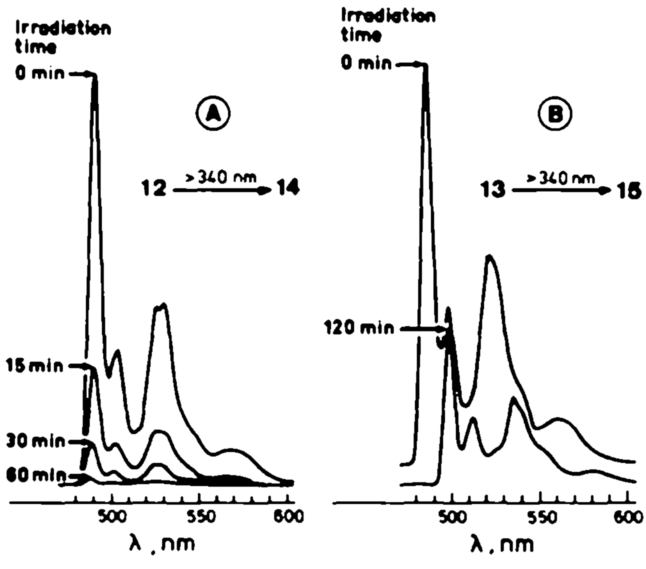


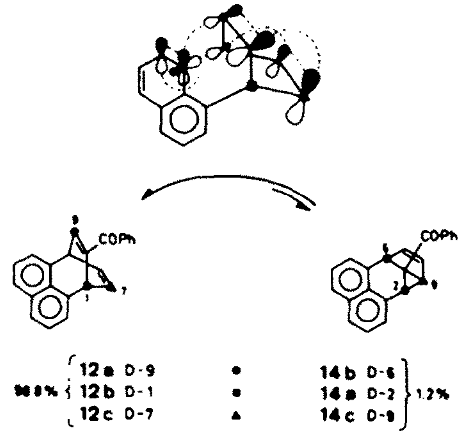
Fig. 8. Phosphorescence at 77 K as a function of irradiation time at room temperature for the systems **12**→**14** (A) and **13**→**15** (B) in ether–isopentane–ethanol 5:5:2. All spectra corrected.

alternative chemical dissipation of the excitation energy, e.g. through cleavage of the cyclopropane bonds *A* or *B* in **14** (Scheme 8). In either case, extensively delocalized diradicals, **31** and **46**, respectively, would result for which the most likely dark reaction would be ring closure and restitution of starting material. A close analogy to process *A* has previously been encountered in the *cis-trans* photoisomerization of 1 - benzoyl - 2 - vinylcyclopropane.[38]

The phosphorescence results at 77 K, shown in Fig. 8, indicate that process *B* may in fact very well account for the "stabilization", *without excluding* the parallel contribution by reversible bond *A* rupture. Product **14** did not emit at all, which is unusual for a naphthalene unless photochemical deactivation plays an important role. Bond cleavages from the excited state, which thermally revert, can therefore be anticipated here as energy wasting processes. This latter condition is less fully met in the dihydro system, and product **15** showed a reasonably intense phosphorescence of Φ_p 0.15 (Fig. 8B). Cleavage of bond *B* in **15** (to **47**), which is not bis-allylic as in **14**, is undoubtedly less favorable than fission of *A*. Based on this merely qualitative mechanistic interpretation, **14** may thus have two efficient funnels for nonradiative deactivation to **31** and **46**, whereas **15** has only one (to **41**).

THE THERMAL INTERCONVERSION OF 12 AND 14

Compounds **12** and **14** interconvert thermally in the dark. While no rearrangement was observed with **12** and **14** below 453 K, a thermally equilibrated mixture of 98.8% **12** and 1.2% **14** was obtained when either of the two components was heated in benzene to 493 K. Table 4 summarizes the results of several runs with **12a** and with the mixture of 58% **14a**, 32% **14b** and 10% **14c**, carried out to various degrees of conversion (runs 2 and 4–7). These results show that the rearrangement **14**→**12** is initially highly regioselective, i.e. **14b**→**12a** and **14a**→**12b** (and implicitly, **14c**→**12c**; Scheme 9). With increasing conversion, however, the deuterium positions were progressively scrambled until a 1:1 ratio of **12a** and **12b** was attained after maximum conversion of the mixture **14a–c** (run 7). A stepwise rearrangement mechanism as delineated in Scheme 10 is compatible with this regioequilibrating process as well as with the corresponding result with **12a** (→**12b**, run 2). The experiments do not discriminate between positional scrambling through **12**⇄**14** and through **12a**⇄**12b** and/or **14a**⇄**14b**. In any event, the diradicals (*E*)- and (*Z*)-**27** are likely intermediates common to all these regioequilibrating processes.



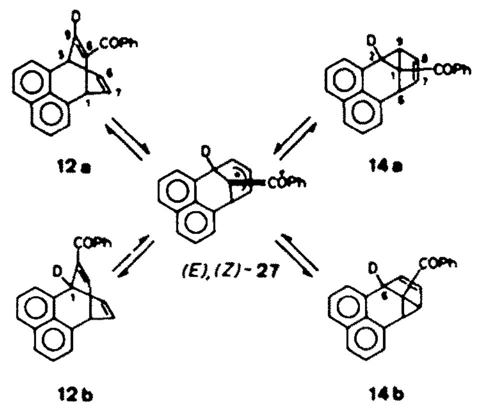
Scheme 9. Regiospecific path for the thermal interconversion of 12 and 14.[39]

The high regioselectivity of the rearrangement **14**→**12** during the initial phase of the thermolyses is clearly seen when the deuterium distributions resulting in product **12** (runs 4–7) are extrapolated to *zero* conversion. This finding can be accommodated by either the concerted mechanism illustrated in Scheme 9 or the stepwise alternative of Scheme 10. The experiments do not differentiate between the two. The latter would require that the *E* and *Z* conformers of **27** react regioselectively in either or both directions, and that conformational equilibration be slower. A

Table 4. Thermolysis of **12a** and **14a**

Run no	Starting material	Reaction time, h	Product ratio 12:14	Relative deuterium distribution, %[b]			
				in 12[c]		in 14[d]	
				C(1)=12b	C(9)=12a	C(2)=14a	C(6)=14b
1	12a	0	100:0	0	100		
2	12a	140[e]	98.8:1.2[e]	6	94	n.d.	n.d.
3	14a-c	0	0:100			64	36
4	14a-c	48	19:81	63	37	58	42
5	14a-c	103	61:39	58	42	53	47
6	14a-c	140	89:11	53	47	n.d.	n.d.
7	14a-c	160	98.8:1.2	50	50	n.d.	n.d.

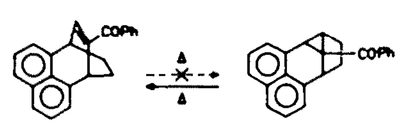
[a] $2 \cdot 10^{-3}$ M benzene solutions, 493 K. [b] Deuteration of 12 at C(5) and C(7) (= 12c), and of 14 at C(7) and C(9) and C(9) (= 14c) in runs 2 and 4-7 was qualitatively in evidence by NMR (totally 10% in 12a-c and in 14a-c) but too low for quantitative measurement. The deuterium percentages given equal 100% for 12a + 12b and for 14a + 14b. [c] Combination of ^1H and ^2H NMR analyses; experimental error ± 3%. [d] ^1H NMR analysis; experimental error ± 3%. [e] The 98.8:1.2 ratio was attained already after 48 h.



Scheme 10. Paths for positional deuterium scrambling in 12a/12b and 14a/14b.

fortuitous combination of two or more parallel equilibrating mechanisms which might have simulated regioselectivity, had been excluded by measurements at different temperatures. No variation of the deuterium distribution was found in these cases. In kinetic terms, the latter experiments exclude significant isotope effects.

The concerted mechanism, if operative, would represent a novel example of orbital symmetry-controlled pericyclic reactions in terms of a "tri - π - methane$\rightleftarrows$cyclopropyldi - π - methane" interconversion. It is a thermally allowed $\sigma^2 + \pi^2 + \pi^2 + \pi^{10}$ process or 16-electron Möbius cyclic array with one nontrivial sign inversion as shown in Scheme 9.[30,39] The observed regioselectivity qualitatively conforms to the regiospecificity expected on this basis. An analogous—photochemically forbidden—three-bridge mechanism had been initially considered by Zimmerman *et al.*[9b] for the photorearrangement of barrelene to semibullvalene, but it was ruled out experimentally in favor of the di-π-methane route. A similar argument now supports the conclusion that the second double bond is mechanistically mandatory in the thermal rearrangement 12→14, unlike the situation found in the photochemistry of 12. The dihydro compound 13 did not convert into 15 even at 523 K during 48 hr. Only the reverse reaction, 15→13, was observed under these drastic conditions.



13 15

In conclusion, we have discovered, with the transformation 12→14, the first example of a ground-state counterpart of a di-π-methane photorearrangement,[40] with requirements characterizing it as a "tri-π-methane" process. The back reaction, 14→12, could also be achieved in the presence of strong electrophiles at room temperature. Treatment of 14 in chloroform with trimethylsilyl trifluoroacetate smoothly led to 12 in a quantitative conversion.[41] The sequence

$$12 \underset{\substack{\text{catalytic}\\ \text{dark reaction}}}{\overset{h\nu;\ \Phi^{366} \sim 1.0}{\rightleftarrows}} 14$$

thus represents a model for chemical light energy storage which can be conducted without detectable destruction of the reactants over many cycles. It is thus among the best approximations to a useful system in organic photochemistry, fulfilling more of the conditions (such as direct excitation at relatively long wavelength, unity quantum yield, quantitative thermal reversal under mild conditions) than any other examples presently known.[42]

EXPERIMENTAL

General remarks. M.ps were determined on a Kofler hot stage microscope and are uncorrected. Mass spectra (MS) were recorded on a Varian MAT CH5 instrument at 70 eV. NMR spectra were determined ($CDCl_3$ unless stated otherwise) in FT mode on Varian XL-100 (for ^2H; 15.4 MHz) and Bruker WH-270 instruments. The chemical shifts are in δ units and the coupling constants (J) in Hz. The abbreviations s, d, t, q, and m refer to singlet, doublet, triplet, quartet and multiplet, respectively. The IR spectra (CCl_4) were recorded on Perkin–Elmer 137 and 700 instruments and are given in cm^{-1}. The UV spectra (isooctane unless stated otherwise) were measured on a Cary 17 spectrophotometer; maxima are given in nm, with ϵ_{max} values in parentheses; sh = shoulder. Glc analyses were made on a Varian Aerograph 1700 instrument with a flame ionization detector coupled to a Spectra Physics Autolab System I computing integrator. The column was an OV 101 glass capillary column, 20 m, with nitrogen as the carrier gas. Preparative thick layer chromatography was carried out on 2 min silica plates (Merck). Column chromatography was performed with silica gel of mesh 70–230 (Merck). Combustion analyses were performed by Dornis and Kolbe, Mülheim a.d. Ruhr. The solvents were purified using standard procedures. 1,3-Cyclohexadiene, used as a quencher, was Fluka UV grade and was distilled prior to use. All solid sensitizers were zone refined, and the liquid sensitizers were purified by spinning-band distillation.

Preparative photolyses were carried out with a 250 W high-pressure Hg lamp (Philips) surrounded by a water-cooled pyrex immersion well. For irradiations at 313 nm the light was passed through an aqueous filter jacket (10 mm path), containing a solution of 567 mg of K_2CrO_4 and 2.056 g of Na_2CO_3 in 1 L of water. For irradiations at wavelengths > 340 nm the filter solution was prepared from 750 g NaBr and 8 g $Pb(NO_3)_2$ per 1 L of water. Prior to irradiations, the solns were deoxygenated by flushing with argon for 20 min. A positive pressure of argon was maintained over the stirred solns throughout the course of the irradiations.

Syntheses and preparative photolyses

2 - *Benzoylbicyclo*[2.2.2]*oct* - 2 - *ene* (2). Diels–Alder addition of 1.0 g (7.7 mmol) of benzoylacetylene[16] to 3.0 g (37.5 mmol) of 1,3-cyclohexadiene gave after 72 hr at 60°, column chromatography with benzene–EtOAc 50:1 and crystallization from MeOH 526 mg (2.52 mmol, 33%) of 2-*benzoylbicyclo*[2.2.2]*octa-2,5-diene* (32), m.p. 59–60° (decomposition to benzophenone at ≥ 80°). UV 345 (87), 244 (11300), 203 (14400). IR 3060, 2970, 2880, 1663, 1592, 1456, 1282, 1155, 912, 850, 722, 700. ^1H NMR 1.40 (broad s, 4 H, ethylene), 3.78 (m, 1 H, $H_{(4)}$, on decoupling at 1.40 d, $J_{3,4} = 6.2$, of d, $J_{4,5} = 6.5$, of d, $J_{4,6} = 2.2$), 4.40 (m, 1H, $H_{(1)}$, on decoupling at 1.40 d, $J_{1,3} \sim 2$, of d, $J_{1,5} \sim 2$, of d, $J_{1,6} = 5.8$), 6.24–6.54 (*AA'MM'*, 2 H, $H_{(5\ \text{and}\ 6)}$), 6.93 (dd, 1 H, $H_{(3)}$), 7.24–7.69 (m, 5 H, phenyl). MS thermal decomposition to benzophenone, *m/e* 180, and ethene.

Hydrogenation of 322 mg (1.5 mmol) of 32 with 150 mg tris(triphenylphosphin)rhodium(I) chloride in 4 mL benzene for 18 hr in the dark at room temp gave after column chromatography with benzene and crystallization from MeOH 240 mg (1.14 mmol, 76%) of 2, m.p. 85–86°. UV 348 (85), 244 (15000), 203 (14400). IR 3070, 2950, 2880, 1663, 1615, 1455, 1298, 1160, 924, 841, 720, 705. ^1H NMR 1.22–1.80 (m, 8 H, four methylenes), 2.73 (broad d, 1 H, $H_{(4)}$), 3.36 (broad s, 1 H, $H_{(1)}$), 6.98 (d, $J_{1,3} = 1.8$, of d, $J_{3,4} = 6.8$, 1 H, $H_{(3)}$), 7.22–7.84 (m, 5H, phenyl). MS *m/e* 212 ($C_{15}H_{16}O^+$), 184, 183, 105 (base peak), 77.

1 - *Phenyl* - 3 - *deuterioprop* - 2 - *yn* - 1 - *one*. A soln of 1.155 g (8.9 mmol) benzoylacetylene[16] and 2 mg cupric acetate in 50 mL of Me_3OD (99.5% d_1) was stirred for 3 days at r.t. The

mixture was concentrated *in vacuo* and the residue was sublimated (60°/0.1 Torr) to give 1.054 g (91%) of colorless product, m.p. 46–48°. IR ($CHCl_3$) 3050, 1655, 1597, 1580, 1450, 1412, 1173, 1030, 1005, 998. NMR 3.50 (s, < 0.05 H). MS *m/e* 131 ($C_9H_5OD^+$).

8 - *Benzoyl* - 9 - *deuterionaphtho*[de - 2.3.4]*bicyclo*[3.2.2]*nona* - 2,6,8 - *triene* (**12a**). A mixture of 930 mg (5.2 mmol) 1 - phenyl - 3 - deuterioprop - 2 - yn - 1 - one and 680 mg (5.2 mmol) cyclohepta[*de*]naphthalene ("pleiadiene")[17] was stirred at 120° under argon for 24 hr. The dark brown mixture was chromatographed on 200 g silica with toluene. The first fractions contained 184 mg of an unidentified, red orange material. Further elution gave 1.25 g of a yellowish oil. This oil was rechromatographed on 200 g silica with 2.5% ether–hexane. Another 110 mg unidentified orange oil were followed by 1.094 g of **12a** in 96% glc purity. Sublimation (175°/0.1 Torr) followed by two crystallizations from CH_2Cl_2 gave 1.024 g (63%) of **12a** (glc purity 100%), m.p. 127°. (Found: C, 89.24; H, 5.36. Calc. for $C_{23}H_{15}OD$: C, 89.23; H, 5.50%). IR 3050, 2940, 1640, 1605, 1593, 1442, 1346, 1333, 1264, 1240, 1000, 890. UV 385 (sh), 375 (110), 350 (350), 302 (6000), 282 (6700), 222 (51700). ^1H NMR 4.26 (d, $J_{5,6} = 6.0$, of d, $J_{5,7} = 3.0$, 1 H, $H_{(5)}$), 5.06 (broad d, $J_{1,7} = 6.0$, 1 H, $H_{(1)}$), 6.52 and 6.66 (*ABXY*, $J_{6,7} = 7.9$, $J_{1,6} = 3.0$, 2 H, $H_{(6)}$ and $H_{(7)}$), 7.10–7.72 (m, 11 H, Ar–H). ^2H NMR 7.29 (m, < 0.05 ^2H, $^2H_{(9)}$). In non-deuteriated sample (12) the $H_{(9)}$ position which was superimposed by the aromatic proton signals, was confirmed by INDOR. MS 309 (M^+), 204 (base peak), 105, 77.

8 - *Benzoyl* - 9 - *deuterionaphtho*[de - 2.3.4]*bicyclo*[3.2.2.]*nona* - 2,8 - *diene* (**13a**). A soln of 150 mg (0.48 mmol) of **12a** and 55 mg (0.60 mmol) tris(triphenylphosphin)rhodium(I) chloride in 6 mL benzene was stirred at r.t. under H_2 in the dark during 24 hr. The orange soln was filtered through 10 g silica and the short column was then washed with toluene. Crystallization from hexane of the crude oily product yielded 121 mg (0.39 mmol, 81%) of **13a** (> 98% by glc), m.p. 149°. (Found: C, 88.75; H, 5.95. Calc. for $C_{23}H_{17}OD$: C, 88.75, H, 6.10%). IR 3055, 2940, 2860, 1646, 1595, 1444, 1263, 1240, 1178, 1120, 709. UV 385 (sh), 375 (165), 319 (6000), 307 (7100), 303 (7200), 282 (8500), 273 (9300), 223 (48500). ^1H NMR 2.08–2.40 (m, 4 H), 3.87 (broad s, 1 H), 4.62 (broad s, 1 H), 7.11 (m, < 0.005 H), 7.20–7.74 (m, 11 H). MS 311 (M^+), 283, 206 (base peak), 105, 77.

2-, 6-, *and* 9-*deuteriated* 1 - *benzoylnaphtho*[de - 2.3.4]*tricyclo* - [4.3.0.0^{2,9}]*nona*-3,7 - *diene* (**14a–c**)

Direct (*preparative*) *irradiations*. $7 \cdot 10^{-3}$ M Solns of **12a** (2.16 mg/mL) in benzene and in t-BuOH were irradiated at 313 and > 340 nm at r.t. The reactions were monitored by glc. Complete conversions were generally achieved after about 4 hr. After evaporation of the solvent, the residue was passed through a column of 50 fold weight of silica with 2.5% ether–hexane. The crystalline product **14a–c** was obtained in > 98% glc purity and yields of 85–90%, m.p. 130–132°. Recrystallization from EtOH afforded a 100% product purity. (Found: C, 89.07; H, 5.44. Calc. for $C_{23}H_{15}OD$: C, 89.32; H, 5.50%). IR 3060, 3030, 2920, 1666, 1598, 1446, 1262, 1240, 1107, 1025. UV 346 (105), 310 (7000), 301 (9000), 292 (7700), 230 (55000). ^1H NMR 3.32 (broad s, 1.3 H, $H_{(2)}$ and $H_{(9)}$), 4.78 (d, 0.7 H, $J_{6,7} = 2.3$, $H_{(6)}$), 5.32 (d, $J_{6,7} = 2.3$, of d, $J_{7,8} = 5.5$, 1 H, $H_{(7)}$), 5.68 (d, $J_{7,8} = 5.5$, of d, $J_{8,9} = 0.8$, 1 H, $H_{(8)}$), 7.17–7.78 (m, 11 H, Ar–H). The deuterium distribution at C(2) and C(9) was analyzed after hydrogenation to **15a–c** (for the results see runs 1, 3 and 4 in Table 1). MS 309 (M^+), 204 (base peak), 105, 77, 57.

Sensitized irradiations. These runs were conducted at > 340 nm as described for the direct irradiations, except that the sensitizers listed in Table 1 were added in concentrations allowing for a > 95% light absorption by the sensitizers (i.e., $3.25 \cdot 10^{-1}$ M benzophenone, $4.6 \cdot 10^{-2}$ M thioxanthone, and $5.8 \cdot 10^{-1}$ M phenanthrene, with $7 \cdot 10^{-3}$ M **12a**). The sensitizers were readily separated from the reaction mixtures in the first chromatographic fractions. The photoproducts **14a–c** were again isolated in > 99% glc purity and yields of > 85%. See above for the analysis of the deuterium distribution and runs 9–11 in Table 1 for the results.

1 - *Benzoylnaphtho*[de - 2.3.4]*tricyclo*[4.3.0.0^{2,9}]*non* - 3 - *ene* (**15a–c**)

(a) The mixture of **14a–c** was hydrogenated as described above for the preparation of **13a**. Routine yields of > 85% **15a–c** (> 96% glc purity) were achieved, m.p. 120°. (Found: C, 88.75; H, 6.10. Calc. for $C_{23}H_{17}OD$: C, 88.69; H, 5.91%). IR 3060, 2950, 2870, 1664, 1596, 1448, 1393, 1271, 1180, 1052. UV 350 (50), 340 (105), 321 (3400), 312 (4800), 299 (7300), 289 (5600), 230 (58000). ^1H NMR 1.20 (m, $J_{8,9} = 3.2$, 1 H, *endo*-$H_{(8)}$), 1.65 (d, $J_{7,8endo} = 12.0$, of d, $J_{7,8exo} = 6.0$, 1 H, *endo*-$H_{(7)}$), 1.95 (m, $J_{7endo,8} = 12.0$, $J_{8,9} = 6.5$, 1 H, *exo*-$H_{(8)}$), 2.66 (m, $J_{6,7} = 7.8$, 1 H, *exo*-$H_{(7)}$), 3.09 (m, $J_{2,9} = 9.4$, $J_{8exo,9} = 6.5$, 0.9 H, $H_{(9)}$), 3.20 (d, $J_{2,9} = 9.4$, 0.4 H, $H_{(2)}$), 4.20 (d, $J_{6,7exo} = 7.8$, 0.7 H, $H_{(6)}$), 7.2–7.9 (m, 11 H, Ar–H). MS 311 (M^+), 206 (base peak), 105, 77.

(b) A mixture of **15a–c** was obtained when $7 \cdot 10^{-3}$ M benzene solutions of **13a** were irradiated at 313 and > 340 nm. The procedure as described above for **14a–c** (direct irradiations) was adopted. The deuterium distribution was determined by ^1H NMR (see (a) and Table 3, runs 1 and 4). The yields of pure **15a,c** were routinely > 85%.

(c) A mixture of **15a, c** was isolated in similar yields and with similar deuterium distribution as described in (b) when $7 \cdot 10^{-3}$ M benzene solns of **13a** were irradiated at > 340 nm in the presence of sensitizers. The procedure for the sensitized irradiations to prepare **14a–c** was adopted here. Concentrations of $3.25 \cdot 10^{-1}$ M benzophenone and Michler ketone ensured > 95% light absorption by these donors. For the deuterium analysis by ^1H NMR see (a) and the results in runs 2 and 3, Table 1.

Diastereoisomeric rac - 9 - *hydroxyphenyl* - 9 - *deuterionaphtho*[de - 2.3.4]*bicyclo*[3.2.2]*nona* - 2,6,8 - *trienes* (1R*)- and (1S*) - **21a**. A soln of 206 mg (0.66 mmol) of **12a** and 152 mg (4 mmol) of $NaBH_4$ in 20 mL MeOH-water 1:1 was stirred at 0° during 1 hr. Excess hydride was then decomposed with 4 mL acetone, the mixture was concentrated *in vacuo*, and the residue was chromatographed on thick-layer plates using 30% ether–hexane. The two major bands were eluted with CH_2Cl_2–20% ether to afford (1*R**)- and (1*S**)-**21a**. The diastereoisomer with a higher R_f value, (1*R**)-**21a**, was isolated as an oil, 62 mg (0.2 mmol, 30%). IR 3610, 3440 (broad), 3060, 3040, 2935, 2860, 1595, 1560, 1495, 1450, 1365, 1170, 1015. UV (EtOH) 318 (1850), 308 (5600), 304 (5850), 296 (7700), 283 (5750). ^1H NMR 1.93 (broad s, 1 H, exchangeable with D_2O), 3.90 (d, $J_{5,6} = 4$, 1 H, $H_{(5)}$), 4.11 (d, $J_{1,7} = 4$, 1 H, $H_{(1)}$), 5.34 (s, 1 H, $H_{(1')}$), 6.38 (d, $J_{5,6} = 4$, of d, $J_{6,7} = 3.5$, 1 H, $H_{(6)}$), 6.48 (d, $J_{1,7} = 4$, of d, $J_{6,7} = 3.5$, 1 H, $H_{(7)}$), 6.55–7.0 (m, 11 H, Ar–H). MS 311 ($C_{23}H_{17}OD^+$), 292, 204 (base peak), 107, 79. The isomer with a lower R_f value, (1*S**)-**21a**, was isolated as an oil, 56 mg (0.18 mmol, 27%). IR 3615, 3440 (broad), 3060, 3040, 2935, 2860, 1600, 1580, 1495, 1450, 1365, 1275, 1015. UV (EtOH) 307 (5530), 295 (7900), 284 (5650). ^1H NMR 1.90 (broad s, 1 H, exchangeable with D_2O), 3.90 (d, $J_{5,6} = 4$, 1 H, $H_{(5)}$), 4.09 (d, $J_{1,7} = 4$, 1 H, $H_{(1)}$), 5.29 (s, 1 H, $H_{(1')}$), 6.40 (d, $J_{5,6} = 4$, of d, $J_{6,7} = 3.5$, 1 H, $H_{(6)}$), 6.50 (d, $J_{1,7} = 4$, of d, $J_{6,7} = 3.5$, 1 H, $H_{(7)}$), 6.55–7.70 (m, 11 H, Ar–H). MS 311 ($C_{23}H_{17}OD^+$), 292, 204 (base peak), 107, 79.

Mixture of 2-, 6-, *and* 9-*deuteriated* 1 - *hydroxyphenylmethylnaphtho*[de - 2.3.4]*tricyclo*[4.3.0.0^{2,9}]*nona* - 3,7 - *dienes* **23a–c**. (1*R**)- and (1*S**)-**21a** were each irradiated (35 mg, 1.12 mmol, in 15 mL benzene) at > 340 nm together with 10 mg (0.055 mmol) benzophenone. The irradiations were completed after 3 hr (glc). A major product (**23a–c**) was isolated in 70% yield in each run by thick-layer chromatography with 30% ether–hexane. The ^1H NMR's (60 MHz) of the two runs were indistinguishable: 2.0 (broad s, 1 H, exchangeable with D_2O), 2.58 (m, 2 H, $H_{(2)}$ and $H_{(9)}$), 4.35 (broad s, 1 H, $H_{(6)}$), 5.0 (s, 1 H, $H_{(1')}$), 5.18 (m, 1 H, $H_{(7)}$), 5.60 (m, 1 H, $H_{(8)}$), 7.0–7.80 (m, 11 H, Ar–H).

The **23a–c** mixtures were oxidized, for the purpose of identification, by mixing 20 mg (0.064 mmol) of each sample with 30 mg (0.14 mmol) pyridinium chlorochromate[43] in 5 mL CH_2Cl_2 at 0°. After stirring for 15 min under argon, the mixtures were filtered and the filtrate was passed through 1 g florisil

(60–100 mesh). The short columns were eluted with 500 mL 25% ether–CH_2Cl_2 to give 17 mg (0.055 mmol) of products which were analyzed by glc (85% **14a–c** in each case). Both samples were hydrogenated without previous purification to afford **15a–c**. The deuterium distributions for both samples were the same and identical with that listed in Table 1 (run 12) for the product obtained from the diastereoisomeric mixture of starting compounds (**21a**).

Irradiation of the mixture of the diastereoisomeric 8 - hydroxyphenylmethyl - 9 - deuterionaphtho[de - 2.3.4]*bicyclo*[3.2.2]*nona - 2.8 - dienes* (1R*)- *and* (1S*)-**22a**. A mixture of diastereoisomers (1*R**)- and (1*S**)-**22a** was prepared following the procedure described for **21a**, except that the isomers could not be separated. Therefore, the 45:55 mixture (glc determination) was directly irradiated (> 340 nm) in the presence of benzophenone (for details, see the preparation of **23a–c**). After 2.5 hr **22a** had disappeared and 82% of **24a** (glc) were formed. After removing the sensitizers by thick-layer chromatography, **24a** was oxidized, according to the procedure for **23a–c** (oxidation), to **15a**.

Irradiations of **32** (for the preparation of **32** see synthesis of **2**). $7 \cdot 10^{-3}$ M Solns of **32** (1.47 mg/mL) in cyclohexane were directly irradiated at 254 (low pressure Hg lamp), 300 (Rayonet RUL lamps) and > 340 nm. In two sensitized runs, acetone was taken as a solvent (λ^{exc} 300 nm) and acetophenone ($3.25 \cdot 10^{-1}$ M) was added to a cyclohexane solution of **32** ($\lambda^{exc} > 340$ nm), respectively. In both runs > 95% of the light were absorbed by the sensitizer. Under all conditions **32** proved unreactive even after prolonged irradiation times of up to 48 hr.

Laser flash photolytic study

The equipment, a Nd laser, has been described elsewhere.[44] The third (λ^{exc} 353 nm, pulse width 10 ns, energy ≤ 50 mJ) and fourth harmonics (λ^{exc} 256 nm) were used. The output of the detection system was fed into a transient digitizer (Tektronix R 7912). The low-temp measurements were performed in a cylindrical suprasil cell (d = L = 1 cm) with evacuated windows. The cell was cooled by means of a N_2 flow. The laser (2 mm dia) and analyzing beams were arranged perpendicular to and along the cylinder axis, respectively. The optical geometry was optimized for maximum transient absorbance in each case. The solutions were purged with argon for 15 min prior to measurements where O_2 was to be removed.

Quenching experiments with **12** *as an acceptor*. The results are summarized in Table 2. Note that the lifetimes of the donors, τ_D, were experimentally determined.

Transient spectra were determined at A^{353} 1.5–8 cm^{-1} for **12** and for **35**. For the results of the lifetimes and activation parameters see text.

Transient absorption coefficient. Two procedures were followed to determine ϵ^{380}:

(a) A method similar to that described by Lachish *et al.*[45] was employed. A solution of $1.1 \cdot 10^{-2}$ M **12** in benzene was irradiated with a laser energy varying from 1 to 20 mJ. The transient absorbance at 380 nm was extrapolated to zero time and plotted vs. the laser energy. In a typical case, a limiting maximum value at high energy of A^{380} 0.7 cm^{-1} was obtained. Taking Φ 1.0 of the product formation (**12** → **14**; run 4 in Table 1) for the efficiency of transient formation (Φ_{trans}), $\epsilon^{380} \leq 200\ M^{-1}cm^{-1}$ was obtained from several runs.

(b) Thioxanthone and pyrene were used as standards with known Φ_{isc} values. Benzene solutions of these compounds and of **12** with similar absorbances (5.1, 7.3, and 6.2 cm^{-1}, respectively) were irradiated at λ^{exc} 353 nm. Low laser energies were used to avoid saturation problems. The ϵ^{380} value for the transient was calculated from

$$\epsilon^{380} \cdot \Phi_{trans} = \frac{1-10^{-A_{stand}}}{1-10^{-A}} \cdot \frac{\epsilon_{T-T} \cdot \Phi_{isc} \cdot A^{380}_{trans}}{A_T},$$

with A_{stand} and A = ground-state absorbances of standard and **12**, respectively, at 353 nm; A_T = triplet absorbance of standard at 650 (thioxanthone) and 420 nm (pyrene); A^{380}_{trans} = transient absorbance at 380 nm; ϵ_{T-T} = absorption coefficient of triplet standard; Φ_{isc} = S–T intersystem crossing yield of standard. The product $\epsilon_{T-T} \cdot \Phi_{isc}$ was measured employing procedure (a). Values of ϵ^{380} $1.2 \cdot 10^2$ (with pyrene) and $2.5 \cdot 10^3\ M^{-1}cm^{-1}$ (with thioxanthone) were obtained. The latter value can be taken as an upper limit.

Variable-temperature emission spectroscopy

A fully computer controlled Spex Fluorolog spectrometer was used for the emission studies. The details of the measurements have been described elsewhere.[46] The irradiation of the samples was carried out with a 250 W high-pressure Hg lamp (*Philips*) surrounded by a water-cooled pyrex immersion well. Aqueous filter solutions were used (see General Remarks).

Variable-temperature ESR spectroscopy

A Varian E9 ESR spectrometer was used with a sensitivity of $5 \cdot 10^{10}$ of ΔH spins. Samples with $(1.0–6.6) \cdot 10^{-2}$ M **12a** were placed, after purging with N_2, in a N_2 flow cavity, and the spectra were recorded at 9.05 GHz microwave frequency. The light source was an SP-1000 W high-pressure Hg lamp (Philips Richtstrahler) combined with liquid filter solutions (see General Remarks) placed in the light beam at the entrance of the cavity.

Variable-temperature IR spectroscopy

The spectra were recorded on a Perkin–Elmer 580 spectrometer. 10^{-1} M solutions of **12a** in 2-methyltetrahydrofuran were used in cell of 25 μm pathlength. The temp. was varied conductively by a Dewar attached to the metallic cell frame. The irradiations were carried out with a 200 W high-pressure Hg lamp (HBO, Osram). Interference filters (Schott, bandwidth 50 nm) were used.

Stern–Volmer quenching analysis

Eleven samples of $7 \cdot 10^{-3}$ M **12a** in benzene in the presence of 0–3 M 1,3-cyclohexadiene were irradiated in a turn-table reactor at > 340 nm. The product formation (**14a–c**) was determined by glc. The plot Φ_O/Φ_q vs quencher concentration gave a straight line with a slope of $k_q \cdot \tau = 1.1\ M^{-1}$.

Quantum yield determinations

All sample solutions were deoxygenated as described in General Remarks. The yields of **14**, **15**, **23** and **24** on $S_0 \rightarrow S_{1\ and\ 2}$ excitation and on sensitization were measured by an electronically integrating actinometer described by Amrein *et al.*[18] Further experimental details and results are given in Tables 1 and 3.

The ε values of **14** at 405 and 436 nm were determined in 10 cm cuvettes with a Zeiss PMQ 3 spectrophotometer.

The yields of **14** obtained by $S_0 \rightarrow T_{1\ and\ 2}$ excitation, were determined by potassium ferrioxalate actinometry.[47] The sample solutions were placed in 5 mm thermostated quartz cells and deoxygenated as above. Direct singlet excitation by irradiation into the long-wavelength tail of the first absorption band or by stray light was excluded for the 405 nm irradiation as follows. In two parallel experiments, one cut-off filter (Schott GG 400; 40% transmission at 400 nm) and a combination of two such filters (16% transmissions at 400 nm) in addition to the interference filters (Schott 405, 15 nm bandwidth) were used. With both arrangements, identical measurements were obtained (Table 1: run 5). For the 436 nm irradiations, an interference filter Schott 436 (bandwidth 12 nm) was used in combination with a cut-off filter (Schott GG 420; 50% transmission at 420 nm) and with two such filters (25% transmission at 420 nm) (Table 1: runs 6–8). Additional experimental details are given in Table 1.

Thermal interconversions

$2 \cdot 10^{-3}$ M (0.6 mg/mL) Benzene solutions of **12a**, **14a–c**, **13a** and **15a–c** were sealed in evacuated Pyrex tubes at −78°. The tubes were then heated in an electric oven and the reactions were monitored by glc over a temperature range of 493–543 K and the time ranges indicated in Table 4. The deuteriation of **12** and **13** was evaluated from the combined spectral data of ^1H NMR for $H_{(1)}$, $H_{(5)}$, $H_{(6)}$, $H_{(7)}$ and ^2H NMR for $D_{(9)}$. **14** was hydrogenated as described earlier affording **15**, the deuterium determination of which was carried out directly by ^1H NMR (see earlier for **15a–c**).

Acknowledgements—We are indebted to Dr. W. Hartmann and Dr. H.-G. Heine, Bayer AG, for a generous gift of pleiadiene, and we thank also Dr. H. Görner (laser flash photolysis), Dr. A. R. Holzwarth (emission spectroscopy), and Mr. W. Riemer (IR spectroscopy) for valuable advice and support, and Mrs. H. Matthäus for able technical assistance. One of us (M.V.G.) was recipient of an Alexander-von-Humboldt fellowship, and the Swiss National Science Foundation and Firmenich SA financially supported initial work carried out at the Department of Organic Chemistry, University of Geneva.

REFERENCES

[1] For preliminary communications of part of the results see [a] M. Demuth, C. O. Bender, S. E. Braslavsky, H. Görner, U. Burger, W. Amrein and K. Schaffner, *Helv. Chim. Acta* **62**, 847 (1979); [b] M. Demuth, U. Burger, H. W. Mueller and K. Schaffner, *J. Am. Chem. Soc.* **101**, 6763 (1979); [c] M. Demuth, D. Lemmer and K. Schaffner, *Ibid.* **102**, 5407 (1980); [d] K. Schaffner and M. Demuth, *Chimia* **34**, 184 (1980); [e] K. Schaffner and M. Demuth, *Rearrangements in Ground and Excited States* (Edited by P. de Mayo), Vol. 3, pp. 281–348. Academic Press, New York (1980).

[2] [a] W. Amrein and K. Schaffner, *Helv. Chim. Acta* **58**, 397 (1975); [b] K. Schaffner, W. Amrein and I.-M. Larsson, *Israel J. Chem.* **14**, 48 (1975); [c] W. Amrein, D. Karanatsios and K. Schaffner, *Chimia* **24**, 28 (1970).

[3] W. Amrein, I.-M. Larsson and K. Schaffner, *Helv. Chim. Acta* **57**, 2519 (1974).

[4] [a] L. M. Jackman, E. F. M. Stephenson and H. C. Yick, *Tetrahedron Letters* 3325 (1970); [b] A. B. Smith, III and W. C. Agosta, *J. Am. Chem. Soc.* **95**, 1961 (1973).

[5] The failure of **2** to photocyclize falls in line with a similar finding for 1-cyclopentenyl phenyl ketone,[4b] suggesting that the reaction either requires an out-of-plane torsion around the double bond in the reactive excited state, or proceeds via $Z \rightarrow E$ photoisomerization and subsequent ground-state cyclization of a highly strained (E)-cyclohexenyl ketone. Such a structural condition is met by **4** ($\Phi_{cycl} = 0.14$[6]). Interestingly, Φ_{cycl} of the 1-cycloheptenyl homolog drops to 0.003,[6] possibly owing to more facile $Z \rightarrow E$ isomerization as an alternative photochemical pathway, or to the lower electrophilicity of the hypothetical (E)-cycloheptenyl ketone intermediate.

[6] W. Amrein and K. Schaffner, Unpublished results.

[7] [a] W. Amrein and K. Schaffner, *Helv. Chim. Acta* **58**, 380 (1975); [b] W. Amrein, Ph.D. Thesis No. 5390, E.T.H. Zürich (1974).

[8] The preparation of **8** and its photochemical rearrangement to **9** has independently been described also by N. K. Saxena, Maya and P. S. Venkataramani, *Indian J. Chem.* 13, 1075 (1975).

[9] [a] H. E. Zimmerman and G. L. Grunewald, *J. Am. Chem. Soc.* **88**, 183 (1966); [b] H. E. Zimmerman, R. W. Binkley, R. S. Givens and M. A. Sherwin, *Ibid.* **89**, 3932 (1967); [c] R. S. H. Liu, *Ibid.* **90**, 215 (1968); [d] H. E. Zimmerman, R. W. Binkley, R. S. Givens, G. L. Grunewald and M. A. Sherwin, *Ibid.* 91, 3316 (1969); [e] H. E. Zimmerman, R. J. Boettcher, N. E. Buehler, G. E. Keck and M. G. Steinmetz, *Ibid.* **98**, 7680 (1976).

[10] [a] J. P. N. Brewer and H. Heaney, *Chem. Commun.* 811 (1967); [b] H. E. Zimmerman, R. S. Givens and R. M. Pagni, *J. Am. Chem. Soc.* **90**, 4191, 6096 (1968); [c] P. W. Rabideau, J. B. Hamilton and L. Friedman, *Ibid.* **90**, 4465 (1968); [d] H. E. Zimmerman and C. O. Bender, *Ibid.* 91, 7516 (1969); 92, 4366 (1970); [e] C. O. Bender, J. L. M. Elder A. J. Herbst and L. E. Miller, *Can. J. Chem.* **50**, 395 (1972); [f] C. O. Bender and H. D. Burgess, *Ibid.* 51, 3486 (1973); [g] H. E. Zimmerman and D. R. Amick, *J. Am. Chem. Soc.* **95**, 3977 (1973); [h] H. E. Zimmerman, D. R. Amick, and H. Hemetsberger, *Ibid.* **95**, 4606 (1973); [i] C. O. Bender and S. S. Shugarman, *Chem. Commun.* 934 (1974); [j] C. O. Bender and E. H. King-Brown, *Ibid.* 878 (1976); [k] C. O. Bender and J. Wilson, *Helv. Chim. Acta* **59**, 1469 (1976).

[11] [a] E. Ciganek, *J. Am. Chem. Soc.* **88**, 2882 (1966); [b] K. E. Richards, R. W. Tillman and G. J. Wright, *Aust. J. Chem.* **28**, 1289 (1975); [c] R. G. Paddick, K. E. Richards and G. J. Wright, *Ibid.* **29**, 1005 (1976).

[12] T. D. Walsh, *J. Am. Chem. Soc.* 91, 515 (1969); N. J. Turro, M. Tobin, L. Friedman and J. B. Hamilton, *Ibid.* 91, 516 (1969).

[13] H. Hart and R. K. Murray, Jr., *J. Am. Chem. Soc.* 91, 2183 (1969); H. Hart and G. M. Love, *Ibid.* **95**, 4592 (1973).

[14] See W. Adam, N. Carballeira and O. De Lucchi, *J. Am. Chem. Soc.* **102**, 2107 (1980), for a similar generation of diradical di-π-methane intermediates from azoalkanes.

[15] For the most recent review see H. E. Zimmerman, *Rearrangements in Ground and Excited States* (Edited by P. de Mayo), pp. 131–166. Academic Press, New York (1980).

[16] T. Naito, S. Nakagawa and J. Okumura, *US Pat.* 3 360 527 [*Chem. Abstr.* **69**, 36117g (1968)].

[17] For syntheses of pleiadiene see I. K. Lewis and R. D. Topsom, *Austr. J. Chem.* **18**, 923 (1965); I. Murata, and K. Nakasuji, *Tetrahedron Letters* 47 (1973); J. Shields, D. Gavrilovic, J. Kopecky, W. Hartmann and H.-G. Heine, *J. Org. Chem.* **39**, 515 (1974); C. R. Watson, Jr., R. M. Pagni, J. R. Dodd and J. E. Bloor, *J. Am. Chem. Soc.* **98**, 2551 (1976).

[18] W. Amrein, J. Gloor and K. Schaffner, *Chimia* **28**, 185 (1974).

[19] By using the "$S_{1\ \mathrm{and}\ 2}$" and "$T_{1\ \mathrm{and}\ 2}$" as well as the "intersystem crossing" and "internal conversion" terminology for the compounds **12–15** we purposely ignore, for the sake of simplicity, that there are formally, and probably to some extent also in terms of mechanistic relevance, two separate chromophoric moieties (e.g. $S_1(n, \pi^*)$ and $T_2(n, \pi^*)$ are the lowest excited states of the benzoyl chromophore).

[20] R. B. Woodward and R. Hoffmann, *The Conservation of Orbital Symmetry*. Verlag Chemie, Weinheim and Academic Press, New York (1970). H. E. Zimmerman, *J. Am. Chem. Soc.* **88**, 1565 and 1566 (1966); *Acc. Chem. Res.* 4, 272 (1971).

[21] W. G. Herkstroeter and G. S. Hammond, *J. Am. Chem. Soc.* **88**, 4769 (1966).

[22] G. Fischer and E. Fischer, *Mol. Photochem.* **8**, 279 (1977).

[23] O. L. J. Gijzeman, F. Kaufman and G. Porter, *J. Chem. Soc.* Farad. Trans. II **69**, 708 (1973); H. Görner and D. Schulte-Frohlinde, *J. Phys. Chem.* **85**, (1981), in press.

[24] In attempts to observe quenching of the room temp transient from **12** by 1,3-cyclohexadiene (laser flash excitation at 353 nm), a lengthening of the transient lifetime at 380 nm on addition of diene was noticed. Apparently a new species (a diene-transient complex) is formed on encounter.

[25] R. Bensasson and E. J. Land, *Trans. Faraday Soc.* **67**, 1904 (1971). D. Lavalette R. Bensasson, B. Àmand and E. J. Land, *Chem. Phys. Lett.* **10**, 331 (1971). M. V. Alfimov, I. G. Batekha, Y. B. Sheck and V. I. Gerko, *Spectrochim. Acta* **27A**, 329 (1971).

[26] In the sequence hexafluorobenzene, ether–isopentane–ethanol 5:5:2 and 2-methyltetrahydrofuran the ESR signal resolution increased markedly.

[27] E. Wasserman, L. C. Snyder and W. A. Yager, *J. Chem. Phys.* **41**, 1763 (1964).

[28] For the ESR parameters of triplet naphthalene, see Ref. 29.

[29] J. K. S. Wan, *Adv. Photochem.* 9, 1 (1974), and Refs. therein.

[30] J. E. Wertz and J. R. Bolton, *Electron Spin Resonance, Elementary Theory and Practical Applications*, Chap. 10. McGraw–Hill, New York (1972).

[31] Components > 0.05% were detectable by glc i.e. $5 \cdot 10^{-6}$ M at a total concentration of $12\ ^{2}$ M. A further factor of ten derives from the minimum ESR signal detectability for a 10% amplitude in the plot of Fig. 5, safely assuming a maximum diradical concentration of 10^{-2} M for 100% signal amplitude.

[32] P. Dowd, *J. Am. Chem. Soc.* **88**, 2587 (1966), 92, 1066 (1970); J. A. Berson, R. J. Bushby, J. M. McBride and M. Tremelling, *Ibid.* 93, 1544 (1971); C. R. Watson, Jr., R. M. Pagni, J. R. Dodd and J. E. Bloor, *Ibid.* **98**, 2551 (1976); W. R. Roth and G. Erker, *Angew. Chem.* **85**, 510 (1973); *Angew. Chem.*, Int. Ed. Engl. 12, 503 (1973).

[33] S. L. Buchwalter and G. L. Closs, *J. Am. Chem. Soc.* **101**, 4688 (1979).

[34] A weak shoulder in the IR spectrum of the photolysate at 77 K (Fig. 6) may have arisen from some **14** formed in a concerted manner. An increase of this absorption at 92 K owing to **14** produced via the S_H2i route, cannot be seen in the spectrum. In any event, the portion of **14** originating from these mechanisms is clearly insignificant.

[35] The splitting of the room temp Co bond (1640 cm^{-1}) starts at about 200 K, and the ratio of the two components depends on the rate of cooling.

[36] For a recent review see D. I. Schuster, *Rearrangements in Ground and Excited States* (Edited by P. de Mayo), Vol. 3, pp. 167–279. Academic Press, New York (1980).

[37] C. Manning and J. J. McCullough, *Chem. Commun.* 75 (1977); J. J. McCullough and C. Manning, *J. Org. Chem.* **43**, 2839 (1978).

[38] Y. Bahurel, F. Pautet and G. Descotes, *Bull. Soc. Chim. Fr.* 2222 (1971).

[39] The inclusion of a single formal double bond in lieu of the entire naphthalene π system in the orbital array of the transition state (Scheme 9) was chosen for simplicity and does not change the orbital symmetry argument. A six-electron process, which does not involve the naphthalene π electrons, is a formally equivalent alternative (however, see Zimmerman[15] for arguments favoring the participation of the second double bond in di-π-methane photorearrangements).

[40] For a vinylogous di-π-methane-type thermal rearrangement of a bicyclo[4.4.1]undecatetraene to a *cis*-bicyclo[5.4.0]undecatetraene, see T. Sato and S. Itô, *Tetrahedron Letters* 1051 (1979). We thank Prof. Itô for communicating these results prior to publication.

[41] For details see M. Demuth, G. Mikhail and M. V. George, *Helv. Chim. Acta* **64**, in press (1981).

[42] For a review on energy storage in organic photoisomers, see G. Jones, II, S.-H. Chiang and P. T. Xuan, *J. Photochem.* **10**, 1 (1979).

[43] E. J. Corey and J. W. Suggs, *Tetrahedron Letters* 2647 (1975).

[44] H. Görner, H. Gruen and D. Schulte-Frohlinde, *J. Phys. Chem.* **84**, 3031 (1980).

[45] U. Lachish, A. Shafferman and G. Stein, *J. Chem. Phys.* **64**, 4205 (1976).

[46] A. R. Holzwarth, H. Lehner, S. E. Braslavsky and K. Schaffner, *Liebigs Ann. Chem.* 2002 (1978); S. E. Braslavsky, A. R. Holwarth, E. Langer, H. Lehner, J. I. Matthews and K. Schaffner, *Israel. J. Chem.* **20**, 196 (1980).

[47] L. G. Hatchard and C. A. Parker, *Proc. Roy. Soc.* **A235**, 518 (1956).