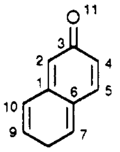
Table VIII. ΔP Values from MNDO-CI Calculations on the Naphthalenone System



bond	ΔP values		
	T_1	T_2	T_3
1-2	−0.50	−0.37	−0.37
4-5	−0.11	−0.27	−0.11
6-7	−0.30	−0.30	−0.24
9-10	−0.17	−0.25	−0.13
3-11	−0.14	−0.14	−0.16
2-3	+0.12	+0.15	+0.15
3-4	+0.06	+0.05	+0.07
5-6	+0.14	+0.18	+0.11
1-6	+0.25	+0.12	+0.21
1-10	+0.13	+0.17	+0.07

electrons was done on the geometry-optimized species of interest to obtain the energies of upper excited states. The bond orders reported are those obtained from the appropriate linear combination of Slater determinants for each CI eigenstate. Single-point ab initio calculations were also performed on the MNDO-optimized geometry of the naphthalenone system using the GAMESS package.[36] Table VIII gives the ΔP values for the naphthalenone system. State energies for species **31***, **33***, and the MNDO and ab initio energies of the triplet excited states for the naphthalenone system are given in Tables 16 and 17 of the supplementary material.

Acknowledgment. Support of this research by the National Science Foundation and NIH Grant GM07487 is gratefully acknowledged. The synthetic portions were supported by the National Institutes of Health while the mechanistic aspects were supported by NSF.

Registry No. **1**, 123208-69-5; **2**, 123208-70-8; **3**, 123208-71-9; **4**, 123208-72-0; **5**, 4528-64-7; **6**, 123208-73-1; **7**, 123208-74-2; **8**, 123208-75-3; **9**, 123208-76-4; **10**, 123208-77-5; **10** (acetate), 123208-78-6; **12**, 123208-79-7; **13**, 123208-80-0; **13** (acetate), 123208-83-3; **14**, 123208-81-1; **15**, 123208-82-2; **17**, 591-31-1; **18**, 123208-84-4; **19**, 123208-85-5; **20**, 72913-59-8; **21**, 123208-86-6; **22**, 123208-87-7; **23**, 123208-88-8; **24**, 123208-89-9; **25**, 123208-90-2; **26**, 123208-91-3; **28**, 123208-92-4; **29**, 123208-93-5; **30a**, 123208-94-6; **30b**, 123285-87-0; **30c**, 123285-88-1; **30d**, 123285-89-2; **48a**, 123208-99-1; **48b**, 123285-90-5; MVK, 78-94-4; HCOOEt, 109-94-4; $BrCH_2COOEt$, 105-36-2; 2-cyclohexen-1-one, 930-68-7; 4,4a,5,6-tetrahydro-2(3*H*)-naphthalenone, 123208-96-8; 4,4a,5,6,10,10a-hexahydro-2(3*H*)-anthracenone, 123208-97-9; 6,6-diphenyl-3-(phenylseleno)-4,4a,5,6-tetrahydro-2(3*H*)-naphthalenone (isomer 1), 123208-95-7; 6,6-diphenyl-3-(phenylseleno)-4,4a,5,6-tetrahydro-2(3*H*)-naphthalenone (isomer 2), 123208-98-0.

Supplementary Material Available: ORTEP drawings and tables of positional parameters, interatomic distances, bond angles, and temperature factors for compounds **1**, **2**, **4**, **10**, **12**, **13**, **14**, **29**, **30a**, **30b**, and **30c**, primary quantum yield data, and additional state energies (59 pages). Ordering information is given on any current masthead page.

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[36] Ab initio calculations were performed with the GAMESS package written by Dupuis, M.; Spangler, D.; Wendoloski, J. J. NRCC, Berkeley, CA.

Photochemistry of (±)-4,4a,5,6-Tetrahydro-4a-methyl-6,6-diphenyl-2(3*H*)-naphthalenone, a Rigid Linear Dienone[1]

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Received June 2, 1989

The rigid linear dienone, (±)-4,4a,5,6-tetrahydro-4a-methyl-6,6-diphenyl-2(3*H*)-naphthalenone (**4**), was synthesized, and its photochemistry was studied. Irradiation in *tert*-butyl alcohol through Pyrex resulted in a normal photoenone rearrangement involving the γ,δ double bond and one of the C-6 geminal phenyls to give products **8** and **9**, incorporating the trans and cis diphenyl [3.1.0] bicyclic subunits, respectively. The reaction was observed to parallel that of the parent 4,4-diphenyl-2-cyclohexen-1-one with comparable stereoselectivity for trans-oriented phenyls in the final product. Finally, the angular methyl exerts a strong steric effect on the reaction such that the three-ring in the final product is anti to this group. Observations suggest that the *trans*- and *cis*-diphenyl photoproducts derive from both primary and secondary processes leading to a photostationary mixture which favors the trans isomer. Finally, it was observed that the trans photoproduct is quantitatively converted back to starting dienone with catalytic acid; the cis product was observed to be stable under these same acidic conditions.

Introduction

One branch of our work has focused on extending studies of the photochemical 4,4-diaryl-2-cyclohexen-1-one rearrangement. The parent reaction, depicted in eq 1, was first described[3] in 1964 and has been thoroughly studied.[4] Low-conversion photolysis of **1** at 300–340 nm $(n \rightarrow \pi^*)$, leads to the formation of the *trans*- and *cis*-5,6-diphenylbicyclo[3.1.0]hexan-2-ones (**2t** and **2c**, respectively) in a ratio of ca. 140:1 as well as a small amount of 3,4-diphenyl-2-cyclohexen-1-one (**3**). Throughout our efforts in this area, this pioneering study has served as a benchmark for comparison of product structures, reaction ste-

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[1] (a) This work was presented at the 197th National ACS Meeting in Dallas, TX, April 1989; ORGN 212. (b) As this work was in progress, we learned that a similar molecule had been studied by H. E. Zimmerman and P. H. Lamers, see accompanying paper. We acknowledge and appreciate several useful suggestions made by the above authors.

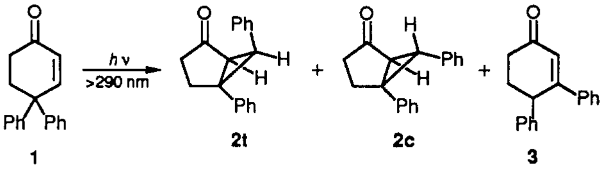
[2] (a) Author to whom correspondence regarding the photochemistry should be addressed. (b) Author to whom correspondence regarding the crystallographic determinations should be addressed.

[3] Zimmerman, H. E.; Keese, R.; Nasielski, J.; Swenton, J. S. *J. Am. Chem. Soc.* 1966, *88*, 4895–4904.

[4] (a) Zimmerman, H. E.; Hancock, K. G. *J. Am. Chem. Soc.* 1968, *90*, 3749–3760. (b) Zimmerman, H. E.; Hancock, K. G.; Licke, G. C. *J. Am. Chem. Soc.* 1968, *90*, 4892–4911. (c) Zimmerman, H. E. *Tetrahedron* 1974, *30*, 1617–1628.

0022-3263/89/1954-5804$01.50/0

reoselectivity, and mechanistic interpretation. We report, here, the synthesis and photochemistry of (±)-4,4a,5,6-tetrahydro-4a-methyl-6,6-diphenyl-2(3*H*)-naphthalenone (**4**), an analogue of compound **1** having an extended π system.



(1)

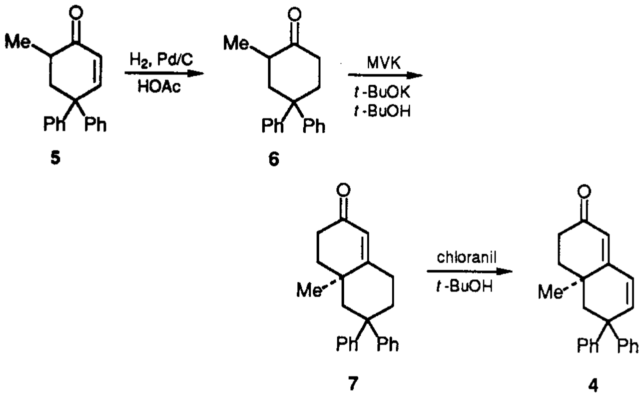
Our initial objective was to determine whether the rearrangement would proceed in the extended dienone system. If reaction occurred, the degree of stereoselectivity in the phenyl migration and the effect of the angular methyl on the product stereochemistry were important questions. The methyl group was incorporated into our substrate to preclude aromatization, help control the regiochemistry of double bond introduction, and prevent migration of the double bond to the β,γ position during irradiation. Finally, with the extended conjugation, it was hoped that further information would be gleaned regarding the energy requirements of the reaction.

Earlier investigations of linear dienone photochemistry[5,6] have shown several characteristic reaction modes depending upon the structure of the substrate. Acyclic 2,4-pentadienone derivatives are generally observed to undergo cis–trans isomerization reactions. Linear homoannular cyclohexadienones rearrange to bicyclohexenones or to diene ketenes, which further react with alcohol solvents. Finally, heteroannular dienones normally do not show any notable unimolecular photoreactivity but, instead, dimerize or enter into reactions with added olefins. The lone exception to this is found in steroidal dienones where intramolecular reactions have been observed when radical-stabilizing functionality (e.g. ethers and alkenes) is present on the angular carbon bound to C-10. These reactions involve hydrogen abstraction by the α-carbon of the excited enone followed by cyclization at the β-enone carbon. In the current substrate, phenyls are positioned such that phenyl migration can occur. Thus, we expected a priori that some normal enone rearrangement would be observed.

Results

Synthesis of the Photoreactant. The synthesis of the photosubstrate used in this study is outlined in Scheme I. The methylated enone **5** was prepared according to the general procedure of Zimmerman and co-workers[4] for the synthesis of the unsubstituted enone. Hydrogenation of this compound[7] followed by Robinson annulation yielded the fused enone **7**. Finally, oxidation of **7** with chloranil in *tert*-butyl alcohol[8] gave the desired (±)-4,4a,5,6-tetrahydro-4a-methyl-6,6-diphenyl-2(3*H*)-naphthalenone (**4**). The overall yield for the sequence was 8.2%.

Scheme I



Exploratory Photochemistry and Structure Elucidation of the Products. The photochemical reactions were carried out using conditions comparable to those reported for 4,4-diphenyl-2-cyclohexen-1-one.[9] Irradiation of a 10^{-3} M solution of **4** in degassed *tert*-butyl alcohol through a Pyrex filter using a 450-W medium-pressure Hanovia immersion apparatus led to the formation of two photoproducts, **8** and **9**. NMR, IR, and UV spectra indicated that both products were α,β-unsaturated cyclohexenyl ketones. Comparison of the high field ^{1}H NMR spectrum of the compounds showed a strong resemblance to the [3.1.0] bicyclic products isolated from the photolysis of 4,4-diphenyl-2-cyclohexen-1-one with the major product **8** resembling the isomer having trans-oriented phenyls. Most notable were the coupling constants for the cis-oriented methine protons (J_{cis} = 9.7 Hz) on the three-ring of the *trans*-diphenyl isomer **8** and for the trans-oriented protons (J_{trans} = 3.4 Hz) on the cyclopropyl of the *cis*-diphenyl isomer **9**.[10] These coupling constants also compared well with those encountered in our previous work.[11]

The orientation of the three-ring relative to the angular methyl was established by a series of spectroscopic observations. In a ^{1}H NOE difference experiment,[12] irradiation of H_8 in **8** led to an 11.6% enhancement in the signal intensity of H_1 and a 6.4% enhancement in the signal for H_7. In **9**, similar irradiation of H_8 resulted in a signal enhancement of 13.3% for H_1 but only 3.0% for H_7. Irradiation of the angular methyl group, on the other hand, showed no enhancement of the H_7 signal as one would expect from a syn cis isomer. A syn trans isomer was ruled out due to the absence of an upfield methyl signal which would have resulted from shielding by the endo phenyl.[10b] The shielding effect of the aromatic ring was most strongly exerted on the α proton at C-4. The signal for $H_{4\alpha}$ was observed as a doublet of triplets at δ 0.98, which is consistent with the anti trans diphenyl structure. In **9**, the cis phenyl rings have a perpendicular orientation relative to one another causing shielding of one set of ortho protons to δ 6.78. Finally, the structures of the two photoproducts were confirmed by single-crystal X-ray structure determinations, which clearly show the stereochemical relationships of the phenyls and the orientation of the three-ring relative to the angular methyl. The ORTEP

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(5) (a) Horspool, W. M. *Photochemistry* **1973**, *4*, 513–577. (b) *Ibid.* **1974**, *5*, 345–407. (c) *Ibid.* **1976**, *7*, 246–299. (d) *Ibid.* **1977**, *8*, 262–313. (e) *Ibid.* **1979**, *10*, 298–357. (f) *Ibid.* **1980**, *11*, 301–361.

(6) Schaffner, K.; Demuth, M. In *Rearrangements in Ground and Excited States*; deMayo, P., Ed.; Academic Press: New York, 1980; Vol. 3, pp 281–348.

(7) Bordwell, F. G.; Wellman, K. M. *J. Am. Chem. Soc.* **1963**, *28*, 2544–2550.

(8) Agnello, E. J.; Laubach, G. D. *J. Am. Chem. Soc.* **1960**, *82*, 4293–4299.

(9) Zimmerman, H. E.; Wilson, J. W. *J. Am. Chem. Soc.* **1964**, *84*, 4036–4042.

(10) (a) Becker, E. D. *High Resolution NMR*; Academic Press: New York, 1969; p 96. (b) Zimmerman, H. E; Weber, A. M. *J. Am. Chem. Soc.* **1989**, *111*, 995–1007.

(11) Bunce, R. A.; Holt, E. M. *J. Org. Chem.* **1987**, *52*, 1549–1554.

(12) (a) Bell, R. A.; Saunders, J. K. In *Topics in Stereochemistry*; Eliel, E. L., Allinger, N. L., Eds.; Wiley Interscience: New York, 1973; Vol. 7, Chapter 1. (b) Croasmun, W. R.; Carlson, R. M. K. in *Two Dimensional NMR Spectroscopy: Applications for Chemists and Biochemists*; Croasmun, W. R., Carlson, R. M. K., Eds.; VCH Publishers: New York, 1987, Chapter 7. (c) Martin, G. E.; Zektzer, A. S. *Two-Dimensional NMR Methods for Establishing Molecular Connectivity: A Chemist's Guide to Experiment Selection, Performance, and Interpretation*; VCH Publishers: New York, 1988, Chapters 6 and 7.

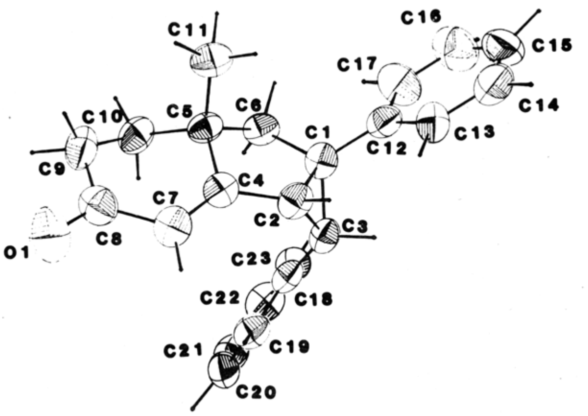


Figure 1. ORTEP diagram for photoproduct **8**.

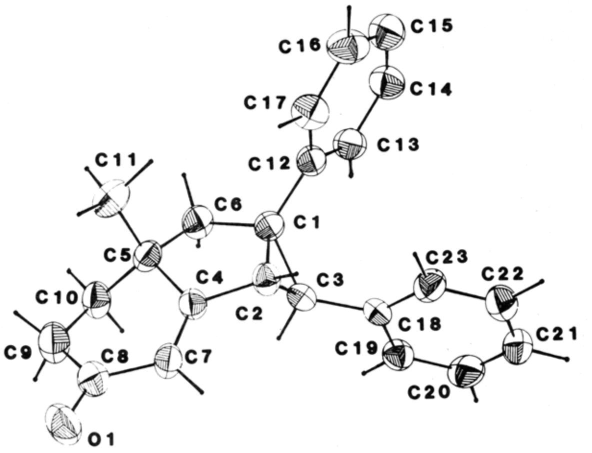


Figure 2. ORTEP diagram for photoproduct **9**.

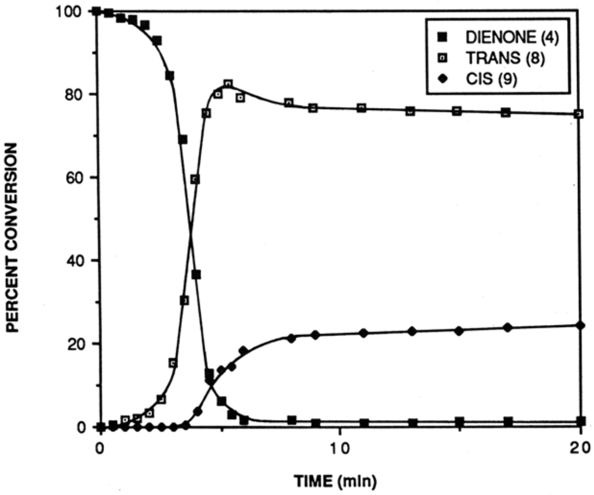
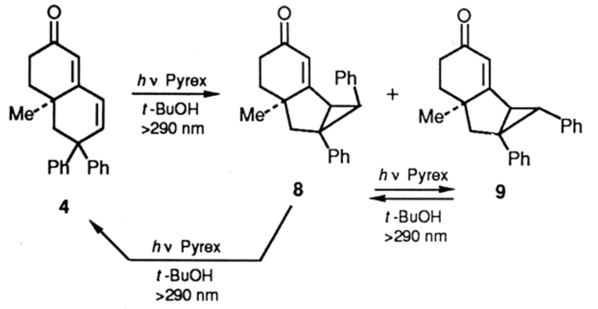
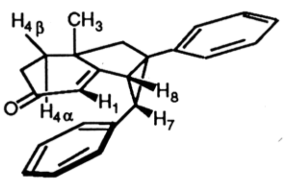


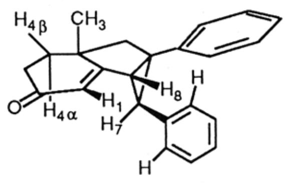
Figure 3. Reaction profile for irradiation of **4**.

Scheme II





8



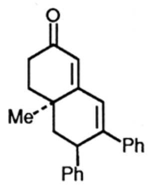
9

diagrams for (±)-(1α,1aβ,5aβ,6aβ)-1a,4,5,5a,6,6a-hexahydro-5a-methyl-1,6a-diphenylcycloprop[*a*]inden-3(1*H*)-one (**8**) (molecule A of the two molecules contained in the acentric unit cell) and (±)-(1α,1aα,5aα,6aα)-1a,4,5,5a,6,6a-hexahydro-5a-methyl-1,6a-diphenylcycloprop[*a*]inden-3-(1*H*)-one (**9**) are given in Figures 1 and 2, respectively.

Compound **8**, the trans diphenyl product, was produced rapidly and appeared initially to be the only photoproduct but, at conversions greater than 30.5%, the *cis*-diphenyl compound **9** was also observed. With longer irradiation times, it became clear that some of compound **9** was formed at the expense of **8**. Independent irradiations of **8** and **9** resulted in interconversion of the two isomers with some return to **4** occurring from **8**. The photochemistry of compound **4** is summarized in Scheme II.

Reaction Profiles and the Behavior of the Photoproducts. Figure 3 depicts the reaction profile for the irradiation of compound **4** performed as described above. Aliquots were removed every 30–90 s without interrupting the photolysis, and the reaction was essentially complete (97% conversion) in 5.5 min. At this point, 83% of the product was compound **8**. Photoproduct **9** was not observed until 30.5% conversion, where 0.3% could be reproducibly detected by GC. Due to this detection limit, it was not possible to unequivocally ascribe the production of **9** to a primary photoprocess. Nevertheless, the 30.2:0.3 mixture of **8**:**9** at this stage of the reaction corresponds to a ca. 100:1 ratio of trans:cis—very comparable to the 140:1 ratio reported for the parent case.^{4,9}

Extended irradiation of **4** resulted in conversion to a photostationary mixture composed of a 76:23:1 ratio of trans:cis:dienone (**8**:**9**:**4**). This equilibrium mixture was obtained after 20 min and remained unchanged even after 6 h. A similar mixture was also formed after irradiation of either **8** or **9** for 30 min. In this latter reaction, a small amount (ca. 1.5%) of the dienone **4** was detected as an intermediate in the reaction of the trans but not in the reaction of the cis. Similar reactivity has been reported in the photochemistry of **1**,^{4b} though in the current reaction, a phenyl-migrated dienone product (e.g. **10**) could not be detected (<0.3%). A separate plot (Figure 4) shows the reaction profile for the conversion of both **8** and **9** to the photostationary mixture. Based upon the observed rates of formation, it is clear that **8** is a primary photoproduct but the secondary interconversion of **8** and **9** makes it more difficult to comment with certainty on the origin of **9**. From our observations, it is clear that **9** arises from a secondary process, but concrete evidence that it is a primary photoproduct remains elusive.



10

An interesting observation was made when the reaction was carried out as a series of short irradiations (<30 s

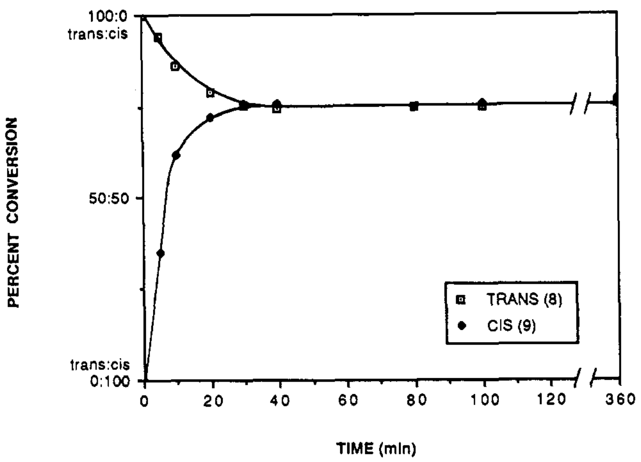


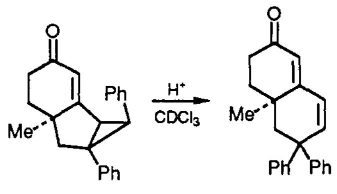
Figure 4. Reaction profile for irradiation of 8 and 9 through Pyrex (ca. 1% of 4 was present after 25 min and remained at 360 min).

each). Under these conditions, in the Hanovia apparatus with a Pyrex filter, compound 8 was the only product of the reaction, even after 90% conversion (25 min). The source of this increased stereoselectivity was intriguing and must derive from a wavelength or a light-intensity effect. Several experiments were, therefore, devised to probe these possibilities.

With short irradiation times, the lamp never comes to full power. Thus, light impinging on the sample is greatly reduced and the spectral output of the lamp more closely resembles that of a low-pressure mercury source (mostly 254-nm light with some low-intensity longer wavelengths).[13] These conditions could not be reproduced exactly by using other means but, in a simulation, irradiating through Pyrex with a Rayonet reactor at 254 nm, no cis isomer formation was detected until 73% conversion (8:9, ca. 190:1). Additional experiments to evaluate this wavelength dependency were done using a series of filter solutions: (A) 0.1 M Na_2VO_3 in 5% NaOH (cutoff 335 nm), (B) 0.1 M $BiCl_3$ in 2 M HCl (cutoff 366 nm), and (C) 0.15 M $FeCl_3$ in 1 M HCl (cutoff 445 nm). With the sodium vanadate filter, both isomers were formed as expected in a ratio similar to that observed on extended irradiation through Pyrex. Irradiation through the bismuth chloride solution, however, gave a more stereoselective reaction (8:9, ca. 160:1), most likely owing to the decreased absorption of light by the photoproducts at this wavelength. Using the ferric chloride filter, no reaction was observed since none of the reactants absorb at this wavelength. These findings support a wavelength dependency in the current reaction.

Since light intensity effects have precedent in ketone photochemistry,[14] it was also necessary to evaluate this parameter. As a simple test, the distance between the light source and the dienone solution was increased from 1 to 40 cm. This reduced the light entering the sample since illuminating power varies inversely with the square of the distance from the source.[15] Additionally, light reaching the reaction vessel was attenuated by air and dust as well as by reflection at the Pyrex surfaces between the source and the reaction mixture. Under these conditions, the reaction, though slower, yielded approximately the same ratio of products at all conversions. Thus, light intensity appears to have little effect on the course of the reaction.

One further interesting observation was made regarding the stability of the photoproducts. Upon prolonged exposure of the product enone 8 to $CDCl_3$ (sealed NMR tube, 1 month, 0 °C, no light), a quantitative reversion back to the starting dienone occurred (see eq 2). This was attributed to catalysis by traces of HCl normally found in this NMR solvent.[16] A control experiment treating 4 with dilute HCl (0.4 mL of 1 M aqueous HCl) in THF (2 mL) further supported this hypothesis. The cis isomer 9, while stable in $CDCl_3$, did react slowly under stronger acid conditions to give up to 20% of a single unidentified product (96–120 h).



8 4 (2)

Mechanistic and Interpretative Discussion. The photochemistry of 4 closely parallels that observed in the parent 4,4-diphenyl-2-cyclohexen-1-one.[4,9] Reaction via the triplet manifold is assumed based upon previous photochemical studies of cyclohexenones. Excitation of the dienone moiety followed by intersystem crossing to the triplet would give an intermediate analogous to that proposed for the simple enone. Bridging of the odd electron center at C-7 in 11 to a C-6 phenyl ring followed by concerted rearomatization–three-ring formation would give the observed product 8. The rigidity of the fused ring structure permits orbital alignment similar to that found in the parent system such that normal concerted phenyl migration may occur. An alternative mechanism[1b,10b] would involve stepwise rearomatization of the bridged intermediate 12 to give a phenyl-migrated diradical having an odd-electron center at C-6. Closure of this species with minimization of phenyl–phenyl steric interference would then give the observed product 8.

The presence of the angular methyl in substrate 4 introduces the possibility of products having a syn or anti relationship between the three-ring and this group. It was expected intuitively that the methyl would exert a steric effect favoring the formation of the anti product. Experimentally, this was found to be the case, and only two products were observed from the reaction, even after extended irradiation times. Additionally, the methyl served to preclude complications resulting from aromatization and double bond migration.

The apparent induction period for initiation of the reaction (see Figure 3) can be attributed to the wavelength variation which occurs during lamp warmup.[13] Repeating the reaction in the same apparatus fitted with a shutter permitted the lamp to attain full power prior to irradiation of the substrate. Under these conditions, products were produced immediately, but the ratio of trans to cis at the earliest point of detection remained ca. 100:1. Thus, the question of whether the cis isomer is a primary photoproduct remains unresolved.

Though the present study has shown that the photochemistry of the dienone 4 bears considerable similarity to that of 1, a difference is found in the composition of the photostationary mixture. While 1 shows a 43:57 trans:cis ratio in the photostationary state,[4b,c] dienone 4 and photoproducts 8 and 9 all lead to approximately the same

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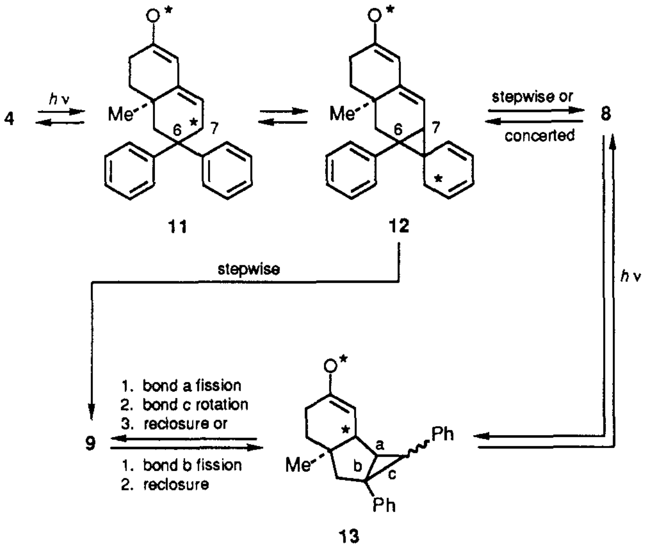
(13) Phillips, R. *Sources and Applications of Ultraviolet Radiation*; Academic Press: New York, 1983; pp 227–230, 247–249.

(14) Schuster, D. I.; Barile, G. C.; Liu, K.-C. *J. Am. Chem. Soc.* **1975**, *97*, 4441–4443.

(15) Giancoli, D. C. *Physics: Principles with Applications*; Prentice-Hall: Englewood Cliffs, NJ, 1980; pp 292–293.

(16) Sohár, P. *Nuclear Magnetic Resonance Spectroscopy*; CRC Press: Boca Raton, FL, 1983; Vol. I, Chapter 2, p 160.

Scheme III. Mechanistic Summary of the Photorearrangement of 4[a]



[a] * = •/• or +/−.

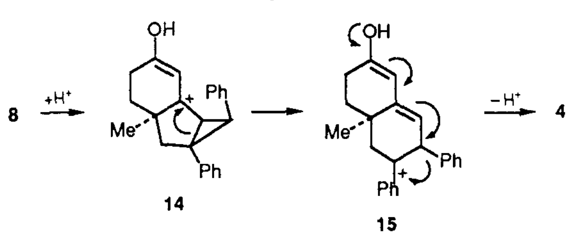
76:23:1 mixture of trans:cis:dienone. Thus, the kinetic (trans) product is also the most stable product in this case. Reference to molecular models and to the X-ray data show that there is no apparent steric bias favoring the trans over the cis stereochemistry in the final product. Thus, the preponderance of trans product likely reflects orbital overlap effects (concerted mechanism) or steric control in the phenyl-migrated diradical (stepwise mechanism).

The preference for production of the trans product at low conversions suggests that the current reaction closely approximates that observed for 1. This seems reasonable since the skeletal rigidity of the system should permit orbital alignment comparable to that found in the parent system if the rearrangement is concerted. Additionally, if the stepwise mechanism is operating, steric interactions during the phenyl migration process would be roughly similar in both molecules. The 100:1 ratio of trans:cis products at low conversion compares well with the parent system and, in all probability, constitutes a lower limit considering the increased photolability of the β-cyclopropyl enone products from 4 (relative to the less conjugated systems derived from 1) and our inability to detect smaller amounts of the products at the initial stages of the reaction.

It seems reasonable that the mechanisms by which 8 and 9 interconvert also parallel those observed in the parent compound 1. These are summarized in Scheme III. Excitation and intersystem crossing of the enone chromophore to give 13 would be followed by fission of the external three-ring bond (bond a), rotation about bond c, and reclosure to give the cis isomer. Alternatively, opening of the internal cyclopropyl bond (bond b) would generate an intermediate which could reclose to give either trans or cis. The minor pathway leading back to the starting dienone can be envisioned from the intermediate obtained from fission of the internal three-ring bond (bond b). Regeneration of the dienone would then occur with migration of the C-7 phenyl back to C-6 by a reversal of the bridging process.

Interestingly, the reaction proceeds normally despite the decreased energy requirements for excitation of 4. Based on a simple comparison of the λ_{max} of the n → π^* band in 1 and 4, the dienone (λ_{max}(n → π^*) = 345 nm) requires less energy for excitation than the simple enone (λ_{max}(n → π^*) = 320 nm). Further extension of the π system might be expected to eventually afford a substrate reactive to light in the visible range. Recent studies by Zimmerman and Lamers,[1b] however, have demonstrated that a linear trienone related to our system is photochemically inert.

Scheme IV



Previous studies[4,17] have revealed significant solvent polarity effects in the photochemistry of 4,4-disubstituted cyclohexenones. For the parent case 1, solvent polarity (benzene vs *tert*-butyl alcohol) had little effect on the trans:cis ratio of the bicyclic products but the more polar *tert*-butyl alcohol gave a 16-fold increase in the production of phenyl-migrated enone (3) as well as an overall increase in quantum efficiency for the disappearance of the enone. These observations were attributed to a possible inversion of close-lying n → π^* and π → π^* triplets brought on by stabilization of the more polar π → π^* state by the alcohol solvent. In the current study, photolyses were run in both benzene and *tert*-butyl alcohol in an attempt to evaluate solvent effects in the extended system. As in the parent case, no significant change in trans:cis product ratio was observed; additionally, a phenyl-migrated enone **10** was not observed in either solvent.

The acid-catalyzed conversion of the trans photoproduct to the starting dienone is the first case of such a reverse process.[18] This reaction presumably proceeds by protonation of the enone carbonyl by traces of HCl in the $CDCl_3$[16] to give the enol cyclopropylcarbinyl carbocation 14 followed by three-ring opening to give the phenyl-stabilized carbocation 15. Regeneration of the dienone system with concomitant phenyl migration and loss of the proton would then regenerate 4 (see Scheme IV).

This quantitative reversion of 8 back to 4 under mild acid conditions suggests that the current reaction represents a photoendothermic process where a considerable portion of the irradiating energy is stored in the carbon framework of the product. The more facile rearrangement of 8 relative to 9 presumably results from more favorable orbital overlap between the enone and the three-ring in the trans isomer. We are continuing our studies of this interesting system.

Experimental Section[19]

6-Methyl-4,4-diphenyl-2-cyclohexen-1-one (5). The general procedure of Zimmerman[3] was used. To a 0 °C solution of 8.9 g (45.4 mmol) of diphenylacetaldehyde and 6.7 g (79.8 mmol) of isopropenyl methyl ketone[20] in 70 mL of ether was added a 4.95-mL ethanol solution of 0.83 g (14.8 mmol) of potassium hydroxide dropwise during 45 min. The mixture was stirred at 23 °C for 6 h, and then poured onto ice, and 25 mL of benzene was added to dissolve the yellow solid. The mixture was neutralized with 1 M HCl to a pH of 7, and the aqueous layer was ether extracted. The organic extracts were combined, washed with saturated NaCl, dried over anhydrous Na_2SO_4, and concentrated in vacuo. The resulting pale yellow oil was crystallized from absolute ethanol to yield 7.67 g (29.0 mmol, 65%) of 6-

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[17] Dauben, W. G.; Spitzer, W. A.; Kellogg, M. S. *J. Am. Chem. Soc.* 1971, *93*, 3674–3677.

[18] The *trans*- and *cis*-5,6-diphenylbicyclo[3.1.0]hexan-2-one photoproducts from 4,4-diphenyl-2-cyclohexen-1-one (1) were observed to be stable in $CDCl_3$ and in THF containing dilute HCl.

methyl-4,4-diphenyl-2-cyclohexen-1-one as a white solid, mp 96–98 °C. Spectral data: IR ($CHCl_3$) 3065, 1680, 1600 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.39–7.18 (cplx, 11 H), 6.20 (d, 1 H, J = 10.1 Hz), 2.65 (m, 1 H), 2.51 (m, 2 H), 1.15 (d, 3 H, J = 6.2 Hz); ^{13}C NMR ($CDCl_3$) δ 201.7, 155.5, 148.1, 143.8, 129.0, 128.9, 128.8, 128.3, 128.0, 127.5, 127.3, 127.0, 50.3, 44.8, 38.7, 15.1; MS m/e (%) 262 (M^+, 26), 234 (18), 206 (100), 191 (24), 165 (14), 115 (17), 77 (10); HRMS, exact mass calcd for $C_{19}H_{18}O$ m/e 262.1357, found m/e 262.1358.

2-Methyl-4,4-diphenylcyclohexanone (6). The general procedure of Bordwell[7] was used. A 150-mL acetic acid solution of 11.8 g (45.0 mmol) of **5** containing 0.5 g of 10% Pd/C was shaken under 60 psi of H_2 in a Parr apparatus at 25 °C for 8 h (H_2 uptake, 12 psi). The crude reaction mixture was filtered through Celite, and the solution was concentrated under vacuum. The residue was taken up in ether, and the solution was washed with $NaHCO_3$, water, and saturated NaCl, dried over anhydrous Na_2SO_4, and concentrated in vacuo. The resulting pale yellow solid was recrystallized twice from absolute ethanol to yield 10.0 g (38.0 mmol, 84%) of 2-methyl-4,4-diphenylcyclohexanone as a white solid, mp 102–103 °C (lit.[3] mp 102–103 °C). Spectral data: IR ($CHCl_3$) 3095, 3060, 1720, 1600, 1500 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.51 (d, 2 H, J = 7.5 Hz), 7.41 (t, 2 H, J = 7.5 Hz), 7.33–7.12 (complex, 6 H), 2.95 (m, 2 H), 2.65–2.30 (complex, 4 H), 2.11 (t, 1 H, J = 13.4 Hz), 1.07 (d, 3 H, J = 6.5 Hz); ^{13}C NMR ($CDCl_3$) δ 212.5, 148.7, 143.5, 128.9, 128.7, 128.3, 127.3, 126.7, 126.5, 126.0, 46.4, 45.8, 41.5, 38.7, 37.3, 14.5; MS m/e (%) 264 (46), 207 (32), 193 (48), 180 (100), 165 (28), 115 (24), 91 (26); HRMS, exact mass calcd for $C_{19}H_{20}O$ m/e 264.1514, found m/e 264.1514.

4,4a,5,6,7,8-Hexahydro-4a-methyl-6,6-diphenyl-2(3*H*)-naphthalenone (7). To a 60-mL benzene solution of 6.0 g (23.0 mmol) of **6** was added 10 mL of a 2.37 M solution of potassium *tert*-butoxide (23.7 mmol). The mixture was stirred for 1 h, and 3.22 g (3.82 mL, 46 mmol) of methyl vinyl ketone was added dropwise. The reaction was stirred for 48 h at 23 °C, diluted with ether, washed with saturated NH_4Cl, water, and saturated NaCl, dried over anhydrous Na_2SO_4, and concentrated in vacuo. The dark brown viscous oil was purified by column chromatography on an 80 cm × 2.5 cm slurry-packed silica gel column eluted with increasing concentrations of ether in hexane. The compounds eluted as follows: 2% ether in hexane, 1.97 g (7.46 mmol, 32.4%) of **6**, 7.5% ether in hexane, 2.18 g (6.90 mmol, 30%) of **7** as a white solid, mp 179–180 °C. Spectral data for **7**: IR ($CHCl_3$) 3060, 2840, 1670, 1625, 1600 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.44 (d, 2 H, J = 7.5 Hz), 7.32 (t, 2 H, J = 7.5 Hz), 7.21 (m, 6 H), 5.77 (s, 1 H), 3.01–2.78 (cplx, 3 H), 2.49–2.22 (cplx, 4 H), 1.88 (m, 3 H), 0.70 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 199.4, 169.8, 150.5, 144.9, 128.4, 128.2, 127.3, 125.9, 125.7, 125.6, 123.8, 50.3, 45.0, 38.9, 36.8, 36.7, 33.5, 30.3, 23.5; UV (abs EtOH) λ_{max} (ϵ) 327 (50.3), 227 (20 353), 208 (20 174); MS m/e (%) 316 (81), 225 (21), 193 (56), 184 (47), 180 (100), 165 (36), 115 (33), 91 (53), 77 (23); HRMS exact mass calcd for $C_{23}H_{24}O$ m/e 316.1827, found m/e 316.1827.

Anal. Calcd for $C_{23}H_{24}O$: C, 86.66; H, 7.59. Found: C, 86.98; H, 7.79.

(±)-4,4a,5,6-Tetrahydro-4a-methyl-6,6-diphenyl-2(3*H*)-naphthalenone (4). The procedure of Agnello and Laubach[8] was used. A stirred mixture of 0.20 g (0.63 mmol) of **7** and 0.90 g (3.67 mmol) of chloranil in 20 mL of *tert*-butyl alcohol was heated at reflux for 3 h. The crude reaction was filtered and concentrated in vacuo. The residue was dissolved in chloroform, washed three times with water and one time with 5% NaOH, washed again with water until reappearance of yellow color, washed with saturated NaCl, dried over anhydrous Na_2SO_4, and concentrated under vacuum. The crude product was separated on a 20 cm × 20 cm PTLC plate eluted six times with 20% ether in hexane. The fastest eluting band yielded 0.1 g (0.32 mmol, 50%) of **4** as a white solid, mp 147–149 °C. The slower eluting band yielded 0.03 g (0.09 mmol, 15%) of **7**, recovered starting material. Spectral data: IR ($CHCl_3$) 1660, 1630, 1610, 1500 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.44–7.34 (cplx, 4 H), 7.25 (m, 3 H), 7.14 (m, 3 H), 6.67 (d, 1 H, J = 10.8 Hz), 6.43 (d, 1 H, J = 10.8 Hz), 5.81 (s, 1 H), 2.69 (A of AB d, 1 H, J = 13.9 Hz), 2.57 (m, 1 H), 2.45 (m, 1 H), 2.38 (B of AB d, 1 H, J = 13.9 Hz), 2.01–1.80 (cplx, 2 H), 0.78 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 199.6, 161.1, 148.8, 145.7, 143.3, 128.4, 128.3, 128.0, 127.2, 126.9, 126.5, 126.3, 124.1, 49.0, 48.9, 37.5, 34.3, 33.8, 23.6; UV (abs EtOH) λ_{max} (ϵ) 337 (500), 287 (24 199), 209 (19 068); MS m/e (%) 314 (100), 299 (8), 286 (17), 257 (19), 243 (23), 210 (20), 195 (19), 165 (27), 115 (15), 91 (22), 77 (10); HRMS exact mass calcd for $C_{23}H_{22}O$ m/e 314.1670, found m/e 314.1670.

Anal. Calcd for $C_{23}H_{22}O$: C, 87.90; H, 7.01. Found: C, 88.09; H, 7.16.

Exploratory Direct Photolysis of (±)-4,4a,5,6-Tetrahydro-4a-methyl-6,6-diphenyl-2(3*H*)-naphthalenone (4). A. In *tert*-Butyl Alcohol. The general procedure described by Zimmerman[9] for the photolysis of 4,4-diphenyl-2-cyclohexenone was followed. A solution of 100 mg (0.32 mmol) of **4** in 320 mL of degassed *tert*-butyl alcohol in a Kreil flask (Ace no. 6963) was irradiated through Pyrex using a 450-W medium-pressure Hanovia immersion apparatus. The rearrangement was followed by GC, and the source was turned off at ca. 98% conversion, concentrated under vacuum, and purified on a 20 cm × 20 cm silica gel PTLC plate eluted 10 times with 8% ether in hexane. The fastest moving of three bands yielded 70 mg (0.22 mmol, 69.7%) of (±)-(1α,1aβ,5aβ,6aβ)-1a,4,5,5a,6,6a-hexahydro-5a-methyl-1,6a-diphenylcycloprop[*a*]inden-3(1*H*)-one (**8**) as a white solid. Recrystallization from $CHCl_3$/ether/hexane afforded an analytical sample: mp 133–134 °C; IR ($CHCl_3$) 3060, 2865, 2830, 1658, 1600 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.39 (m, 4 H), 7.33–7.20 (complex, 6 H), 6.08 (s, 1 H), 3.18 (A of AB d, 1 H, J = 9.6 Hz), 2.89 (B of AB d, 1 H, J = 9.6 Hz), 2.39 (ddd, 1 H, J = 19.0, 13.4, 5.6 Hz), 2.17 (dd, 1 H, J = 19.0, 5.6 Hz), 2.11 (A of AB d, 1 H, J = 13.2 Hz), 1.92 (B of AB d, 1 H, J = 13.2 Hz), 1.50 (dd, 1 H, J = 12.9, 5.6 Hz), 1.33 (s, 3 H), 0.98 (dt, 1 H, J = 13.0, 5.6 Hz); ^{13}C NMR ($CDCl_3$) δ 198.6 (C), 176.8 (C), 144.1 (C), 135.1 (C), 131.1 (CH), 128.7 (CH), 128.4 (CH), 127.0 (CH), 126.8 (CH), 126.5 (CH), 124.2 (CH), 124.2 (CH), 49.8 (C), 44.1 (CH_2), 43.0 (C), 40.7 (CH), 36.4 (CH), 33.6 (CH_2), 31.8 (CH_2), 27.8 (CH_3); UV (abs EtOH) λ_{max} (ϵ) 325 (549), 258 (14 381), 207 (20 881); MS m/e (%) 314 (M^+, 100), 257 (19), 195 (27), 165 (33), 91 (31); HRMS exact mass calcd for $C_{23}H_{22}O$ m/e 314.1670, found m/e 314.1671.

Anal. Calcd for $C_{23}H_{22}O$: C, 87.90; H, 7.01. Found: C, 87.72; H, 7.13.

The second band yielded 12 mg (0.04 mmol, 11.9%) of (±)-(1α,1aα,5aα,6aα)-1a,4,5,5a,6,6a-hexahydro-5a-methyl-1,6a-diphenylcycloprop[*a*]inden-3(1*H*)-one (**9**) as a white solid. Recrystallization from $CHCl_3$/ether/hexane afforded an analytical sample: mp 212–214 °C; IR ($CHCl_3$) 1660, 1605, 1500 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.25–7.00 (complex, 8 H), 6.79 (dd, 2 H, J = 7.8, 2.1 Hz), 6.02 (s, 1 H), 3.06 (d, 1 H, J = 3.4 Hz), 2.56 (m, 1 H), 2.43 (m, 1 H), 2.32 (A of AB d, 1 H, J = 12.8 Hz), 2.31 (d, 1 H, J = 3.4 Hz), 2.12 (B of AB d, 1 H, J = 12.8 Hz), 1.97 (m, 2 H), 1.39 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 198.9 (C), 178.2 (C), 138.8 (C), 137.1 (C), 129.3 (CH), 128.3 (CH), 127.8 (CH), 127.4 (CH), 126.6 (CH), 126.0 (CH), 122.0 (CH), 53.3 (CH_2), 48.9 (C), 46.5 (CH), 45.6 (C), 36.9 (CH), 34.7 (CH_2), 33.8 (CH_2), 26.9 (CH_3); UV (abs EtOH) λ_{max} (ϵ) 325 (463), 260 (7991), 203 (12 898); MS m/e (%) 314 (100), 286 (18), 258 (23), 243 (30), 203 (38), 167 (41), 115 (22),

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(19) Melting points were obtained on a Fisher-Johns melting point apparatus and are uncorrected. IR spectra were recorded with a PE-681 instrument and are referenced to polystyrene. ^1H NMR and ^{13}C NMR were measured as solutions in $CDCl_3$ at 300 MHz and 75 MHz, respectively, on a Varian XL-300 superconducting FT instrument; chemical shifts are reported in δ units relative to internal Me_4Si. UV spectra were recorded in absolute ethanol using a Varian DMS-200 spectrophotometer. Mass spectra were recorded at 70 eV on a VG ZAB-2SE or a VG TS-250 instrument. Elemental analyses (±0.4%) were performed by Galbraith Laboratories, Knoxville, TN. All reactions were run under an atmosphere of dry nitrogen. Solvents used in photochemical runs were purified in the following manner: *tert*-butyl alcohol was distilled from CaH_2; benzene was sequentially washed with concentrated H_2SO_4 (2×), 5% $KMnO_4$ in 10% aqueous H_2SO_4 (2×), and 10% aqueous KOH, dried over anhydrous $MgSO_4$, and distilled from CaH_2. All photochemical reactions were degassed with dry, oxygen-free nitrogen for 1 h prior to and during irradiation. Column chromatography was performed on silica gel (Grace, grade 62, 60–200 mesh) mixed with Sylvania 2282 phosphor and slurry packed into Vycor columns such that band elution could be monitored with a hand-held UV lamp. Preparative thick-layer chromatography (PTLC) was performed on Analtech (No. 02015) preparative silica gel uniplates with fluorescent indicator. Reactions were monitored and kinetic measurements were made on a capillary GC (Varian 3400) with FI detection on a 0.1 mm × 6 m SE-30 column programmed between 100 and 300 °C.

(20) Cook, K. L.; Waring, A. J. *J. Chem. Soc., Perkin Trans. 1* **1973**, 529–537.

Table I. Crystal Data for 8 and 9

	8 (trans)	**9** (cis)
formula	$C_{23}H_{22}O$	$C_{23}H_{22}O$
MW	314.2	314.2
a, Å	9.194(3)	12.639(5)
b, Å	10.567(6)	5.680(2)
c, Å	9.867(5)	23.835(8)
α, deg	106.74(4)	90.0
β, deg	101.68(3)	90.25(3)
γ, deg	99.56(4)	90.0
V, Å^3	872.8(7)	1711.0(10)
F(000)	336	672
μ(Mo Kα), cm^{-1}	0.663	0.677
λ(Mo Kα), Å	0.71069	0.71069
D_{calcd}, g cm^{-3}	1.196	1.220
Z	2	4
obsd refl	2265	1367
R/R_w, %	6.1/7.7	5.5/7.2
space group	$P1$	$P2_1/c$
goodness of fit	0.38	0.33

91 (36), 77 (13); HRMS exact mass calcd for $C_{23}H_{22}O$ m/e 314.1670, found m/e 314.1670.

Anal. Calcd for $C_{23}H_{22}O$: C, 87.90; H, 7.01. Found: C, 87.69; H, 6.97.

A third band, overlapping with **9**, proved to be unreacted starting material.

B. In Benzene. A solution of 100 mg (0.32 mmol) of **4** in 320 mL of degassed purified benzene was photolyzed using conditions identical with those described above. After 3.5 min, there was observed a 36.0:0.40:63.6 ratio of **8**:**9**:**4**, which corresponded to a ca. 90:1 ratio of **8**:**9**. After 11 min a photostationary state was reached having a 75:24:1 ratio of **8**:**9**:**4**. The products:reactant ratios were all within 10% of those observed in the photolysis reaction of **4** in *tert*-butyl alcohol.

Single-Crystal X-ray Structure Determination of the *trans*-Diphenyl Photoproduct 8. A crystal of **8** was mounted on a Syntex P3 automated diffractometer. Unit cell dimensions (Table I) were determined by least-squares refinement of the best angular positions for 15 independent reflections ($2\theta > 15°$) during normal alignment procedures using molybdenum radiation (λ = 0.71069 Å). Data (3096 independent points after removal of space group forbidden and redundant data) were collected at room temperature using a variable scan rate, a $\theta - 2\theta$ scan mode and a scan width of 1.2° below $K\alpha_1$ and 1.2° above $K\alpha_2$ to a maximum 2θ value of 45°. Backgrounds were measured at each side of the scan for a combined time equal to the total scan time. The intensities of three standard reflections were remeasured after every 97 reflections. As the intensities of these reflections showed less than 5% variation, corrections for decomposition were deemed unnecessary. Data were corrected for Lorentz, polarization, and background effects. Observed reflections [2265, $I > 3.0\sigma(I)$] were used for solution of carbon and oxygen positions of the structure by direct methods using SHELX86.[21] Refinement[22] of scale factor and positional and anisotropic thermal parameters for all non-hydrogen atoms was carried out to convergence. The positions of the hydrogen atoms were located from a difference Fourier synthesis and were included (with hydrogen positional and thermal parameters fixed) in the final cycles of refinement [function minimized, $\sum(|F_o| - |F_c|)^2$] leading to a final agreement factor, R = 6.1%. [$R = (\sum||F_o| - |F_c||/\sum|F_o|) \times 100$]. Scattering factors were taken from Cromer and Mann.[23] In the final stages of refinement, a weight of $1/\sigma(F)^2$ was used. R_w = 7.7%.

The unit cell contains two molecules of the trans isomer which display enantiomeric chiralities at C-1, C-2, C-3, and C-5 but which are packed in the accentric cell in a manner which does not involve a crystallographic symmetry element.

Single-Crystal X-ray Structure Determination of the *cis*-Diphenyl Photoproduct 9. A crystal of **9** was mounted on a Syntex P3 automated diffractometer. Unit cell dimensions (Table I) were determined by least-squares refinement of the best angular positions for 15 independent reflections ($2\theta > 15°$) during normal alignment procedures using molybdenum radiation (λ = 0.71069 Å). Data (2237 independent points after removal of space group forbidden and redundant data) were collected at room temperature using a variable scan rate, a $\theta - 2\theta$ scan mode and a scan width of 1.2° below $K\alpha_1$ and 1.2° above $K\alpha_2$ to a maximum 2θ value of 45°. Backgrounds were measured at each side of the scan for a combined time equal to the total scan time. The intensities of three standard reflections were remeasured every 97 reflections. As the intensities of these reflections showed less than 5% variation, corrections for decomposition were deemed unnecessary. Data were corrected for Lorentz, polarization and background effects. Observed reflections [1367, $I > 3.0\sigma(I)$] were used for solution of carbon and oxygen positions of the structure by direct methods using MULTAN80.[24] Refinement[22] of scale factor and positional and anisotropic thermal parameters for all non-hydrogen atoms was carried out to convergence. The positions of all hydrogen atoms, except those associated with the methyl group (C-11), were calculated and included (with hydrogen and positional and thermal parameters held fixed) in three cycles of least-squares refinement. A difference Fourier synthesis then allowed location of the three hydrogens of C-11. All hydrogen parameters were included but constrained in the final cycle of refinement [function minimized, $\sum(|F_o| - |F_c|)^2$ leading to a final agreement factor, R = 5.5%. [$R = (\sum||F_o| - |F_c||/\sum|F_o|) \times 100$]. Scattering factors were taken from Cromer and Mann.[23] In the final stages of refinement, a weight of $1/\sigma(F)^2$ was used. R_w = 7.2%.

Reaction Profiles. Solutions of 100 mg (0.32 mmol) of **4** in 320 mL of *tert*-butyl alcohol, 50 mg (0.15 mmol) of **8** in 160 mL of *tert*-butyl alcohol, and 50 mg (0.15 mmol) of **9** in 160 mL of *tert*-butyl alcohol were irradiated as before in the Hanovia apparatus. The reactions were monitored by GC analysis of 0.2-mL aliquots removed by syringe from the reaction mixture. Compound **4** was irradiated at 0.5-min intervals for the first 6 min and at 1-min intervals thereafter for a total time of 20 min. Compounds **8** and **9** were irradiated at 5-min intervals for the first 40 min and at 40-min intervals thereafter for a total time of 6 h. The samples were injected onto a 0.25 mm × 6 m SE-30 column, temperature programmed between 150 and 300 °C; the individual compounds were found to be stable to these thermal conditions. Peak areas were determined from electronic integration of the peaks relative to internal benzophenone standard.

Control Experiment. Photostability of the Photoproducts. In a typical control run, 0.29 mmol of the photoproduct was photolyzed as a 0.001 M solution in *tert*-butyl alcohol using conditions identical with those described for the exploratory irradiations. The reactions were monitored by GC as above; the individual compounds were found to be stable to these thermal conditions. After 30 min, compound **8** had reached a photostationary state having a 76:23:1 ratio of **8**:**9**:**4**, which remained unchanged even after 6 h. Irradiation of **9** yielded a 76:24 ratio of **8**:**9** after 30 min with no formation of **4**; this ratio remained constant after 6 h.

Acid-Catalyzed Reactions of the Photoproducts. A sealed sample of **8** (25 mg, 0.08 mmol) dissolved in 0.75 mL of $CDCl_3$ for 1 month in the dark was transformed to **4** in quantitative yield. A sealed sample of **9** (25 mg, 0.08 mmol) dissolved in 0.75 mL of $CDCl_3$ for 1 month in the dark was found to be stable under these conditions. In a typical control run, 10 mg (0.03 mmol) samples of **8** and **9** were treated with 2 mL of THF containing 0.4 mL of 1.0 M HCl and allowed to stir at 23 °C in the dark under N_2. After 2 days, **8** had undergone 80% conversion (by GC) back to **4**. After 4 days, **9** had undergone 20% conversion (by GC) to an unidentified compound; this conversion was not increased upon extended reaction.

Wavelength Dependency Experiments. The photoreaction of **4** was run in *tert*-butyl alcohol using the following filter solutions. A: 0.1 M $NaVO_3$ in 5% NaOH (cutoff 335 nm). B: 0.1 M $BiCl_3$ in 2.0 M HCl (cutoff 366 nm). C: 0.15 M $FeCl_3$ in 1.0 M HCl (cutoff 445 nm). The reactions using the filter solutions

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[21] Sheldrick, G. Institut für Anorganische Chemie der Universität Gottingen, 1986.

[22] The X-ray System-Version of 1980, Technical Rpt TR446 of the Computer Center, Stewart, J. M., Ed.; University of Maryland: College Park, MD.

[23] Cromer, D. T.; Mann, I. B. *Acta Crystallogr.* **1968**, *A24*, 321–324.

[24] Main, P.; Fiske, S. J.; Hull, S. E.; Lessinger, L.; Germain, G.; DeClerq, J. P.; Woolfson, M. M., University of York, England, 1980.

were monitored by GC as above. The reaction using filter solution A was followed by removing aliquots at 0.5-min intervals for the first 6 min and at 1-min intervals for a total time of 20 min. The cis photoproduct was not observed until 38% conversion of **4**, where 0.39% of the cis isomer was detected. This corresponds to a ca. 100:1 ratio of **8**:**9**. After 11 min, there was obtained a 76:23:1 equilibrium ratio of **8**:**9**:**4**. The reaction using filter solution B was followed by removing aliquots at 1-min intervals for the first 10 min, 2-min intervals for the next 30 min, and 4-min intervals for an additional 80 min. The earliest detected ratio (49% conversion) of **8**:**9**:**4** was 48.7:0.3:5.1, which corresponds to an **8**:**9** ratio of ca. 160:1. Extended irradiation of **4** resulted in a photostationary mixture composed of a 79:20:1 ratio of **8**:**9**:**4**. No reaction was seen using filter solution C, even after a 6-h photolysis time.

Irradiation Using a Rayonet Reactor. The photochemical reaction of **4** (80 mg, 0.25 mmol) in 260 mL of *tert*-butyl alcohol was run in a 500-mL Pyrex round-bottom flask using a Rayonet reactor (254-nm lamps). The reaction was monitored by GC as above, and aliquots were removed at 2-min intervals for the first 20 min and at 4-min intervals thereafter for a total time of 2 h. After 24 min, a 73.0:0.4:26.6 ratio of **8**:**9**:**4** was detected. This corresponds to ca. 180:1 ratio of **8**:**9**. At 95% conversion, there was observed an 88:5 ratio of **8**:**9** with 2% of an unknown product. After photolyzing 92 min there was observed a 73:24:1 ratio of **8**:**9**:**4** with 2% of an unknown product.

Irradiation Using a Shutter. A solution of 50 mg (0.15 mmol) of **4** in 160 mL of *tert*-butyl alcohol was irradiated using a Hanovia apparatus fitted with an opaque cylindrical shutter between the Pyrex filter and the immersion well cooling jacket. The shutter fit snugly into a multilayered piece of aluminum foil, which prevented light from passing out the bottom of the well. The lamp was turned on for 3 min with the shutter in place to enable the lamp to warm up. Once the source was at full power, the shutter was removed and the solution was photolyzed as before. The reaction was monitored by GC; aliquots were taken at 0.5-min intervals for the first 6 min and at 1.0-min intervals thereafter, for a total photolysis time of 20 min. The earliest detected ratio of products and reactant was seen after 1 min. There was observed a 39.6:0.4:60.0 ratio of **8**:**9**:**4**, which corresponds to ca. 100:1 ratio of **8**:**9**. Though the production of **9** appeared to be somewhat slower, the previously encountered photostationary state of 76:23:1 (**8**:**9**:**4**) was reached after 10 min.

Light Intensity Experiment. The photochemical reaction of **4** (40 mg, 0.13 mmol) in 130 mL of *tert*-butyl alcohol was run in a 250-mL Pyrex flask positioned 40 cm from the Pyrex-filtered 450-W light source. The reaction was monitored by GC; aliquots were removed at 1-min intervals for the first 40 min and at 3-min intervals for an additional 80 min. The earliest detected ratio, 36.0:0.4:63.6 of **8**:**9**:**4** occurred after 20 min. This corresponds to ca. 100:1 ratio. Upon extended irradiation (2 h), the equilibrium (**8**:**9**:**4**) ratio of 76:23:1 was observed.

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Supplementary Material Available: Tables 2–7 listing positional parameters, final anisotropic thermal parameters, and bond angles and distances for **8** and **9** (10 pages). Ordering information is given on any current masthead page. A listing of calculated and observed structure factors as well as the ORTEP drawing of molecule B from the unit cell of **8** is available from R.A.B.

Notes

Preparative Flash Vacuum Thermolysis.[1] Selective Elimination of 6-Chloro-1-hexene from Esters of 6-Chloro-1-hexanol with Schönberg Rearrangement of the *S*-Methyl Xanthate

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Thermal elimination from carboxylic esters, often acetates,[2] tosylates,[3] and at milder temperatures in the Chugaev reaction from *S*-methyl xanthates,[4] is a classic route for the preparation of olefins.[5] We have recommended[6] the use of flash vacuum thermolysis (FVT) as a general method for such preparations, instead of applying the traditional reaction procedures by dropping in,[7] or by vaporizing the esters with a flow of nitrogen[2-5] into a filled hot tube. FVT utilizes an unfilled quartz tube and low pressure, which prevents tar formation and generally gives quantitative mass recovery, since the pyrolysate is captured in liquid nitrogen cooled traps.[6]

As part of our polymer research program, considerable amounts of 6-chloro-1-hexene (**1**) were needed. This compound is utilized in the synthesis of natural products,[8,9] bicyclic olefins,[10] and polymers,[11] in solvomercuration reactions,[12] and as a radical probe for studying electron-transfer mechanisms.[13-15] Most workers use 5-hexen-1-ol

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[1] Previous paper in this series: Batelaan, J. G.; Weber, A. J. M.; Wiersum, U. E. *J. Chem. Soc., Chem. Commun.* **1987**, 1397.

[2] DePuy, C. H.; King, R. W. *Chem. Rev.* **1960**, *60*, 431.

[3] Boyd, J.; Overton, K. H. *J. Chem. Soc., Perkin Trans. 2* **1972**, 2533.

[4] Nace, H. R. In *Organic Reactions*; J. Wiley & Sons Inc.: New York, 1962; Vol. 12, p 57.

[5] Saunders, W. H.; Cockerill, A. F. In *Mechanisms of Elimination Reactions*; J. Wiley & Sons Inc.: New York, 1973.

[6] (a) Wiersum, U. E. *Recl. Trav. Chim., Pays-Bas* **1982**, *101*, 317 and 365. (b) Wiersum, U. E. *Aldrichimica Acta* **1984**, *17*, 31.

[7] Benson, R. E.; McKusick, B. C. In *Organic Synthesis*; J. Wiley & Sons Inc.: New York, 1963; Collect. Vol. IV, p 746.

[8] Black, H. K; Weedon, B. C. L. *J. Chem. Soc.* **1953**, 1785.

[9] Mihara, S.; Tateba, H.; Nishimura, O.; Machii, Y.; Kishino, K. *J. Agric. Food Chem.* **1987**, *35*, 532.

[10] Criegee, R.; Bolz, G.; Askani, R. *Chem. Ber.* **1969**, *102*, 275.

[11] Backskai, R. *J. Pol. Sci., A* **1965**, *3*, 2491.

[12] Brown, H. C.; Lynch, G. J. *J. Org. Chem.* **1981**, *46*, 930.

[13] Jenkins, C. L.; Kochi, J. K. *Ibid.* **1971**, *36*, 3103.

[14] Ashby, E. C.; Oswald, J. *Ibid.* **1988**, *53*, 6068.

[15] Cf.: (a) Giese, B.; Kretzschmar, G. *Chem. Ber.* **1984**, *117*, 3160. (b) Newcomb, M.; Curran, D. P. *Acc. Chem. Res.* **1988**, *21*, 206. (c) Stork, G. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 149.

0022-3263/89/1954-5811$01.50/0