Photocyclization Reactions of Substituted 2,2′-Divinylbiphenyl Derivatives

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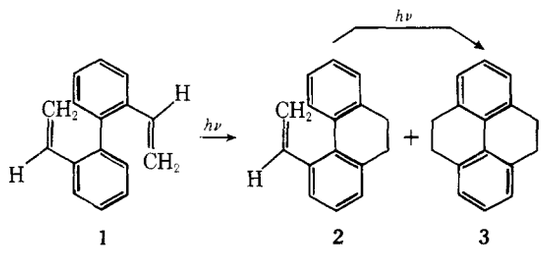
The direct and sensitized photochemistry of substituted 2,2′-divinylbiphenyl derivatives is reported. Direct irradiation of these compounds results in smooth nonoxidative cyclization to tetrahydropyrenes. This reaction may be conveniently viewed as proceeding by a mechanism which involves an initial stilbene–phenanthrene type cyclization, followed by a 1,5-sigmatropic hydrogen shift to give a vinyl-substituted dihydrophenanthrene which is subsequently converted to the tetrahydropyrene system on further irradiation. The photochemistry of several divinylbiphenyls possessing a styryl group was also studied. In contrast to the photocyclizations observed with the simple divinylbiphenyls, these compounds were found to undergo an intramolecular [2 + 2]-cycloaddition reaction. The difference in photobehavior of these systems and the low intersystem crossing efficiency noted is discussed. Calculations by the Hückel molecular orbital method of the sum of the free valence indices in the first excited state (ΣF^*) of the terminal atoms concerned in the photocyclizations were carried out and serve as a guide in predicting the direction of cyclization. The photochemistry of several 2-vinyl-2′-acylbiphenyls was also studied and compared to that encountered in the divinylbiphenyl system.

The photochemical [2 + 2]-cycloaddition reaction has a long history[1] and its utility in the construction of four-membered rings has been amply demonstrated.[2] Similarly, the photocyclization–oxidation reaction of stilbene-like molecules has been widely investigated[3-11] and in many cases has led to the synthesis of a variety of interesting polyaromatic compounds,[12,13] some of which would be tedious to synthesize by other routes.[14] Somewhat related nonoxidative cyclizations have also received wide attention in recent years from both the preparative and mechanistic points of view.[15-22] As part of a general study dealing with intramolecular [2 + 2]-cycloaddition and 6π-electrocyclic reactions, we recently investigated the excited state behavior of several 2,2′-divinylbiphenyl derivatives.[15] During the course of these studies we found that the resulting photochemistry depends not only on the experimental conditions used, but also on the choice of the substituent groups attached to the double bond.[16] In this paper we wish to describe the results of our study and to delineate the effect of the substituent groups and biphenyl geometry on the course of the photoreaction.

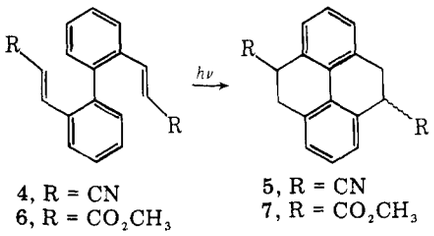
Results

Irradiation of a 0.05 M solution of 2,2′-divinylbiphenyl (**1**) in benzene with a 450-W Hanovia lamp equipped with a Pyrex filter for 3 h gave a mixture of two products isomeric with starting material. The two isomers could be separated by preparative gas chromatography and are assigned structures **2** and **3** on the basis of their spectral data. The structure of **3** was unambiguously established as 4,5,9,10-tetrahydropyrene (70%), mp 134–135 °C, by comparison with an authentic sample.[23] The minor component was identified as 4-vinyl-9,10-dihydrophenanthrene (**2**) (30%) on the basis of its characteristic NMR spectrum and its quantitative conversion to **3** on further irradiation. The quantum yield for the cyclization of **1** → **2** is 0.042 while that for **2** → **3** is 0.014. The quantum yields were not affected when the irradiation was carried out in the presence of piperylene. The photocyclization of **1** to **2** (and **3**) could also be induced by triplet excitation. Thus, irradiation of a solution of **1** through a uranium glass filter containing sufficient benzophenone to absorb >95% of the incident light gave **2** as well as **3**. In this case, the quantum yield for cyclization was significantly reduced (i.e., $\Phi_{1\rightarrow 2}$ = 0.003 and $\Phi_{2\rightarrow 3}$ = 0.004). These results would tend to indicate that the singlet state of **1** is the reactive state responsible for the cyclization in the direct irradiation experiment.



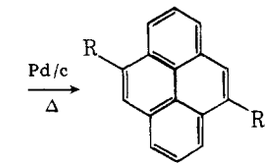
1 2 3

Similar irradiation of 2,2′-biphenyldiacrylonitrile (**4**) afforded 4,5,9,10-tetrahydro-4,9-dicyanopyrene (**5**) (71%), mp 260–262 °C, as the major photoproduct. When the photolysis of dimethyl 2,2′-biphenyldiacrylate (**6**) was conducted in benzene, a mixture of *cis*- and *trans*-4,5,9,10-tetrahydro-4,9-dicarbomethoxypyrene (**7**) was obtained in good yield (60%). Oxidation of photoproducts **5** and **7** to the corresponding 4,9-disubstituted pyrene system (**8**) could be readily achieved by heating **5** and **7** in benzene which contained a catalytic quantity of palladium on carbon.



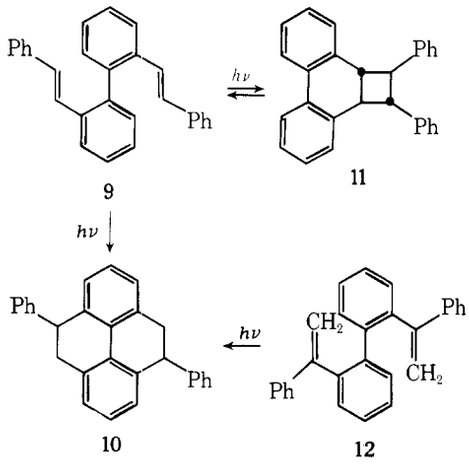
4, R = CN
6, R = CO_2CH_3

5, R = CN
7, R = CO_2CH_3



8a, R = CN
8b, R = CO_2CH_3

Laarhoven and Cuppen had previously reported[24] that the extended photolysis of 2,2′-distyrylbiphenyl (**9**) gave tetrahydro-4,9-diphenylpyrene (**10**) as the thermodynamically controlled photoproduct. Irradiation of **9** for shorter periods of time, however, was reported to give 1,2-diphenylcyclobuta[*l*]phenanthrene (**11**) as the kinetically controlled product[25] which was ultimately converted into **10** on further irradiation.[24] We have confirmed these findings and have also observed that the irradiation of 2,2′-bis(1-phenylvinyl)biphenyl (**12**) gave only **10**, mp 221–213 °C, even under kinetically controlled conditions. It should be pointed out that the irradiation of divinylbiphenyl derivatives **1**, **4**, **6**, and **12** did not lead to any detectable quantities of [2 + 2] internal cycloadducts, even when short irradiation times were used. This

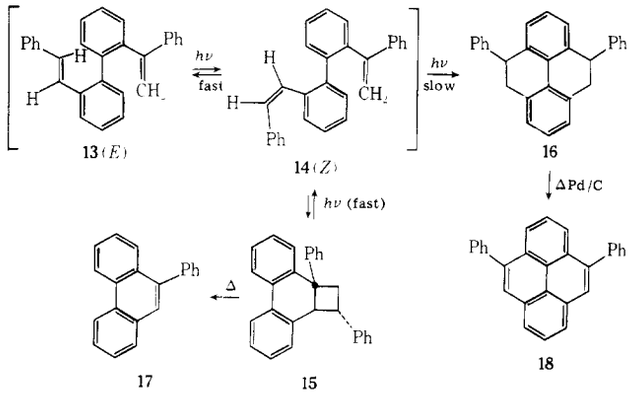


stands in marked contrast to the results of Laarhoven and Cuppen[24] with distyrylbiphenyl system (**9**).

During the course of these studies we found that [2 + 2] cycloaddition is the main reaction which occurs on photoexcitation of the 2-(1-phenylvinyl)-2′-styrylbiphenyl system (**13** or **14**). Thus, irradiation of either the *E* (**13**) or *Z* (**14**) isomer in benzene gave 1,2,2a,10b-tetrahydro-1,2a-diphenylcyclobuta[*l*]phenanthrene (**15**) and 4,5,9,10-tetrahydro-4,10-diphenylpyrene (**16**). Photoequilibration of the *Z* and *E* isomers

$$13 \overset{h\nu}{\rightleftharpoons} 14$$

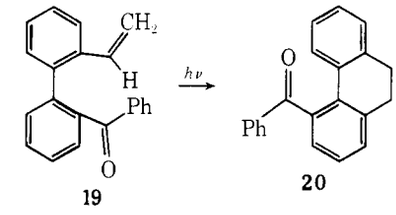
was rapidly established (1:1) before intramolecular cycloaddition occurred. The [2 + 2]-cycloaddition product **15** was identified on the basis of its spectral properties; mass spectrum *m/e* 358 (M^+), 104 (base); UV (methanol) 268 and 300 nm (ϵ 13 200, 5100); NMR ($CDCl_3$, 100 MHz) τ 7.23 (d, 2 H, J = 8.0 Hz), 5.98 (d, 1 H, J = 12.0 Hz), 5.63 (td, 1 H, J = 12.0 and 8.0 Hz), and 2.21–3.03 (m, 18 H). On further irradiation, this material was converted to tetrahydropyrene **16** in quan-



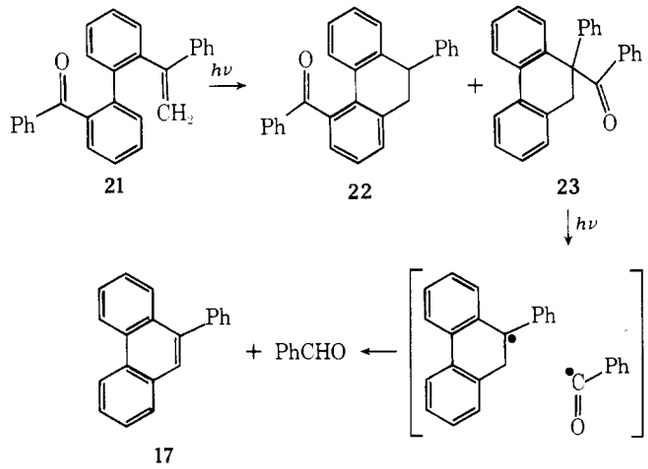
titative yield. Chemical confirmation of the structure of **16** was obtained by its ready oxidation to 4,10-diphenylpyrene (**18**), mp 152–153 °C, on heating with palladium on carbon. When a sample of **15** was subjected to pyrolysis at 150 °C, the major products were 9-phenylphenanthrene (**17**) and polystyrene.

The photochemical results observed with this system are very similar to those encountered by Laarhoven and Cuppen with the 2,2′-distyrylbiphenyl system.[24] Apparently, the photocyclization of **13** (or **14**) to tetrahydropyrene **16** is slow in comparison with the [2 + 2]-cycloaddition reaction. Tetrahydropyrene **16** is only obtained after long irradiation times and its formation can be attributed to a subsequent photocleavage reaction of cyclobutane **15**. These results demonstrate that the [2 + 2] intramolecular photocycloaddition reaction of divinylbiphenyl derivatives only occurs when a stilbene moiety is present in the system.

In view of the extremely interesting substituent effect uncovered during our studies with the divinylbiphenyl system, we felt that it would be worthwhile to determine whether a comparable effect would occur with the related carbonyl system. One of the more common photoreactions of carbonyl compounds is their addition to olefins to form oxetanes, i.e., the Paterno–Buchi reaction.[26,27] Contributions from many laboratories suggest that the cycloaddition of simple phenyl ketones with π bonds proceeds via their n $-$ π^* triplet state.[28–33] Ketones with low-lying π–π^* states generally do not undergo the Paterno–Buchi reaction,[28] although some exceptions have appeared in the literature.[28,31,34] For example, the irradiation of 2-phenylbenzophenone in the presence of olefins does not lead to oxetanes,[28] presumably because the lowest excited state of this system possesses a π–π^* triplet state.[28] However, 3-phenylbenzophenone does undergo efficient cycloaddition with isobutylene (Φ = 0.1),[35] even though this ketone phosphoresces from a π–π^* triplet state.[28] Although 2-(*o*-vinylphenyl)benzophenone and its derivatives would be expected to possess a low-lying π–π^{*3} state, the ready availability of these compounds made it attractive, nonetheless, to examine their photochemical behavior in order to determine whether [2 + 2] cycloaddition would occur. The first system studied was 2-(*o*-styryl)benzophenone (**19**). Irradiation of **19** with Pyrex filtered light gave no recognizable [2 + 2]-cycloaddition product but instead gave 4-benzoyl-9,10-dihydrophenanthrene (**20**) in high yield.



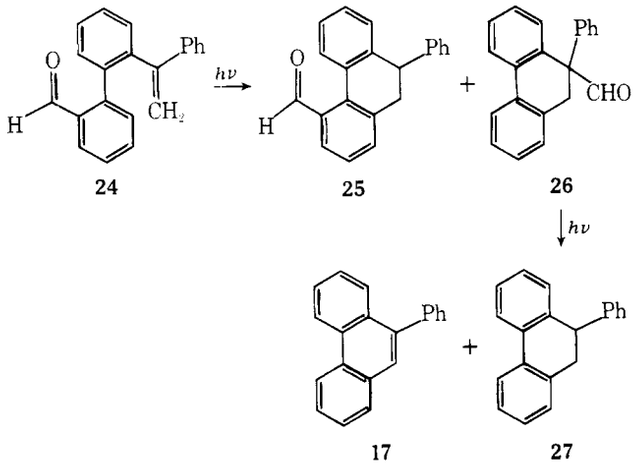
In contrast to the photochemistry of **19**, where only one dihydrophenanthrene was observed, irradiation of 2-[*o*-(1-phenylvinyl)phenyl]benzophenone (**21**) in benzene with 365-nm light furnished a mixture of two isomeric ketones [**22** (60%) and **23** (20%)]. The structures of these two products were assigned as 4-benzoyl-9-phenyl- (**22**) and 9-benzoyl-9-phenyl-9,10-dihydrophenanthrene (**23**) on the basis of their analytical and spectroscopic data (see Experimental Section for details). Structure **23** was further verified by a photochemical degradation. Photolysis of **23** should cause efficient



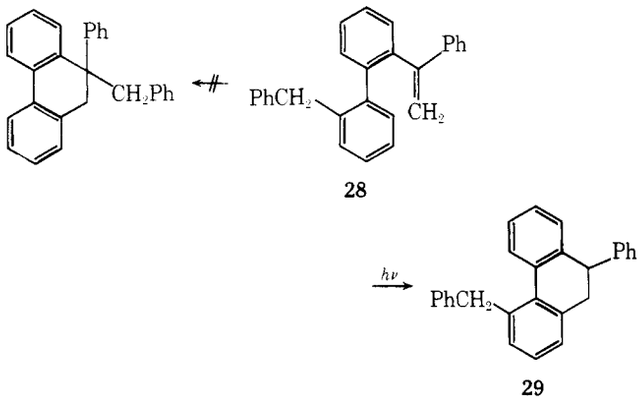
α cleavage and formation of a tight radical pair. Subsequent hydrogen transfer from the 9-phenylphenanthryl radical to the benzoyl radical would be expected to give benzaldehyde and 9-phenylphenanthrene (**17**). Indeed, irradiation of **23** with a low-pressure mercury lamp produced the suspected products in excellent yield. Thus, the photochemical behavior of **23**

provided a simple and effective method of confirming its structure.

We also prepared and irradiated 2′-(1-phenylvinyl)-2-biphenylcarboxaldehyde (**24**) with 365-nm light. The products obtained from this photolysis were 9-phenyl-9,10-dihydro-4-phenanthrenecarboxaldehyde (**25**) (13%) and 9-phenyl-9,10-dihydro-9-phenanthrenecarboxaldehyde (**26**) (50%). The structure of aldehyde **26** was assigned on the basis of its spectroscopic properties (see Experimental Section) and its ready conversion to 9-phenylphenanthrene (**17**) and 9-phenyl-9,10-dihydrophenanthrene (**27**) on irradiation with 2537-Å light.



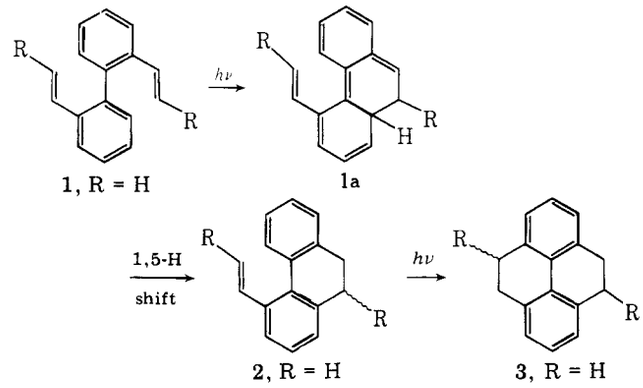
The photocyclization of 2-(1-phenylvinyl)-2′-benzylbiphenyl (**28**) was also studied. In contrast with the results obtained with ketone **21** and aldehyde **24**, this compound afforded a single dihydrophenanthrene (i.e., **29**) whose structure was established as 9-phenyl-9,10-dihydro-4-benzylphenanthrene (**29**), mp 105–106 °C, on the basis of its characteristic



spectral data. It would appear, therefore, that ipso cyclization only occurs when a carbonyl group is present in the 2′-(ortho) position of the biphenyl ring.

Discussion

The most stable conformation of ground-state biphenyl is strongly dependent on the medium. The dihedral angle between the two rings is 40–45° in the gas phase,[36] 20–25° in solution,[37] and 0° in the crystalline state.[38] By contrast, theoretical calculations by Hoffmann[39] predict a planar excited state and some experimental work by Wagner[40] shows that triplet biphenyl prefers to be planar. A planar biphenyl excited state should favor bond formation between the ortho position of the biphenyl ring and an unsaturated 2-substituent. The present study reveals that the irradiation of several 2,2′-divinylbiphenyl derivatives results in a smooth nonoxidative cyclization and represents a convenient route for the preparation of the tetrahydropyrene ring system. This reaction may be conveniently viewed as proceeding by a mechanism which involves an initial stilbene–phenanthrene type cyclization followed by a 1,5-sigmatropic hydrogen shift to give a vinyl-substituted dihydrophenanthrene. On further irradiation, this material is converted to the tetrahydropyrene system. This mechanistic proposal is supported by the isolation of 4-vinyl-9,10-dihydrophenanthrene (**2**) from a short-term irradiation of 2,2′-divinylbiphenyl (**1**).

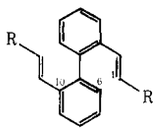
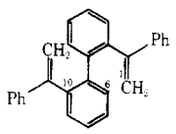
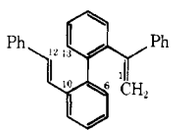
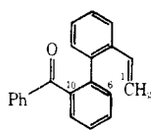
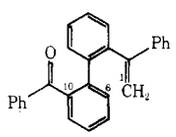
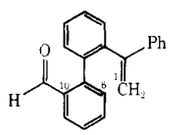
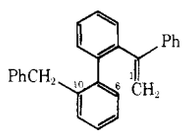


The relative ease of photocyclization of hexatriene-type analogues has been related to the sum of the free-valence indices in the first excited state, ΣF*, at the two positions which become bonded during the cyclization.[41-43] Laarhoven and co-workers showed that only if the sum of free valence indices in the first excited state of the terminal atoms concerned in the photocyclization of stilbene-like compounds exceeds a critical value (unity in this case (i.e., $\Sigma F^* > 1.0$)) will cyclization occur.[43] In some stilbene-like molecules, photocyclization can occur in a number of possible ways. By using Laarhoven's calculations,[43] one can predict the preferred mode of cyclization in these cases. When more than one mode of cyclization has a value of unity or greater for ΣF* of the terminal atoms concerned in the photocyclization, cyclization usually occurs for the highest calculated value as long as the difference in the values of ΣF* is more than 0.1; otherwise both photocyclizations can occur.[43,44] It seemed that calculation of the ΣF* of the terminal atoms involved in the cyclization of the 2,2′-divinylbiphenyl systems could yield useful information and aid us in predicting the direction of cyclization when multiple modes of cyclization are possible. Using the relation $F^* = \sqrt{3} - \Sigma_s \rho_{rs}^*$ in which ρ_{rs}^* is the π-bond order in the first excited state between the atom r and a neighboring atom s,[45] the ΣF* of the terminal atoms involved in the cyclization was calculated for a number of 2,2′-divinylbiphenyl derivatives. These values are calculated for planar molecules in the usual way and are based on the HMO approximation. All possible modes of cyclization are included in the calculations, and these are outlined in Table I.

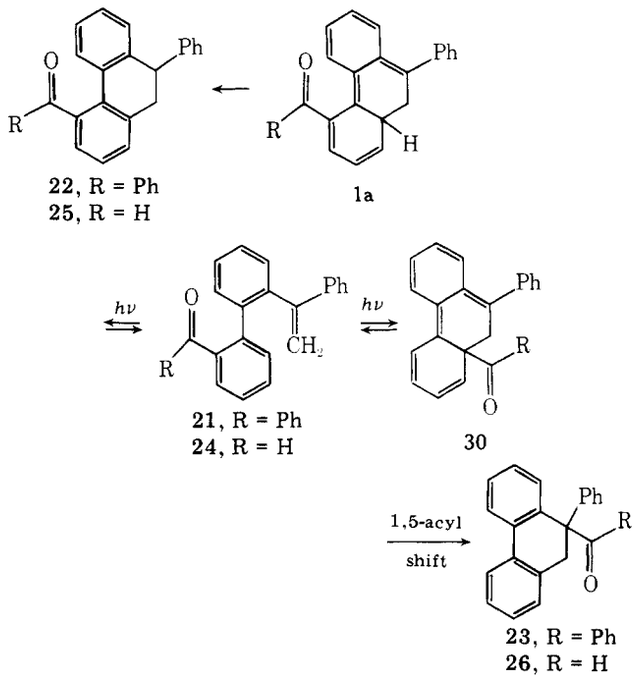
As shown in the table, all compounds with $\Sigma F^* > 1.0$ undergo cyclization under the influence of light. Of the systems examined, only one, the cyclization of dinitrile **5**, occurs with a value of ΣF* less than unity. This system, however, has a ΣF* which is only slightly less than the critical value, and this exception may be ascribed to the fact that numerical evaluation of ΣF* for compound **5** by the HMO method is a rather rough approximation. Photocyclization of divinylbiphenyl derivatives **1**, **4**, **6**, and **9** at the 1 and 10 positions did not occur as the values of ΣF* at these atoms were much less than the corresponding values at positions 1 and 6 (see Table I). Similarly, structures **12**, **16**, and **19** cyclize only in the direction predicted by the Laarhoven rule.[43]

The rule breaks down, however, with structures **21** and **24**. Calculation of the free valence numbers of the various carbon atoms in the excited state of these systems reveals that the difference between ΣF* is significantly greater than 0.1.

Table I. Results of SHMO Calculations

Compound	ΣF*	Product
 4	R = H 1,6 = 1.454 1,10 = 1.221 R = CN 1,6 = 0.979 1,10 = 0.699	3 (obsd) Not obsd 8a (obsd) Not obsd
6	R = CO_2CH_3 1,6 = 1.137 1,10 = 0.850	8b (obsd) Not obsd
9	R = Ph 1,6 = 1.022 1,10 = 0.746	10 (obsd) Not obsd
 12	1,6 = 1.525 1,10 = 1.286	10 (obsd) Not obsd
 16	1,6 = 1.437 12,13 = 1.067 1,10 = 1.175 2,12 = 0.809	Obsd Not obsd Not obsd
 19	1,6 = 1.465 1,10 = 1.166	20 (obsd) Not obsd
 21	1,6 = 1.544 1,10 = 1.252	22 (obsd) 23 (obsd)
 24	1,6 = 1.557 1,10 = 1.254	25 (obsd) 26 (obsd)
 28	1,6 = 1.727 1,10 = 1.727	29 (obsd) Not obsd

Hence, photocyclization of **21** and **24** should have given only dihydrophenanthrenes **22** and **25**. Irradiation of these compounds, however, also produced structures **23** and **26**. In fact, structure **26** was the major product obtained from the photolysis of **24**. The most likely mechanism to rationalize the formation of these products involves ipso cyclization to give **30** as a transient intermediate which then undergoes a facile 1,5-acyl shift. The 1,5-sigmatropic shift probably proceeds via a thermally allowed concerted pathway[46,47] since the yield of **23** or **26** was unaffected when the irradiation was carried out in the presence of *n*-dodecanethiol. Lewis and Magyar[48] had previously demonstrated that this thiol is an efficient radical scavenger which is capable of trapping photochemically generated acyl radicals. The absence of benzaldehyde in the above reaction implies that either the benzoyl group is



22, R = Ph
25, R = H

1a

21, R = Ph
24, R = H

30

23, R = Ph
26, R = H

transferred in a concerted fashion or else that geminate recombination of the radical pair is proceeding within a radical cage.

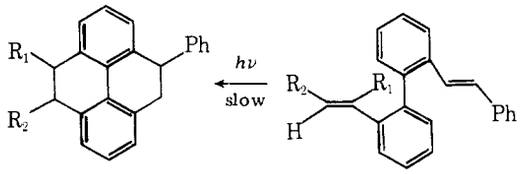
It is not clear why **21** (or **24**) produces a mixture of dihydrophenanthrenes **22** and **23**, whereas the related divinylbiphenyl system **12** cyclizes in only one direction. The slight difference in the magnitude of the free valence numbers (i.e., $\Delta\Sigma F^*$ **21** = 0.292 vs. $\Delta\Sigma F^*$ **12** = 0.239) of the two systems seems to be too small to account for the nonselectivity exhibited by structure **21**. One possibility to account for this nonselectivity is that **21** is polarized in such a direction that the cyclizing atom attached to the carbonyl group may be regarded as being electron deficient. As a result of this polarization, the normally electron-rich ortho position of the excited biphenyl system[49] becomes electron deficient at the position bearing the benzoyl group. This, in turn, creates an electrostatic attraction between the electron-deficient ortho carbon of the biphenyl ring with the electron-rich terminus of the neighboring vinyl group, thereby promoting cyclization between these two atoms. In support of this explanation, we find that the ratio of **22**/**23** is increased on changing the solvent from benzene (3/1) to methanol (1.7/1). The inherent hydrogen bonding capabilities of methanol would be expected to increase the polarization of the carbonyl group in the excited state and thereby promote cyclization on the ortho carbon atom bearing the carbonyl group. Another rationale which could account for the nonselectivity exhibited by structures **21** and **24** is based on the assumption that the initial cyclization step affords cyclohexadienes **1a** and **30** which can regenerate starting material by a retrocyclization reaction. The distribution of products (i.e., **22** or **23**) could then be controlled by the rates of hydrogen or acyl group migration of the transient cyclohexadienes. Thus, the poor ΣF^* correlation encountered with these systems may be related to the fact that the 1,5-acyl shift is faster than the 1,5-hydrogen shift. Further work is needed to distinguish between the above two possibilities.

The finding that 2-(1-phenylvinyl)-2′-benzylbiphenyl (**28**) cyclizes only in one direction, even though the free valence numbers on both ortho positions have the same value, must be related to steric factors. By incorporating a benzyl group on the 2′ position, the concentration of the conformation necessary for ipso cyclization is significantly decreased. The exclusive formation of **29** from **28** is undoubtedly a reflection

of the greater steric interactions involved in ipso cyclization. This phenomenon is not without precedent as other reports in the literature have shown that conformational factors can markedly influence the direction of both photo and thermal electrocyclic reactions.[50-53] Alternatively, the exclusive formation of **29** from **28** may be related to the fact that a 1,5-hydrogen shift of one of the initially formed cyclohexadiene intermediates is much faster than a 1,5-alkyl shift.

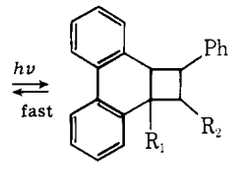
Our inability to detect an oxetane from the photolysis of **21** (or **24**) can be attributed to the π–π^* singlet nature of the excited state. The excited singlet seemingly prefers to cyclize to a dihydrophenanthrene rather than to undergo the Paterno–Buchi reaction. The apparent low intersystem crossing efficiency noted with **21**[54] could either be the result of an exceptionally fast decay process of the singlet state or an especially low rate of intersystem crossing.

One final point worthy of discussion concerns the photochemistry of divinylbiphenyls having an aryl group at the β position. These systems prefer to undergo a fast intramolecular 2 + 2 cycloaddition to give cyclobuta[*l*]phenanthrenes rather than to undergo cyclization to the tetrahydropyrene ring system. Apparently the formation of the tetrahydropyrene is slow in comparison with the formation of the cyclobutane. Only on extended irradiation is the tetrahydropyrene ring produced and its formation can be traced to a subsequent cycloreversion reaction of the initially formed cycloadduct. Calculation of free valence numbers of the various carbon atoms of **9** or **13** in the excited state reveals that the photocyclization should be a favorable process [i.e., $\Sigma F^*_9 = 1.022$ and $\Sigma F^*_{13} = 1.437$ (or 1.067)]. Thus the preferential internal cycloaddition reaction observed with these systems cannot be attributed to an unfavorable cyclization process.



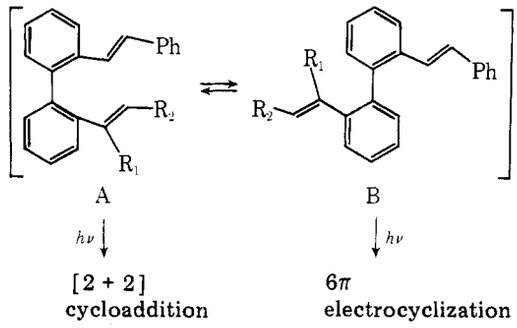
10, R_1 = H, R_2 = Ph
16, R_1 = Ph, R_2 = H

9, R_1 = H, R_2 = Ph
13, R_1 = Ph, R_2 = H



11, R_1 = H, R_2 = Ph
15, R_1 = Ph, R_2 = H

Electronic excitation of these β-aryl substituted divinylbiphenyl derivatives results in energy localization on the stilbene portion of the molecule. Stilbenes are known to undergo 2 + 2 cycloaddition to olefins from the excited singlet state.[55-59] The formation of the cyclobuta[*l*]phenanthrene ring system can be readily ascribed to such a process. When the divinylbiphenyl derivative is devoid of a β-phenyl group, no detectable quantities of a [2 + 2] cycloadduct were found.[60] The distribution of products obtained from the irradiation of these β-aryl substituted divinylbiphenyl derivatives may be related to conformational factors. Two different conformations (A and B) are possible with these systems. One conformation (A) will lead to [2 + 2] cycloaddition while the other conformer (B) will result in cyclization. Lewis and co-workers have previously pointed out that two limiting cases are possible for a situation where two different conformers of a substrate give rise to different photoproducts.[61] In one case, the activation energy for conformational isomerization is lower than that for formation of the products. With this situation,



the ratio of products will depend upon the difference in energy for the transition states leading to the products (Curtin–Hammett principle). In the other case, the activation energy for conformation isomerization is greater than that for formation of the products. For this situation, the ratio of products will depend upon the population of the different conformers and their efficiencies of product formation. If the two conformers of **9** (or **13**) interconvert more rapidly than they react, it follows that the relative distribution of products will depend only on the rates of reaction. According to this argument, the preferential formation of the cyclobuta[*l*]phenanthrene ring system stems from the fact that the 2 + 2 cycloaddition proceeds at a much faster rate than the cyclization reaction. The rapid rate of cycloaddition from conformer A can be ascribed to the close proximity of the excited stilbene moiety and the neighboring vinyl group and the relief of steric crowding which results upon bond closure. It should also be pointed out that the energy barrier for conformational isomerization in the ground and excited state will not necessarily be the same. If conformations A and B are not interconverted in the excited state, then the distribution of products will depend upon the population of A* and B*.[62] The distribution of A* and B* will, in turn, be determined by the ground state equilibrium between the two conformations. Since the 2 + 2 cycloaddition predominates, this reasoning would demand that A be the more stable conformer. The predominance of conformer A could be attributed to the existence of attractive van der Waal forces between the atoms of the aryl-substituted vinyl groups. These weak but effective forces would lead to an overall attractive interaction between the aryl-substituted vinyl groups, much the same as was suggested by Martin in the helicene series.[63] While we consider it instructive to point out the available mechanistic possibilities, the exact situation which operates with these β-aryl substituted divinylbiphenyl derivatives remains to be established.

Experimental Section[64]

Preparation of 2,2′-Biphenyldiacrylonitrile. A solution containing 2.1 g of diphenaldehyde and 6.2 g of cyanomethyltriphenylphosphorane[65] in 200 mL of benzene was heated at reflux for 4 h. The solvent was partially removed and the precipitated triphenyl phosphine oxide was filtered. The resulting crude oil was chromatographed on a 4 × 75 cm Florisil column using a 1:1 pentane–ether mixture as the eluent. The major component isolated (1.1 g, 44%) was a white solid, mp 119–120 °C, which was shown to be a 2:3 mixture of the cis and trans isomers of 2,2′-biphenyldiacrylonitrile (**4**): IR (KBr) 4.53, 6.24, 6.30, 8.40, 10.42, and 13.00 μ; UV (methanol) 223 (ϵ 28 100) and 274 nm (ϵ 32 000); NMR ($CDCl_3$, 100 MHz) τ 4.63 (d, 1 H, J = 12.0 Hz), 4.23 (d, 1 H, J = 16.0 Hz), 3.23 (d, 1 H, J = 12.0 Hz), 3.03 (d, 1 H, J = 16.0 Hz), and 1.80–2.87 (m, 8 H); *m/e* 256 (M^+, base), 228, 179, 178, and 165.

Anal. Calcd for $C_{18}H_{12}N_2$: C, 84.35; H, 4.72; N, 10.93. Found: C, 83.95; H. 4.76; N, 10.86.

Preparation of Dimethyl 2,2′-Biphenyldiacrylate. A solution containing 2.1 g of diphenaldehyde and 7.0 g of carbomethoxymethyltriphenylphosphorane[66] in 200 mL of benzene was heated at reflux for 24 h. The solvent was removed under reduced pressure, and the resulting residue was chromatographed on a 4 × 75 cm Florisil column using a 10% ethyl acetate–benzene mixture as the eluent. The major component isolated was a white solid (1.75 g, 55%) whose structure

was assigned as dimethyl 2,2′-biphenyldiacrylate (**6**): mp 126–127 °C (lit.[67] 123–124 °C); IR (KBr) 5.93, 6.10, 6.30, 6.96, 7.62, 8.40, 10.22, 11.50, and 13.15 μ; UV (methanol) 225 (ε 18:500) and 278 nm (ε 22 500); NMR ($CDCl_3$, 60 MHz) τ 6.35 (s, 6 H), 3.74 (d, 2 H, J = 16.0 Hz), and 2.26–2.94 (m, 10 H); m/e 322 (M^+), 291, 262, 231, 203 (base), 178, and 133.

Anal. Calcd for $C_{20}H_{18}O_4$: C, 74.52; H, 5.63. Found: C, 74.30; H, 5.62.

Preparation of 2,2′-Bis(1-phenylvinyl)biphenyl. To a solution containing 3.57 g of methyltriphenylphosphonium bromide in 75 mL of ether was added 4.3 mL of a 2.3 M n-butyllithium solution at 25 °C. The resulting orange solution was allowed to stir at 25 °C for 20 min prior to the addition of 1.0 g of 2,2′-dibenzoylbiphenyl[68] in 75 mL of ether. The mixture was heated at reflux for 4 days and filtered to remove triphenylphosphine oxide. The residual oil was chromatographed on a 3 × 50 cm Florisil column using a 1:1 pentane–ether mixture as the eluent. The major component isolated contained 900 mg (90%) of 2,2′-bis(1-phenylvinyl)biphenyl (**12**), mp 98–100 °C (lit.[69] 100–101 °C); IR (KBr) 6.22, 6.70, 7.15, 9.41, 11.05, 12.85, and 13.35 μ; UV (methanol) 240 nm (ε 29 300); NMR ($CDCl_3$, 60 MHz) τ 5.07 (d, 2 H, J = 1.5 Hz), 4.67 (d, 2 H, J = 1.5 Hz), and 2.80–3.10 (m, 18 H).

Preparation of 2-(1-Phenylvinyl)-2′-(*Z*)-styrylbiphenyl. A solution containing 2.1 g of diphenylaldehyde, 0.78 g of 2,2-dimethyl-1,3-propanediol, and a trace of p-toluenesulfonic acid in 100 mL of benzene was heated at reflux for 15 h using a Dean–Stark tube to remove the water. The crude oil obtained on removal of the solvent was chromatographed on a 4 × 75 cm Florisil column using a 20% ether–pentane mixture as the eluent. The major component contained 1.3 g (4) of diphenyl monoacetal: IR (neat) 3.40, 5.88. 6.24, 6.81, 7.19, 8.35, 9.05. 9.80, 10.70, 12.05, and 13.10 μ; NMR ($CDCl_3$, 60 MHz) τ 9.40 (s, 3 H), 8.84 (s, 3 H), 6.28–6.99 (m, 4 H), 5.05 (s, 1 H), 1.98–2.98 (m, 8 H), and 0.30 (s, 1 H),

To a solution containing 1.94 g of phenylmethyltriphenylphosphonium chloride[70] in 30 mL of ether was added 2 mL of a 2.5 M n-butyllithium solution at room temperature. The orange solution obtained was allowed to stir at room temperature for 20 min prior to the addition of 1.3 g of the above diphenylaldehyde monoacetal in 20 mL of ether. The solution was stirred at 25 °C for 24 h, filtered, and concentrated under reduced pressure. The resulting oil was taken up in 60 mL of acetone and then 12 mL of a 55% formic acid solution was added. After stirring at 25 °C for 3 days, the solution was diluted with water and extracted with ether. The ether extracts were washed with 10% sodium hydroxide and water, dried over anhydrous magnesium sulfate, concentrated under reduced pressure, and chromatographed on a 3 × 50 cm Florisil column using a 1:1 pentane–ether mixture as the eluent. Removal of the solvent from the major fraction left 905 mg (70%) of 2′-(*Z*)-styryl)-2-biphenylcarboxaldehyde as a pale oil: NMR ($CDCl_3$, 60 MHz) τ 3.82 (d, 1 H, J = 12.0 Hz), 3.60 (d, 1 H, J = 12.0 Hz), 2.03–2.99 (m, 13 H), and 0.21 (s, 1 H).

To a sample containing 284 mg of the above aldehyde was added 0.6 mL of a 1.8 M phenylithium solution. Workup in the normal fashion gave 335 mg (93%) of 2-hydroxybenzyl-2′-(*Z*)-styrylbiphenyl: NMR ($CDCl_3$, 60 MHz) τ 7.83 (br s, 1 H), 4.17–4.50 (m, 1 H), 3.67 (d, J = 2.0 Hz, 2 H), and 2.30–3.30 (m, 18 H). A 362-mg sample of this alcohol in 25 mL of acetone which contained 0.2 mL of Jones reagent was allowed to stir at 25 °C for 5 min. The excess reagent was destroyed by addition of 2-propanol, and the resulting mixture was taken up in 59 mL of water and extracted with ether. The ether extracts were washed with 10% sodium bicarbonate and water, dried over magnesium sulfate, and recrystallized from methanol to give 234 mg (68%) of 2-[o-(*Z*)-styryl)phenyl]benzophenone, mp 85–87 °C; NMR ($CDCl_3$, 60 MHz) τ 3.73 (s, 2 H) and 2.25–3.19 (m, 18 H).

To a solution containing 393 mg of methyltriphenylphosphonium bromide in 20 mL of ether was added 0.44 mL of a 2.5 M n-butyllithium solution at room temperature, followed by 358 mg of 2-[o-(*Z*)-(styryl)phenyl]benzophenone in 20 mL of ether. After stirring at 25 °C for 48 h, the solution was filtered, concentrated under reduced pressure, and purified by thick-layer chromatography using a 20% ether–pentane mixture as the eluent. The major band contained 112 mg (31%) of 2-(1-phenylvinyl)-2′-(*Z*)-styrylbiphenyl (**14**): mp 87–88 °C; IR (KBr) 6.24, 6.95, 7.60, 8.65, 9.05, 9.70, 10.85, and 13.26 μ; UV (methanol) 255 nm (ε 19 500); NMR ($CDCl_3$, 60 MHz) τ 4.83 (d, 1 H, J = 1.5 Hz), 4.59 (d, 1 H, J = 1.5 Hz), 3.86 (d, 1 H, J = 12.0 Hz), 3.61 (d, 1 H, J = 12.0 Hz), 2.62–3.12 (m, 18 H); m/e 358 (M^+) and 255 (base).

Anal. Calcd for $C_{28}H_{22}$: C, 93.81; H, 6.19. Found: C, 93.65; H, 5.88.

Preparation of 2-(1-Phenylvinyl)-2′-(*E*)-styrylbiphenyl. A solution containing 360 mg of 2-[o-(*Z*)-(styryl)phenyl]benzophenone and three crystals of iodine in 50 mL of benzene was heated at reflux for 4 days. Removal of the solvent followed by thick-layer chromatography gave 280 mg (74%) of 2-[o-(*E*)-(styryl)phenyl]benzophenone: mp 111–113 °C; IR (KBr) 603, 6.24, 6.94, 7.82, 8.65, 9.34, 10.38, 10.76, 13.33, 13.97, and 14.35 μ; NMR ($CDCl_3$) 2.47–3.17 (m, 20 H).

To a solution containing 393 mg of methyltriphenylphosphonium bromide in 20 mL of ether was added 0.44 mL of a 2.5 M n-butyllithium solution at room temperature, followed by 358 mg of 2-[o-(*E*)-(styryl)phenyl]benzophenone in 20 mL of ether. After stirring at 25 °C for 48 h, the solution was filtered, concentrated under reduced pressure, and purified on a 1 × 20 cm Florisil column using a 40% ether–pentane mixture as the eluent. The major fraction contained 230 mg (64%) of 2-(1-phenylvinyl)-2′-(*E*)styrylbiphenyl (**13**): mp 80–87 °C; IR (KBr) 6.26, 6.74, 8.55, 9.72, 10.32, 11.08, 13.06, 14.01, and 14.52 μ; UV (methanol) 224 (ε 36 900), 305 (ε 2400), and 315 nm (ε 23 700); NMR ($CDCl_3$, 100 MHz) τ 4.83 (s, 1 H), 4.62 (s, 1 H), and 2.43–3.20 (m, 20 H); m/e 358 (M^+), 257, 181, 178 (base), 126, 104, and 103.

Preparation of 2-[*o*-(1-Phenylvinyl)phenyl]benzophenone. To a solution containing 4.64 g of methyltriphenylphosphonium bromide in 100 mL of ether was added 5.65 mL of a 2.3 M n-butyllithium solution at room temperature, followed by 3.60 g of 2,2′-dibenzoylbiphenyl in 200 mL of a 1:1 ether–benzene mixture. After stirring for 4 days at 25 °C, the solution was filtered, concentrated under reduced pressure, and chromatographed on a dry column (alumina, 5 × 70 cm) using a 20% ether–pentane mixture as the eluent. Three components were isolated and identified as 2,2′-bis(1-phenylvinyl)biphenyl [500 mg (14%)], 2-[o-(1-phenylvinyl)phenyl]benzophenone [2.03 g (56%)], and recovered starting material. The desired 2-[o-(1-phenylvinyl)phenyl]benzophenone (**21**) was a white solid: mp 111–112 °C; IR (KBr) 6.01, 6.28, 6.75, 6.85, 6.96, 7.62, 7.81, 7.94, 9.97, 10.75, 12.84, 13.32, and 14.14; UV (methanol) 242 nm (ε 26 300); NMR (60 MHz, $CDCl_3$) τ 4.92 (d, 1 H, J = 1.5 Hz), 4.61 (d, 1 H, J = 1.5 Hz), and 2.3–3.0 (m, 18 H); m/e 360 (M^+), 225 (base), 105, and 77.

Anal. Calcd for $C_{27}H_{20}O$: C, 89.97; H, 5.59. Found: C, 89.95; H, 5.60.

Preparation of 2′-(1-Phenylvinyl)-2-biphenylcarboxaldehyde. To a solution containing 296 mg of diphenaldehyde monoacetal in 15 mL of ether at 0 °C was added 0.6 mL of a 1.8 M phenyllithium solution. After stirring for 30 min at room temperature, the solution was poured over cracked ice which contained 2 drops of hydrochloric acid. The mixture was extracted with ether, and the ether extracts were washed with a 10% sodium bicarbonate solution and water, dried over magnesium sulfate, and concentrated to a pale oil which contained 320 mg (86%) of 2′-(hydroxybenzyl)-2-biphenylcarboxaldehyde acetal: NMR ($CDCl_3$, 60 MHz) τ 9.42 (s, 3 H), 8.84 (s, 3 H), 6.23–6.98 (m, 5 H), 4.86–5.39 (m, 1 H), 4.38–4.53 (m, 1 H), and 2.22–3.08 (m, 13 H).

A solution containing 1.12 g of the above alcohol in 15 mL of pyridine was added to 10 mL of a 1.0 M solution of Cornforth's reagent. The mixture was stirred at room temperature for 15 h, diluted with water, and extracted with ether. The ether extracts were washed with a 5% hydrochloric acid solution, followed by a 10% sodium bicarbonate solution, and then water. After drying over magnesium sulfate, the solvent was removed under reduced pressure to give 882 mg (79%) of 2′-benzoyl-2-biphenylcarboxaldehyde acetal as a pale oil: NMR (60 MHz, $CDCl_3$) τ 9.38 (s, 3 H), 8.71 (s, 3 H), 6.21–6.81 (m, 4 H), 4.87 (s, 1 H), and 2.18–3.03 (m, 13 H). To a solution containing 393 mg of methyltriphenylphosphonium bromide in 20 mL of ether was added 0.44 mL of a 2.5 M n-butyllithium solution, followed by 372 mg of the above ketone. After stirring for 3 days at 25 °C, the solution was filtered, concentrated, and chromatographed on a 2 × 40 cm Florisil column using a 20% ether–pentane mixture as the eluent. The major component contained 285 mg (77%) of 2′-(1-phenylvinyl)-2-biphenylcarboxaldehyde acetal: mp 108–110 °C; NMR τ 9.32 (s, 3 H), 8.72 (s, 3 H), 6.71 (d, 2 H, J = 11.0 Hz), 6.38 (d, 2 H, J = 11.0 Hz), 5.03 (s, 1 H), 4.85 (s, 1 H), and 2.36–3.17 (m, 13 H).

A solution containing 740 mg of the above acetal and 10 mL of a 55% formic acid solution in 50 mL of acetone was stirred at room temperature for 3 days. The solution was extracted with ether, and the ether extracts were washed with 10% sodium hydroxide and water and dried over magnesium sulfate. Removal of the solvent left a crude oil which was purified on a 2 × 40 cm Florosil column using a 20% ether–pentane mixture. The major component isolated from the column was a pale oil (315 mg, 55%) which crystallized on standing, mp 60–62 °C, and whose structure was assigned as 2′-(1-phenylvinyl)-2-biphenylcarboxaldehyde (**24**): IR (KBr) 3.34, 3.45, 3.55, 5.93, 6.23, 6.97, 7.25, 8.40, 9.17, 11.05, 12.10, 13.10, and 14.20 μ; UV (methanol) 235 (ε 25 700) and 292 nm (ε 3200); NMR ($CDCl_3$, 100 MHz) τ 4.67 (s, 1 H), 4.54 (s, 1 H), 2.18–3.24 (m, 13 H), and 0.33 (s, 1 H); m/e 284 (M^+), 255 (base), 241, 240, 239, 179, 178.

Anal. Calcd for $C_{21}H_{16}O$: C, 88.70; H, 5.67. Found: C, 88.71; H, 5.69.

Preparation of 2-(1-Phenylvinyl)-2′-benzylbiphenyl. To a mixture containing 190 mg of lithium aluminum hydride and 1.07 g of aluminum chloride in 20 mL of ether was added 600 mg of 2-[o-(1-phenylvinyl)phenyl]benzophenone in 10 mL of ether. The mixture was heated for 1 h at reflux, cooled, and then added to 10 mL of a 20% sulfuric acid solution. The ether layer was separated, washed with 10% aqueous sodium bicarbonate and water, dried over magnesium sulfate, and concentrated under reduced pressure. The pale oil was recrystallized from methanol to give 420 mg (72%) of 2-(1-phenylvinyl)-2′-benzylbiphenyl (**28**): mp 88–89 °C; IR (KBr) 3.31, 6.25, 6.72, 6.94, 7.57, 8.55, 9.32, 9.75, 9.94, 11.06, 12.64, 13.02, 13.33, and 14.30 μ; UV (methanol) 245 nm (ε 17 300); NMR ($CDCl_3$, 60 MHz) τ 6.59 (d, 1 H, J = 15.0 Hz), 6.29 (d, 1 H, J = 15.0 Hz), 4.98 (d, 1 H, J = 1.5 Hz), 4.70 (d, 1 H, J = 1.5 Hz), and 2.63–3.31 (m, 18 H); m/e 346 (M^+), 255 (base), 241, 240, 239, 178, 165, and 91.

Anal. Calcd for $C_{27}H_{22}$: C, 93.60; H, 6.40. Found: C, 93.53; H, 6.42.

Preparation of 2-(o-Styryl)benzophenone. To a solution containing 25.0 g of methyltriphenylphosphonium bromide in 150 mL of ether was added 28.0 mL of a 2.5 M n-butyllithium solution, followed by the addition of 10.2 g of diphenylaldehyde acid methyl ester[71] in 200 mL of ether. After stirring for 24 h at 25 °C, the mixture was filtered, concentrated under reduced pressure, and chromatographed on a 3 × 50 cm Florisil column using a 40% ether–pentane mixture. The major fraction isolated [5.0 g (49%)] was identified as o-styrylbenzoic acid methyl ester: NMR ($CDCl_3$, 60 MHz) τ 6.50 (s, 3 H), 5.00 (dd, 1 H, J = 10.0 and 1.5 Hz), 4.49 (dd, 1 H, J = 18.0 and 1.5 Hz), 3.62 (dd, 1 H, J = 18 and 10.0 Hz), 2.03–2.99 (m, 8 H).

A 4.0-g sample of the above ester was reduced with 360 mg of lithium aluminum hydride in 25 mL of ether. The usual lithium aluminum hydride workup afforded 3.0 g (89%) of o-styrylbenzyl alcohol: NMR ($CDCl_3$, 60 MHz) τ 8.00 (s, 1 H), 5.71 (s, 2 H), 4.98 (dd, 1 H, J = 10.0 and 1.5 Hz), 4.48 (dd, 1 H, J = 18 and 1.5 Hz), 3.66 (dd, 1 H, J = 18.0 and 10.0 Hz), 2.32–3.07 (m, 8 H). To a solution containing 2.16 g of pyridinium chlorochromate in 25 mL of methylene chloride at 25 °C was added 1.05 g of the above alcohol. After stirring for 1.5 h, the mixture was filtered and concentrated under reduced pressure to give 900 mg (86%) of o-styrylbenzaldehyde: NMR ($CDCl_3$) τ 4.96 (d, 1 H, J = 11.0 Hz), 4.40 (d, 1 H, J = 16.0 Hz), 3.67 (dd, 1 H, J = 16.0 and 11.0 Hz), 2.33–2.98 (m, 7 H).

To a solution containing phenylmagnesium bromide (prepared from 1.73 g of bromobenzene and 292 mg of magnesium turnings in 40 mL of ether) was added 2.08 g of the above aldehyde in 40 mL of ether. Normal work-up procedures afforded 2.42 g (85%) of 2-(o-styryl)benzhydrol which was oxidized with Jones reagent to give 62% of 2-(o-styryl)benzophenone (**19**) as a colorless oil: IR (neat) 3.32, 6.01, 6.28, 6.86, 6.95, 7.62, 7.80, 8.69, 9.98, 10.76, 13.01, 13.33, and 14.13 μ; NMR ($CDCl_3$, 100 MHz) τ 5.03 (d, 1 H, J = 10.0 Hz), 4.61 (d, 1 H, J = 16.0 Hz), 3.62 (dd, 1 H, J = 16.0 and 10.0 Hz), and 2.63–3.22 (m, 13 H); m/e 284 (M^+), 105 (base) and 77.

Irradiation of 2,2′-Divinylbiphenyl. A solution containing 150 mg of 2,2′-divinylbiphenyl (**1**) in 150 mL of benzene was irradiated with a 450-W Hanovia lamp equipped with a Pyrex filter sleeve for 18 h. The solvent was removed under reduced pressure, and the crude photolysate was chromatographed on a 1 × 15 cm Florisil column using a 1:1 pentane–ether mixture as the eluent. The major fraction contained 125 mg (85%) of 4,5,9,10-tetrahydropyrene (**3**), mp 134–136 °C (lit.[72] 135–136 °C). The structure of this material was unambiguously established by comparison with an authentic sample. When the irradiation of 1 was carried out for 3 h, a new product was present (30%) and was isolated by preparative gas chromatography (0.5 in. × 4 ft 3% SE-30 on Chromosorb W at 160 °C) and shown to be 4-vinyl-9,10-dihydrophenanthrene (**2**) on the basis of the following data: IR (neat) 6.15, 6.32, 6.72, 6.90, 7.08, 7.94, 9.94, 10.88, 12.45, and 13.40 μ; UV (methanol) 244 (ε 17 200) and 274 nm (ε 14 700); NMR ($CDCl_3$, 60 MHz) τ 7.26 (s, 4 H), 4.75 (dd, 1 H, J = 11.0 and 1.5 Hz), 4.32 (dd, 1 H, J = 18.0 and 1.5 Hz), and 2.28–3.20 (m, 8 H); m/e 206 (M^+ and base). Further irradiation of this material afforded 4,5,9,10-tetrahydropyrene (**3**).

Irradiation of 2,2′-Biphenyldiacrylonitrile. A solution containing 160 mg of 2,2′-biphenyldiacrylonitrile (**4**) in 125 mL of benzene was irradiated through a Corex filter sleeve for 5 h. Removal of the solvent followed by chromatography on a 1 × 15 cm Florisil column with a 20% ethyl acetate–benzene mixture gave 114 mg (71%) of 4,5,9,10-tetrahydro-4,9-dicyanopyrene (**5**) as a pale-yellow solid: mp 258–260 °C: IR (KBr) 4.43, 6.90, 7.75, 8.05, 8.45, 9.10, 10.00, 12.35, and 13.52 μ; UV (methanol) 231 (ε 9800), 267 (ε 14 900), 277 (ε 17 000), and 290 nm (ε 11 700); NMR ($CDCl_3$, 100 MHz) τ 6.83 (d, 2 H, J = 7.0 Hz), 5.73 (t, 1 H, J = 7.0 Hz), and 2.57–2.78 (m, 6 H); m/e 256 (M^+ and base). The structure of this material was verified heating a 120-mg sample with 10 mg of 5% paladium on carbon in 10 mL of toluene at 160 °C for 20 h. Separation of the catalyst followed by removal of the solvent gave 4,9-dicyanopyrene (**8a**) as a yellow solid: mp 392–397 °C (lit.[73] mp 405–406 °C); IR (KBr) 4.48, 6.70, 6.90, 8.20, 10.88, 11.20, 12.50, and 13.90 μ; UV (methanol) 243, 268, 280, 333, and 348 nm (ε 10 900, 3100, 6300, 1900, and 2900); m/e 252 (M^+ and base).

Irradiation of Dimethyl 2,2′-Biphenyldiacrylate. A 410-mg sample of **6** in 125 mL of benzene was irradiated through a Corex filter sleeve for 7 h. Removal of the solvent followed by chromatography on a 2 × 40 cm Florisil column using a 10% ethyl acetate–benzene mixture afforded 246 mg (60%) of 4,5,9,10-tetrahydro-4,9-dicarbomethoxypyrene (**7**), mp 122–129 °C. This material was a 2:1 mixture of isomers as evidenced by examination of the NMR spectrum (100 MHz, $CDCl_3$) τ 6.71–7.19 (m, 4 H), 6.57 and 6.47 (s, 6 H total), 6.17–6.37 (m, 2 H), and 3.20 (s, 6 H); IR (KBr) 5.75, 6.67, 7.00, 7.88, 8.35, 9.01, 9.42, 12.35, and 14.00 μ; UV (methanol) 268 (ε 14 200), 278 (ε 16 900), and 290 nm (ε 12 000); m/e 322 (M^+) and 203 (base). This material was oxidized with 5% palladium on charcoal at 160 °C in toluene (24 h) to give 4,9-dicarbomethoxypyrene (**8b**): mp 239–240 °C; IR (KBr) 5.74, 6.75, 7.00, 7.92, 8.38, 9.46, 11.00, 12.30, and 14.00 μ; UV (methanol) 243 (ε 46 400), 271 (ε 18 600), 282 (ε 29 400), and 346 nm (ε 15 900); m/e 318 (M^+ and base).

Anal. Calcd for $C_{20}H_{14}O_4$: C, 75.46; H, 4.43. Found: C, 75.36; H, 4.43.

Irradiation of 2,2′-Bis(1-phenylvinyl)biphenyl. A 200-mg sample of **12** in 140 mL of benzene was irradiated through a Corex filter sleeve for 4 h. Removal of the solvent followed by chromatography through a 1 × 20 cm Florisil column with a 1:1 benzene–pentane mixture gave 75 mg (38%) of 4,5,9,10-tetrahydro-4,9-diphenylpyrene (**10**), mp 211–213 °C (lit.[24] 213–215 °C). This material was compared with an authentic sample synthesized according to the procedure of Laarhoven and Cuppen.[24]

Irradiation of 2-(1-Phenylvinyl)-2′-styrylbiphenyl. A solution containing 150 mg of either the (*E*) or (*Z*) isomer of 2-(1-phenylvinyl)-2′-styrylbiphenyl (**13** or **14**) in 350 mL of benzene was irradiated through Pyrex for 16 h. Removal of the solvent followed by chromatography on a 1 × 12 cm Florosil column using a 5% ether–pentane mixture gave 120 mg of 4,5,9,10-tetrahydro-4,10-diphenylpyrene (**16**), mp 152–158 °C, as a mixture of stereoisomers: IR (KBr) 6.30, 6.75, 6.94, 7.74, 8.69, 9.33, 9.74, 12.70, 13.08, 13.63, and 14.25 μ; UV (methanol) 272 (ε 13 200), 282 (ε 14 900), and 294 nm (ε 10 400); NMR ($CDCl_3$, 100 MHz) τ 6.67–6.85 (d, 4 H, J = 8.0 Hz), 5.70 (t, 2 H, J = 8.0 Hz), and 2.08–3.22 (m, 16 H); m/e 358 (M^+ and base). This material was oxidized with 5% palladium on carbon at 160 °C for 16 h to give 4,10-diphenylpyrene (**18**): mp 152–153 °C; IR (KBr) 6.32, 6.75, 6.98, 7.37, 9.11, 9.35, 11.25, 11.89, 12.61, 12.95, 13.83, and 14.33 μ; UV (methanol) 244 (ε 43 200), 279 (ε 40 100), 315 (ε 10 200), 328 (ε 19 800), and 344 nm (ε 26 000); m/e 354 (M^+), 225, 133, 131, 89 (base), and 73.

Anal. Calcd for $C_{28}H_{18}$: C, 94.88; H, 5.12. Found: C, 94.49; H, 5.04.

The irradiation of the 2-(1-phenylvinyl)-2′-styrylbiphenyl system was also carried out for a much shorter period of time. A 150-mg sample of either (*E*)-**13** or (*Z*)-**14** in 140 mL of benzene was irradiated through a Pyrex filter sleeve for 40 min. Removal of the solvent followed by thick-layer chromatography using a 1% ether–pentane mixture resulted in the separation of three bands. The two minor components were recovered starting material (42%) [(*Z*) and (*E*) mixture (1:1)], 4,5,9,10-tetrahydro-4,10-diphenylpyrene (**16**) (5 mg, 3%), and 82 mg (55%) of 1,2,2a,10b-tetrahydro-1,2a-diphenylcyclobuta[*l*]phenanthrene (**15**): mp 147–148 °C; IR (KBr) 6.25, 6.72, 6.95, 8.36, 9.15, 9.31, 9.68, 10.24, 10.98, 12.73, 13.24, 13.51, and 14.14 μ; UV (methanol) 268 (ε 13 200 and 300 nm (ε 5080); NMR ($CDCl_3$, 100 MHz) τ 7.23 (d, 2 H, J = 8.0 Hz), 5.98 (d, 1 H, J = 12.0 Hz), 5.63 (td, 1 H, J = 12.0 and 8.0 Hz) and 2.21–3.03 (m, 18 H); m/e 358 (M^+), 104 (base), and 77.

Anal. Calcd for $C_{28}H_{22}$: C, 93.81; H, 6.19. Found: C, 93.77; H, 6.19.

Photolysis of 1,2,2a,10b-tetrahydro-1,2a-diphenylcyclobuta[*l*]-phenanthrene (**15**) in benzene through Pyrex resulted in the quantitative formation of 4,5,9,10-tetrahydro-4,10-diphenylpyrene (**16**). Thermolysis of **15** at 150 °C for 48 h, on the other hand, resulted in the formation of 9-phenylphenanthrene (**17**) and polystyrene.

Irradiation of (*E*,*E*)-2,2′-Distyrylbiphenyl. A 200-mg sample of **9** in 140 mL of benzene was irradiated through Pyrex for 64 h. Removal of the solvent followed by chromatography on a 2 × 20 cm Florosil column using a 1:1 benzene–hexane mixture gave 105 mg (52%) of 4,5,9,10-tetrahydro-4,9-diphenylpyrene (**10**), mp 211–213

°C (lit.[24] 213–215 °C). When the irradiation was carried out for 1 h, the major component isolated from the thick-layer plate (135 mg, 68%) was 1,2,2a,10b-tetrahydro-1,2-diphenylcyclobuta[*l*]phenanthrene (**11**), mp 136–137 °C (lit.[24] 136–137 °C), whose spectral properties were identical with those reported in the literature.[24]

Irradiation of 2-[*o*-(1-Phenylvinyl)phenyl]benzophenone. A solution containing 140 mg of **21** in 275 mL of benzene was irradiated through a Vycor filter sleeve for 22 h. Removal of the solvent followed by thick-layer chromatography using a 20% ether–pentane mixture gave 9-phenylphenanthrene (**17**) (16 mg (10%) and 4-benzoyl-9-phenyl-9,10-dihydrophenanthrene (**22**) [85 mg (60%)]: mp 116–117 °C; IR (KBr) 6.04, 6.30, 6.72, 6.92, 7.61, 7.82, 8.38, 8.65, 9.88, 10.10, 10.87, 11.47, 12.30, 12.61, 13.02, and 13.06 μ; UV (methanol) 255 nm (ε 21 100); NMR ($CDCl_3$, 100 MHz) τ 6.79 and 6.77 (two overlapping doublets, 2 H, J = 7.0 Hz), 5.84 (t, 1 H, J = 7.0 Hz), and 2.48–3.20 (m, 17 H); *m/e* 360 (M^+), 254, 202, and 105 (base).

Anal. Calcd for $C_{27}H_{20}O$: C, 89.97; H, 5.59. Found: C, 89.94; H, 5.60.

The irradiation of **21** was also carried out with wavelength of light >365 nm. A 300-mg sample of **21** in 410 mL of benzene was irradiated through a uranium glass filter for 60 h. Removal of the solvent followed by chromatography on a 2 × 40 cm silica gel column using a 20% ether–pentane mixture gave 185 mg of 4-benzoyl-9-phenyl-9,10-dihydrophenanthrene (**22**) as well as 60 mg (20%) of 9-benzoyl-9-phenyl-9,10-dihydrophenanthrene (**23**): mp 147–148 °C; IR (KBr) 5.98. 6.74, 6.92, 7.93, 8.24, 10.90, 13.05, 13.25, and 14.09 μ; UV (methanol) 260 nm (ε 18 300); NMR (100 MHz, $CDCl_3$) τ 6.32 (s, 2 H) and 2.42–3.47 (m, 18 H). When europium shift reagent was added, the singlet at τ 6.32 was converted to an AB quartet (J_{AB} = 14.0 Hz); *m/e* 358 (M^+), 256, 126 (base), 119, 105, and 98.

Anal. Calcd for $C_{27}H_{20}O$: C, 89.97; H, 5.59. Found: C, 89.65; H, 5.47.

The ratio of **22** and **23** did not change when the irradiation of **21** was carried out in the presence of 1-dodecanethiol. Further irradiation of **23** with 2537-Å light resulted in the formation of 9-phenylphenanthrene (**17**) and benzaldehyde.

Irradiation of 2′-(1-Phenylvinyl)-2-biphenylcarboxaldehyde. A 100-mg sample of **24** in 350 mL of benzene was irradiated through a Pyrex filter sleeve for 4.5 h. Removal of the sovlent followed by thick-layer chromatography using a 20% ether–pentane mixture gave three bands which were identified as 9-phenyl-9,10-dihydrophenanthrene (**27**) [58 mg (58%)], 9-phenylphenanthrene (**17**) [12 mg (1)] and 9-phenyl-9,10-dihydro-4-phenanthrenecarboxaldehyde (**25**) [10 mg (10%)]. The first two products were identified by comparison with authentic samples. The assignment of the third component as **25** rests on its analytical and spectral data: mp 116–117 °C; IR (KBr) 5.96, 6.29, 6.94, 7.28, 8.15, 8.63, 9.33, 10.27, 12.64, 13.16, 13.64, and 14.24 μ; UV (methanol) 243 (ε 16 600), 269 (ε 10 600), and 324 nm (ε 5300); NMR ($CDCl_3$, 100 MHz) τ 6.65–6.81 (two overlapping doublets, 2 H, J = 7.0 Hz), 5.67–5.84 (t, 1 H, J = 7.0 Hz), 2.40–2.98 (m, 11 H), 1.98–2.10 (m, 1 H), and −0.37 (s, 1 H); *m/e* 284 (M^+ and base) 283, 255, 178, 91, and 77.

Anal. Calcd for $C_{21}H_{16}O$: C, 88.70; H, 5.67. Found: C, 88.35; H, 5.66.

The photolysis of **24** was also carried out using light of wavelength >365 nm. A 80-mg sample of **24** in 140 mL of benzene was irradiated through a uranium glass filter for 28 h. Removal of the solvent followed by thick-layer chromatography using a 3% ether–pentane mixture gave a mixture of 9-phenyl-9,10-dihydro-4-phenanthrenecarboxaldehyde [(**25**) (10 mg (13%)] and 9-phenyl-9,10-dihydro-9-phenanthrenecarboxaldehyde (**26**) [40 mg (50%)]: mp 111–112 °C; IR (KBr) 5.81, 6.75, 6.97, 9.17, 10.53, 12.14, 12.99, 13.39, and 14.13 μ; UV (methanol) 269 (ε 6500) and 300 nm (ε 1300); NMR ($CDCl_3$, 100 MHz) τ 6.60 (d, 1 H, J = 15.0 Hz), 6.38 (d, 1 H, J = 15.0 Hz), 1.88–3.06 (m, 13 H), and −0.11 (s, 1 H); *m/e* 284 (M^+) 255 (base), 178, 146, and 126.

Anal. Calcd for $C_{21}H_{16}O$: C, 88.70; H, 5.67. Found: C, 88.68; H, 5.55.

On further photolysis using 2537-Å light, **26** was converted to 9-phenylphenanthrene (**17**) and 9-phenyl-9,10-dihydrophenanthrene (**27**).

Irradiation of 2-(1-Phenylvinyl)-2′-benzylbiphenyl. A 100-mg sample of **28** in 140-mL of benzene was irradiated through a Pyrex filter sleeve for 48 h. Removal of the solvent followed by chromatography on a 1 × 10 cm silica column using a 20% ether–pentane mixture as the eluent gave 9-phenyl-9,10-dihydro-4-benzylphenanthrene (**29**) as the only detectable photoproduct: mp 105–106 °C; IR (KBr) 6.27, 6.72, 6.92, 7.80, 8,70, 10.61, 12.66, 12.89, 13.39, and 14.30 μ; UV (methanol) 265 nm (ε 16 100); NMR ($CDCl_3$, 60 MHz) τ 6.83 (d, 2 H, J = 7.0 Hz), 5.90 (t, 1 H, J = 7.0 Hz), 5.62 (s, 2 H), and 2.63–3.07 (m, 17 H); *m/e* 346 (M^+ and base).

Anal. Calcd for $C_{27}H_{22}$: C, 93.60; H, 6.40. Found: C, 93.55; H, 6.44.

Irradiation of 2-(*o*-Styryl)benzophenone. A solution containing 80 mg of **19** in 140 mL of benzene was irradiated through a Pyrex filter sleeve for 24 h. Removal of the solvent followed by chromatography on a 1 × 10 cm neutral alumina column using a 1:1 pentane–ether mixture as the eluent gave 4-benzoyl-9,10-dihydrophenanthrene (**20**) [60 mg (75%)] as the major product: IR (neat) 3.50, 6.01, 6.25, 6.96, 7.85, 8.61, 8.96, 9.96, 11.11, 12.76, 13.46, and 14.08 μ; UV (methanol) 253 (ε 26 900) and 293 nm (ε 5900); NMR (100 MHz, $CDCl_3$) τ 7.03 (s, 4 H) and 2.28–3.13 (m, 12 H); *m/e* 284 (M^+), 283 (base), 255, 207, 179, 178, 105, and 77.

Quantum Yield Determination. Quantitative measurements were made on a rotating assembly with a series of 2537- or 3130-Å lamps in a Rayonet reactor. Samples in 13-mm Pyrex or quartz ampules were placed in holders on the assembly approximately 6 cm from the light source. All studies were made at room temperature. Samples were degassed to 10^{-4} mm in several freeze-pump-thaw cycles and then sealed. Benzophenone–benzhydrol solutions were used as the chemical actinometer.[74] After irradiation, the degree of reaction was determined by quantitative NMR or vapor-phase chromatography. The conversions were run to 15% or less. In no case was the amount of product formed affected by added piperylene. The quencher was present in concentrations sufficiently high to suppress established triplet processes.[75] Sensitization experiments used benzophenone and were made on a rotating assembly with a central light source (internal water-cooled mercury arc lamp, Hanovia Type L-450W) equipped with a uranium filter sleeve. The concentrations were such that benzophenone absorbed greater than 98% of the light.

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Registry no.—**1**, 34919-47-6; **2**, 55006-42-3; *cis*-**4**, 63104-60-9; *trans*-**4**, 63104-61-0; **5**, 55006-99-0; **6**, 55006-97-8; *cis*-**7**, 55007-00-6; *trans*-**7**, 55007-01-7; **8a**, 55006-40-1; **8b**, 55006-41-2; **9**, 33510-35-9; **12**, 55006-98-9; **13**, 63104-62-1; **14**, 63104-63-2; **15**, 63104-64-3; *cis*-**16**, 63104-65-4; *trans*-**16**, 63104-66-5; **18**, 63104-67-6; **19**, 63104-68-7; **20**, 63104-69-8; **21**, 63104-70-1; **22**, 63104-71-2; **23**, 63104-72-3; **24**, 63104-73-4; **25**, 63104-74-5; **26**, 63104-75-6; **28**, 63104-76-7; **29**, 63104-77-8; diphenaldehyde, 1210-05-5; cyanomethyltriphenylphosphorane, 63104-78-9; carbomethoxymethyltriphenylphosphorane, 63104-79-0; methyltriphenylphosphonium bromide, 1779-49-3; 2,2′-dibenzoylbiphenyl, 24018-00-6; 2,2-dimethyl-1,3-propanediol, 126-30-7; diphenyl monoacetal, 63104-80-3; phenylmethyltriphenylphosphonium chloride, 1100-88-5; 2′-((*Z*)-styryl)-2-biphenylcarboxaldehyde, 63104-81-4; 2-hydroxybenzyl-2′-(*Z*)-styrylbiphenyl, 63104-82-5; 2-[*o*-(*Z*)-(styryl)phenyl]benzophenone, 63104-83-6; 2[*o*-(*E*)-(styryl)phenyl]benzophenone, 63104-84-7; 2′-(hydroxylbenzyl)-2-biphenylcarboxaldehyde acetal, 63104-85-8; 2′-benzoyl-2-biphenylcarboxaldehyde acetal, 63104-86-9; 2′-(1-phenylvinyl)-2-biphenylcarboxaldehyde acetal, 63104-87-0; diphenylaldehyde acid methyl ester, 16231-67-7; *o*-styrylbenzoic acid methyl ester, 63104-88-1; *o*-styrylbenzyl alcohol, 4393-04-8; *o*-styrylbenzaldehyde, 63104-89-2; bromobenzene, 108-86-1.

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Dipolar Micelles. 5. Micellar Effects on the Hydrolysis of Neutral and Charged Esters

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The specific base catalyzed hydrolyses of positively charged and neutral esters in three betainelike micelles of structures I–III, and five dipolar micelles IV–VIII, have been studied. These comprised nine different esters: $C_{10}H_{21}N^+(CH_3)_2ZBr^-$, Z = 2-(*p*-nitrobenzoyloxy)ethyl (CPNBA), Z = 3-(*p*-nitrobenzoyloxy)propyl (HCPNBA), Z = 3-(2,4-dinitrophenyloxycarbonyl)propyl (DNPDE$^+$); *p*-nitrophenyl acetate (PNPA); *p*-nitrophenyl hexanoate (PNPH); *p*-nitrophenyl decanoate (PNPD); 2,4-dinitrophenyl acetate (DNPA); 2,4-dinitrophenyl decanoate (DNPD); and decyl *p*-nitrobenzoate (DPNBA). Study has shown that the second-order rate coefficients of PNPA, PNPH, and PNPD enhance with increasing concentration of premicelle aggregates (subunits) and decrease in the presence of micelles. The betainelike micelles exhibit inhibitory effect on rates of hydrolyses of most substrates included in this study. The inhibitory efficiency was found to depend on the positions of both the reaction site and the carboxylate anion of the zwitterionic micelle. It is suggested that proximity of microenvironmental factors affects primarily the course of hydrolyses on the micellar surface.

In parts 3 and 4[1,2] we have shown that proximity and microenvironmental factors are important in determining the catalytic efficiency of micelle-forming cationic surfactants containing hydroxy head groups at various positions around the cationic surface. It is well known that reactions which occur at the micellar surface are highly affected by the hy-