diluted with methanol (10 mL), and the colorless precipitate (637 mg) was removed by filtration. Recrystallization by dissolving the precipitate in methylene chloride followed by addition of methanol gave 561 mg (72%) of *p,p* dimer 15, mp 307–311 °C. Its UV absorption spectrum in cyclohexane is virtually identical with that of *p,p* dimer 11: 270-MHz ^{1}H NMR (CDCl$_3$) 7.28 (d, 4 H, J = 8 Hz), 6.85 (t, 4 H, J = 8 Hz), 6.40 (s, 4 H, methylene H), 6.27 (d, 4 H, J = 8 Hz), 4.01 (s, 2 H). Anal. Calcd for C$_{30}$H$_{18}$Cl$_4$ (mol wt 520.28): C, 69.26; H, 3.49. Found: C, 69.10; H, 3.56.

Thermodynamic and Kinetic Measurements. Thermodynamic and kinetic data for the equilibration of tetrachlorolepidopterenes 10-L-1 ⇌ 10-L-2 were obtained in CDCl$_3$ solution at 10, 25, and 35 °C by integration over the ABX spectra shown

in Figure 4. The solubility of 10-L-1 in CDCl$_3$ is about 1 mg/mL.

Photosensitized Electron-Transfer-Induced Reactions of Some Cyclopropene Derivatives

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The 9,10-dicyanoanthracene-sensitized rearrangement of several 3-phenyl-substituted cyclopropenes to indenes in acetonitrile has been studied. When an unsymmetrically 1-phenyl-2-methyl-substituted cyclopropene was used, the major indene obtained corresponds to cleavage of the cyclopropene bond attached to the phenyl group. This stands in marked contrast to the results obtained on direct irradiation. The mechanism proposed to rationalize the results involves a number of steps. The first step consists of selective excitation of dicyanoanthracene. Step 2 involves an electron transfer which ultimately leads to a solvent-separated radical ion pair. The calculated ΔG value for this process indicates that the electron-transfer reaction should be spontaneous. The initially produced radical cation undergoes cleavage of the ring followed by a subsequent cyclization onto the ortho position of the neighboring aromatic ring. Reaction of the resulting radical cation with dicyanoanthracene radical anion leads to an isoindene which undergoes rearomatization. The radical cation path nicely accommodates the regioselectivity observed. Thus, ring opening occurs in the direction leading to the most stable radical cation.

The reactions of exciplexes and electron-transfer processes have attracted considerable attention in recent years.[1–5] It is clear that, in many cases where electronic energy transfer is endothermic, the primary process leading to quenching is formation of an exciplex, the stability of which should depend on the electron-donating and -accepting properties of the quencher and excited state, respectively. Whereas exciplexes are usually formed in nonpolar solvents, the formation of solvated radical ions occurs on irradiation in polar solvents. The electron-transfer reactions of cyclopropenes are particularly interesting because of the unusual intermediates that are involved. Independent work by Arnold[7] and Farid[8] has shown that the [2 + 2] photocycloaddition of cyclopropenes with electron-deficient olefins proceeds via an electron-transfer reaction. Diphenyl-substituted cyclopropenes have also been found to react with the singlet-state of

Scheme I
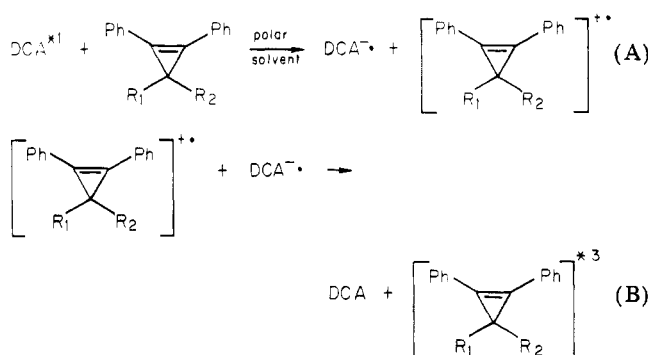
9,10-dicyanoanthracene (DCA*^{1}) at a diffusion-controlled rate to produce the radical ions of the cyclopropene and anthracene (see Scheme I).[7,8] The free-energy (ΔG) change for such a process, leading to the formation of a radical-ion pair, can be calculated from the Weller equation (eq 1).[3]

$$\Delta G_1 = (E_D^{Ox} - E_A^{Red}) - \Delta E(A^{*1}) \qquad (1)$$

In this expression E_D^{Ox} and E_A^{Red} are the electrochemically determined potentials for the one-electron oxidation of the donor and reduction of the acceptor, respectively. $\Delta E(A^{*1})$ is the zero–zero transition energy of the lowest excited singlet state of the acceptor. Substitution of the appropriate values into the Weller equation results in the conclusion that electron transfer from a diphenyl-substituted

(1) A. Weller in "The Exciplex", M. S. Gordon and W. R. Ware, Eds., Academic Press, New York, 1975, Chapter 2.
(2) D. Rehm and A. Weller, *Isr. J. Chem.*, **8**, 259 (1970).
(3) A. Weller, *Nobel Symp.*, No. 5, 413 (1967).
(4) H. Beens and A. Weller, *Acta Phys. Pol.*, **34**, 593 (1968).
(5) H. Knibbe, D. Rehm and A. Weller, *Ber. Bunsenges. Phys. Chem.*, **72**, 257 (1968).
(6) T. Okada, H. Oohari, and N. Mataga, *Bull. Chem. Soc. Jpn.*, **43**, 2750 (1970).
(7) D. R. Arnold and R. M. Morchat, *Can. J. Chem.*, **55**, 393 (1977); P. C. Wong and D. R. Arnold, *ibid.*, **57**, 1037 (1979).
(8) S. Farid and K. A. Brown, *J. Chem. Soc., Chem. Commun.*, **564** (1976); K. A. Brown-Wensley, S. L. Mattes, and S. Farid, *J. Am. Chem. Soc.*, **100**, 4162 (1978).

Scheme II

Scheme III

4, $n = 1$
8, $n = 2$

5, $n = 1$ **6,** $n = 1$
9, $n = 2$ **10,** $n = 2$
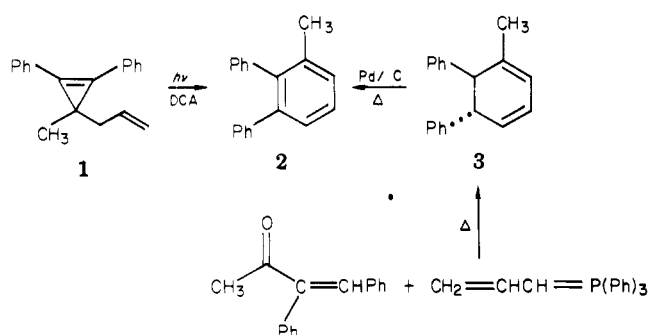
cyclopropene to DCA* is favorable by 9 kcal/mol.[8]

Photophysical studies by the Farid group have established that recombination of the DCA–cyclopropene radical-ion pair results in the formation of the triplet state of the cyclopropene (B, Scheme I).[8] The free energy associated with this recombination is given by eq 2.[3] The

$$\Delta G = \Delta E(D^{*3}) - (E_D^{Ox} - E_A^{Red}) \qquad (2)$$

first term represents the triplet energy of the diphenyl-substituted cyclopropene. From electrochemical data and the triplet energy of the cyclopropene ($E_T \approx 53$ kcal/mol),[9] it has been estimated that reaction B (Scheme I) is exothermic by 6 kcal/mol. This phenomenon is potentially useful for generating the triplet state of cyclopropenes since the singlet state is known to have a very inefficient intersystem crossing efficiency.[9,10] In this paper we report the results of a study using dicyanoanthracene as a photosensitizer for several diphenyl-substituted cyclopropenes. The reactions observed are best rationalized as proceeding via initial electron transfer from the cyclopropene to the excited DCA to give a radical cation which then undergoes a subsequent rearrangement.

Results

Previous work in our laboratory has shown that 3-allyl-substituted cyclopropenes undergo smooth intramolecular [2 + 2] cycloaddition on triplet sensitization to give tricyclo[2.2.0.0²,⁶]hexanes.[11] If the triplet state of the 3-allyl-substituted cyclopropene is generated by using DCA as the sensitizer, then the same tricyclohexane should be formed as was obtained when thioxanthone was used as the photosensitizer.[11] This turned out not to be the case. Solutions of variously substituted diphenyl-substituted cyclopropenes in acetonitrile were found to readily quench the fluorescence of DCA. No exciplex emission was observed in this solvent system. Farid had previously shown that the rate of quenching of the fluorescence of DCA by a representative cyclopropene is diffusion controlled.[8] Irradiation of an argon-purged acetonitrile solution of DCA and 1,2-diphenyl-3-methyl-3-allylcyclopropene (1) produced 1,2-diphenyl-3-methylbenzene (2) as the major photoproduct (Scheme II). The structure of this material was determined by comparison with an independently synthesized sample prepared from the Wittig reaction of 3,4-diphenyl-3-buten-2-one and allyltriphenylphosphorane followed by 6π electrocyclization and subsequent oxidation with palladium on carbon. When the irradiation of the isomeric 1,3-diphenyl-2-methyl-3-allylcyclopropene (4) was
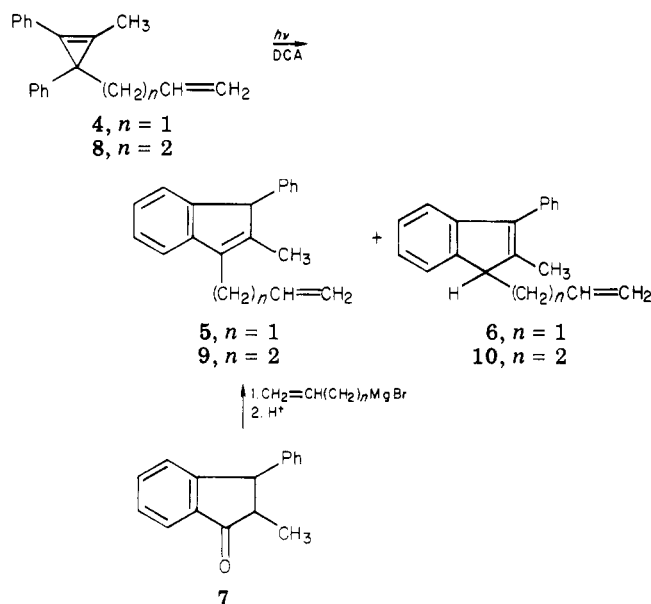
carried out in acetonitrile with DCA as the sensitizer (Scheme III), a 2:1 mixture of 1-phenyl-2-methyl-3-allyl-(5) and 1-allyl-2-methyl-3-phenylindene (6) was obtained. The structure of indene 5 was confirmed by comparison with an authentic sample prepared by treating 2-methyl-3-phenyl-1-indanone (7) with allylmagnesium bromide, followed by dehydration of the resulting alcohol. Heating a benzene–pyridine solution of 5 at 160 °C gave the isomeric indene 6 as well as recovered starting material. This base-induced isomerization undoubtedly involves a 1,3 hydrogen shift.

The photosensitized reaction of the closely related 1,3-diphenyl-2-methyl-3-(4-butenyl)cyclopropene (8) was also studied in order to further assess the excited-state behavior of these systems. The DCA-sensitized reaction of 8 produced a 3:1 mixture of indenes 9 and 10. The structures of the resulting photoproducts were verified by comparison with independently synthesized samples. The above results clearly indicate that the DCA-sensitized reactions do not proceed via the electronically excited triplet state since no detectable quantities of an intramolecular [2 + 2] cycloadduct were present in the crude photolysate (i.e., <3%). This is in dramatic contrast to the thioxanthone-sensitized reaction where internal cycloaddition is the only path followed.

One of the more frequently encountered photochemical reactions of 3-aryl-substituted cyclopropenes involves rearrangement to indenes.[12,13] The reaction has been proposed to involve a sequence consisting of ring opening of the electronically excited singlet state to a vinylcarbene intermediate.[14] Cyclization of the carbene onto the ortho position generates an isoindene which subsequently undergoes a thermally allowed sigmatropic 1,5 hydrogen shift. Studies dealing with the photochemistry of a number of unsymmetrically 3-aryl-substituted cyclopropenes revealed the existence of an unusual substituent effect on the mode of ring opening.[15-18] Thus, the major product obtained

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(9) C. D. DeBoer, D. H. Wadsworth, and W. C. Perkins, *J. Am. Chem. Soc.*, **95**, 861 (1973).

(10) A. Padwa, T. J. Blacklock, C. S. Chou, and N. Hatanaka, *J. Am. Chem. Soc.*, **101**, 5743 (1979).

(11) A. Padwa and T. J. Blacklock, *J. Am. Chem. Soc.*, **99**, 2345 (1977); **101**, 3390 (1979).

(12) H. Durr, *Tetrahedron Lett.*, 1649 (1967).

(13) B. Halton, M. Kulig, M. A. Battiste, J. Perreten, D. M. Gibson, and G. W. Griffin, *J. Am. Chem. Soc.*, **93**, 2327 (1971).
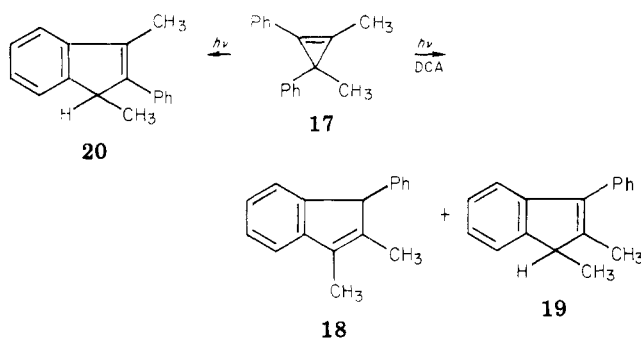
(14) M. A. Battiste, B. Halton, and R. H. Grubbs, *Chem. Commun.*, 907 (1967).

(15) A. Padwa, T. Blacklock, D. Getman, and N. Hatanaka, *J. Am. Chem. Soc.*, **99**, 2344 (1977); A. Padwa, R. Loza, and D. Getman, *Tetrahedron Lett.*, 2847 (1977); A. Padwa, T. J. Blacklock, D. Getman, N. Hatanaka, and R. Loza, *J. Org. Chem.*, **43**, 1481 (1978).
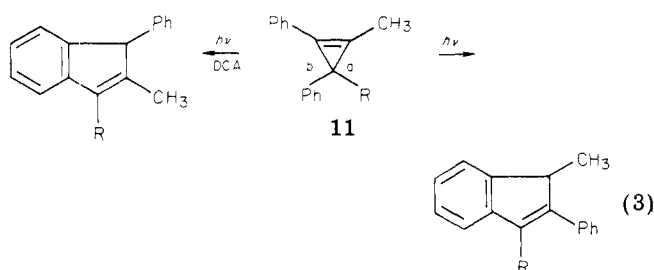
Scheme IV
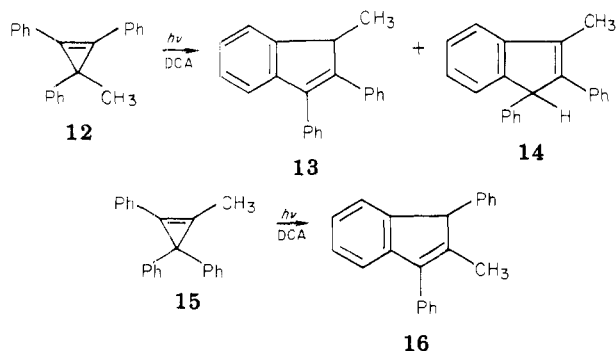
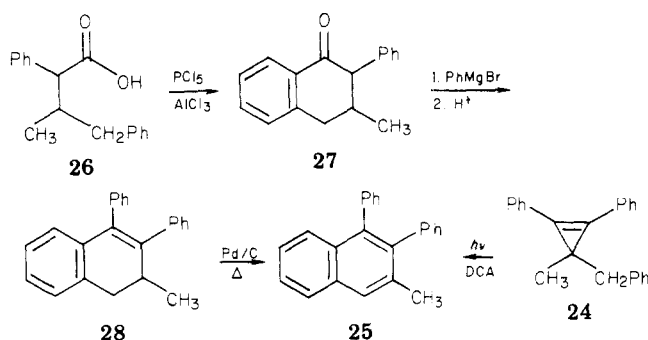**Scheme V**

from the irradiation of a 1,3-diphenyl-2-methyl-substituted cyclopropene (11, eq 3) was always found to correspond

$$(3)$$

to preferential cleavage of the cyclopropene bond which is methyl rather than phenyl substituted (i.e., bond a). This unusual regioselectivity was attributed to a funneling of the excited state of the cyclopropene to the energy surface of the higher lying carbene state.[15] In marked contrast to the direct photolysis, the DCA-sensitized irradiation of cyclopropenes 4 and 8 resulted in the exclusive cleavage of the cyclopropene bond attached to the phenyl group (bond b). This observation clearly eliminates the involvement of the electronically excited singlet state of the cyclopropene in the DCA-sensitized reaction.

In order to further define the factors and mechanism associated with the DCA-sensitized reaction of cyclopropene derivatives, we studied the photochemistry of a number of related systems. The DCA-sensitized irradiation of 1,2,3-triphenyl-3-methylcyclopropene (12) afforded a 3:1 mixture of indenes 13 and 14 (Scheme IV). The structures of these compounds were verified by comparison with independently synthesized samples. Irradiation of an acetonitrile solution of the isomeric 1,3,3-triphenyl-2-methylcyclopropene (15) produced 1,3-diphenyl-2-

Scheme VI

methylindene (16) as the exclusive photoproduct.

Subjection of 1,3-diphenyl-2,3-dimethylcyclopropene (17) to conditions similar to those used with 12 and 15 gave rise to a mixture of indenes 18 and 19 (Scheme V). The structures of these indenes were established by comparison with authentic samples. It should be noted that the direct irradiation of 17 resulted in the exclusive formation of 1,3-dimethyl-2-phenylindene (20).

Another commonly observed reaction that the electronically excited singlet state of a diphenyl-substituted cyclopropene undergoes consists of an insertion into a C–H bond. For example, Arnold and co-workers found that irradiation of 1,2-diphenyl-3,3-dimethylcyclopropene (21) produced the isomeric dienes 22 and 23 in a 3:1 ratio (eq 4).[19] Similar results were observed with 1,2-diphenyl-3-

$$(4)$$
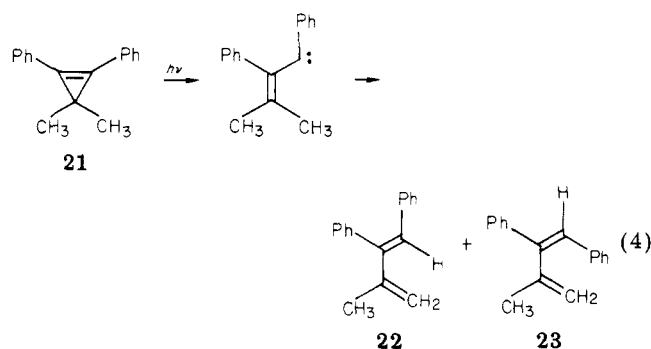
benzyl-3-methylcyclopropene (24). Direct irradiation of this compound leads to ring fragmentation to give products derived from a vinylcarbene intermediate.[20] In contrast, we find that the sensitized (electron transfer) irradiation of 24, with dicyanoanthracene as an electron-accepting sensitizer, produced 1,2-diphenyl-3-methylnaphthalene (25) as the exclusive photoproduct (Scheme VI). The irradiation was carried out in acetonitrile under conditions where only the sensitizer absorbed light. In the time required to complete the conversion of 24, little if any of the sensitizer was consumed. Confirmation of the structure of naphthalene 25 was obtained from its spectroscopic properties and, more firmly, from its independent synthesis. This involved an intramolecular Friedel–Crafts acylation of 2,4-diphenyl-3-methylbutyric acid (26) followed by phenyl Grignard addition, dehydration, and oxidation with palladium on carbon.

The DCA-sensitized photolysis of the isomeric 1,3-diphenyl-2-methyl-3-benzylcyclopropene (29) was also studied (eq 5). With this system a 3:1 mixture of 1-phenyl-2-methyl-3-benzylindene (30) and 1,3-diphenyl-2-

(16) H. E. Zimmerman and S. M. Aaasen, *J. Am. Chem. Soc.*, **99**, 2342 (1977); *J. Org. Chem.*, **43**, 1493 (1978); H. E. Zimmerman and M. C. Hovey, *ibid.*, **44**, 2331 (1979).

(17) J. A. Pincock and A. Moutsokapas, *Can. J. Chem.*, **55**, 979 (1979).

(18) R. M. Morchat and D. R. Arnold, *J. Chem. Soc., Chem. Commun.*, 743 (1978).

(19) D. R. Arnold, J. A. Pincock, and R. Morchat, *J. Am. Chem. Soc.*, **95**, 7536 (1973).

(20) A. Padwa, U. Chiacchio, and N. Hatanaka, *J. Am. Chem. Soc.*, **100**, 3928 (1978); A. Padwa and R. Loza, unpublished results.

29

30   31   (5)
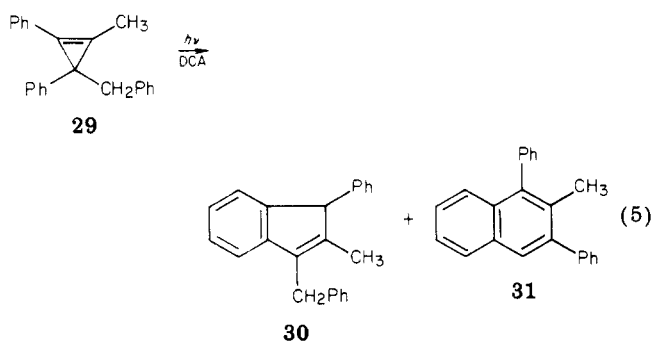
methylnaphthalene (31) was obtained. The structures of these compounds were verified by comparison with authentic samples.

In an earlier study we observed that the triplet-sensitized irradiation of tetrasubstituted cyclopropenes which possess γ-hydrogens leads to products involving intramolecular transfer of hydrogen from the side chain to the $\pi-\pi^*$ triplet state.[10,20] In order to determine whether intramolecular γ-hydrogen transfer would also occur on electron-transfer sensitization, we examined the DCA-sensitized photolysis of cyclopropenes 32 and 33 (eq 6). Both of these com-

32, R_1 = H; R_2 = Ph
33, R_1 = R_2 = CH_3

34   35   (6)
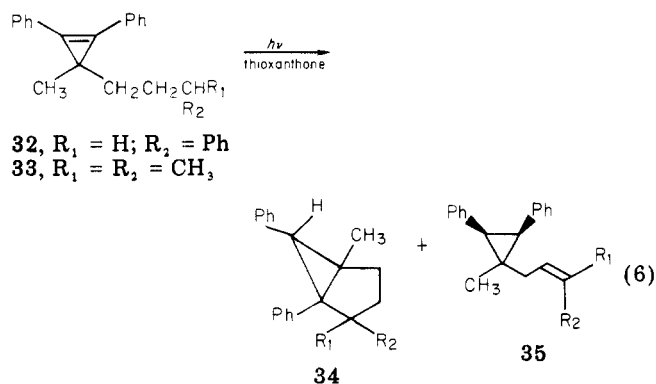
pounds, however, were found to be stable on irradiation in the presence of DCA. The thioxanthone-sensitized reaction of these compounds, on the other hand, gave rise to products (i.e., 34 and 35) derived from a 1,5-diradical intermediate.

One additional system which was also studied involved the photochemistry of 1,2-diphenyl-3-methyl-3-(o-ethylphenyl)cyclopropene (36). Previous work from our laboratory has shown that the direct and thioxanthone-sensitized photolysis of this system afforded completely different products.[20] Thus, direct irradiation of 36 produced indene 37 in quantitative yield (Scheme VII). Thioxanthone-sensitized photolysis of 36, on the other hand, gave benzobicyclo[3.1.0]hexane 38 as a mixture of diastereomers. The DCA-sensitized photolysis of 36 followed an entirely different course and gave rise to a mixture of indenes 37, 39, and 40. The structure of indene 40 was established by comparison with an authentic sample prepared by treating the indenyl anion derived from 1-methyl-2,3-diphenylindene with ethyl bromide.

Discussion

The photochemistry of cyclopropene derivatives has been shown to be markedly dependent on the multiplicity of the excited state involved.[21] Singlet states react by σ-bond cleavage to give products which are explicable in terms of the chemistry of vinyl carbenes.[21] Recent MO calculations by Pincock and Boyd indicate that the triplet

(21) A. Padwa, *Acc. Chem. Res.*, 12, 310 (1979).

Scheme VII

37 (25%)   39 (67%)   40 (8%)

hv | DCA

37   36

38
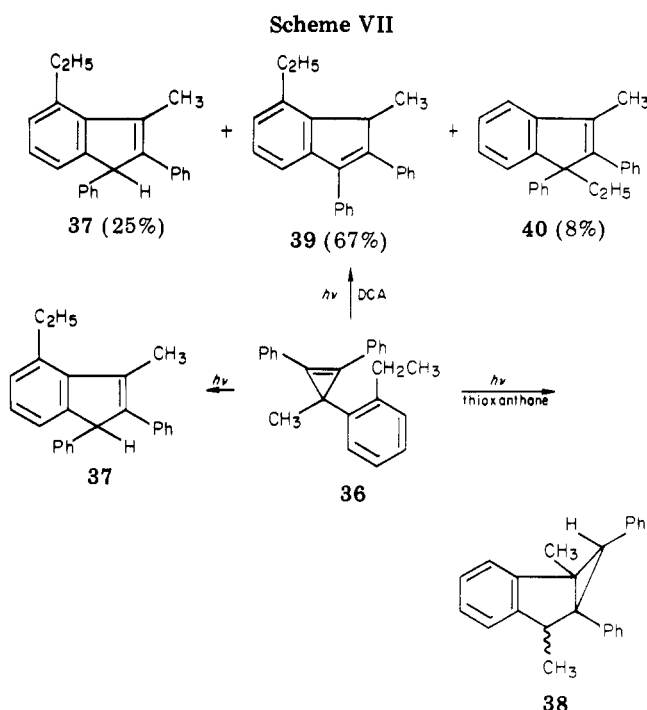
state of cyclopropene possesses a large barrier ($\sim$13 kcal/mol) to ring opening.[22] Previous work by DeBoer has shown that trisubstituted cyclopropenes dimerize on triplet sensitization to give tricyclo[3.1.0.0^{2,4}]hexanes.[9] Triplet states of tetrasubstituted cyclopropenes, however, do not dimerize as a consequence of the severe steric factors which exist in the transition state. Instead, these systems abstract a hydrogen from the γ-carbon atom of the side chain via a six-membered transition state to produce a 1,5-biradical which either couples or disproportionates.[10] We have recently found that by incorporating a π bond into the 3-position of the cyclopropene ring, it is possible to induce an intramolecular [2 + 2] cycloaddition on triplet sensitization. Thus, 3-allyl-substituted cyclopropenes produce tricyclo[2.2.0.0^{2,6}]hexanes (eq 7) on irradiation in the presence of a triplet sensitizer.[23]


41   42   (7)
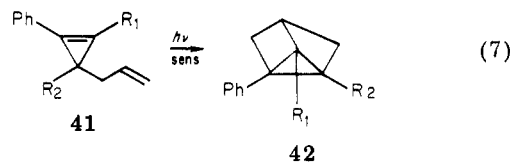
The dicyanoanthracene-sensitized reactions of the above cyclopropenes are particularly interesting because they give rise to products which are different from those obtained on direct irradiation or on triplet sensitization with thioxanthone. For example, the direct irradiation of cyclopropene 36 leads to indene 37 while sensitization with thioxanthone produces benzobicyclohexane 38. In contrast, we find that the sensitized irradiation of 36 using DCA gives rise to a mixture of three indenes (37, 39, and 40). The photochemistry of cyclopropene 4 provides still another example of a system in which the products of the direct, triplet-sensitized, and DCA-sensitized photolyses are completely different. The direct irradiation of 4 is known to produce indene 43 (eq 8) as the major photoproduct.[15] This indene is derived from cleavage of the cyclopropene bond attached to the methyl substituent. In contrast, we find that the DCA-sensitized irradiation of

(22) J. A. Pincock and R. J. Boyd, *Can. J. Chem.*, 55, 2482 (1977).
(23) A. Padwa, *Org. Photochem.*, 4, 261 (1979).

(8)
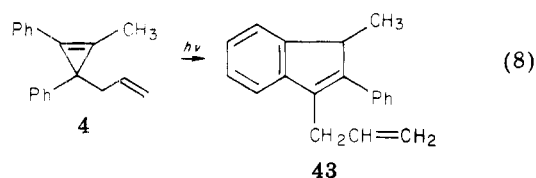
4 produces indenes **5** and **6** derived from cleavage of the cyclopropene bond attached to the phenyl group. The thioxanthone-sensitized photolysis of **4**, on the other hand, gave tricyclohexane **42** (R_1 = Ph, R_2 = CH_3) as the exclusive photoproduct. Thus, an important point requiring discussion is the regioselectivity associated with the DCA-sensitized ring-opening reaction of the unsymmetrical cyclopropenes. In all of the cases studied, the products obtained are derived from cleavage of the cyclopropene bond attached to the phenyl ring. This stands in marked contrast with the regioselectivity encountered on direct irradiation.

Electron-transfer quenching of singlet excited sensitizers by olefins has recently received considerable attention.[24-30] Radical-ion intermediates have been characterized by transient absorption spectroscopy[31] and CIDNP methods.[32,33] 9,10-Dicyanoanthracene (DCA) is a typical sensitizer for photogeneration of radical ions. Electron-transfer quenching of the fluorescence of DCA by a variety of substrates has been postulated from correlations of quenching rate constants and free energies of electron transfer,[34] from solvent-dependent exciplex emissions,[35] and on the basis of distinctive photochemistry.[36,37] The structural and regiochemical features of the DCA-sensitized reactions of the diphenyl-substituted cyclopropenes are nicely rationalized by using the electron-transfer mechanism presented in Scheme VIII. This mechanism is similar to that proposed for the photosensitized electron-transfer cycloaddition reactions encountered with 1,2-diphenylcyclopropene-3-carboxylate.[8] The first step involves excitation of the dicyanoanthracene. The second step involves an electron transfer which ultimately produces a solvent-separated radical-ion pair. As was mentioned earlier, the calculated ΔG value for this reaction indicates that the electron transfer should be spontaneous. One rationale to account for the formation of indenes **13** and **14** from cyclopropene **12** is that the radical cation derived from **12** (i.e., **43**) undergoes an initial ring scission followed by cyclization onto the ortho position of the
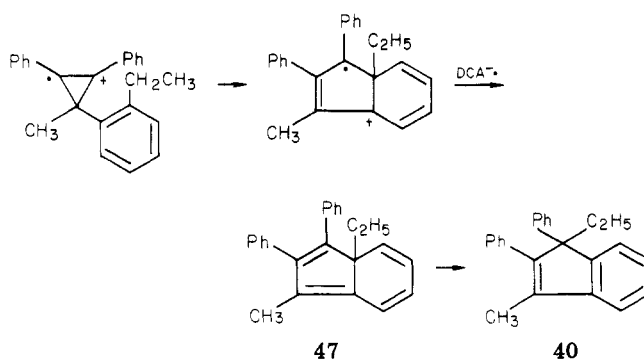
Scheme VIII

Path A
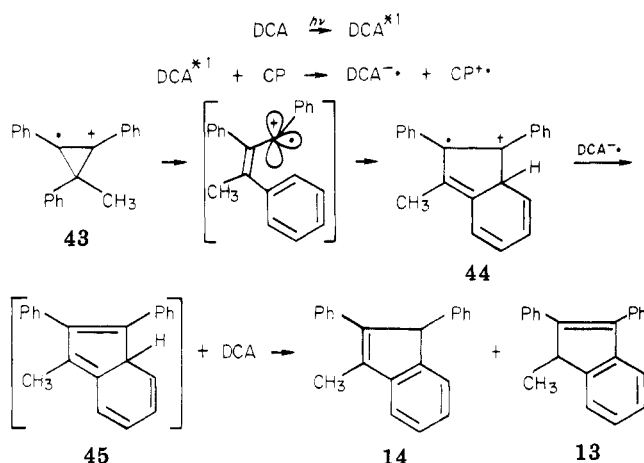
Path B
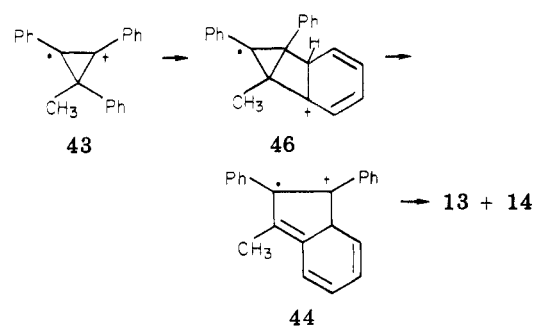
Scheme IX

neighboring aromatic ring (path A). Reaction of the resulting radical cation **44** with dicyanoanthracene radical anion (DCA⁻·) leads to isoindene **45** which then gives rise to indenes **13** and **14**. An alternate possibility (path B) involves initial cyclization of radical cation **43** followed by a subsequent ring opening and back electron transfer from the DCA radical anion.

The formation of 1,2-diphenyl-3-methylbenzene (**2**) from cyclopropene **1** is also compatible with a radical cation intermediate. In this case, ring opening followed by cyclization would be expected to lead to a species which should be readily oxidized to the observed aromatic compounds (eq 9). A similar sequence would account for the

(9)
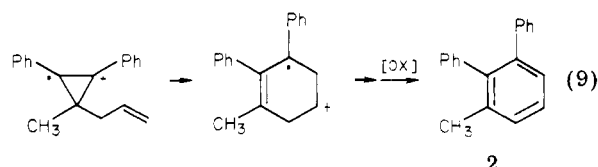
conversion of 1,2-diphenyl-3-benzyl-3-methylcyclopropene

(24) W. K. Smothers, K. S. Schanze, and J. Saltiel, *J. Am. Chem. Soc.*, **101**, 1895 (1979).

(25) D. V. O'Connor and W. R. Ware, *J. Am. Chem. Soc.*, **101**, 121 (1979).

(26) A. J. Maroulis, Y. Shigemitsu, and D. R. Arnold, *J. Am. Chem. Soc.*, **100**, 535 (1978).

(27) P. S. Mariano, J. L. Stavinoha, G. Pepe, and E. F. Meyer, Jr., *J. Am. Chem. Soc.*, **100**, 7114 (1978).

(28) T. Miyamoto, Y. Tsujimoto, T. Tsuchinaga, Y. Nishimura, and Y. Odaira, *Tetrahedron Lett.*, 2155 (1978).

(29) J. J. McCullough, R. C. Miller, D. Fung, and W. S. Wu, *J. Am. Chem. Soc.*, **97**, 5942 (1975).

(30) D. R. Arnold and R. W. R. Humphreys, *J. Am. Chem. Soc.*, **101**, 2743 (1979).

(31) R. A. Neunteufel and D. R. Arnold, *J. Am. Chem. Soc.*, **95**, 4080 (1973).

(32) D. R. Arnold and P. C. Wong, *J. Am. Chem. Soc.*, **101**, 1894 (1979).

(33) H. D. Roth and M. L. M. Schilling, *J. Am. Chem. Soc.*, **101**, 1898 (1979), and references cited therein.

(34) R. W. Ware, J. D. Holmes, and D. R. Arnold, *J. Am. Chem. Soc.*, **96**, 7861 (1974).

(35) J. Eriksen and C. S. Foote, *J. Phys. Chem.*, **82**, 2659 (1978).

(36) J. Eriksen, C. S. Foote, and T. L. Parker, *J. Am. Chem. Soc.*, **99**, 6455 (1977).

(37) W. Ando, T. Nagashima, K. Saito, and S. Kohmoto, *J. Chem. Soc., Chem. Commun.*, 154 (1979).

(24) to naphthalene 25. The nature of the oxidizing agent involved in these transformations is unclear.

The DCA-sensitized formation of indene 40 from cyclopropene 36 represents a novel reaction and merits some comment. This compound is not formed from either the electronically excited singlet or triplet state of the cyclopropene. A possible mechanism for its formation involves ipso cyclization followed by electron transfer from DCA⁻· to the intermediate radical cation to give isoindene 47 (Scheme IX). This species would then have to undergo a [1,5] sigmatropic ethyl shift to give the observed product. The last step is not unreasonable since it is known that many carbon functional groups can participate in [1,5] sigmatropic shift reactions.[38,39] As was mentioned earlier, triplet formation of the cyclopropene via recombination of the radical-ion pairs is an exothermic process. The fact that the triplet state is not produced in these DCA-sensitized reactions suggests that the initially produced radical cations rearrange with great facility.

Turning now to the matter of regioselectivity associated with the DCA-sensitized ring-opening reaction, we note that the scission of the cyclopropene bond to which the phenyl group is attached (i.e. bond b, eq 10) can be nicely
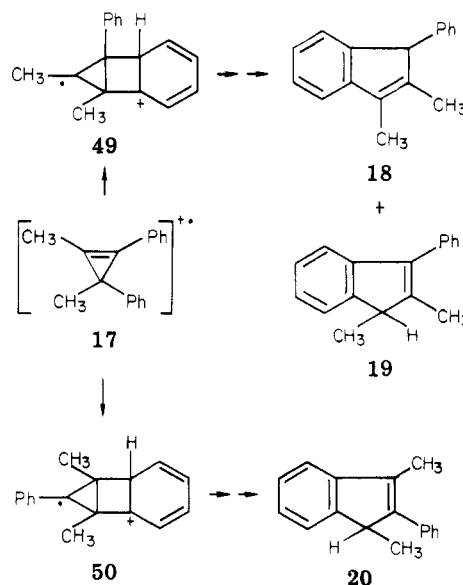
(10)
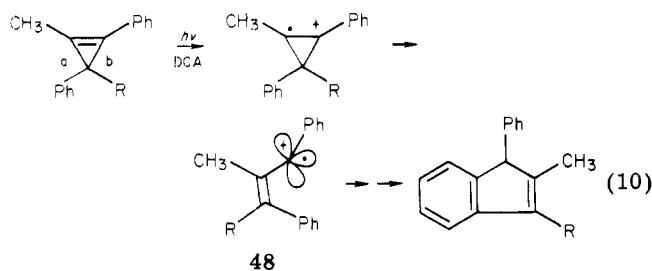
accommodated by the radical cation pathway. According to this mechanism ring opening will occur so as to give the most stable radical cation. The preferential cleavage of bond b is undoubtedly related to the fact that the radical cation produced (i.e., 48) allows for maximum delocalization of the reactive centers. Conjugation of the radical center in the sp²-hybridized orbital of the ring-opened species 48 with the adjacent phenyl group will be more important than that with an adjacent methyl group.

It should be pointed out that path B (Scheme VIII) is not compatible with the regioselectivity noted in the DCA-sensitized reaction of the unsymmetrically substituted cyclopropenes. Thus, if the radical cation derived from 17 were to cyclize to an intermediate like 46, two possible species could result (i.e., 49 or 50, Scheme X). According to path B, the initial cyclization would be expected to give the most stable radical cation (i.e., 50) and consequently produce 1,3-dimethyl-2-phenylindene (20). This is clearly not the case. The exclusive formation of indenes 18 and 19 from the DCA-sensitized irradiation of 17 is best interpreted as arising from an initial ring-scission reaction followed by a subsequent cyclization (i.e., path A, Scheme VIII).

In conclusion, the mechanism suggested for these DCA-sensitized reactions is patterned after Arnold[7] and Farid's[8] rationale of electron-transfer reactions. The rearranged indenes are the end products of a sequence initiated by an electron transfer from the cyclopropene to the excited state of the dicyanoanthracene. We are investigating the electron-transfer-mediated reactions of other arylcyclopropene radical cations and will report additional findings at a later date.

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(38) C. W. Spangler, *Chem. Rev.*, **76**, 187 (1976).
(39) P. Schiess and H. Stalder, *Tetrahedron Lett.*, 1417 (1980).

Scheme X

Experimental Section[40]

Dicyanoanthracene-Sensitized Irradiation of 1,2-Diphenyl-3-allyl-3-methylcyclopropene (1) in Acetonitrile. A solution containing 272 mg of 1 and 73 mg of 9,10-dicyanoanthracene in 450 mL of acetonitrile was irradiated for 60 h under an argon atmosphere with a 450-W Hanovia lamp equipped with a uranium-glass filter sleeve. Removal of the solvent left a yellow residue which was subjected to thick-layer chromatography using a 1:1 benzene-hexane mixture as the eluent. The major component isolated (38 mg, 14%) was identified as 1,2-diphenyl-3-methylbenzene (2) on the basis of its spectral properties: mp 60–61 °C (lit.[41] 62–63 °C); IR (neat) 3.26, 3.29, 6.25, 6.71, 6.87, 6.97, 7.27, 8.51, 8.69, 9.39, 9.76, 10.01, 11.05, 11.90, 12.66, 13.07, 13.33, 13.60, 14.49 µm; NMR (CDCl₃, 90 MHz) δ 2.12 (s, 3 H), 6.97–7.32 (m, 13 H); mass spectrum, m/e 244 (M⁺, base), 229, 228, 178.

The structure of this material was further verified by comparison with an independently synthesized sample. To a stirred suspension of 7.7 g of triphenylallylphosphonium bromide in 60 mL of ether was added 8.7 mL of a 2.79 M solution of n-butyllithium in hexane. To the resulting red solution was added a solution containing 4.4 g of 3,4-diphenyl-3-buten-2-one in 20 mL of ether. After the mixture was stirred for 24 h at room temperature, the solution was washed with water. The organic extracts were dried and concentrated under reduced pressure. The resulting oil was chromatographed on a silica gel column with hexane as the eluent. The major product obtained was a clear oil (1.2 g, 25%) whose structure was assigned as trans-1-methyl-5,6-diphenylcyclohexa-1,3-diene (3) on the basis of its spectral properties: IR (neat) 3.30, 3.37, 3.45, 6.25, 6.72, 6.90, 9.28, 9.68, 11.02, 11.73, 12.18, 13.25, 13.30, 13.90, 14.30 µm; NMR (CDCl₃, 100 MHz) δ 1.59 (br s, 3 H), 3.37 (d, 1 H, J =4.0 Hz), 3.53 (dd, 1 H, J = 6.0, 4.0 Hz), 5.61, (dd, 1 H, J = 10.0, 6.0 Hz), 5.93 (dq, 1 H, J = 5.0, 1.0 Hz), 6.09 (dd, 1 H, J = 10.0, 5.0 Hz), 7.15–7.38 (m, 10 H).

A solution containing 1.2 g of the above compound and 100 mg of palladium on charcoal in 30 mL of benzene was heated in a sealed tube at 180 °C for 7 h. The mixture was filtered to remove the catalyst, and the solvent was removed under reduced pressure. The resulting white solid (810 mg, 68%) was identical in every detail with a sample of 1,2-diphenyl-3-methylbenzene (2) isolated

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(41) J. Colonge and J. Brunie, *Bull. Soc. Chim. Fr.*, 42 (1963).

from the DCA-sensitized irradiation of cyclopropene 1.

Dicyanoanthracene-Sensitized Irradiation of 1,3-Diphenyl-2-methyl-3-allylcyclopropene (4) in Acetonitrile. A solution containing 274 mg of 4 and 96 mg of 9,10-dicyanoanthracene in 250 mL of acetonitrile was irradiated for 8 h under an argon atmosphere with a 450-W Hanovia mercury arc lamp equipped with a uranium-glass filter sleeve. Removal of the solvent under reduced pressure left a yellow oil which was chromatographed on a silica gel column with hexane as the eluent. The first component isolated was a colorless oil (31 mg, 13%) whose structure was assigned as 1-allyl-2-methyl-3-phenylindene (6) on the basis of its spectral properties: IR (neat) 3.28, 3.32, 3.47, 3.53, 6.25, 6.71, 6.83, 6.94, 7.27, 7.38, 9.30, 9.80, 9.90, 10.05, 10.93, 12.90, 13.33, 13.99, 14.28 μm; NMR (CDCl$_3$, 90 MHz) δ 1.98 (s, 3 H), 2.23–2.98 (m, 2 H), 3.40 (br t, 1 H, J = 5.3 Hz), 4.82–5.16 (m, 2 H), 5.15–5.78 (m, 1 H), 7.03–7.48 (m, 9 H); UV (95% ethanol) 260 nm (ϵ 9600); mass spectrum, m/e 246 (M$^+$), 206, 205 (base), 204, 203, 202.

The structure of this material was further supported by comparison with an independently synthesized sample prepared from the base-induced isomerization of 1-phenyl-2-methyl-3-allylindene (5).

The second component isolated from the chromatography column contained 73 mg (27%) of a clear oil whose structure was assigned as 1-phenyl-2-methyl-3-allylindene (5) on the basis of the following spectral data: IR (neat) 3.32, 3.45, 6.12, 6.24, 6.71, 6.90, 9.75, 10.05, 10.90, 12.85, 13.30, 13.65, 14.35 μm; NMR (CDCl$_3$, 100 MHz) δ 1.84 (s, 3 H), 3.32 (d, 2 H, J = 5.5 Hz), 4.28 (s, 1 H), 5.05 (d, 1 H, J = 7.0 Hz), 5.12 (d, 1 H, J = 18.0 Hz), 5.72–6.18 (m, 1 H), 6.90–7.36 (m, 9 H); UV (95% ethanol) 263, nm (ϵ 6800), 220 (17 800); mass spectrum, m/e 246 (M$^+$), 206, 205 (base), 108; mass spectrum, calcd for C$_{19}$H$_{18}$ (P$^+$) m/e 246.140 832, found 246.140 820.

The structure of indene 5 was further established by comparison with an independently synthesized sample. To a stirred solution containing 1.0 g of *cis*-2-methyl-3-phenyl-1-indanone (7)[42] in 25 mL of ether was added 7.5 mL of a 0.67 N solution of allylmagnesium bromide in ether. After being stirred for 1 h, the solution was quenched with a saturated ammonium chloride solution. The organic layer was separated, washed with water, and dried over magnesium sulfate. Removal of the solvent left 1.0 g (84%) of *cis*-1-allyl-2-methyl-3-phenyl-1-indanol: NMR (CDCl$_3$, 100 MHz) δ 0.66 (d, 3 H, J = 7.0 Hz), 1.90 (br s, 1 H), 2.60 (d, 2 H, J = 7.0 Hz), 2.62 (p, 1 H, J = 7.0 Hz), 4.34 (d, 1 H, J = 7.0 Hz), 5.05 (d, 1 H, J = 15.5 Hz), 5.10 (d, 1 H, J = 9.0 Hz), 5.46–5.97 (m, 1 H), 6.8–7.4 (m, 9 H). A 1.0-g sample of this indanol was added to 10 mL of a solution containing 85% glacial acetic acid, 10% sulfuric acid, and 5% water. The reaction mixture was stirred at 25 °C for 5 min and was then poured into water. The excess acid was neutralized with sodium bicarbonate, and the mixture was extracted with ether. The ether layer was washed with water and dried over magnesium sulfate. Removal of the solvent left a clear oil which was chromatographed on silica gel with hexane to give 0.65 g (63%) of 1-phenyl-2-methyl-3-allylindene (5) which was identical in all respects with the major fraction obtained from the DCA-sensitized reaction of cyclopropene 4.

A solution containing 413 mg of indene 5 in 10 mL of a benzene–pyridine solution (4:1) was heated in a sealed tube at 160 °C for 25 h. The solution was taken up in ether and washed with a 10% hydrochloric acid solution followed by a sodium bicarbonate solution. The ether layer was dried over magnesium sulfate, and the solvent was removed under reduced pressure. The resulting yellow oil was chromatographed on a silica gel column with hexane to give 1-allyl-2-methyl-3-phenylindene (6) as the major product (155 mg, 38%) in addition to recovered starting material (141 mg, 34%). The structure of indene 6 was identical with the sample obtained from the DCA-sensitized reaction of cyclopropene 4.

Dicyanoanthracene-Sensitized Irradiation of 1,3-Diphenyl-2-methyl-3-(4-butenyl)cyclopropene (8) in Acetonitrile. A solution containing 238 mg of 8 and 37 mg of 9,10-dicyanoanthracene in 250 mL of anhydrous acetonitrile was ir-

radiated for 8 h under an argon atmosphere with a 450-W Hanovia lamp equipped with a uranium-glass filter sleeve. Removal of the solvent left a yellow oil which was chromatographed on a silica gel column with hexane as the eluent. The first component isolated from the column consisted of a clear oil (29 mg, 12%) whose structure was identified as 1-(4-butenyl)-2-methyl-3-phenylindene (10) on the basis of its spectral properties: IR (neat) 3.26, 3.32, 3.36, 3.42, 6.13, 6.28, 6.73, 6.87, 6.97, 7.40, 8.70, 9.39, 9.85, 10.01, 10.10, 11.04, 12.98, 13.42, 14.39 μm; NMR (CDCl$_3$, 90 MHz) δ 1.69–2.28 (m, 4 H), 2.00 (s, 3 H), 3.44 (br t, 1 H, J = 6.8 Hz), 4.82–5.10 (m, 2 H), 5.78 (ddt, 1 H, J = 17.0, 10.2, 5.7 Hz), 7.06–7.57 (m, 9 H); UV (95% ethanol) 259 nm (ϵ 9130), 223 (19 600); mass spectrum, m/e 260 (M$^+$), 221, 219 (base), 218, 205, 191, 189, 165, 91.

Anal. Calcd for C$_{20}$H$_{20}$: C, 92.26; H, 7.74. Found: C, 92.01; H, 7.78.

The structure of this material was further supported by comparison with an independently synthesized sample prepared from the base-induced isomerization of 1-phenyl-2-methyl-3-(4-butenyl)indene (9).

The second component isolated from the chromatography column contained 90 mg (38%) of a colorless oil whose structure was identified as 1-phenyl-2-methyl-3-(4-butenyl)indene (9): IR (neat) 3.26, 3.30, 3.41, 3.49, 6.25, 6.71, 6.89, 9.34, 9.71, 9.80, 10.10, 10.98, 12.90, 13.51, 13.69, 14.25 μm; NMR (CDCl$_3$, 90 MHz) δ 1.76 (s, 3 H), 2.13–2.47 (m, 2 H), 2.51–2.73 (m, 2 H), 4.22 (br s, 1 H), 4.87–5.17 (m, 2 H), 5.87 (ddt, 1 H, J = 17.2, 10.0, 6.0 Hz), 6.87–7.28 (m, 9 H); UV (95% ethanol) 262 nm (ϵ 11 000).

Anal. Calcd for C$_{20}$H$_{20}$: C, 92.26; H, 7.74. Found: C, 92.11; H, 7.82.

The structure of indene 9 was further established by comparison with an independently synthesized sample. To a stirred solution of 2-methyl-3-phenyl-indanone[42] in 25 mL of ether was added the Grignard reagent derived from 4-bromo-1-butene (1.22 g of bromide). After the mixture was stirred for 12 h at 25 °C, the solution was quenched with ammonium chloride. The organic layer was washed, dried, and concentrated to give 0.88 g (70%) of 1-(4-butenyl)-2-methyl-3-phenyl-1-indanol. This material was dehydrated by using an acetic acid, sulfuric acid, and water mixture according to the procedure previously described. The oil obtained was chromatographed on a silica gel column to give 0.74 g (90%) of 1-phenyl-2-methyl-3-(4-butenyl)indene (9) which was identical in all respects with the major fraction obtained from the DCA-sensitized reaction of cyclopropene 8. Treatment of this material with pyridine at 160 °C for 14 h resulted in a 32% yield of 1-(4-butenyl)-2-methyl-3-phenylindene (10) which was identical with the minor indene isolated from the DCA-sensitized reaction of cyclopropene 8.

Preparation of 1,2,3-Triphenyl-3-methyl- (12) and 1,3,3-Triphenyl-2-methylcyclopropene (15). To a stirred suspension containing 4.0 g of 1-methyl-2,3-diphenylcyclopropenylium perchlorate in 100 mL of anhydrous ether at 0 °C was added 10 mL of a 3.2 M solution of phenylmagnesium bromide in ether. The reaction was stirred for 12 h, and a saturated ammonium chloride solution was added. The organic layer was washed with water and dried over magnesium sulfate. Removal of the solvent under reduced pressure left a yellow oil which was chromatographed on a silica gel column with hexane as the eluent. The first component eluted from the column contained 2.1 g (54%) of 1,2,3-triphenyl-3-methylcyclopropene (12): mp 97–98 °C (lit.[43] mp 96–98 °C); NMR (CDCl$_3$, 60 MHz) δ 1.95 (s, 3 H), 7.03–8.25 (m, 15 H).

The second component isolated from the column contained 520 mg (13%) of a crystalline solid (mp 95–96 °C) whose structure was assigned as 1,3,3-triphenyl-2-methylcyclopropene (15) on the basis of its spectroscopic properties: IR (KBr) 3.28, 3.31, 5.43, 6.21, 6.66, 6.97, 7.30, 9.51, 11.20, 12.60, 13.31, 14.20 μm; UV (95% ethanol) 262 nm (ϵ 18 000); NMR (CDCl$_3$, 60 MHz) δ 2.48 (s, 3 H), 7.13–7.80 (m, 15 H); mass spectrum, m/e 282 (M$^+$), 267, 205, 165, 149, 100 (base), 77.

Anal. Calcd for C$_{22}$H$_{18}$: C, 93.57; H, 6.43. Found: C, 93.52; H, 6.47.

Dicyanoanthracene-Sensitized Irradiation of 1,2,3-Triphenyl-3-methylcyclopropene (12) in Acetonitrile. A solution

(42) H. E. Zimmerman, *J. Am. Chem. Soc.*, **78**, 1168, (1956).

(43) R. Breslow and P. Dowd, *J. Am. Chem. Soc.*, **85**, 2729 (1963).

containing 158 mg of cyclopropene 12 and 25 mg of dicyano-anthracene (DCA) in 170 mL of anhydrous acetonitrile was irradiated with a 450-W Hanovia lamp equipped with a uranium-glass filter sleeve under an argon atmosphere for 30 min. Removal of the solvent under reduced pressure left a yellow oil which was shown to contain a mixture of two compounds (3:1) by NMR spectroscopy. Chromatography of the mixture on a silica gel column with hexane as the eluent resulted in the complete separation of the two compounds. The first component isolated from the column contained 30 mg (19%) of 1-methyl-2,3-diphenylindene (13): mp 105–106 °C; IR (KBr) 3.30, 3.38, 3.43, 6.24, 6.70, 6.76, 6.81, 6.98, 7.28, 9.45, 13.20, 13.51, 14.71 μm; NMR (CDCl$_3$, 60 MHz) δ 1.08 (d, 3 H, J = 7.0 Hz), 4.02 (q, 1 H, J = 7.0 Hz), 7.05–7.38 (m, 14 H); UV (95% ethanol) 238 nm (ϵ 22 300), 303 (17 000).

Anal. Calcd for C$_{22}$H$_{18}$: C, 93.57; H, 6.43. Found: C, 93.49; H, 6.47.

The structure of this material was further verified by comparison with an independently synthesized sample. Treatment of 2-phenyl-3-methyl-indanone[44] with phenylmagnesium bromide followed by dehydration of the resulting alcohol with a catalytic quantity of p-toluenesulfonic acid in benzene gave indene 13 which was identical in every detail with the minor component isolated from the photolysis of cyclopropene 12.

The second component isolated from the silica gel column contained 78 mg (49%) of a crystalline solid (mp 90–91 °C) whose structure was assigned as 1,2-diphenyl-3-methylindene (14) on the basis of the following data: IR (KBr) 3.30, 3.34, 6.24, 6.71, 6.82, 6.90, 6.96, 7.28, 9.31, 12.73, 13.18, 13.35, 13.49, 13.85, 14.37 μm; UV (95% ethanol) 295 nm (ϵ 16 700), 230 (15 800); NMR (CDCl$_3$, 60 MHz) δ 2.32 (d, 3 H, J = 2.0 Hz), 4.91 (q, 1 H, J = 2.0 Hz), 6.9–7.40 (m, 14 H); mass spectrum, m/e 282 (M$^+$, base) and 267.

Anal. Calcd for C$_{22}$H$_{18}$: C, 93.57; H, 6.43. Found: C, 93.21; H, 6.61.

The structure of this material was established by comparison with an authentic sample prepared according to the procedure of Koelsch and Johnson.[44]

Subjection of indenes 13 or 14 to DCA-sensitized conditions resulted in a 3:1 mixture of indenes 13 and 14.

Dicyanoanthracene-Sensitized Irradiation of 1,3,3-Triphenyl-2-methyl-cyclopropene (15) in Acetonitrile. A solution containing 115 mg of cyclopropene (15) and 25 mg of DCA in 170 mL of anhydrous acetonitrile was irradiated with a 450-W Hanovia lamp equipped with a uranium-glass filter sleeve under an argon atmosphere for 90 min. Removal of the solvent under reduced pressure left a crude oil which was chromatographed on a silica gel column with hexane as the eluent. The major component isolated contained 104 mg (90%) of a white solid (mp 109–110 °C) whose structure was assigned as 1,3-diphenyl-2-methylindene (16) on the basis of the following data: IR (KBr) 3.38, 3.42, 3.48, 5.15, 6.24, 6.74, 6.90, 7.01, 8.50, 9.45, 9.75, 10.20, 13.30, 14.40 μm; UV (95% ethanol) 227 nm (ϵ 29 800), 263 (10 800); NMR (CDCl$_3$, 60 MHz) δ 1.86 (s, 3 H), 4.39 (br s, 1 H), 6.88–7.47 (m, 14 H); mass spectrum, m/e 282 (M$^+$, base), 267, 205, 203.

Anal. Calcd for C$_{22}$H$_{18}$: C, 93.57; H, 6.43. Found: C, 93.51; H, 6.43.

Dicyanoanthracene-Sensitized Irradiation of 1,3-Diphenyl-2,3-dimethylcyclopropene (17) in Acetonitrile. A solution containing 337 mg of 17 and 103 mg of 9,10-dicyano-anthracene in 250 mL of acetonitrile was irradiated for 4 h under an argon atmosphere with a 450-W Hanovia mercury arc lamp equipped with a uranium-glass filter sleeve. Removal of the solvent under reduced pressure left a yellow oil which was chromatographed on a silica gel column with hexane as the eluent. The two major fractions isolated were identified as 1,2-dimethyl-3-phenylindene [19; 48% yield; NMR (CDCl$_3$, 90 MHz) δ 1.29 (d, 3 H, J = 7.5 Hz), 1.95 (s, 3 H), 3.27 (q, 1 H, J = 7.5 Hz), 7.12–7.52 (m, 9 H)] and 1-phenyl-2,3-dimethylindene [18; 40% yield; NMR δ 1.75 (br s, 3 H), 2.01 (br s, 3 H), 4.18 (br s, 1 H), 6.85–7.37 (m, 9 H)] by comparison with authentic samples.[45,46]

Direct Irradiation of 1,3-Diphenyl-2,3-dimethylcyclopropene (17). A solution containing 75 mg of 17 in 230 mL of benzene was irradiated for 60 min under an argon atmosphere with a 450-W Hanovia lamp equipped with a Corex filter sleeve. Removal of the solvent left a yellow oil which was subjected to thick-layer chromatography using a 3:1 pentane–ether mixture as the eluent. The major component isolated from the plate contained 67 mg (90%) of a white crystalline solid (mp 72–73 °C) which was identified as 1,3-dimethyl-2-phenylindene (20) on the basis of its spectral properties: NMR (CDCl$_3$, 100 MHz) δ 1.15 (d, 3 H, J = 7.0 Hz), 2.21 (d, 3 H, J = 3.0 Hz), 3.65–4.00 (m, 1 H), 7.08–7.52 (m, 9 H); IR (KBr) 3.54, 6.24, 7.05, 13.23, 13.50, 14.45 μm; UV (95% ethanol) 292 nm (ϵ 25 800), 228 (15 200); mass spectrum, m/e 220 (M$^+$, base), 205. The structure of this material was further verified by comparison with an authentic sample.[47]

Dicyanoanthracene-Sensitized Irradiation of 1,2-Diphenyl-3-benzyl-3-methylcyclopropene (24) in Acetonitrile. A solution containing 110 mg of cyclopropene 24 and 20 mg of DCA in 170 mL of acetonitrile was irradiated with a 450-W Hanovia lamp equipped with a uranium-glass filter sleeve for 30 min. Removal of the solvent under reduced pressure left a yellow oil which was chromatographed on a 1.5 × 100 cm column of silica gel impregnated with silver nitrate (10%) and eluted with a 2% ether–hexane mixture. The first component isolated from the column contained 81 mg of recovered starting material. The second component isolated from the column contained 23 mg (20%) of a white solid (mp 149–150 °C) whose structure was assigned as 1,2-diphenyl-3-methylnaphthalene (25) on the basis of the following data: IR (KBr) 3.38, 6.23, 6.74, 7.10, 7.24, 9.41, 9.92, 11.35, 11.73, 13.50, 14.75 μm; UV (95% ethanol) 228 nm (ϵ 59 400), 282 (8800); NMR (CDCl$_3$, 60 MHz) δ 2.20 (s, 3 H), 6.9–7.95 (m, 15 H); mass spectrum, m/e 294 (M$^+$, base), 279, 217, 215, 202, 100.

Anal. Calcd for C$_{23}$H$_{18}$: C, 93.84; H, 6.16. Found: C, 93.72; H, 6.19.

The structure of this material was further verified by comparison with an independently synthesized sample. A solution containing 3.1 g of phenylacetic acid in 25 mL of tetrahydrofuran was added to a solution containing 0.048 mol of lithium diisopropylamide (LDA) in tetrahydrofuran at 0 °C. After the mixture was stirred at 0 °C for 20 min, 9 mL of freshly distilled hexamethylphosphoramide (HMPA) was added. The mixture was stirred for an additional 20 min, and then 4.8 g of 2-bromophenylpropane in 20 mL of tetrahydrofuran was added to the clear solution. The reaction mixture was stirred at 25 °C for 1 h followed by heating at reflux for 2 h. The solution was quenched with a 10% hydrochloric acid solution and was extracted with ether. The ether extracts were dried over magnesium sulfate, and the solvent was removed under reduced pressure to give 3.8 g (68%) of 2,4-diphenyl-3-methylbutyric acid (26) as a crystalline solid: mp 134–135 °C; NMR (CDCl$_3$, 60 MHz) δ 0.59 (d, 3 H, J = 6.0 Hz), 2.20–3.18 (m, 3 H), 3.46 (d, 1 H, J = 10.0 Hz), 7.27–7.68 (m, 10 H), 10.37 (br s, 1 H); mass spectrum, m/e 254 (M$^+$), 135 (base), 118.

A solution containing 1.35 g of the above acid and 2.5 g of phosphorus pentachloride in 25 mL of benzene was heated at reflux for 10 min. After addition of 2.0 g of aluminum chloride to the mixture, the reaction mixture was heated at reflux for 30 min and was then quenched with a 10% ice-cold solution of hydrochloric acid. The organic layer was taken up in ether, washed with water, and dried over magnesium sulfate. The solvent was removed under reduced pressure, and the resulting yellow solid was chromatographed on a silica gel column with a 10% ether–hexane mixture as the eluent. The major component contained 1.04 g (83%) of a clear oil whose structure was assigned as 2-phenyl-3-methyl-1-tetralone (27) on the basis of its spectral data: IR (neat) 3.28, 3.30, 3.38, 3.43, 4.46, 5.90, 6.23, 6.92, 7.30, 7.84, 8.33, 9.10, 9.91, 11.10, 13.50, 14.32 μm; NMR (CDCl$_3$, 60 MHz) δ 0.96 (d, 3 H, J = 6.0 Hz), 2.33–3.18 (m, 3 H), 3.45 (d, 1 H, J = 10.0 Hz), 7.14–8.38 (m, 9 H).

To a solution containing 220 mg of the above tetralone in 25 mL of anhydrous ether at 0 °C under a nitrogen atmosphere was added 2 mL of a 3.2 M phenylmagnesium bromide solution in

(44) C. R. Koelsch and P. R. Johnson, *J. Am. Chem. Soc.*, **65**, 567 (1943).

(45) W. J. Baron, M. E. Hendrick, and M. Jones, Jr., *J. Am. Chem. Soc.*, **95**, 6286 (1973).

(46) L. I. Smith and L. I. Hanson, *J. Am. Chem. Soc.*, **57**, 1326 (1935).

(47) A. Padwa, T. J. Blacklock, R. Loza, and R. Polniaszek, *J. Org. Chem.*, **45**, 2181 (1980).

ether. After being heated at reflux for 12 h, the mixture was quenched with a saturated ammonium chloride solution. The organic layer was taken up in ether, washed with water, and dried over magnesium sulfate. The solvent was removed under reduced pressure, and the resulting residue was heated in a solution containing 30 mL of methanol and 10 mL of concentrated hydrochloric acid. After the mixture was heated at reflux for 3 h, the organic layer was taken up in ether, washed with water, and dried over magnesium sulfate. Removal of the solvent left a yellow oil which was chromatographed on a preparative thick-layer plate with a 2% ether–hexane mixture as the eluent. The major component isolated from the plate contained 130 mg (47%) of 3,4-dihydro-1,2-diphenyl-3-methylnaphthalene (28): NMR (CDCl$_3$, 60 MHz) 1.14 (d, 3 H, J = 6.0 Hz), 2.57–3.50 (m, 3 H), 6.86–7.89 (m, 14 H). By use of the procedure of Linstead and Thomas,[48] dihydronaphthalene 28 was oxidized to the corresponding aromatic hydrocarbon in high yield. A solution containing 130 mg of the above 3,4-dihydronaphthalene in 50 mL of *p*-cymene containing 160 mg of 10% palladium on carbon was heated at reflux for 3 h under an atmosphere of carbon dioxide. Removal of the solvent under reduced pressure left 120 mg (93%) of 1,2-diphenyl-3-methylnaphthalene (25) as a crystalline solid (mp 149–150 °C) which was identical in every detail with the product obtained from the photolysis of cyclopropene 24. The 3,4-dihydronaphthalene 28 could also be converted to naphthalene 25 by irradiation in the presence of DCA.

Dicyanoanthracene-Sensitized Irradiation of 1,3-Diphenyl-2-methyl-3-benzylcyclopropene (29) in Acetonitrile. A solution containing 650 mg of cyclopropene 29 and 110 mg of DCA in 550 mL of acetonitrile was irradiated with a 450-W Hanovia lamp equipped with a uranium-glass filter sleeve under an argon atmosphere for 70 min. Removal of the solvent under reduced pressure left a yellow oil which was chromatographed over silica gel with hexane as the eluent. The first component isolated contained 52 mg (24%) of a crystalline solid (mp 117–118 °C) whose structure was assigned as 1,3-diphenyl-2-methyl-naphthalene (31) on the basis of its spectral properties: IR (KBr) 3.22, 3.30, 3.40, 6.27, 6.72, 6.95, 7.27, 9.35, 11.22, 14.32, 15.20 μm; NMR (CDCl$_3$, 60 MHz) δ 2.10 (s, 3 H), 7.12–7.97 (m, 15 H); UV (95% ethanol) 234 nm (ε 52000), 286 (8000); mass spectrum, *m/e* 294 (M$^+$), 279, 100 (base).

Anal. Calcd for C$_{23}$H$_{18}$: C, 93.84; H, 6.16. Found: C, 93.77; H, 6.18.

The structure of naphthalene 31 was unambiguously established by comparison with an authentic sample provided by Professor H. E. Zimmerman.[49]

The second component isolated from the column contained 422 mg of recovered starting material. The third fraction (69%) obtained from the column was a crystalline solid (mp 103–104 °C) whose structure was assigned as 1-phenyl-2-methyl-3-benzylindene (30) on the basis of its spectral data: IR (KBr) 6.25, 6.72, 8.43, 9.31, 9.72, 10.60, 13.26, 13.80, 14.54 μm; NMR (CDCl$_3$, 60 MHz) δ 1.94 (s, 3 H), 3.99 (s, 2 H), 4.43 (br s, 1 H), 6.85–7.57 (m, 14 H); UV (95% ethanol) 265 nm (ε 9400); mass spectrum, *m/e* 296 (M$^+$), 206, 205 (base), 91.

Anal. Calcd for C$_{23}$H$_{20}$: C, 93.20; H, 6.80. Found: C, 93.34; H, 6.49.

The structure of this material was further verified by comparison with an authentic sample.[15]

Dicyanoanthracene-Sensitized Irradiation of 1,2-Diphenyl-3-methyl-3-(*o*-ethylphenyl)cyclopropene (36) in Acetonitrile. A solution containing 170 mg of cyclopropene 36 and 40 mg of DCA in 170 mL of acetonitrile was irradiated with a 450-W Hanovia lamp equipped with a uranium-glass filter sleeve under an argon atmosphere for 30 min. Removal of the solvent under reduced pressure left a yellow oil which was chromatographed on a silica gel column with hexane as the eluent. The first component isolated from the column contained 14 mg of a crystalline solid whose structure was assigned as 1-ethyl-1,2-diphenyl-3-methyl-indene (40): mp 84–85 °C; IR (KBr) 3.25, 3.28, 3.35, 3.40, 6.28, 6.73, 6.84, 6.89, 6.94, 7.27, 9.09, 9.76, 9.95, 12.74, 12.90, 13.42, 13.69, 14.49 μm; NMR (CDCl$_3$, 90 MHz) δ 0.46 (t,

3 H, J = 6.1 Hz), 1.87–2.62 (m, 2 H), 2.18 (s, 3 H), 6.74–7.44 (m, 14 H); UV (95% ethanol) 290 nm (ε 2260), 222 (5190).

Anal. Calcd for C$_{24}$H$_{22}$: C, 92.86; H, 7.14. Found: C, 92.82; H, 7.18.

The structure of this material was further established by comparison with an independently synthesized sample. To a solution containing 1.0 g of *cis*-2-phenyl-3-methylindanone[30] in 30 mL of anhydrous ether was added 2.0 mL of a 3.2 M solution of phenylmagnesium bromide in ether at 0 °C. After being stirred for 1 h, the mixture was quenched with an ammonium chloride solution. The ether layer was washed with water and dried over magnesium sulfate. Removal of the solvent under reduced pressure afforded 1,2-diphenyl-3-methyl-1-indanol: NMR (CDCl$_3$, 90 MHz) δ 1.25 (d, 3 H, J = 6.0 Hz), 2.19 (br s, 1 H), 2.28 (d, 1 H, J = 9.0 Hz), 3.78 (dq, 1 H, J = 6.0, 9.0 Hz), 6.57–7.61 (m, 14 H). The above indanol was taken up in 20 mL of acetic acid, 2 mL of sulfuric acid, and 2 mL of water. The mixture was stirred at 25 °C for 30 min and then poured into water. The aqueous solution was neutralized and extracted with ether. The ether layer was washed with water and dried over magnesium sulfate. Removal of the solvent gave 1.12 g (88%) of 1-methyl-2,3-diphenylindene as a crystalline solid: NMR (CDCl$_3$, 90 MHz) δ 1.26 (d, 3 H, J = 7.0 Hz), 3.98 (q, 1 H, J = 7.0 Hz), 7.12–7.65 (m, 14 H).

To a stirred solution containing 0.5 g of the above indene and 0.32 mL of tetramethylethylenediamine in 25 mL of hexane at –78 °C was added 1.17 mL of a 1.25 M solution of *n*-butyllithium in hexane. After being stirred at room temperature for 3 h, the solution was cooled to –78 °C, and 0.5 g of ethyl bromide was added. The mixture was allowed to stir for 2 h and was then quenched with an ammonium chloride solution. The organic layer was washed with water and dried over magnesium sulfate. Removal of the solvent left a yellow oil which was chromatographed on a silica gel column with hexane. The major component isolated from the column (64%) was a clear oil whose structure was assigned as 1-methyl-1-ethyl-2,3-diphenylindene on the basis of its characteristic NMR spectrum (CDCl$_3$, 90 MHz): δ 0.57 (t, 3 H, J = 6.8 Hz), 1.40 (s, 3 H), 1.86 (q, 2 H, J = 6.8 Hz), 6.95–7.64 (m, 14 H). The minor isomer was a crystalline solid (mp 84–85 °C) whose spectral properties were identical with those of a sample of 1-ethyl-1,2-diphenyl-3-methylindene (40) isolated from the DCA-sensitized reaction of cyclopropene 36.

The second component isolated from the crude photolysate contained 110 mg (67%) of a white solid whose structure was assigned as 1-methyl-2,3-diphenyl-7-ethylindene (39) on the basis of the following data: mp 107–108 °C; IR (KBr) 3.28, 3.36, 3.50, 5.14, 5.34, 6.23, 6.76, 6.94, 7.24, 9.41, 12.50, 13.51, 14.25 μm; UV (95% ethanol) 238 nm (ε 22800), 303 (17300); NMR (CDCl$_3$, 60 MHz) δ 1.20 (d, 3 H, J = 8.0 Hz), 1.25 (t, 3 H, J = 8.0 Hz), 2.81 (q, 2 H, J = 8.0 Hz), 4.09 (q, 1 H, J = 8.0 Hz), 6.98–7.57 (m, 13 H); mass spectrum, *m/e* 310 (M$^+$), 295, 281, 264, 219 (base).

Anal. Calcd for C$_{24}$H$_{22}$: C, 92.86; H, 7.14. Found: C, 92.80; H, 7.17.

The third component isolated from the column contained 38 mg (25%) of a colorless oil whose structure was assigned as 1,2-diphenyl-3-methyl-4-ethylindene (37) on the basis of its spectral properties: IR (neat) 3.30, 3.40, 3.48, 6.24, 6.71, 6.80, 6.92, 7.31, 7.85, 8.50, 9.30, 9.40, 9.65, 9.85, 10.02, 10.90, 11.67, 12.40, 12.70, 13.05, 13.55, 14.35 μm; UV (95% ethanol) 288 nm (ε 10300); NMR (CDCl$_3$, 60 MHz) δ 1.33 (t, 3 H, J = 8.0 Hz), 2.52 (d, 3 H, J = 1.5 Hz), 3.13 (q, 2 H, J = 8.0 Hz), 4.92 (q, 1 H, J = 1.5 Hz), 6.88–7.60 (m, 13 H); mass spectrum, *m/e* 310 (M$^+$, base), 295, 281, 265, 203, 202, 194, 166, 139, 105, 84.

Anal. Calcd for C$_{24}$H$_{22}$: C, 92.86; H, 7.14. Found: C, 92.78; H, 7.24.

This compound was also obtained from the direct irradiation of cyclopropene 36 in benzene. Indenes 37 and 39 could be readily interconverted (photostationary-state ratio of 2:1 for 39 to 37) by carrying out the irradiation in the presence of dicyanoanthracene with a uranium-glass filter sleeve.

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Cycloaddition Reactions of Indenes. 2. Reactions with Dimethyl Acetylenedicarboxylate and Maleic Anhydride[1]

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1H-Indenes (1) react with dimethyl acetylenedicarboxylate (DMAD), unlike maleic anhydride and other ethylenic dienophiles, without prior isomerization to 2H-indenes (2), giving a 1:1 Diels-Alder adduct (6) formed with destruction of the aromaticity of the benzene ring. This intermediate, not isolated in the present work, appears to serve as the precursor for all further adducts. Thus, 1H-indene (1a) and 1-methyl-1H-indene (1b), but not the more sterically hindered 1-ethyl-1H-indene, react with DMAD in refluxing benzene (with 1a) or toluene (with 1b) via a 1,2-cycloaddition to 6 to give solid 1:2 adducts (7a, 34%; 7b, 30%). In refluxing xylene the reaction goes further to give a 1:3 adduct (11a; 40% from 1a, 71% from 7a) formed by a Diels-Alder addition of a third molecule of DMAD across the remaining diene system of 7a. Reaction of 2-methyl-1H-indene (1c) with DMAD in refluxing xylene gave the corresponding 1:3 adduct (11c, 5-6%), but an attempt in refluxing toluene to isolate a solid 1:2 adduct (7c) was unsuccessful. A 3-substituent in the 1H-indene, which becomes a 4-substituent in 6, blocks the 1,2-cycloaddition (to give 7) and diverts the DMAD to the cyclohexadiene system of 6, where a Diels-Alder reaction occurs in refluxing xylene to give another type of 1:2 adduct (8). The following 3-substituted 1H-indenes (1) gave 1:2 adducts of type 8: 3-methyl- (8d, 41%), 3-ethyl- (8e, 40%), 1,3-dimethyl- (8f, 31%), 2,3-dimethyl- (8g, 19%), 3-carboxy- (8l, 74%), 3-(methoxycarbonyl)- (8m, 66%), and 3-cyano-1H-indene (8n, 63%). Alkaline hydrolysis of 8l and acidification to pH <2 gave the monosodium salt (91%) of the corresponding pentacarboxylic acid (13l). Hydrogenation of 8l over PtO₂ gave a tetrahydro derivative (14l, 100%). That maleic anhydride can take the place of the second (but not the first) molecule of DMAD in 8 is shown by the formation of a 1:1:1 mixed adduct (10l, 17%) along with the 1:2 adduct (8l, 18%) from reaction of 1l, DMAD, and maleic anhydride in a 1:2:2 molar ratio in refluxing xylene. A similar 1:1:1 mixed adduct (10n, 59%), but no 1:2 adduct (8n), was isolated from the corresponding reaction of 1n, DMAD, and maleic anhydride in a 1:1:1 molar ratio. Similarly, maleic anhydride can take the place of the third molecule of DMAD in the 1:3 adduct 11. Thus, reaction of 7a and 7b with maleic anhydride in refluxing xylene gave the corresponding 1:2:1 mixed adducts (12a, 69%; 12b, 32%), formed by Diels-Alder addition across the cyclohexadiene system of 7a and 7b. Reaction of 1-methyl-1H-indene (1b), DMAD, and maleic anhydride in a 1:2:1 molar ratio in refluxing xylene also gave 12b (31%) but no 1:3 adduct (11b). Methyl esterification of 12a gave the corresponding hexamethyl ester (15a, 52%). On the basis of the shielding effects of neighboring ethylene groups on the methylene bridge protons, an NMR rationale has been developed for assignment of stereochemistry to the adducts 8-12.

The previous paper[1] reports that 1H-indene-3-carboxylic acid (1l) and its less reactive methyl ester (1m) react upon heating (in refluxing xylene or, when necessary, in 1,2-dichlorobenzene), via intermediate 2H-indenes (isoindenes, 2), with the more reactive ethylenic dienophiles, such as maleic anhydride or N-phenylmaleimide, or the less reactive dimethyl fumarate, to give 1:1 Diels-Alder adducts (3 and 4, 1,2,3,4-tetrahydro-1,4-methanonaphthalene-1-carboxylic acid 2,3-derivatives). 1H-Indene (1a) itself reacts with maleic anhydride at 250[3] or 180 °C[4] in benzene or at 198 °C in tetralin[3b] solution to give the corresponding

1:1 adduct (3a)[3a] by the same mechanism.[3a,4] The dimer[5] formed by heating 1l at 180 °C has been shown[2b] to have the corresponding structure 5,[1,2b] formed by one molecule of 1l isomerizing to 2H-indene-3-carboxylic acid (2l) and another molecule of 1l, acting as an ethylenic dienophile, adding to it in a head-to-head Diels-Alder fashion (Scheme I).

With the more reactive acetylenic dienophile dimethyl acetylenedicarboxylate (DMAD, dimethyl 2-butynedioate),[6] however, the reactions with indenes take a different course. 1H-Indene (1a) with DMAD gave a 1:2 adduct[3,7] in refluxing benzene,[3a] or more slowly at room temperature[7] or even at 0-5 °C,[8] the structure of which was shown to be 7a by X-ray analysis of its 6,9-dibromide.[7] The four vinylene protons of 7a were shown to come from

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