values are expected, but the trends are invariant.

When this methodology is used, the resulting valence electron affinity of CH_4 is −65 kcal/mol and $b^2 = 0.34$. Using these values and $I_{H\cdot} = 19.0$ kcal/mol yields a barrier of 43.12 kcal/mol, with $S = 2$ (see Table I) and $f = b^2S = 0.68$. The reasonable size of the barrier gives some confidence that our recipe for f in eq 12 is a reasonable one.[31] Note the values of A_{CH_4} in ref 18e,f refer to a localized anionic form.

All the values of A_{RX} and b^2 refer to a standard S_{R-X} overlap (0.5). For details, see ref 18f.

Registry No. CH_3Cl, 74-87-3; $ClCH_2Cl$, 75-09-2; FCH_2Cl, 593-70-4; Cl_2CHCl, 67-66-3; Cl_3CCl, 56-23-5; CH_3Br, 74-83-9; $BrCH_2Br$, 74-95-3; CH_3I, 74-88-4; ICH_2I, 75-11-6; $(HO)CH_2Cl$, 15454-33-8; $(FCH_2)CH_2Br$, 762-49-2; Cl, 16887-00-6; Br, 24959-67-9; I, 20461-54-5; $NCCH_2Cl$, 107-14-2; $NCCH_2Br$, 590-17-0; $NCCH_2I$, 624-75-9.

Photochemistry of β,γ-Enones. 7.[1] Intramolecular Competition between Di-π-methane and Oxa-di-π-methane Rearrangements. On the Intermediacy of Charge-Transfer Complexes and Zwitterions in the Di-π-methane Rearrangements

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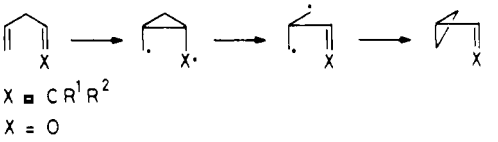
Abstract: The intramolecular competition between the di-π-methane (DPM) rearrangement and the oxa-di-π-methane (ODPM) rearrangement of 3-(3,4-dihydro-2-naphthyl)-3-methylpent-4-en-2-one (**1**), (*E*)-3-methyl-3-vinyl-5-phenylpent-4-en-2-one (**2**), and 2-cyclopent-1-enyl-2-vinylcyclopentanone (**3**) has been examined. Dienone **1** in benzene upon triplet photosensitization with 4-benzoylbiphenyl leads to the formation of one DPM isomer and two ODPM isomers in a ratio of 35:17:10. The results are consistent with a stepwise mechanism via 1,4- and 1,3-biradicals as the subsequent intermediates. The occurrence of only one instead of the expected two DPM isomers is explained in terms of the specific charge-transfer complexation in the 1,3-biradical rotamer intermediate in which the phenylene and acetyl group are "cisoid" (CTC). The preference of the DPM over the ODPM rearrangement has been explained in terms of the lower bond strength of the C=C as compared with the C=O π-bond. Dienone **2**, under similar conditions as **1**, exhibits only *E*–*Z* isomerization, even after prolonged irradiation. This may be explained in terms of the free rotor theory in which presumably the 1,4-biradicals of the DPM and ODPM rearrangements (E and F) are involved. Dienone **3** upon irradiation in acetone as solvent and triplet sensitizer decomposes rapidly; use of the sensitizers acetophenone, *m*-methoxyacetophenone, and benzene also leads to the formation of nonvolatile products only. No rearrangement products have been observed.

Both the DPM[2,3] and the ODPM rearrangements[3-5] are currently under investigation, and excellent reviews on these photochemical reactions were recently published. Our interest in these topics originated from our photochemical studies on the ionones and the noted absence of the ODPM rearrangement with the retro-α-ionones.[6-8] Later van der Weerdt, in a detailed study on acyclic γ-phenyl-β,γ-enones,[9] showed that the occurrence of

Scheme I



an ODPM rearrangement, which is in competition with *E*–*Z* isomerization, is strongly dependent on the degree and type of α-alkyl substitution.[8] On the basis of a relation between homoconjugation and the occurrence of the ODPM rearrangement,[4,9c] it was suggested that conformational effects in β,γ-enones lead in some cases to a sufficient orbital overlap to effect the ODPM rearrangement.[9b]

Based on single-photon counting studies Zimmerman[2,10] showed that the rate of the DPM rearrangement is affected by the degree of α-alkyl substitution between the two unsaturated bonds. He suggested that the rate variation results from a difference in stabilization of the transition state for the conversion of the 1,4- into the 1,3-biradical intermediate. The same could apply to the ODPM rearrangement,[9] but this still awaits experimental evidence.

DPM and ODPM rearrangements occur upon triplet photosensitization of suitable 1,4-dienes and β,γ-unsaturated ketones,

(1) For part 6, see R. H. van der Veen, C. Kruk, and H. Cerfontain, *Recl. Trav. Chim. Pays-Bas*, **101**, 272 (1982).
(2) H. E. Zimmerman in "Rearrangements in Ground and Excited States", Vol. 3, P. de Mayo, Ed., Academic Press, New York, 1980, pp 131–161.
(3) S. S. Hixson, P. S. Mariano, and H. E. Zimmerman, *Chem. Rev.*, **73**, 531 (1973).
(4) D. I. Schuster in "Rearrangements in Ground and Excited States", Vol. 3, P. de Mayo, Ed., Academic Press, New York, 1980, pp 167–279.
(5) K. N. Houk, *Chem. Rev.*, **76**, 1 (1976).
(6) A. van Wageningen, P. C. M. van Noort, and H. Cerfontain, *J. Chem. Soc., Perkin Trans. 2*, 1662 (1974); A. van Wageningen, J. A. J. Geenevasen, and H. Cerfontain, *Ibid.*, 1283 (1975).
(7) In a study on the acetone-photosensitized irradiation of three spiro-β,γ:δ,ε-dienones Fuchs[8] very recently reported that the 1,2-acyl shift product formation can be explained in terms of an ODPM type mechanism involving one or both double bonds.
(8) S. Abramson and B. Fuchs, *J. Chem. Soc., Chem. Commun.*, 1376 (1982).
(9) (a) A. J. A. van der Weerdt and H. Cerfontain, *J. Chem. Soc., Perkin Trans. 2*, 592 (1980); (b) A. J. A. van der Weerdt, Thesis (in English), University of Amsterdam, 1978; (c) A. J. A. van der Weerdt and H. Cerfontain, *Recl. Trav. Chim. Pays-Bas*, **96**, 247 (1977).
(10) H. E. Zimmerman and P. S. Mariano, *J. Am. Chem. Soc.*, **91**, 1718 (1969); H. E. Zimmerman and J. A. Pincock, *Ibid.*, **95**, 2957 (1973).

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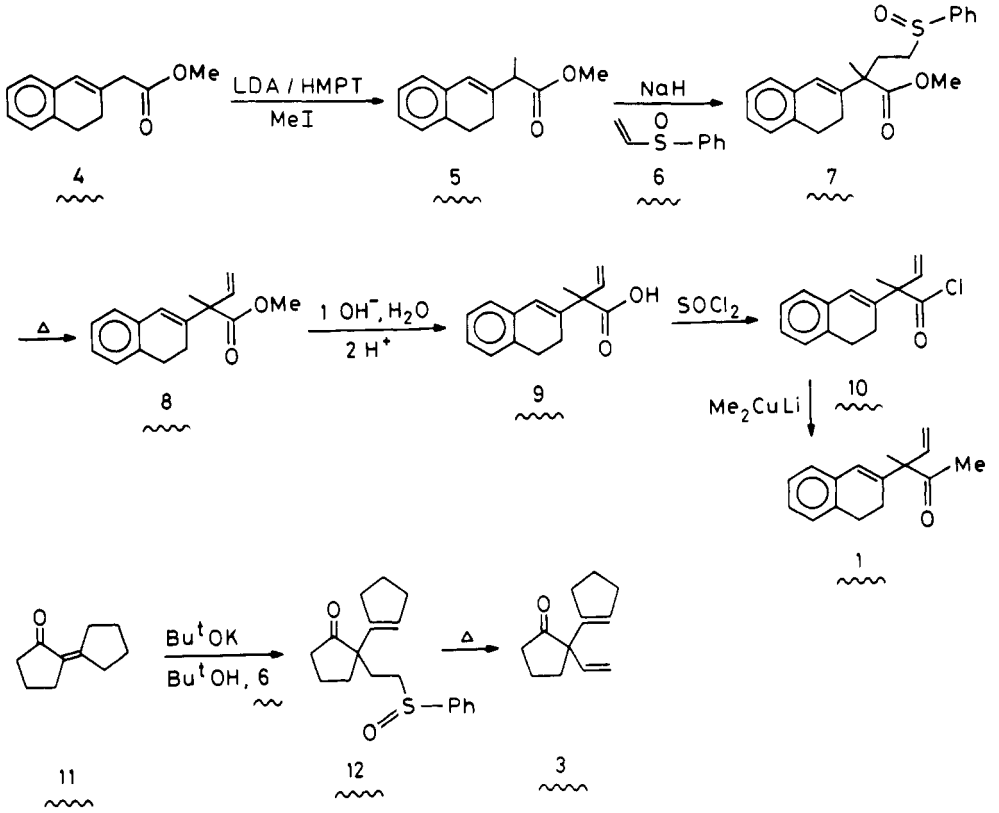
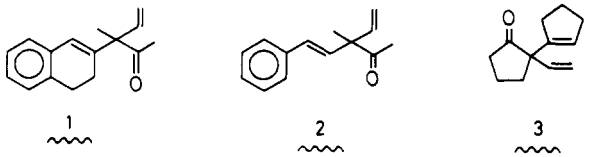
Scheme II. Synthesis of Photochemical Reactants



respectively. Most of these observed rearrangements were explained in terms of a *stepwise* mechanism involving the 1,4- and 1,3-biradicals as subsequent intermediates.[11] Recently Schaffner[12] did show that at low temperature these two species are the subsequent stable transients in the DPM rearrangement (Scheme I). The ODPM rearrangement in most cases also follows a stepwise mechanism[13] and the 1,3-biradical is in fact considered to be responsible for the racemization at the central α-carbon. Some ODPM rearrangements, however, were explained in terms of a *concerted* mechanism.[14]

In order to obtain more insight into the mechanism of the DPM and ODPM rearrangements it was thought of interest to study the photochemistry of substrates that would allow competition between the DPM and ODPM rearrangements. To this end we have chosen substrates in which the three unsaturated π-bond moieties are all substituted at one (i.e., the central) carbon atom, viz., the acyclic $\beta,\gamma,\beta',\gamma'$-dienones **1–3**. These dienones are almost



free of conformational and configurational constraints. A preliminary account of the reaction products of triplet excited **1** has been given.[1]

Results

Synthesis of the Dienones 1–3. The synthesis of the dienones **1** and **3** is outlined in Scheme II and described in the Experimental Section. A prerequisite for the conversion of **4** into the monovinyl ester **8**[15] is the blocking of one position of the α-carbon by alkylation with methyl iodide. The unsaturated sulfoxide **6** appears to be a strong and aselective electrophile; upon reaction of **6** with the unsaturated ester **4**, the main product after pyrolysis is the α,α-divinyl ester. The dienone **2** was prepared similarly to **1**.

Irradiation of the Dienones.[16,18] In a typical run 100 mg of the dienone **1** in 10 mL of benzene with 100 mg of 4-benzoylbiphenyl in a Pyrex tube was irradiated at λ 350 nm for 30 min to complete conversion. The products were separated by recycling HPLC (N = 11 000, nucleosil 10 μm) to obtain 52 mg of the DPM isomer and 34 mg of the ODPM isomers (**13**, **14**, and **15**, respectively). The two unseparable ODPM isomers were slightly contaminated with the sensitizer. The dienone (*E*)-**2** was irradiated under the same conditions as **1**. Even after 10 days of irradiation only the *Z* isomer (≥95%) was detected. Dienone **3** (5 mg/mL) was irradiated with λ 254 nm in acetone, which served as both solvent and triplet sensitizer, and found to decompose. The decomposition was complete in 6 h. No low molecular weight products were found, as was concluded from ^{1}H NMR, GLC, and TLC analysis.

Product Identification. The ^{1}H NMR spectrum of the DPM isomer **13** is similar to the spectra of the two ODPM isomers **14**

(11) See, for example, H. E. Zimmerman and R. E. Factor, *Tetrahedron*, **37**, 125 (1981); W. Adam and O. de Luchi, *J. Org. Chem.*, **46**, 4133 (1981); P. S. Mariano, E. Bay, D. G. Watson, T. Rose, and C. Bracken, *Ibid.*, **45**, 1753 (1980); H. E. Zimmerman, T. P. Gannett, and G. E. Keck, *J. Am. Chem. Soc.*, **100**, 323 (1978); H. E. Zimmerman, T. P. Gannett, and G. E. Keck, *J. Org. Chem.*, **44**, 1982 (1979); W. Adam, O. de Lucchi, K. Peters, E.-M. Peters and H. G. von Schnering, *J. Am. Chem. Soc.*, **104**, 5747 (1982).

(12) M. Demuth, W. Amrein, C. O. Bender, S. E. Braslavsky, U. Burger, M. V. George, D. Lemmer, and K. Schaffner, *Tetrahedron*, **37**, 3245 (1981).

(13) (a) W. G. Dauben, G. Lodder, and J. D. Robbins, *J. Am. Chem. Soc.*, **98**, 3030 (1976); (b) B. Winter and K. Schaffner, *Ibid.*, **98**, 2022 (1976).

(14) (a) R. L. Coffin, W. W. Cox, R. G. Carlson, and R. S. Givens, *J. Am. Chem. Soc.*, **101**, 3261 (1979); (b) J. I. Seeman and H. Ziffer, *Tetrahedron Lett.*, 4413 (1973).

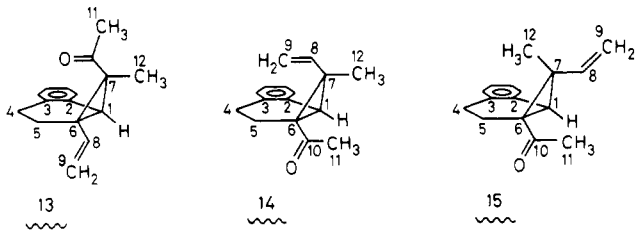
(15) R. Tanikaga, H. Sugihara, K. Tanaka, and A. Kaji, *Synthesis*, 299 (1977).

(16) The UV spectra (cyclohexane, λ_{max} in nm, ϵ in L/(mol cm)) of the dienones **1** (253, 20 500; 284, 2720; 293, 2290) and **2** (252, 11 600; 284, 1640; 293, 1320) are very similar to the β,γ-enones investigated before.[17] Dienone **3** exhibits only one absorption band at $\lambda > 220$ nm, viz., an n,π^* absorption with λ_{max} 303 nm (ϵ = 135 L/(mol cm)) which is 10–15 nm shifted to longer wavelength in comparison with the n,π^* absorption of the α-alkyl-substituted β,γ-enones, probably due to a larger degree of homoconjugation.

(17) A. J. A. van der Weerdt and H. Cerfontain, *Tetrahedron*, **37**, 2121 (1981).

(18) The dienones **1–3** both in acetonitrile and cyclohexane are photostable for irradiation at λ 300 nm. The mechanistic implications of this photostability will be discussed in the forthcoming Thesis of R. H. van der Veen.

and **15**. It consisted of the following absorptions (in ppm):



DPM - isomer ODPM - isomers

7.35–6.95 (m, 4H, Ar), 6.05 (dd, J_Z = 11.5, J_E = 18 Hz, 1 H, olefinic), 5.21 (dd, J_Z = 11.5, J_{vic} = 1.5 Hz, 1 H, olefinic), 5.18 (dd, J_E = 18, J_{vic} = 1.5 Hz, 1 H, olefinic), some multiplets of the dihydronaphthyl group at 2.35–2.15 (1 H), 2.70–2.55 (2 H), 2.00–1.80 (1 H), and finally three singlets at 1.90 (3 H, CH_3CO), 1.33 (3 H, CH_3), and 1.24 (1 H, cyclopropyl H).

The spectrum of the second (i.e., the ODPM isomers) fraction is very similar to that of the DPM isomer as to the chemical shifts of the absorptions. All the absorptions are double with an intensity ratio (*after* separation) of ca. 1.3 in favor of **14** over **15**. The NMR spectrum of the irradiated mixture as such contained the same absorptions, but the relative ratio of the three isomers was somewhat different, viz., **13**:**14**:**15** = 35:17:10.

The definite structural assignments of **13**–**15** have been made on the basis of NOE difference and $Eu(fod)_3$ shift experiments (Table I and Figure 1). As to the NOE difference experiments, irradiation of the acetyl hydrogens led to a signal of the methyl hydrogens only in the case of the DPM isomer **13** and to a signal of the cyclopropyl hydrogen only with the two ODPM isomers. This infers that the acetyl group in **13** must be trans with respect to the cyclopropyl hydrogen. The configuration of **13** was further confirmed by the irradiation of the methyl hydrogens: only with the DPM isomer **13** *signals of both the acetyl hydrogens and the 6.05 ppm olefinic hydrogen* were found. No signals were found upon irradiation of the methyl hydrogens of the ODPM isomers, even after prolonged accumulation of signals.

The $Eu(fod)_3$ experiments (Figure 1) confirm the interpretation: complexation shifts the cyclopropyl hydrogens of the two ODPM isomers downfield in contrast to the cyclopropyl hydrogen of the DPM isomer, which does not shift. Furthermore, only in the ODPM isomer **15** (i.e., the one with the vinyl and acetyl groups in cis orientation) a strong shift of the 5.67 ppm olefinic hydrogen was observed. Both the other ODPM isomer, **14** (in which the vinyl and acetyl group are trans), and the DPM isomer **13** exhibit no shift of the olefinic hydrogen upon adding $Eu(fod)_3$. Finally the methyl group only shifts considerably with the DPM isomer **13**.

Chemical evidence for the structure of products **13**–**15** has been obtained from their high-temperature isomerization. Upon GLC analysis of the irradiation mixtures two products, **16** and **17**, have been isolated of which **16** was found to result exclusively from the DPM isomer **13** and **17** exclusively from both **14** and **15**. The structure elucidation of **16** and **17** was based on normal and double-resonance ^1H NMR, NOE difference ^1H NMR, and off-resonance ^{13}C NMR spectroscopy (Table II).

The thermal rearrangements are outlined in Scheme III. The isomerization of **13** into **16** is a thermal homo-Cope rearrangement of which many examples are known.[19] The thermal isomerization of **14** and **15** into **17** is a retro ODPM rearrangement.[12,20] It is of interest[19d] to note that **14** (in contrast to **13**) does not exhibit a homo-Cope rearrangement, which would yield eventually the ketone **18**.

(19) (a) T. Hudlicky, F. J. Koszyk, T. M. Kutchan, and J. P. Sheth, *J. Org. Chem.*, **45**, 5020 (1980); (b) R. A. Cormier, W. L. Schreiber, and W. C. Agosta, *J. Am. Chem. Soc.*, **95**, 4873 (1973); (c) S. Sard, A. Schlossman, and M. Langbeheim, *Tetrahedron Lett.*, **22**, 691 (1981); (d) F. G. Klärner, W. Rüngeler, and W. Maifeld, *Angew. Chem.*, **93**, 613 (1981); (e) D. A. Clark, C. A. Bunnell, and P. L. Fuchs, *J. Am. Chem. Soc.*, **100**, 7777 (1978).

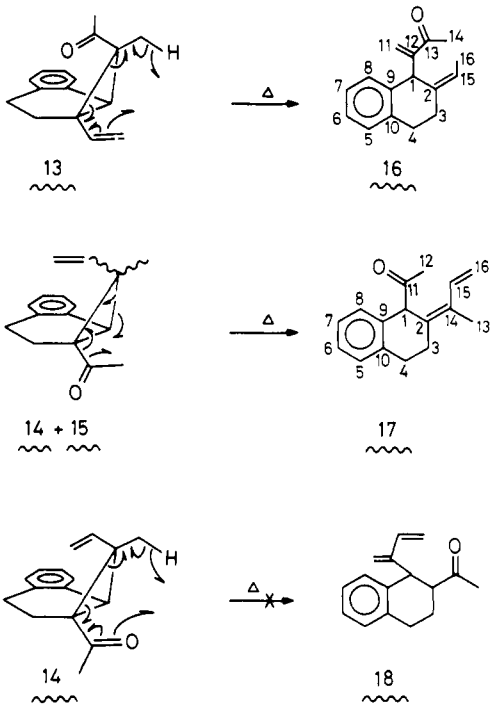
(20) J. Ipaktschi, *Tetrahedron Lett.*, 3179 (1970); A. Padwa, T. J. Blacklock, D. M. Cordova, and R. Loza, *J. Am. Chem. Soc.*, **102**, 5648 (1980).

Table I. NOE Difference Signals for **13**–**15**

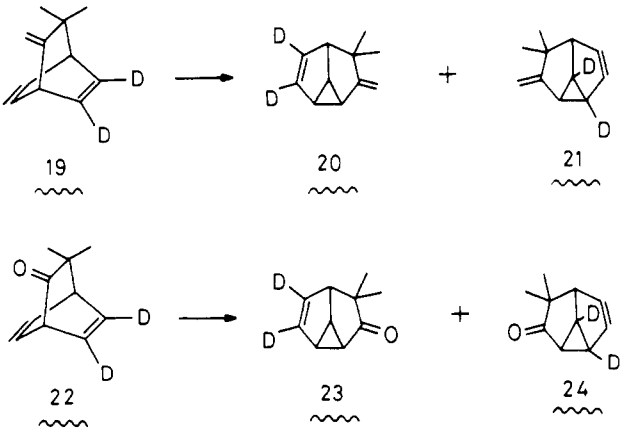
products	NOE difference signals[a,b] H(1)	H_α(5)	H_β(5)	H(8)	H_E-(9)	H_Z-(9)	H(11)	H(12)
13	–	+	+	–	–	–	I	+
	nd	–	–	+	–	–	+	I
	I	–	–	–	–	–	–	–
14	+	nd	w	–	–	–	I	–
	–	nd	–	–	–	–	–	I
	I	nd	–	–	–	–	–	+
15	+	nd	w	–	–	–	I	–
	–	nd	–	–	–	–	–	I
	I	nd	–	–	–	–	–	+

[a] I = irradiated, nd = not detected, + = signal, – = no signal, w = weak signal. [b] H_α and H_β are defined cis and trans relative to the cyclopropane C(6)–C(7) bond, respectively.

Scheme III. Thermal Conversion of **13**–**15**



Scheme IV. Sensitized Irradiation of 2-Methylenebicyclo[2.2.2]octadiene (**19**) and 3,3-Dimethylbicyclo[2.2.2]octa-5,7-dien-2-one (**22**)



Irradiation of 1 in Methanol. In order to examine the possible intermediacy of dipolar intermediates, the 4-benzoylbiphenyl-sensitized irradiation of **1** has been performed in methanol as trapping solvent. The only photoproducts were again **13**–**15**, which were formed in exactly the same ratio as in benzene, as was

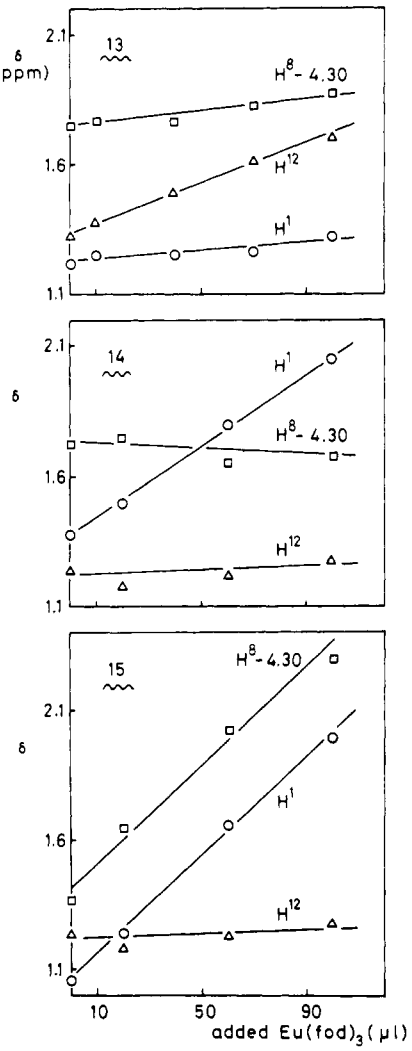
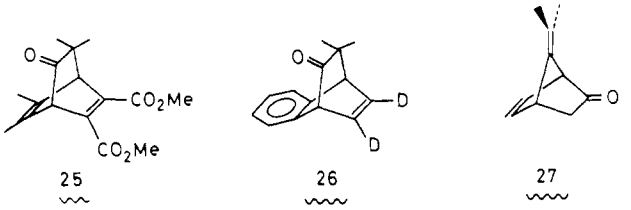


Figure 1. Shift reagent study of the isomers **13–15**. ^{1}H NMR chemical shift δ (in ppm) vs. amount of added shift reagent solution.

established with ^{1}H NMR, GLC, and HPLC.

Discussion

Several authors have sought in a given substrate for intramolecular competition[21a,b,22] between two DPM rearrangements and for intramolecular competition[21c-e,23,24] between the DPM and ODPM rearrangements. Luibrand observed[22] that upon irradiation of 3,3-dimethyl-2-methylenebicyclo[2.2.2]octa-5,7-diene (**19**) in acetone as triplet sensitizer only two DPM isomers were obtained, viz., **20** and **21** (Scheme IV). Both these isomers were formed by conversion of the triplet excited substrate into one and the same 1,4-biradical intermediate. The alternative DPM rearrangement in which the exocyclic double bond would be involved was not observed. In another study Luibrand reported[23a] that from the triplet-sensitized irradiation of 3,3-dimethylbicyclo[2.2.2]-octa-5,7-dien-2-one (**22**) only two DPM isomers were isolated, which resulted from cleavage of (only) *one* of the two possible 1,4-biradical intermediates and its subsequent conversion along *two* different pathways, i.e., via two 1,3-biradical intermediates, to the two DPM isomers **23** and **24**. There was no evidence for products resulting from an ODPM rearrangement. These results agree with those of Becker,[23b] who investigated several substituted dimethylbicyclo[2.2.2]octa-5,7-diene-5,6-dicarboxylates (**25**) that



25 **26** **27**

yielded only one DPM isomer. He proposed that only one of the two possible 1,3-biradical intermediates is formed from the initial 1,4-biradical, due to the difference in bond strength of the two unsaturated carbon–carbon bonds involved. The preferred 1,3-biradical leads to the DPM product by cyclopropanation over the dicarboxylated carbon–carbon bond.[25]

With the present substrate **1** the DPM isomer is the major product and the ODPM isomers are the minor ones. The preferred formation of the DPM isomer cannot be explained in terms of stabilization of the 1,3-biradical intermediates. A vinyl group would stabilize the 1,3-biradical intermediate of the ODPM rearrangement much better than an acetyl group would in the corresponding 1,3-biradical intermediate of the DPM rearrangement, and if this stabilization would be the decisive factor, then the major product would be the ODPM isomers. Instead we propose that the preferred formation of the DPM isomer must be explained in terms of relative stabilities of the initially formed 1,4-biradical intermediates (Scheme V). The π-bond strength is greater for the carbonyl than for the ethylene π-bond.[19b,26] In normal sterically nonconstrained dienones the formation of the 1,4-biradicals gives approximately the same energy release for the DPM and the ODPM rearrangement. On the assumption that the structure of the transition state is close to that of the resulting 1,4-biradicals it then follows that the major product will be the DPM isomer. The observation of additional formation of the ODPM isomers confirms our initial supposition (see the first two paragraphs of this section) that the regioselectivity in the barrelenones **22** and **25**[23] is much more determined by both the mutual interaction between the radical sites and the interaction of the radical sites with the carbon–oxygen π-bond in the triplet 1,4-biradicals of the "conjugated" DPM rearrangement[23b,27] than by the relative stability of the oxo- vs. the carbo-radical site. The absence of such interactions in the 1,4-biradical of the ODPM rearrangement disfavors the formation of this biradical. The same explanation, rather than the one advocated by Luibrand[23a] on the basis of the free rotor effect,[30] can be used for the barrelene **19** in which the exocyclic methylene group is not directly involved

(21) (a) M. Nitta, O. Inoue, and M. Tada, *Chem. Lett.*, 1065 (1977); (b) M. Nitta, I. Kasahara, and T. Kobayashi, *Bull. Chem. Soc. Jpn.*, **54**, 1275 (1981); (c) J. Ipaktschi, *Chem. Ber.*, **105**, 1840 (1972); (d) M. Nitta and H. Sugiyama, *Bull. Chem. Soc. Jpn.*, **55**, 1127 (1982); (e) A. Hassner, D. Middlemiss, J. M. Rust, and P. M. Rust, *Tetrahedron*, **38**, 2539 (1982).

(22) R. T. Luibrand and E. M. Fujinari, *J. Org. Chem.*, **45**, 958 (1980).

(23) (a) R. T. Luibrand, B. M. Broline, K. A. Charles, and R. W. Drues, *J. Org. Chem.*, **46**, 1874 (1981); (b) H. D. Becker and B. Ruge, *Ibid.*, **45**, 2189 (1980).

(24) R. S. Givens and W. F. Oettle, *J. Am. Chem. Soc.*, **93**, 3963 (1971).

(25) The schemes of the mechanisms of the DPM and ODPM rearrangements of **19**, **22**, and **25** via 1,4- and 1,3-biradicals as the subsequent intermediates are depicted in detail in the papers by Luibrand[22,23a] and Becker.[23b]

(26) S. L. Murov, "Handbook of Photochemistry", Marcel Dekker Inc., New York, 1973.

(27) It was recently pointed out by Verhoeven that transoid 1,4-biradicals are slightly more stabilized by through-bond interaction (TBI) than cisoid 1,4-biradicals as a result of σ assistance.[28a] The cisoid DPM 1,4-biradicals of the barrelenones **22** and **25**[23] have, however, an additional 1,3-biradical interaction in contrast with the corresponding transoid ODPM 1,4-biradicals in which the exocyclic C=O bond is involved. 1,3-Biradicals are stabilized by TBI over the two intermediate carbon–carbon bonds as a result of σ-assistance.[28b] This type of stabilization is absent in the transoid 1,4-biradicals of **22** and **25**,[23] and consequently rearrangements derived from these 1,4-biradicals, in which the exocyclic carbonyl bond is involved, do not occur. The 1,4-biradicals of **1**, shown in Scheme V, are all drawn cisoid, although the transoid configurations will be lower in energy on the basis of σ-assistance. The occurrence of a cisoid 1,4-biradical as a detectable intermediate has a precedent in the reported intermediate (Scaiano) formed upon photoexcitation of *cis*-2-ethylcyclopropyl phenyl ketone in a Norrish type II reaction.[29]

(28) (a) J. W. Verhoeven, private communication; (b) J. W. Verhoeven, *Recl. Trav. Chim. Pays-Bas*, **99**, 143, 369 (1980).

(29) J. C. Scaiano, *Acc. Chem. Res.*, **15**, 252 (1982).

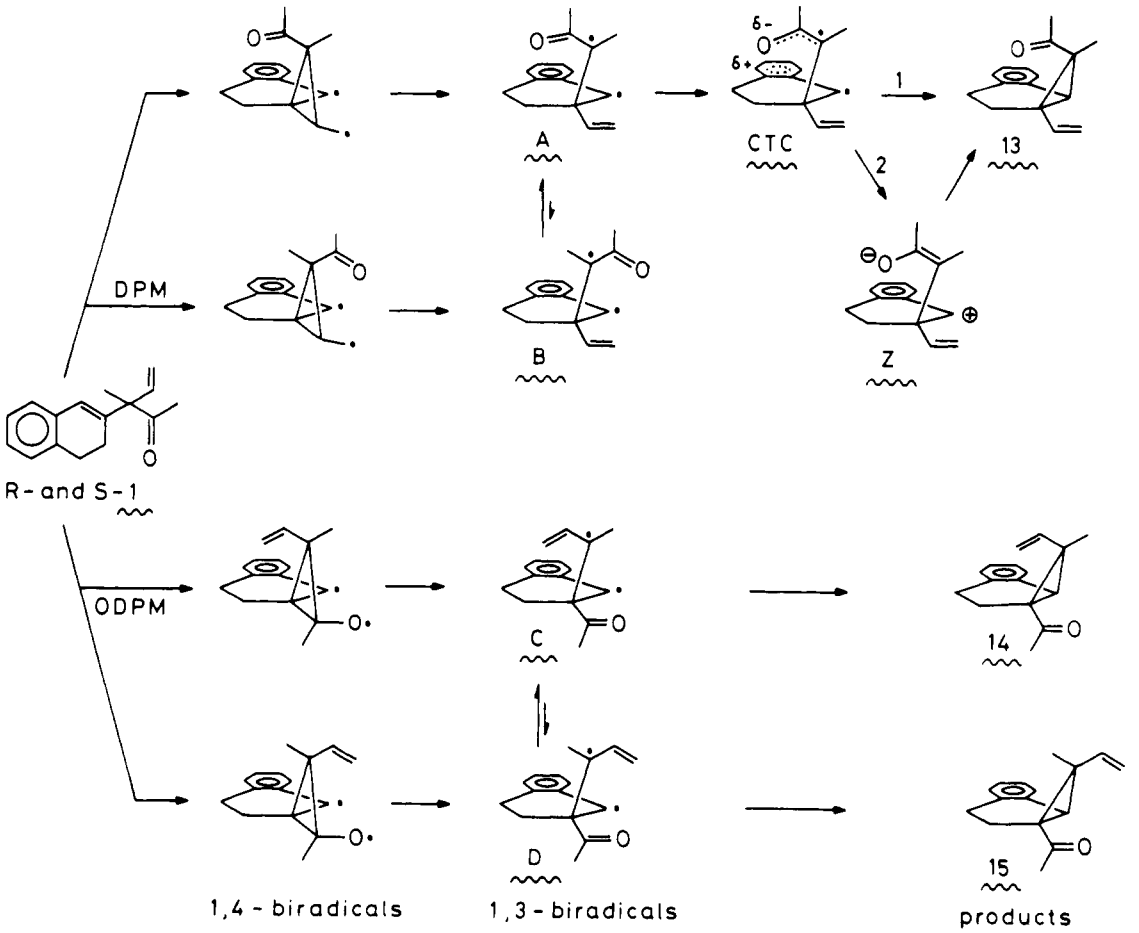
Table II. NOE Difference and Double Resonance Signals for **16** and **17**

compd	^{1}H NMR method	irradiated hydrogens[a] H(1)	H(3a)	H(3b)	H(4a)	H(4b)	H(8)	H_{trans}-(11)	H_{cis}-(11)	H(14)	H(15)	H(16)
16	NOE difference	I	–	–	–	–	+	–	–	–	–	+
		–	–	–	–	–	–	+	I	–	–	–
		–	–	–	–	–	–	–	+	I	–	–
		–	–	w	–	–	–	–	–	–	I	+
		+	–	–	–	–	–	–	–	–	+	I
16	double resonance	○	I	*	*	*	○	○	○	○	○	*
		○	○	○	○	○	○	I	*	○	○	○
		○	*	○	○	○	○	○	○	○	*	I

compd	NOE difference	H(1)	H(8)	H(12)	H(13)	H(15)	H_{trans}(16)	H_{cis}(16)
17		I	+	–	–	+	nd	nd
		+	–	I	nd	+	–	–
		–	–	–	I	+	–	–

[a] I = irradiated, nd = not detected, + = signal, – = no signal, w = weak signal, * = reduced multiplicity, ○ = no effect.

Scheme V. Mechanism for the Triplet Photosensitized Formation of the DPM and ODPM Products of **1**. Only One of the Two Possible Enantiomeric Structures of the Various Intermediates and Products is Shown

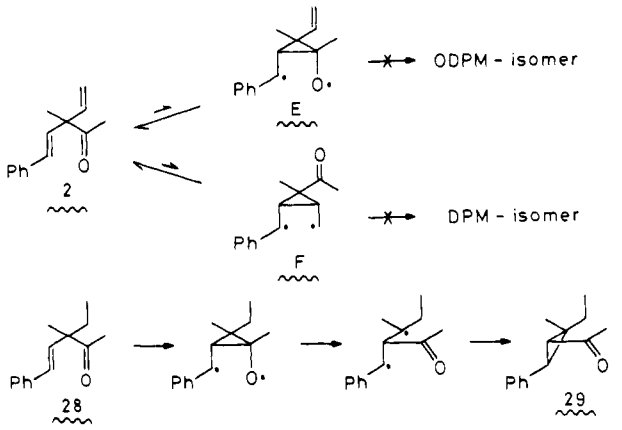


in the formation of the 1,4-biradicals.[22] There is, however, one exception. Givens and Oettle reported[24] that upon triplet photosensitization benzobarrelenone **26** undergoes an ODPM rearrangement in which in the initial step vinyl bridging occurred with the exocyclic carbonyl group; the alternative is energetically disfavored in view of the required loss of the resonance energy of the benzo moiety. Further, Ipaktschi[21c] reported that the irradiation of **27** yielded only one ODPM isomer. Clearly this must be the result of the relatively low degree of strain of the 1,4-biradical leading eventually to the ODPM product as compared with the strain in the three other possible 1,4-biradicals.

Finally our observation that there are only one DPM and two ODPM isomers deserves discussion. It is thought that formation of the DPM and ODPM products both proceeds via the 1,4- and 1,3-biradicals as the subsequent intermediates (Scheme V). Clearly two routes, viz., the DPM and ODPM one, are involved. The formation of only one DPM isomer is ascribed to the charge-transfer stabilization in the "cisoid" rotamer of the 1,3-biradical CTC in which the acetyl and phenylene groups are in

(30) (a) H. E. Zimmerman, F. X. Albrecht, and M. J. Haire, *J. Am. Chem. Soc.*, **97**, 3726 (1975); (b) H. E. Zimmerman and A. C. Pratt, *Ibid.*, **92**, 1409, 6259, 6267 (1970); P. S. Mariano, D. G. Watson, and E. Bay, *Tetrahedron*, **33**, 11 (1977); R. G. Weiss and G. S. Hammond, *J. Am. Chem. Soc.*, **100**, 1172 (1978); H. E. Zimmerman, K. S. Kamm, and D. P. Werthemann, *Ibid.*, **96**, 439, 7821 (1974).

Scheme VI



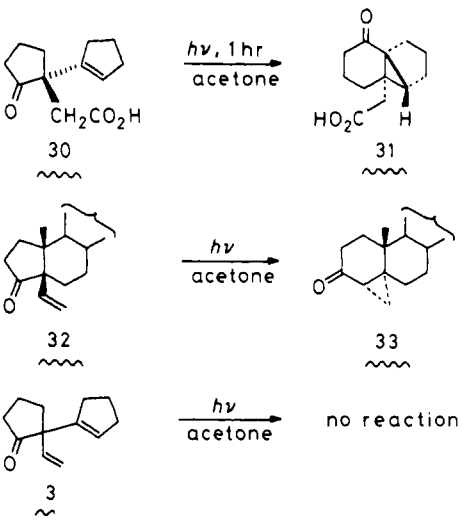
close vicinity and which cannot occur in the "transoid" rotamer B. Cyclopropanation of CTC will then yield the DPM isomer in which the acetyl and phenylene groups have a cis orientation, which is in fact the only observed DPM isomer, **13**. It is not known whether the charge-transfer complex CTC yields directly or by further charge separation via the zwitterion Z as intermediate the DPM isomer **13**. Although zwitterions rarely occur in photochemical reactions, they were established as intermediates in the well-known type A rearrangement of cyclohexadienones in which an allyl radical moiety transfers an electron to the alkoxy radical site.[31] In the present DPM rearrangement a similar electron transfer could occur between the benzyl and the enolate radical moieties. Attempts to trap the possible zwitterion intermediate Z in the DPM rearrangement with methanol did not lead to products derived from addition of methanol to the zwitterion in methanol: **13**, **14**, and **15** were formed in the same ratio as in benzene as solvent. As to the rotameric ODPM 1,3-biradicals there will be at most a weak charge-transfer interaction in the "cisoid" rotamer C which is absent in D. Accordingly, as expected,[13a] two ODPM isomers will be formed with **14** in excess of **15**, which is in fact observed.

At this point (cf. ref 32a) it is of interest to note that the proposed mechanism for the triplet-photosensitized conversion of **1** via 1,4-and 1,3-biradicals as the subsequent intermediates (cf. Scheme V) is in agreement with the stepwise mechanism proposed by Schaffner[32b] on the basis of his study on steroidal β,γ-enones of which the CD_3 and CH_3 substituents at the central carbon atom are completely racemized in the ODPM products.

The failure of dienone **2** to form any DPM or ODPM product may be ascribed either to radiationless decay of the triplet excited state of **2** or to rapid energy dissipation of the 1,4-biradicals E and F, which prevents the formation of 1,3-biradicals (Scheme VI). The carbon–carbon π-bond is broken more easily than the carbon–oxygen π-bond (see before), and accordingly the energy dissipation is thought[30] to proceed mainly via the 1,4-biradical F.[17] In this connection it is surprising that the related (*E*)-3-ethyl-3-methyl-5-phenylpent-4-en-2-one (**28**) yields upon triplet photosensitization the ODPM product **29**.[13a]

Finally we have investigated the dienone **3** for which it would be expected that both DPM and ODPM rearrangements proceed concertedly. A few examples of this type of rearrangements were reported.[14b,21a,b,33] However, upon triplet-sensitized irradiation of **3** in acetone no products have been observed at all. This

Scheme VII. Sensitized Irradiation of β,γ-Enones Which Exhibit a Concerted ODPM Rearrangement



contrasts with the rapid conversion of **30** and **32** into the ODPM isomers **31** and **33**, respectively (Scheme VII). The absence of the ODPM rearrangement with **3** may be explained in terms of *E–Z* isomerization of the vinyl group. It should be realized, however, that certain α-vinyl ketones[14b] and dienes[30a] lead with high efficiency to the ODPM and DPM product, respectively, via a *concerted* mechanism.

Experimental Section

Melting points were determined on a Reichert hot stage microscope and are uncorrected. Elemental analyses were performed at the Institute for Organic Chemistry, TNO, Utrecht. NMR spectra were recorded on a Varian A60-D, a Varian XL-100-15 FT (both ^1H) and a Bruker WM 250 (^1H and ^{13}C) spectrometer with Me_4Si as internal standard. IR spectra were taken with a Perkin-Elmer 257 grating infrared spectrophotometer and a Perkin-Elmer 298 instrument. The GLC analyses were carried out on a Varian Model 3700 chromatograph and the GLC separations were conducted with a Varian Model 2700 chromatograph. Mass spectra were obtained on a Varian MAT-711 double focusing mass spectrometer or a Varian AEI-MS-902 instrument equipped with an all-glass heated inlet system at 15 and 70 eV.

THF and ether were freshly distilled from sodium wire with benzophenone as indicator under a nitrogen atmosphere prior to use. *t*-BuOH was distilled from anhydrous K_2CO_3 and stored over molecular sieves (4 Å). Hexamethylphosphortriamide (HMPT) was distilled from CaH_2 and stored over molecular sieves (4 Å). Benzene was extracted 4 times with concentrated sulfuric acid, washed with water, dried over $MgSO_4$, distilled, and stored over sodium wire. $SOCl_2$ was purified as described.[34] All the synthetic and photochemical reactions have been performed under an atmosphere of dry nitrogen using flame-dried apparatus.

Methyl 2-(3,4-Dihydro-2-naphthyl)propanoate (5). To a solution of 5.15 g (51 mmol) of diisopropylamine in 250 mL of THF, was added 32.5 mL (49 mmol) of *n*-BuLi in hexane ($\simeq$1.5 mmol/mL) dropwise over 30 min at −78 °C, followed by addition of 10.5 g (59 mmol) of HMPT. The solution was stirred for 1 h and remained colorless. Then 10 g (49 mmol) of the ester **4**[35] was added slowly over 30–45 min. The solution immediately colored deep yellow and the solution was stirred for another hour. Finally the mixture was allowed to warm to −40 °C and 1.1 equiv (7.0 g) of MeI was added at once. The reaction mixture decolored to slightly yellow after 1 h. The temperature of the solution was then raised to −10 °C and the mixture was quenched with 10% aqueous NH_4Cl. The ester was extracted with ether, and the organic layer was washed with 5% aqueous HCl (twice), water, and brine and then dried with anhydrous $MgSO_4$. The solvents were removed under reduced pressure, leaving a yellow oil (10.2 g) of **5**. It was distilled at 98 °C (0.01 mmHg), yielding 9.3 g (43 mmol, 88%): ^1H NMR (CCl_4, 60 MHz) δ 6.90 (m, 4 H, Ar), 6.20 (br, s, 1 H, olefinic), 3.60 (s, 3 H, OCH_3), 3.8–3.0 (m, 1 H, methine), 3.5–3.0 (m, 2 H, methylene), 2.15–2.0 (m, 2 H, methylene), 1.30 (d, J = 7 Hz, 3 H, CH_3); IR (liquid capillary) 3070 (m), 3020 (m),

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2960 (s), 2955 (s), 2840 (m), 1735 (s), 1460 (s), 1440 (s), 1245 (s), 1205 (s), 1175 (s), 890 (m), 765 (s) cm^{-1}. Anal. Calcd for $C_{14}H_{16}O_2$: C, 77.25; H, 7.46. Found: C, 77.45; H, 7.37.

Methyl 2-(3,4-Dihydro-2-naphthyl)-2-[2-(phenylsulfinyl)-1-ethyl]-propanoate (7). Ester **5** (19.0 g) in 100 mL of benzene was added dropwise to 0.4 g of 55% sodium hydride suspension in 200 mL of dry benzene. After the addition the solution was stirred for 3 h. Then the solution was refluxed gently and a solution of phenyl vinyl sulfoxide **6** (13.0 g in 100 mL of dry benzene) was added during 1 h. After one night of refluxing the reaction mixture was cooled and extracted with 200 mL of 5% aqueous ammonium chloride. The organic layer was separated and washed with water. The combined water layers were extracted with benzene. The combined organic layers were extracted with brine and dried with $MgSO_4$ and the solvents were evaporated under reduced pressure to yield a very viscous oil (31 g), which failed to crystallize. Elution of the oil on SiO_2 using CH_2Cl_2 yielded about 150 mg of the unreacted ester **5**. By use of 30% ethyl acetate in dichloromethane as the subsequent eluent the sulfoxide **7** was obtained. The yield was 25 g (80%): ^1H NMR ($CDCl_3$, 60 MHz) δ 7.5–7.4 (m, 5 H, Ar), 7.0 (m, 4 H, Ar), 6.25 (br s, 1 H, olefinic), 3.6 (s, 3 H, OCH_3), 3.0–2.5 (m, 4 H), 2.4–1.9 (m, 4 H) (the eight methylene protons), 1.35 (s, 3 H, CH_3). The oil was very viscous and therefore no analytically pure sample could be obtained. It was slightly contaminated with the unsaturated sulfoxide **6** (TLC) and traces of solvents.

Methyl 2-Methyl-2-(3,4-dihydro-2-naphthyl)but-3-enoate (8). The sulfoxide **7** (28.0 g) was pyrolysed in a distillation flask at 200 °C and distilled in vacuo (0.03 mmHg). A colorless liquid distillate was obtained and became slightly yellow after some time. Slowly the temperature of the distillate increased from 110 to 145 °C, at which temperature the diphenyl disulfide was distilled off. The distillate was eluted on SiO_2 by using CH_2Cl_2 in hexane (1:4, v/v), yielding the disulfide; the ester **8** was subsequently collected by using a CH_2Cl_2–hexane mixture (1:1, v/v): yield 11.8 g (64%); ^1H NMR ($CDCl_3$, 60 MHz) δ 7.0 (s, 4 H, Ar), 6.2 (br s, 1 H, olefinic), 6.20 (dd, J = 10, 18 Hz, 1 H, olefinic), 5.18 (dd, J = 1.5, 10 Hz, 1 H, olefinic), 5.15 (dd, J = 1.5, 18 Hz, olefinic), 3.65 (s, 3 H, OCH_3), 2.7 (m, 2 H, methylene), 2.1 (m, 2 H, methylene), 1.50 (s, 3 H, CH_3); IR (liquid capillary) 3090 (w), 3060 (w), 2990 (m), 2890 (m), 2830 (m), 1735 (s), 1635 (m), 1600 (w), 1450 (m), 1430 (m), 1240 (s), 1110 (s), 920 (m), 750 (s) cm^{-1}. Anal. Calcd for $C_{16}H_{18}O_2$: C, 79.31; H, 7.49. Found: C, 78.92, H, 7.47.

2-Methyl-2-(3,4-dihydro-2-naphthyl)but-3-enoic Acid (9). The ester **8** (11.0 g) was hydrolized by refluxing it with 10% KOH in water containing 20% EtOH for 1 night. After cooling the reaction mixture was neutralized with 5% aqueous HCl to pH 4 and extracted with ether. The organic layer was washed with water and brine and dried over anhydrous $MgSO_4$, and the solvents were evaporated. The isolated solid acid **9** was dried over P_2O_5 for 2 days, yielding 10.2 g (98%) of the acid **9**: mp 85–88 °C; ^1H NMR ($CDCl_3$, 60 MHz) δ 7.1 (s, 4 H, Ar), 6.4 (br s, 1 H, olefinic), 6.30 (dd, J = 10, 18 Hz, 1 H, olefinic), 5.30 (dd, J = 1, 10 Hz, 1 H, olefinic), 5.20 (dd, J = 1, 18 Hz, 1 H, olefinic), 3.0–2.6 (m, 2 H, methylene), 2.4–2.0 (m, 2 H, methylene), 1.50 (s, 3 H, CH_3); IR ($CHCl_3$) 3300–2800 (br, m), 2940 (m), 2890 (m), 1705 (s), 1635 (w), 1485 (w), 1450 (w), 1270 (m), 925 (m) cm^{-1}. Anal. Calcd for $C_{15}H_{16}O_2$: C, 78.92; H, 7.06. Found: C, 78.62; H, 7.04.

3-Methyl-3-(3,4-dihydro-2-naphthyl)pent-4-en-2-one (1). Acid **9** (500 mg, 2.48 mmol) was dissolved in 25 mL of anhydrous benzene and the mixture was stirred in 2.5 mL of freshly distilled thionyl chloride for 4 h. The benzene and the excess of thionyl chloride were removed under reduced pressure. The remaining viscous oil, **10**, was dissolved in 25 mL of anhydrous ether. The resulting solution was injected rapidly into a solution of 1.2 equiv (2.97 mmol) of dimethyl cuprate[34] in 50 mL of anhydrous ether at −35 °C. The colorless cuprate solution became yellow immediately and a precipitate was formed. After 30 min the reaction mixture was warmed to 0 °C and quenched with 5% aqueous ammonium chloride. The water layer was washed with ether and the combined ether layers were washed with water and finally with brine and dried over $MgSO_4$. Then the ether was evaporated, leaving 330 mg of a yellow oil. Elution on SiO_2 with CH_2Cl_2 in hexane (3:7 v/v) as eluent afforded traces of the ester **8** and 292 mg (≃60%) of the colorless ketone **1**, which was further purified by preparative GLC: ^1H NMR ($CDCl_3$, 250 MHz) δ 7.2–7.0 (m, 4 H, Ar), 6.45 (s, 1 H, olefinic), 6.35 (dd, J = 10, 17 Hz, 1 H, olefinic), 5.30 (dd, J = 1.5, 10 Hz, 1 H, olefinic), 5.15 (dd, J = 1.5, 17 Hz, olefinic), 2.75 (m, 2 H, methylene), 2.15 (m, 2 H, methylene), 2.20 (s, 3 H, acetyl), 1.40 (s, 3 H, CH_3); IR (liquid capillary) 3060 (w), 3020 (w), 2980 (m), 2930 (m), 2880 (w), 2820 (w), 1720 (s), 1630 (w), 1485 (m), 1450 (m), 1350 (m), 920 (m), 760 (m), 750 (s) cm^{-1}. Anal. Calcd for $C_{16}H_{18}O$: C, 84.91; H, 8.02. Found: C, 85.13; H, 7.98.

The dienone **2** was prepared from **35** in a similar fashion as **1**.

Methyl (*E*)-2-Methyl-4-phenylbut-3-enoate (36). Alkylation of methyl (*E*)-4-phenylbut-3-en-1-oate (**35**)[17] with methyl iodide afforded 75% monomethylated ester **36**, which was contaminated with the dimethylated ester and the starting compound **35**. An analytical sample was obtained by preparative GLC: ^1H NMR (CCl_4, 60 MHz) δ 7.3–7.0 (m, 5 H, Ar), 6.40 (d, J = 16 Hz, 1 H, olefinic), 6.10 (dd, J = 6, 16 Hz, 1 H, olefinic), 3.60 (s, 3 H, OCH_3), 3.2 (m, 1 H, methine), 1.30 (d, J = 7 Hz, CH_3); IR (liquid capillary) 3100 (w), 3040 (w), 3000 (m), 2960 (m), 1735 (s), 1600 (w), 1500 (m), 1450 (m), 1250 (m), 1170 (s), 970 (s), 750 (s), 695 (s) cm^{-1}. Anal. Calcd for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42. Found: C, 75.68; H, 7.27.

Methyl 2-Methyl-2-[2-(phenylsulfinyl)-1-ethyl]-4-phenylbut-3-enoate (37). Reaction of **36** with **6** afforded 76% the sulfoxide addition product **37** as a crystalline compound. An analytical sample of the sulfoxide was obtained by recrystallization from CCl_4: mp 119–123 °C (170–180 °C dec); ^1H NMR ($CDCl_3$, 60 MHz) δ 7.5 (m, 5 H, Ar), 7.2 (m, 5 H, Ar), 6.3 (m, 2 H, olefinic), 3.65 (s, 3 H, OCH_3), 3.0–2.5 (br m, 2 H, methylene), 2.3–1.8 (br m, 2 H, methylene), 1.4 (s, 3 H, CH_3); IR ($CHCl_3$) 3090 (w), 3070 (w), 3010 (s), 2960 (m), 1750 (s), 1450 (s), 1440 (m), 1040 (s) cm^{-1}. Anal. Calcd for $C_{20}H_{22}SO_3$: C, 70.15; H, 6.48; S, 9.36. Found: C, 69.71; H, 6.42; S, 9.30.

Methyl 2-Methyl-2-vinyl-4-phenylbut-3-enoate (38). The sulfoxide **37** was heated in vacuo (0.05 mmHg) and started to decompose at 180 °C. The resulting ester **38** and diphenyl disulfide were distilled off at 110–130 °C. The ester was purified in the same way as described for **8** and an analytical sample was obtained by preparative GLC: ^1H NMR ($CDCl_3$, 60 MHz) δ 7.3–7.2 (m, 5 H, Ar), 6.35 (s, 2 H, olefinic), 6.10 (dd, J = 10, 18 Hz, 1 H, olefinic), 5.13 (dd, J = 2, 10 Hz, 1 H, olefinic), 5.10 (dd, J = 2, 18 Hz, 1 H, olefinic), 3.65 (s, 3 H, OCH_3), 1.45 (s, 3 H, CH_3); IR (liquid capillary) 3100 (m), 3070 (m), 3030 (s), 3020 (s), 2960 (s), 1750 (s), 1630 (m), 1500 (m), 1450 (s), 1440 (s), 1420 (s), 1250 (s), 1230 (s), 1210 (s), 990 (s), 975 (s), 700 (s) cm^{-1}. Anal. Calcd for $C_{14}H_{16}O_2$: C, 77.75; H, 7.46. Found: C, 77.45; H, 7.21.

(*E*)-2-Methyl-2-vinyl-4-phenylbut-3-enoic Acid (39). The ester **38** was saponified by refluxing it with 10% KOH in water containing 20% EtOH for one night. After it was cooled, the reaction mixture was treated as described before for **9**, yielding 94% of the acid **39**. Recrystallization from hexane afforded an analytical sample: mp 81–84 °C, ^1H NMR ($CDCl_3$, 60 MHz) δ 7.3 (m, 5 H, Ar), 6.4 (s, 2 H, olefinic), 6.20 (dd, J = 10, 17 Hz, 1 H, olefinic), 5.20 (dd, J = 0.5, 10 Hz, 1 H, olefinic), 5.20 (dd, J = 0.5, 17 Hz, 1 H, olefinic), 1.55 (s, 3 H, CH_3); IR ($CHCl_3$) 3050 (br m), 2650 (br m), 1700 (s), 1635 (m), 1600 (w), 1500 (w), 1450 (m), 1270 (m), 975 (m), 690 (m) cm^{-1}. Anal. Calcd for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98. Found: C, 76.98; H, 7.03.

(*E*)-3-Methyl-3-vinyl-5-phenylpent-4-en-2-one (2). The dienone **2** was prepared from **39** via the acid chloride **40** as described for compound **1**. Preparative GLC afforded an analytically pure sample: ^1H NMR (CCl_4, 60 MHz) δ 7.2 (m, 5 H, Ar), 6.35 (s, 2 H, olefinic), 6.10 (dd, J = 10, 17 Hz, 1 H, olefinic), 5.20 (dd, J = 1, 10 Hz, 1 H, olefinic), 5.10 (dd, J = 1, 17 Hz, 1 H, olefinic), 2.15 (s, 3 H, acetyl), 1.40 (s, 3 H, CH_3); IR (liquid capillary) 3080 (w), 3060 (w), 2980 (s), 2940 (m), 1720 (s), 1630 (m), 1600 (w), 1500 (m), 1450 (s), 1350 (s), 980 (s), 920 (s), 750 (s), 700 (s) cm^{-1}. Anal. Calcd for $C_{14}H_{16}O$: C, 83.96; H, 8.05. Found: C, 83.67; H, 8.01.

2-Cyclopent-1-enyl-2-[2-(phenylsulfinyl)-1-ethyl]cyclopentanone (12). A solution of 4.4 g of cyclopentylidenecyclopentanone (**11**) in 20 mL of *t*-BuOH was added dropwise to 0.28 g of *t*-BuOK dissolved in 80 mL of *t*-BuOH. After the solution was stirred for 2 h at room temperature a solution of phenyl vinyl sulfoxide **6** (4.0 g) in 50 mL of *t*-BuOH was added slowly (during 8 h) under reflux. After one night of refluxing the solution was cooled and the solvent evaporated in part. The sulfoxide **12** was extracted with chloroform and the extract washed with water. The solvent of the organic layer was evaporated. From the residue 1.2 g of the ketone **11** was recovered by column chromatography on SiO_2 with CH_2Cl_2 as eluent. Sulfoxide **12** (5.0 g, 57%) was isolated by using subsequently CH_2Cl_2 in EtOAc (7:4 v/v). The sulfoxide **12** was slightly contaminated with **6** and traces of ethyl acetate. ^1H NMR ($CDCl_3$, 60 MHz) δ 7.5 (br s, 5 H, Ar), 5.5–5.3 (m, 1 H, olefinic), 3.0–2.5 (m, 2 H, CH_2SO), 2.4–1.5 (m, 14 H). IR (liquid capillary) 3000 (s), 2970 (s), 2880 (m), 2860 (m), 1770 (s), 1760 (s), 1660 (s), 1450 (s), 1050 (s), 990 (s) cm^{-1}.

2-Cyclopent-1-enyl-2-vinylcyclopentanone (3). The sulfoxide **12** was pyrolized at 180–200 °C (1 mmHg) and the distillate eluted with CH_2Cl_2 in hexane (1:4 v/v) to remove diphenyl disulfide and subsequently with CH_2Cl_2 in hexane (1:1 v/v) to obtain dienone **3**. An analytical sample was obtained by preparative GLC: ^1H NMR (CCl_4, 60 MHz) δ 5.4 (dd, J = 10, 17 Hz, 1 H, olefinic), 4.85 (br t, J = 2 Hz, 1 H, olefinic), 4.50 (dd, J = 1.5, 10 Hz, 1 H, olefinic), 4.40 (dd, J = 1.5, 16 Hz, 1 H, olefinic), 2.4–1.4 (m, 12 H); IR (liquid capillary) 3080 (m), 3050 (m), 2950 (s), 2880 (s), 2840 (s), 1735 (s), 1630 (m), 1450 (m), 1040 (m), 995 (m), 920 (m) cm^{-1}. Anal. Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 81.62; H, 9.12.

Photochemical Experiments. The irradiations were carried out in a Rayonet RPR-208 photoreactor, equipped with eight RUL 3500 lamps and Pyrex vessels and a Rayonet RPR-204 photoreactor, equipped with four RUL 2537 lamps and quartz vessels.

Isolation of the Photoproducts. The excess of the sensitizer 4-benzoylbiphenyl was removed by crystallization from *n*-hexane. Then the residual oil was separated by high-pressure LC with a 20 cm × 4.6 cm column packed with 10-μm Nucleosil. The eluent was 0.20% CH_3CN in hexane at a flow rate of 4.2 mL/min, yielding three bands: band A, retention time 5.0 min, 34 mg of ODPM isomers **14** and **15**; band B, retention time 5.5 min, 15 mg of 4-benzoylbiphenyl; band C, retention time 7.0 min, 52 mg of DPM isomer **13**.

Fraction A: ^{1}H NMR ($CDCl_3$, 250 MHz) δ 7.4–7.0 (m, 4 H, Ar), 6.03 (dd, J = 9, 17 Hz, 1 H, olefinic H of **14**), 5.67 (dd, J = 10, 16 Hz, 1 H, olefinic H of **15**), 5.30–5.05 (m, 4 H, methylene H's of **14** and **15**), 2.8–2.5 (m, 2 H), 2.4–2.2 (m, 4 H), 2.17 (s, 3 H, acetyl H's of **15**), 1.90 (s, 3 H, acetyl H's of **14**), 1.85–1.60 (m, 2 H), 1.38 (s, 1 H, cyclopropyl H of **14**), 1.08 (s, 1 H, cyclopropyl H of **15**); IR (liquid capillary) 3060 (w), 3050 (w), 2980 (m), 2940 (m), 2870 (m), 1705 (s), 1630 (w), 1490 (m), 1450 (m) 1355 (m), 765 (m), 750 (m), 740 (m) cm^{-1}. (N.b.: Fraction A contained about equal amounts of **14** and **15**.)

Fraction C: ^{1}H NMR ($CDCl_3$, 250 MHz) δ 7.35–6.95 (m, 4 H, Ar), 6.04 (dd, J = 11, 16 Hz, 1 H, olefinic), 5.21 (dd, J = 1.5, 11 Hz, 1 H, olefinic), 5.18 (dd, J = 1.5, 17 Hz, 1 H, olefinic), 2.73–2.57 (m, 1 H), 2.40–2.15 (m, 2 H), 2.00–1.80 (m, 1 H), 1.90 (s, 3 H, acetyl), 1.35 (s, 3 H, methyl), 1.26 (s, 1 H, cyclopropyl); IR (liquid capillary) 3060 (w), 3020 (w), 2930 (m), 2880 (w), 1700 (s), 1630 (w), 1490 (m), 1450 (w), 1355 (m), 770 (m), 750 (m), 740 (m) cm^{-1}.

Pyrolysis of the DPM and ODPM isomers. The isomers **16** and **17** were isolated by preparative GLC by using a copper column, 5 m × 0.25 in. with Chromosorb W-AW (60–80 mesh) coated with 15% DC-550 at 260 °C. The carrier gas employed was helium at a flow rate of 60 mL/min. Upon pyrolysis of **13**, a new compound, viz. the isomer **16**, was obtained: ^{1}H NMR ($CDCl_3$, 250 MHz) δ 7.15–7.00 (m, 3 H, Ar), 7.00–6.90 (m, 1 H, Ar), 6.05 (s, 1 H, H_Z olefinic), 5.38 (q, J = 7 Hz, 1 H, olefinic), 5.28 (s, 1 H, H_E olefinic), 5.18 (s, 1 H, aliphatic), 2.98–2.85 (m, 1 H), 2.83–2.70 (m, 1 H), 2.60–2.40 (m, 1 H), 2.32 (s, 3 H, acetyl), 2.25–2.13 (m, 1 H), 1.73 (dd, J = 2, 7 Hz, 3 H, methyl); IR (liquid capillary) 3100 (w), 3060 (m), 3020 (m), 2940 (m), 2920 (s), 2850 (m), 1680 (s), 1620 (m), 1490 (m), 1450 (m), 1360 (m), 1235 (m), 1115 (m), 1100 (m), 940 (m), 700 (w), 675 (m) cm^{-1}. Anal. Calcd for $C_{16}H_{18}O$: C, 83.96; H, 8.05. Found: C, 83.60; H, 8.02. High-resolution mass spectrum (70 eV): calcd for $C_{14}H_{16}O$, m/z 226.1355; found, m/z 226.1355.

Upon pyrolysis of the mixture of **14** and **15**, complete conversion into one new isomer, viz., **17**, was observed: ^{1}H NMR ($CDCl_3$, 250 MHz) δ 7.5–7.1 (m, 4 H, Ar), 5.95 (dd, J = 9, 16 Hz, 1 H, olefinic), 5.18 (dd, J = 1, 9 Hz, 1 H, olefinic), 5.17 (s, 1 H, aliphatic), 5.09 (dd, J = 1, 16 Hz, 1 H, olefinic), 2.75–2.60 (m, 2 H), 1.95–1.75 (m, 2 H), 1.77 (s, 3 H, acetyl), 1.56 (s, 3 H, methyl); IR (liquid capillary) 3080 (m), 3060 (m), 3020 (m), 2920 (s), 2880 (m), 2850 (m), 1705 (s), 1660 (m), 1490 (m), 1450 (s), 1430 (s), 1385 (s), 1210 (m), 1160 (m), 985 (s), 940 (s), 910 (s), 700 (w), 650 (m) cm^{-1}. Anal. Calcd for $C_{16}H_{18}O$: C, 83.96; H, 8.05. Found: C, 83.70; H, 8.03. High-resolution mass spectrum (70 eV): calcd for $C_{14}H_{16}O$, m/z 226.1355; found, m/z 226.1356.

Eu(fod)$_3$ Complexation. For the Eu(fod)$_3$ experiments a solution Eu(fod)$_3$, purchased from Aldrich Chemical Co. (Gold Label 99%), in deuterated chloroform was used (50 mg/mL). This solution was added (in portions) to a solution of 1 mg/0.3 mL of isomer in $CDCl_3$.

Attempted Trapping of the DPM Intermediate with MeOH.[36] A solution of **1** (10 mg/mL) was irradiated at λ 350 nm in methanol with 4-benzoylbiphenyl as triplet sensitizer (10 mg/mL). After 35 min **1** had disappeared and the irradiation mixture was treated in the same way as described under isolation of the photoproducts. The ^{1}H NMR spectrum consisted of the same absorptions of **13–15** in the same ratio as observed for the irradiation of **1** in benzene.

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Registry No. (±)-**1**, 85553-98-6; (±)-(*E*)-**2**, 85553-99-7; (±)-(*Z*)-**2**, 85554-00-3; (±)-**3**, 85554-01-4; **4**, 41791-31-5; (±)-**5**, 85554-02-5; **6**, 20451-53-0; **7**, 85554-03-6; (±)-**8**, 85554-04-7; (±)-**9**, 85554-05-8; **11**, 825-25-2; **12**, 85554-06-9; (±)-**13**, 85611-56-9; (±)-**14**, 85611-57-0; (±)-**15**, 85611-58-1; (±)-(*Z*)-**16**, 85554-07-0; (±)-(*Z*)-**17**, 85554-08-1; (*E*)-**35**, 34541-74-7; (±)-(*E*)-**36**, 85554-09-2; (*E*)-**37**, 85554-10-5; (±)-(*E*)-**38**, 85554-11-6; (±)-(*E*)-**39**, 85554-12-7.

(36) D. J. Patel and D. I. Schuster, *J. Am. Chem. Soc.*, **90**, 5137 (1968).

Four-at-Once Dedeuteration of Cyclopentanone-2,2,5,5-d_4[1]

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Abstract: In aqueous solutions containing 3-(dimethylamino)propylamine (**1**) or 2,2-dimethyl-3-(dimethylamino)propylamine (**2**), cyclopentanone-2,2,5,5-d_4 undergoes dedeuteration largely by forming iminium ions. In the iminium ions deuterium is exchanged with the solvent via internal basic catalysis by the dimethylamino group from the catalyst. At most pH's studied the most common result of iminium-ion formation was exchange of all four deuterium atoms from the ketone. This contrasts with earlier studies of acetone-d_6 and certain diamines, in which the most common result of iminium-ion formation was exchange of all three deuterium atoms on one side of the ketone. Apparently, in the present case, but not in the earlier cases, the intermediate iminium ion undergoes cis–trans isomerization more rapidly than it is hydrolyzed back to ketone. It is proposed that this isomerization can take place via reaction of the iminium ion with a second molecule of diamine catalyst to give a *gem*-diamine or *gem*-diamine derivative that can revert to either geometric isomer of the iminium ion. Rapid transimination via *gem*-diamine formation apparently also takes place in the presence of other primary amines. The dedeuteration of cyclopentanone-d_4 catalyzed by 0.005 M **1** was studied in the presence of added 2-(dimethylamino)ethylamine (**3**), an amine that forms iminium ions rapidly but is a poor catalyst for deuterium exchange. At about pH 8, 0.05 M **3** increases the rate of formation of the iminium ions derived from cyclopentanone and **1** by about 16-fold; simultaneously, the ratio of the rate of dedeuteration to the rate of hydrolysis of these iminium ions decreases by about 16-fold. Other possible mechanisms for cis–trans isomerization of the intermediate iminium ions are discussed as are reasons why such isomerization is faster than iminium-ion hydrolysis in some cases but not in others.

Three types of α-hydrogen exchange have been observed for ketones. (1) Many achiral monofunctional bases and acids give one-at-a-time exchange nonstereoselectively.[2-5] (2) Certain primary–tertiary diamines give exchange by the mechanism shown

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