Substituent Effects on the Efficiency and Selectivity of Photochemical 1,5 Shifts in Benzonorcaradienes

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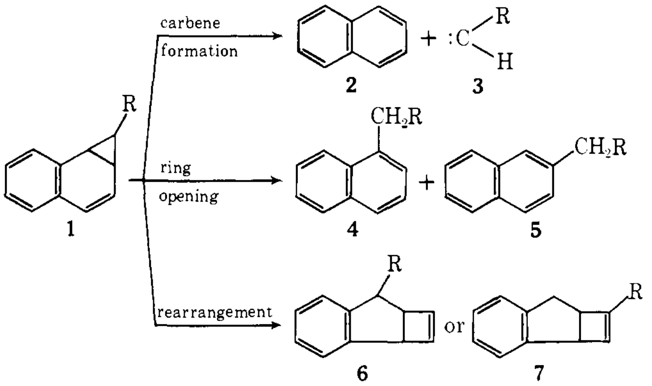
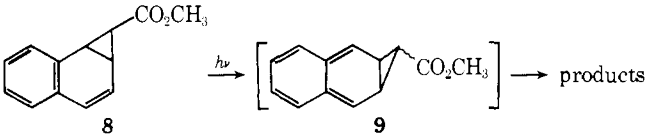
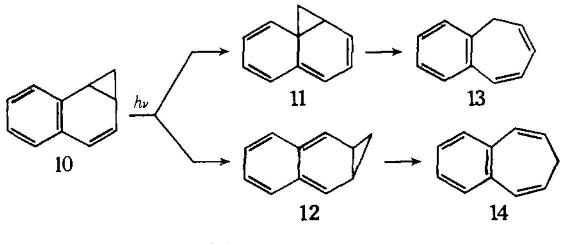
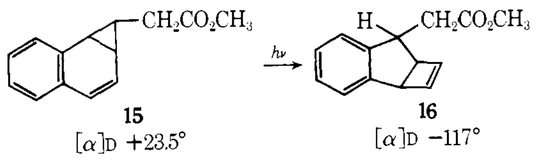
Abstract: The photochemistry of 7-carbomethoxy- (**8**), 6-carbomethoxy- (**17**), 6-cyano- (**26**), 1-carbomethoxy- (**29**), and 1-cyanobenzonorcaradiene (**30**) has been studied. The major photochemical process in all these systems is 1,5-sigmatropic migration to produce after tautomerization a 1,2- and/or 3,4-benzotropilidene. Substituents may produce a marked effect on the direction of migration. Thus, whereas **8** and the unsubstituted benzonorcaradiene (**10**) show little specificity in the direction of migration, **17** and **26** produce exclusively a 5-substituted 1,2-benzotropilidene, and **30** yields preferentially a 2-substituted 3,4-benzotropilidene. The nonselectivity in the 1,5-sigmatropic shift in **29** is attributed to steric hindrance between the ester function and the perihydrogen. The basic processes in the photochemistry of benzonorcaradienes are discussed in view of the results reported here.

The photochemical reactions of benzonorcaradienes have been of interest for the past several years. Early investigations in this area showed that carbene formation, ring-opening reactions, and rearrangement processes could all be involved in the photochemistry of this moiety.[2a-d] The rearrangement reactions were especially intriguing, and Swenton and Krubsack[2d] first proposed an intermediate such as **9** to be involved in the photochemistry of the 7-carbomethoxybenzonorcaradiene (**8**). Pomerantz and Gruber[2e] subsequently showed that the rearrangement products from irradiation of the parent hydrocarbon (**10**) were nicely accommodated by the intervention of two 1,5-shift intermediates, **11** and **12**, and termed the process a Berson-Willcott-Bones Rearrangement.[3,4] While the question of retention or inversion of the migrating carbon in the reaction has not been answered, it has been shown that irradiation of optically active **15** yields optically active **16**.[5] More recently analogous examples of this basic process have been noted in the photochemistry of a heterocyclic norcaradiene[6a] and arene oxides.[6b-d]

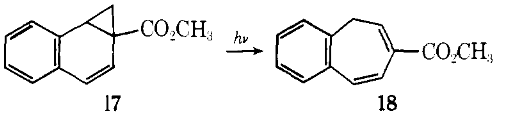






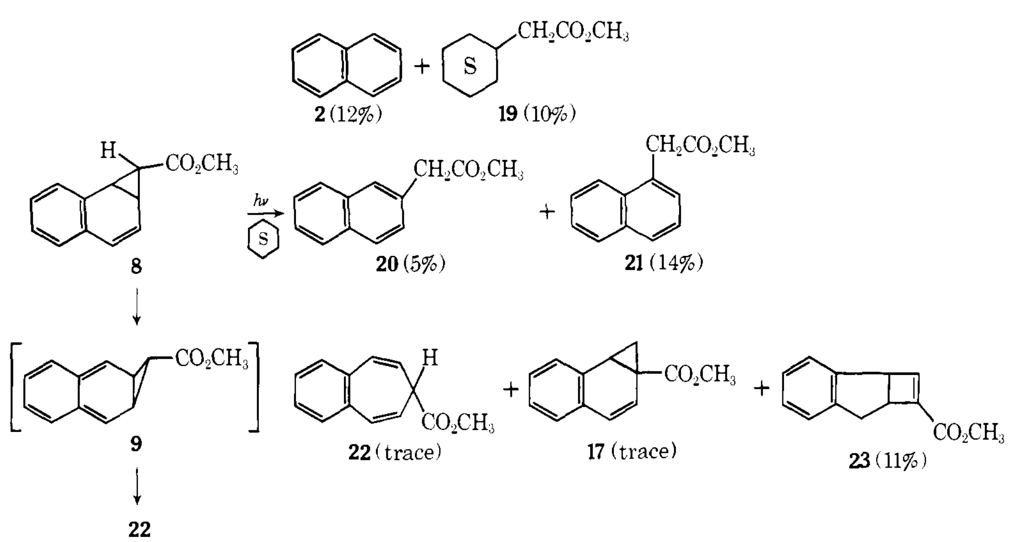


An especially interesting aspect of the reaction to us was the dramatic effect of substituents in altering the relative efficiencies of the three basic processes. Thus, whereas irradiation of **8**[2d] and **10**[2b,e] yielded products derived from all three routes, the 6-carbomethoxybenzonorcaradiene (**17**) afforded nearly exclusively **18** in high quantum efficiency at low conversion.[7] A clear interpretation of the photochemistry of these benzonorcaradienes is complicated by the photolability of the initial 1,5-shift products, 1,2- and 3,4-benzotropilidenes. Because of the strong uv absorption of these compounds relative to benzonorcaradienes, even the photoproducts of benzonorcaradienes often detected at low conversion arise from secondary irradiation of the initially formed 1,2- and 3,4-benzotropilidene.

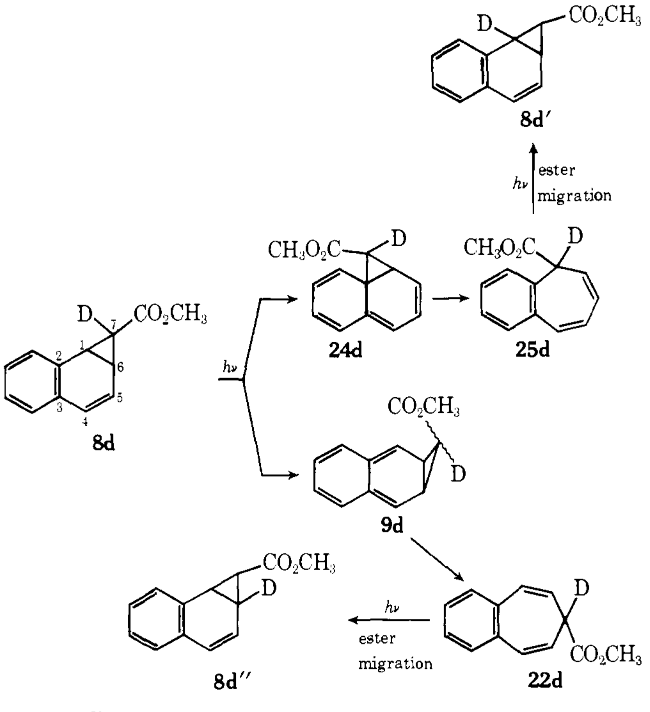


We have independently studied the photochemistry of 1,2-[8] and 3,4-[9] benzotropilidenes. This information together with the results presented here allows a reasonable interpretation of the basic processes and substituent effects observed in benzonorcaradiene photochemistry.

Irradiation of 7-Carbomethoxybenzonorcaradiene. While this system was studied only at long wavelength, several facets of its photochemistry are apparent from these efforts. Preparative irradiation of **8** with Corex-filtered light from a 450-W Hanovia source produced a complex, time-dependent ratio of the products as shown below, with a typical product distribution as indicated. The structures of these products were rigorously established by VPC isolation of these materials and comparison of their ir spectra with those of authentic compounds.[8,9] The mechanism for formation of the rearrangement products **17**, **22**, and **23** is consistent with 1,5-sigmatropic shift in excited **8** to produce the photolabile **22**. The formation of **17** and **23** from **22** and of **23** from **17** has been previously discussed.[9b] The quantum yield for disappearance of **8** measured at 3-5% conversion was 0.01-0.02.

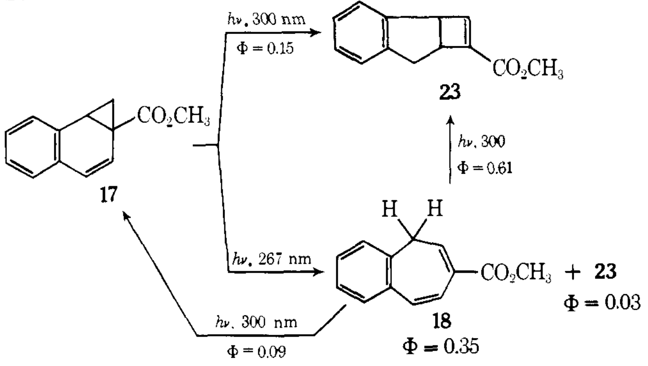


A question remaining was the apparent absence of products arising from 1,5 migration toward the aromatic ring (i.e., **24d**). In view of the complexity of the product mixture, it seemed appropriate to seek additional evidence for this apparent specificity of the 1,5 shift. Irradiation of the 7-deuterio compound, **8d**, to 34% conversion followed by VPC isolation of the starting material and NMR integration for hydrogen content revealed 9% loss of hydrogen at C_1 and C_6 accompanied by an increase of hydrogen content at C_7. This deuterium scrambling is consistent with the scheme noted above wherein 1,5-sigmatropic migration is occurring in both directions. The subsequent irradiations of **25d** and **22d** would necessarily involve migration of carbomethoxy vs. deuterium, a point which has previously been established for **22d**.[9b] An analogous scheme had been previously invoked to explain deuterium scrambling in the parent system.[2e] Thus, in both of these compounds, **8** and **10**, little directional specificity is noted in the initial 1,5-shift process.



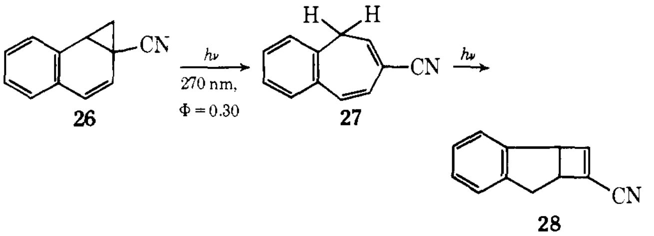
Photochemistry of 6-Carbomethoxy and 6-Cyanobenzonorcaradiene. In contrast to the small perturbing effect of a 7-carbomethoxy group on the photochemistry of the parent hydrocarbon, the 6-carbomethoxy compound exerted a pronounced effect on the photochemistry of this ring system. Irradiation of **17** at 300 nm led solely to the production of **23** with an "operational quantum efficiency" of 0.15. Evidence that this was not the sole initial photochemical process was deduced by studying the reaction at 267.5 nm, a wavelength where the uv absorption of **17** was maximized vs. that of an expected 1,5-shift product **18**. Irradiation at this shorter wavelength produced major amounts of **18** ($\Phi = 0.35$) and minor amounts of **23** ($\Phi = {\sim}0.03$). The interrelations of these various photochemical processes are presented in Scheme I.

Scheme I



The difference in results at these two wavelengths could arise from a bona fide wavelength effect on the photochemistry of **17**. However, the operation of a common route at both wavelengths is possible if the absence of **18** in the 300-nm irradiation of **17** were due to its rapid photochemical rearrangement to the cyclobutene. Indeed, **18** possesses a much stronger uv absorption at 300 nm than **17** and is efficiently converted to **23** upon irradiation. In calculating the overall efficiency for the production of **23** via the route **17** → **18** then **18** → **23**, a value of 0.11 is obtained. The observed efficiency for the **17** → **23** conversion at 300 nm is 0.15. Thus, we cannot exclude a minor photochemical route of low efficiency ($\Phi \sim 0.04$) for production of **23** directly from **17**. Interestingly, this is the magnitude of the measured efficiency for production of **23** from **17** at 267 nm also. Thus, there is no strong evidence for a wavelength effect on the basic photochemical process of **17**. While the major reaction of **17** is to afford **18** via a highly specific 1,5 shift, the data do not exclude a process of lesser importance which would effect a one-step photochemical conversion of **17** to **23**.

In view of the highly specific rearrangement in the ester system, the related cyano system (**26**) was briefly examined. Again preparative irradiation of **26** at 300 nm led to exclusive formation of the cyclobutene **28** in 88% yield, while low



conversion irradiation of **26** at 270 nm afforded the 1,2-benzotropilidene (**27**) with a quantum efficiency of 0.30. While the quantum yields interrelating these three products were not studied in so extensive detail as for the ester system **17**, the results indicate that the cyano group also functions to specifically direct the photochemical 1,5 shift.

Synthesis and Irradiation of 1-Carbomethoxy- and 1-Cyanobenzonorcaradiene. The high selectivity observed in the 1,5-carbon shift of **17** and **26** posed a question as to the origin of this specificity. Our initial hypothesis was that some effect involving the conjugating ability of these groups was related to the selectivity of migration. Thus, of the two pathways for 1,5 shift in the excited benzonorcaradienes **17** and **26**, only path a (migration toward the ring) has the carbomethoxy or cyano group situated for conjugative interaction with the π system (Scheme II). By contrast, irradiation of either **29** or **30** would present the opposite situation. The substituent in this case would exert its conjugating effect only if path b were followed. Thus, we felt it informative to study the selectivity of the 1,5-alkyl shift in benzonorcaradienes **29** and **30**.

Scheme II

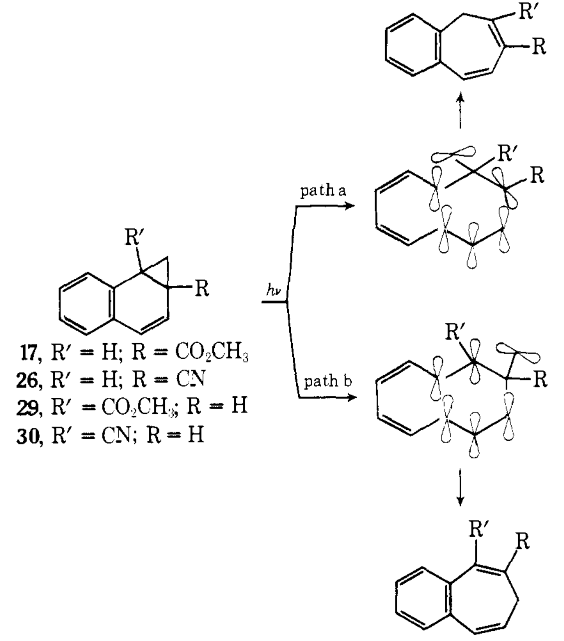
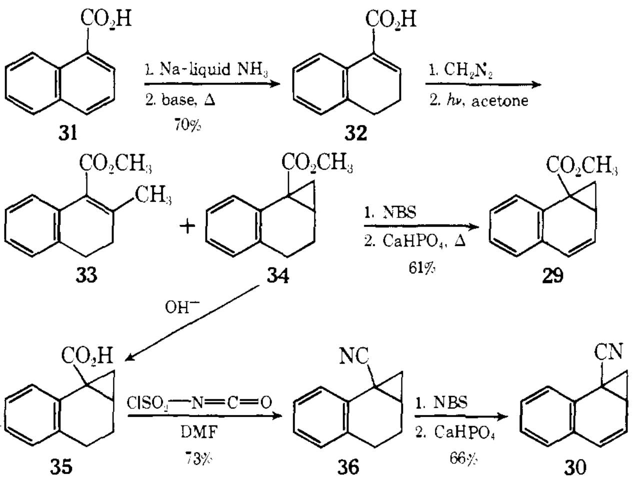


Chart I. Synthesis of 1-Carbomethoxy and 1-Cyanobenzonorcaradiene



The synthesis of the requisite compounds is outlined in Chart I. This synthetic procedure was especially useful since it also allowed the preparation of the 7,7-dideuterio compound **29d** when dideuteriodiazomethane was substituted for diazomethane in the sequence. Irradiation of **29** in cyclohexane showed by VPC the formation of two major products at 40% conversion in approximately equal amounts.[10] Upon continued irradiation, one of these increased while the other decreased until, at 95% conversion, one product remained in 49% yield. The 49% product was established as **43** and the second material as **42** by spectroscopic comparison with authentic samples synthesized as shown in Chart II. Since the efficiency of this reaction appeared quite low, it was of interest to determine if a recycling process as noted for the parent benzonorcaradiene and **8** was operative here also. Thus, the photochemistry of **29d** was studied. Irradiation of the 7,7-dideuterio compound **29d** afforded **43d** with the deuteriums located exclusively at the benzylic methylene positions. Since **29d** reisolated from a 50% conversion—irradiation showed an NMR spectrum identical with starting **29d**—no recycling process such as noted in the 7-carbomethoxynorcaradiene and parent hydrocarbon was operative in this system.

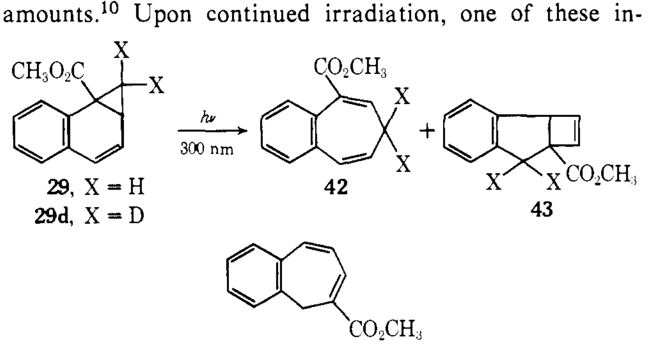
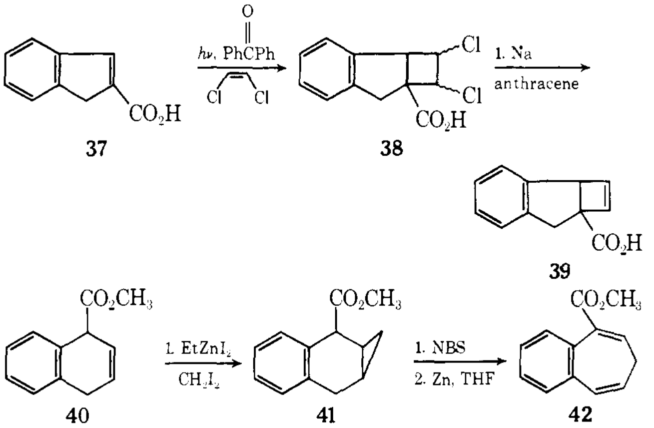
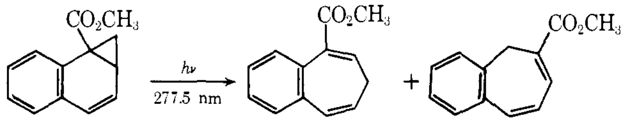


Chart II. Authentic Syntheses of 1-Carbomethoxy-3,4-benzotropilidene and 5-Carboxy-2,3-benzobicyclo[3.2.0]heptadiene



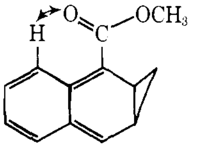
Since it appeared reasonable that **43** was arising from secondary irradiation of **44** initially formed in the reaction, the photochemistry of **29** was examined at 277.5 nm. At this shorter wavelength, the uv absorption of **29** was maximized relative to **42** and **44**. Indeed, irradiation at 277.5 nm afforded **42** and **44** with quantum efficiencies of 0.050 and 0.068, respectively. Since irradiation of **44** produces exclusively **43**, it appears that, as in the related system (i.e., **17**), the cyclobutene product arises primarily from a secon-



29 **42**, $\Phi = 0.050$ **44**, $\Phi = 0.068$

dary photochemical process. The absence of any photochemical products derived from secondary irradiation of **42** apparently derives from its low photochemical reactivity. The independent irradiation of **42** yielded only a 3% yield of an uncharacterized volatile compound.

The lack of specificity noted in the photochemical 1,5-shift process for **29** was both frustrating and interesting. A possible explanation for the nearly random migration in **29** could arise from steric hindrance to effective conjugation in the transition state for the 1,5 shift. Inspection of models of



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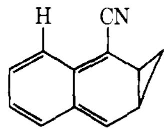

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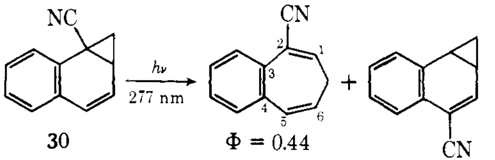
the intermediate **45** suggests that interaction of the perihydrogen with the carbomethoxy group could cause twisting of the carbomethoxy group from planarity with the ring system. Inasmuch as the transition state for migration resembles this intermediate, steric hindrance could also be important here. If this be the case, the effect of ester conjugation in the transition state would be lost, and nonspecific migration could result. To test the suggestion that steric hindrance could be responsible for the lack of directionality in **29**, the nitrile **30** was studied. Studies in the 6-substituted benzonorcaradienes showed that the carbomethoxy and nitrile functions were nearly equally effective in directing the 1,5 shift. Furthermore, any steric interaction in the transition state for this compound should be minimal due to the linear nitrile function in **46**.

Preparative irradiations of **30** at 300 nm up to 30% conversion showed the production of three products in the ratio ca. 1:17:4. The products were isolated by preparative VPC and the structures of the two major products assigned as **47** and **48** on the basis of analytical and spectroscopic data.

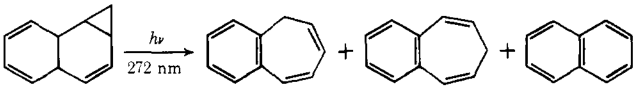


30 $\Phi = 0.44$ **47** $\Phi = 0.15$ **48**

The most informative data on **47** were the NMR spectrum (100 MHz) which showed a lone deshielded aromatic proton at τ 2.35 (m, 1 H), the remaining aromatic protons at 2.74 (m, 3 H), H_1 as a triplet at 3.36 ($J_{1,7} = 7$ Hz) overlapping with the AB doublet of H_5 centered at 3.34 ($J_{5,6} = 10$ Hz), H_6 as a doublet of triplets at 4.22 ($J_{67} = 7$, $J_{56} = 10$ Hz), and the methylene group as a triplet at 7.54 ($J = 7$ Hz). The structure of the minor product was assigned as **48**, again largely on the basis of its NMR spectrum: τ 2.58 (m, 1 H), 2.70 (m, 3 H), 2.92 (d, $J = 5$ Hz), 7.42 (m, 1 H), 7.94 (m, 1 H), 8.16 (m, 1 H), and 10.12 (m, 1 H). The one-hydrogen absorption at 10.12 indicated the compound was a benzonorcaradiene, and comparison with authentic samples indicated it was not the 1- or 6-cyano compound. Since the cyano was not at the apical cyclopropyl position because of the presence of the high-field resonance, the cyano must be at either position 4 or 5. The appearance of the vinyl proton as a clean doublet establishes the cyano group at C_4 and thus the structure as **48**.[11]

Since **48** appeared to be a product from secondary irradiation of **47**, the irradiation of **47** was briefly examined. Indeed irradiation of **47** to ca. 40% conversion at 350 nm produced both **30** (three parts) and 48 (one part) in addition to the unknown photoproduct (one part). While we had been previously successful in isolating the primary photochemical product by conducting low conversion irradiations with monochromatic light, such was not the case in this system. Irradiation of **30** at a number of wavelengths afforded both **47** and **48**. The quantum yield at 277 nm for **47** was 0.44, and for **48** was 0.15. If the **48** observed in these determinations is from secondary irradiation of **47**, then the real efficiency for irradiation of **30** must be approaching unity. Thus, in contrast to the ester **29**, the nitrile **30** undergoes the photochemical 1,5 shift with a high selectivity and high efficiency.

Irradiation of Benzonorcaradiene. The results presented in the previous section suggested an additional point deemed worthy of further study, namely, that those benzonorcaradienes (i.e., **17, 26, 30**) showing a high specificity in the direction of the 1,5 migration likewise show a good quantum efficiency for the reaction (Φ = 0.35, 0.30, and 0.44), whereas **29**, which showed little specificity, rearranged less efficiently (Φ = 0.12). To establish whether the ester group in **29** retarded the 1,5 shift or simply exerted little effect on the rearrangement, the parent system was studied at 272 nm, where the uv absorption of benzonorcaradiene is maximized vs. the tropilidenes. Low conversion irradiation of **10** at 272 nm afforded **13** and naphthalene, with quantum efficiencies of 0.078 and 0.030. The presence of 3,4-benzotropilidene (**14**) could not be determined in these low conversion runs because of the VPC overlap of **14** with starting **10**. However, since the 3,4- and 1,2-benzotropilidenes appear in approximately equal quantities in preparative runs,[2] it seems reasonable that they are formed with comparable efficiency. Thus, using the parent benzonorcaradiene as a model, those substituents which increase the selectivity of the 1,5 shift also cause a modest increase in its efficiency.



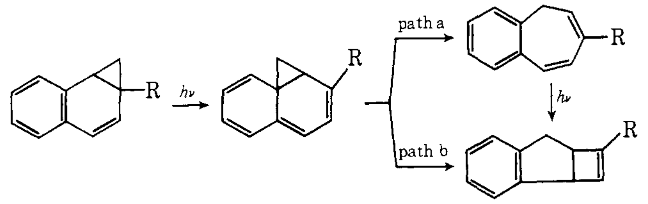
10 **13**, $\Phi = 0.078$ **14** **2**, $\Phi = 0.030$

Discussion

The previous studies in benzonorcaradiene chemistry have involved preparative irradiations and product identification with little information being obtained on the relative efficiency of the photochemical processes involved. The complex product mixtures noted in many of these studies undoubtedly arise from further irradiation of initially formed 1,2- and 3,4-benzotropilidenes. For example, whereas preparative studies of benzonorcaradiene yield naphthalene as a major product,[2e] these studies indicate that the most efficient photochemical process involved is 1,5-alkyl migration. The formation of naphthalene is approximately only ⅕ as efficient as 1,5 migration, and the formation of the 1- and 2-methylnaphthalene must be less efficient yet. Thus, in contrast to what might be inferred from the preparative irradiation studies, the basic photochemical process is reasonably clean and efficient.

While the 1,5-sigmatropic shift affording a 1,2- and/or 3,4-benzotropilidene is certainly the major photochemical process in the system, evidence exists for a minor route affording benzobicyclo[3.2.0]hepta-2,6-dienes (hereinafter termed cyclobutene products). It is important to note that there are actually two routes to form cyclobutenes. One of these involves a two-step process wherein an initially formed 1,2-benzotropilidene undergoes electrocyclic ring closure to afford the product (Scheme III, path a). In those instances wherein substituted benzonorcaradienes (i.e., **17** and **26**) afford cyclobutene products in high yield, this is the major pathway followed. The substituent in these cases alters the photochemistry in two ways. First, at the benzonorcaradiene stage, it specifically directs migration so as to afford exclusively a 1,2-benzotropilidene. Second, at the 1,2-benzotropilidene stage, the substituent favors electrocyclic ring closure relative to 1,7-hydrogen shift. Should the substituent effect at either stage be inoperative (i.e., **29**), then lower yields of cyclobutene products would be produced.

Scheme III. Routes to Bicyclo[3.2.0]hepta-2,6-diene Formation from Benzonorcaradienes



Another mechanism for cyclobutene formation had been noted earlier by Pomerantz and Gruber.[2e] In the parent system, these workers reported that the cyclobutene product was formed faster from benzonorcaradiene than from 1,2-benzotropilidene and proposed bath b as the reaction mechanism. In view of the low yield of the cyclobutene product obtained from preparative irradiation, the overall efficiency of the process appears quite low. While we cannot exclude a portion of the cyclobutene arising via path b in the substituted systems (**17** and **26**), it is much less important than path a for these compounds.

Certainly the most interesting aspect of the work is the dramatic influence of the 1 and 6 substituent in effecting the direction of migration. The substituent effect in each case favors cleavage of the external cyclopropane ring bond which is bonded to the substituted carbon. Whether the origin of the substituent relates to the lower bond energy of this linkage or is a consequence of producing the most conjugated 1,5-shift intermediate is unknown. Since, in fact, these two features are undoubtedly interrelated, further discussion of the matter at this time is unwarranted. While it remains to be established whether substituents other than the conjugating and electron-withdrawing cyano and carbomethoxy groups utilized here can show a directive effect, it would be especially interesting if substituents in general can rationally direct sigmatropic migration. There appear to be few studies along these lines, and one that has been carried out on the photochemistry of substituted cycloheptatrienes does not appear to have a simple interpretation.[12]

A final point concerns the multiplicity of the excited state undergoing rearrangement. While this has not been studied in detail, we have not been able to effect sensitization of these reactions. Thus, the singlet state appears as the most likely reactant.

Conclusion

The basic photochemical process in direct irradiation.of benzonorcaradienes is a novel and interesting 1,5-sigmatropic shift. The final result of this process is the production of a 1,2- and/or 3,4-benzotropilidene. Conjugating electron-withdrawing substituents at the 1 and 6 positions can enhance the efficiency and selectivity of the process. The anomaly associated with the nonselective rearrangement of the 1-carbomethoxybenzonorcaradiene is attributed to steric hindrance preventing effective conjugation in the transition state.

Experimental Section

Melting points were taken in a Thomas-Hoover "Unimelt" apparatus and are corrected. Infrared spectra were taken as neat films or KBr pellets with a Perkin-Elmer Model 137 spectrophotometer. Nuclear magnetic resonance spectra were recorded on a Varian A-60A or a Jeolco MH-100 instrument in chloroform-d_1 or carbon tetrachloride and are reported in τ units using tetramethylsilane as internal standard. Mass spectra were obtained with an AEI-MS-902 instrument with an ionizing potential of 70 eV. Irradiations were performed with two sources: Source I, 450-W Hanovia medium-pressure source; Source II, Rayonet photochemical reactor equipped with 16 RPR-3000 Å lamps. Gas chromatographic analyses were performed on a Varian Aerograph Model 1200 or 1400 flame ionization instrument using the following columns: column A, 10 ft × 0.25 in., 10% PDEAS on 60–80 Chrom W; column B, 12 ft × ⅛ in., 5% PDEAS on 60–80 Chrom W; column C, 5 ft × ⅛ in., 3% SE-30 on 100–120 Varaport 30; column D, 25 ft × ⅛ in., 5% SE-30 on DMCS treated 60–80 Chrom G; column E, 11 ft × 0.25 in., 10% SE-30 on 60–80 Chrom W; column F, 11 ft × 0.25 in., 5% SE-30 on DMCS treated 60–80 Chrom G; column G, 25 ft × ⅜ in., 5% SE-30 on DMCS treated 60–80 Chrom G.

Elemental Analyses were performed by Scandinavian Microanalytical Laboratory, Herlev, Denmark. Some separations as noted were performed by low-pressure liquid chromatography on a 1 × 43 in. column of floatation-graded TLC grade silica gel according to a procedure devised by Dr. John McCall. NMR spectra were recorded at 60 MHz unless otherwise noted.

Irradiation of 7-Carbomethoxy-2,3-benzonorcaradiene (8). The ester **8** was dissolved in 150 ml of purified cyclohexane and irradiated for 10 hr with Corex-filtered light from source I. After irradiation, 0.12 g of diphenyl ether was added and the mixture analyzed by VPC [column A programmed from 100 to 180°]. Using calibration data from known compounds, the following yields were calculated: **19** (10%); **2** (12%); **23** (11%); **17** (trace); **8** (12%); **22** (trace); **21** (14%);[12] and **20** (5%).[13] All the compounds were collected by VPC, and their identity established by ir and NMR comparison with the known compounds.[8,9]

Deuterium Scrambling in the Irradiation of 7-Deuterio-7-carbomethoxy-2,3-benzonorcaradiene (8d). A solution of 82 mg of **8d** and 35 mg of octadecane in 18 ml of cyclohexane was irradiated with source II for 15 hr (34% disappearance of **8d**). The cyclohexane was removed in vacuo and the starting material separated from octadecane and photoproducts by VPC (column A at 150°). NMR analysis showed a decrease in hydrogen of 8% at C_1 and 9% at C_6 with an increase of 27% at C_7. A second determination performed at 21% conversion showed a decrease of 7% at C_1 and 9% at C_6 with an increase of 21% at C_7.

Irradiation of 6-Carbomethoxy-2,3-benzonorcaradiene (17). A solution of 79 mg of **17** in 20 ml of cyclohexane was irradiated for 2.5 hr through Pyrex with source II. Quantitative VPC analysis (column B at 155°) showed an 81% yield of **23** and ca. 1% of starting material present. Some polymerization had occurred prior to analysis, thus accounting for the low yield of **23.** Identity and homogeneity were established by ir and NMR comparison with the known compound.[8a]

Irradiation of 6-Cyano-2,3-benzonorcaradiene (26). A solution of 50 mg of **26** in 20 ml of cyclohexane was irradiated for 3 hr using source II, the progress of the reaction being monitored by VPC (column C at 120°). The sole product detected was **28** in greater than 88% yield.[8]

1-Carbomethoxy-2,3-benzonorcarene (34). The ethereal diazomethane solution obtained from a mixture of 60 ml of 40% potassium hydroxide, 150 ml of ether, and 13.15 g (0.127 mol) of *N*-nitroso-*N*-methylurea was dried for 1 hr over potassium hydroxide pellets and then added to 3.99 g (0.021 mol) of 1-carbomethoxy-3,4-dihydronaphthalene[14] and the solution stored for 48 hr at 5°. The solution was evaporated in a stream of nitrogen and the yellow residue transferred to a Pyrex test tube with 125 ml of acetone. This material was irradiated with source II at 0° until nitrogen evolution had subsided (6 hr). Gas chromatographic analysis (column C at 135°) showed an 83:17 mixture of **34** and a compound tentatively identified as 1-carbomethoxy-2-methyl-3,4-dihydronaphthalene. Short-path distillation of this material afforded 3.96 g (92%) of the ca. 1:5 mixture of **33** and **34**. A sample of **34** purified by preparative VPC showed: ir 3.35 (m), 5.80 (s), 6.71 (m), 7.00 (m), 7.85 (m), 7.97 (m), 8.27 (m), 8.38 (m), 8.57 (m), 8.91 (m), 9.32 (m), 9.43 (m), 9.72 (m), 13.20 (m), and 13.58 μ (m); NMR (CCl_4) τ 2.46–2.77 (m, 1 H), 2.83–3.23 (m, 3 H), 6.46 (s, 3 H), 7.1–8.5 (series of m, 6 H), and 9.13 (m, 1 H).

Anal. Calcd for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98. Found: C, 76.78; H, 6.90.

1-Carbomethoxy-2,3-benzonorcaradiene (29). A mixture of 4.04 g (0.02 mol) of the above material and 3.90 g (0.02 mol) of *N*-bromosuccinimide in 150 ml of carbon tetrachloride was heated to reflux and 10 mg of AIBN added as an initiator. Initiation occurred within 10 min, and the reaction was complete in 0.5 hr. The reaction mixture was cooled, the solid removed by filtration, and the filtrate concentrated, yielding a yellow oil. The oil was immediately dissolved in 100 ml of dimethylformamide, 4 g of calcium biphosphate added, and the suspension stirred at 80° for 8 hr. The cooled mixture was poured into 200 ml of ice–water, extracted with ether (4 × 100 ml), and the combined ether layers were washed with 10% sodium bicarbonate (100 ml), water (2 × 100 ml), and saturated sodium chloride solution (100 ml). After drying over Drierite and solvent removal in vacuo, the oil was chromatographed on silica gel (2.8 × 76 cm column, slurry packed with 3% ether–hexane). Elution proceeded as follows: 1.75 l., 3% ether–hexane, nil; 0.5 l., 5% ether–hexane, nil; 0.125 l., 5% ether–hexane, 0.053 g unidentified oil; 1.625 l., 5% ether–hexane, 3.5987 g of dark solid. Recrystallization of this material from absolute methanol afforded 2.592 g (78% based on the single component of the starting mixture) of 1-carbomethoxy-2,3-benzonorcaradiene (**29**): mp 88–88.5°; ir (KBr) 5.78 (s), 6.95 (m), 7.71 (s), 7.98 (s), 8.32 (m), 8.66 (m), 12.71 (s), and 13.92 μ (m); uv$_{max}$ (cyclohexane) 225 nm (ϵ 21,700), 229 (ϵ 19,400), and 272 (8030); NMR (CCl_4) τ 2.3–2.6 (m, 1 H), 2.8–3.1 (m, 3 H), 3.87 (m, 2 H), 6.37 (s, 3 H), 7.75 (m, 2 H), and 9.81 (m, 1 H); mass spectrum *m/e* (relative intensity) 202 (M, 58), 203 (M + 1, 10), 51 (5), 55 (5), 56 (10), 57 (19), 63 (5), 71 (9), 72 (5), 91 (5), 115 (20), 127 (9), 128 (42), 129 (9), 141 (20), 142 (28), 143 (100), 144 (12), 170 (14), and 171 (8).

Anal. Calcd for $C_{13}H_{12}O_2$: C, 77.98; H, 6.04. Found: C, 77.76; H, 6.14.

2,3-Benzonorcarene-1-carboxylic Acid (35). The neat ester **34**, 0.868 g (4.3 mmol), was added to 12 ml of water containing 0.253 g (4.5 mmol) of potassium hydroxide and 0.5 ml of absolute methanol and heated for 12 hr at 80°. The cooled hydrolysis solution was extracted once with 30 ml of ether, then acidified with concentrated hydrochloric acid to a pH of 2. This mixture was extracted with ether which was then washed with saturated brine, dried over calcium sulfate, and concentrated in vacuo, yielding a white solid. This material was recrystallized once from 50% ether–hexane, yielding 0.731 g (91%) of the corresponding acid: mp 120–122°; ir (KBr) 3.40 (m), 5.93 (s), 6.72 (m), 6.91 (m), 7.04 (m), 7.72 (s), and 7.90 μ (m); NMR ($CDCl_3$) τ 1.76 (s, 1 H), 2.40 (m, 1 H), 2.64–3.08 (m, 3 H), 6.8–8.4 (series of m, 6 H), and 8.94 (m, 1 H).

Anal. Calcd for $C_{12}H_{12}O_2$: C, 76.57; H, 6.43. Found: C, 76.53; H, 6.52.

1-Cyano-2,3-benzonorcarene (36). To a refluxing solution of 0.3 g (1.59 mmol) of **35** dissolved in 2 ml of methylene chloride was added 0.27 g (1.91 mmol) of chlorosulfonyl isocyanate in 1 ml of methylene chloride.[15] The solution was refluxed until gas evolution ceased, ~1 hr. The reaction was cooled to room temperature, and 0.456 g of *N,N*-dimethylformamide was added with further gas evolution. Stirring was continued for 15 min, followed by pouring the reaction into 50 ml of water and extracting with ether. The ether layer was washed with saturated brine solution, dried over calcium sulfate, and concentrated, yielding a clear yellow oil. The oil was chromatographed on silica gel (1.5 × 30 cm, slurry packed in 2% ether–petroleum ether). Elution proceeded as follows: 2% ether–petroleum ether, 150 ml, nil; 2% ether–petroleum ether, 350 ml, 220 mg of a clear oil that was molecularly distilled at 60° (0.15 mm), yielding 0.198 g (73%) of the nitrile ir (neat) 4.48 (s), 6.7 (s), 6.85 (s), 6.92 (s), 6.99 (m), 9.55 (m), 10.5 (s), 12.8 (s), 13.4 (s), and 13.5 μ (s); NMR (CCl_4) τ 2.45 (m, 1 H), 3.0 (m, 3 H), and 7.3–8.8 (broad structured m, 7 H)].

Anal. Calcd for $C_{12}H_{11}N$: C, 85.21; H, 6.51; N, 8.28. Found: C, 84.80; H, 6.81; N, 7.87.

1-Cyano-2,3-benzonorcaradiene (30). To a refluxing mixture of 0.788 g (4.4 mmol) of *N*-bromosuccinimide in 12 ml of carbon tetrachloride containing 0.681 g (4 mmol) of **36** was added ~10 mg of azobisisobutyronitrile. After 15 min, the mixture was filtered hot and the filtrate concentrated. The orange oil was dissolved in 12 ml of *N,N*-dimethylformamide containing ~200 mg of calcium dihydrogen phosphate and heated for 8 hr at 80° under a nitrogen atmosphere. The cooled reaction mixture was poured into 100 ml of water and extracted with ether. The organic layer was washed with saturated brine, dried over calcium sulfate, and concentrated, yielding 0.79 g of crude product. This was combined with 0.24 g of crude product from a previous run and chromatographed on a 1 × 10 cm neutral alumina column with 3% ether–petroleum ether, 300 ml, yielding 0.75 g of a pale-yellow oil, 90% pure by VPC. This material was chromatographed on a 43 × 1 in. TLC grade silica gel column as follows: petroleum ether, 0.9 l., nil; 1% ether–petroleum ether, 0.6 l., nil; 2% ether–petroleum ether, 0.4 l., nil; 3% ether–petroleum ether, 240 ml, 44 mg; 3% ether–petroleum ether, 440 ml, 0.592 g (66%) of **24** as a clear oil [ir (neat) 4.9 (m), 6.71 (m), 6.9 (m), 12.5 (m), 12.8 (s), and 13.5 μ (m); NMR 100 MHz (CCl_4) τ 2.41 (m, 1 H), 2.95 (m, 3 H), 3.72 (d, J = 11 Hz), 3.94 (d of d, J = 11, J = 4.5 Hz, 2 H), 7.48 (five line m, 1 H), 7.98 (d of d, J = 9.9, J = 4.1 Hz, 1 H), and 9.72 (d of d, J = 6.5, J = 4.5 Hz, 1 H)].

Anal. Calcd for $C_{12}H_9N$: C, 86.23; H, 5.40; N, 8.38. Found: C, 86.00; H, 5.67; N, 8.57.

Improved Preparation of Dideuteriodiazomethane. The procedure of Hecht and Kozarich[16] was substantially improved by the following modification. Into a flask were placed 180 ml of dimethoxyethane and 80 ml of 99.8% deuterium oxide containing 2.08 g of sodium hydride dispersion (52%). This mixture was cooled to 0° and swirled to make a single homogeneous phase. To this was added 3.0 g (29 mmol) of *N*-nitroso-*N*-methylurea in portions. After a period of 1.5 hr, the solution was at room temperature. Anhydrous ethyl ether (50 ml) was added to the bright-yellow solution, and the ether–diazomethane mixture was distilled into the cold receiver flask containing 40 ml of anhydrous ether and 10 g of potassium hydroxide pellets. This dry ethereal solution of deuteriodiazomethane is suitable for use after decanting it from the pellets. Esterification of a portion of benzoic acid with this diazomethane, followed by NMR integration, indicated 93% deuterium incorporation into the diazomethane.

Irradiation of 1-Carbomethoxy-2,3-benzonorcaradiene (29) and Its 7,7-Dideuterio Compound 29d. A solution of 50 mg of **29** in 18 ml of cyclohexane in a Pyrex tube was irradiated until disappearance of **29**. At this point, VPC analysis (column D) indicated one major product and two minor products. The major product was isolated by preparative VPC (column E) and shown to be **43** by comparison with a synthesized authentic sample. In a similar experiment, a solution of 25 mg of **29** and 6.5 mg of tetradecane in 18 ml of cyclohexane was irradiated as above. VPC analysis (column C at 125°) showed that, at 41% reaction of **29**, there were equal amounts of **43** and **42** as well as trace amounts of a compound having the retention time of **44**. As the reaction progressed, the amount of **43** increased, and the **42** decreased until at ca. 97% conversion (4.5 hr) the yield of **43** was 49%.

For irradiation of **29d**, 0.125 g of **29d** in 30 ml of cyclohexane was irradiated 6 hr (50% conversion) with source II. The solvent was distilled and the material chromatographed on the TLC grade silica gel column (1 × 43 in.). Elution proceeded as follows: 2% ether–petroleum ether, 1 l., nil; 3% ether–petroleum ether, 1.4 l., nil; 3% ether–petroleum ether, 220 ml, 40 mg (32%) of **29**. This material was further purified by preparative VPC (column F at 150°), and the NMR was found to be identical with that of the starting material, **29d**.

Further elution with 3% ether–petroleum ether, 264 ml, yielded 48 mg (38%) of **43d**. Further purification of this material by preparative VPC (column F at 150°) yielded material with the following NMR: (CCl_4) τ 2.92 (s, 4 H), 3.58 (broad d, J = 2.5 Hz, 1 H), 3.87 (broad d, J = 2.5 Hz, 1 H), 5.61 (broad s, 1 H), and 6.32 (s, 3 H).

Continued elution with 3% ether–petroleum ether, 40 ml, yielded 8 mg (6%) of an oil tentatively assigned **42d** by NMR.

Addition of 1,2-Dichloroethylene to 2-Indenecarboxylic Acid. A solution of 0.50 g (3.1 mmol) of 2-indenecarboxylic acid,[17] 5 ml of freshly distilled 1,2-dichloroethylene (cis-trans mixture), and

Table I. Quantum Yields

Compd	VPC column for analysis	Wavelength, nm	Light output, mE/min	% conversion	Compd (Φ)
8	B	300	0.96/305	5	8 (0.018)
8	B	300	0.811/300	3	8 (0.014)
17	B	300	0.26/100	5	17 (0.17), 23 (0.15)
17	B	300	0.31/115	5	17 (0.18), 23 (0.17)
17	B	300	0.47/200	9	17 (0.25), 23 (0.18)
17	B	270	0.089/290	4	17 (0.45), 18 (0.35), 23 (0.03)
17	B	267.5	0.11/265	6	17 (0.47), 18 (0.37), 23 (0.03)
17	B	267.5	0.14/583	6	17 (0.47), 18 (0.33), 23 (0.03)
26	D	270	0.0094/180	1	27 (0.30)
29	D	277.5	0.057/522	1	42 (0.041), 44 (0.054)
29	D	277.5	0.044/529	1	42 (0.059), 44 (0.082)
30	D	277.5	0.022/358	3	47 (0.45), 48 (0.15)
30	D	277.5	0.029/322	3	47 (0.44), 48 (0.15)
10	D	272	0.035/121	0.5	13 (0.078), naphthalene (0.030)

0.100 g of benzophenone in 35 ml of purified acetone was irradiated in a Pyrex test tube with source II for 20 hr. After removal of the solvent, the yellow semisolid residue was taken up in 5% sodium hydroxide (25 ml) and ether (25 ml). The aqueous layer was separated and the ether layer extracted with 5% sodium hydroxide (2 × 25 ml). The combined base layers were washed with ether (15 ml) and acidified with concentrated sulfuric acid. The precipitated oily solid was extracted into ether (3 × 75 ml). The combined ether layers were washed with water (50 ml) and saturated sodium chloride solution (50 ml) and dried over anhydrous calcium sulfate. Removal of solvent in vacuo gave 0.46 g (58%) of tacky, tan solid mixture of epimers of 6,7-dichloro-2,3-benzobicyclo[3.2.0]hept-2-ene-5-carboxylic acid (**38**).

2,3-Benzobicyclo[3.2.0]hepta-2,6-diene-5-carboxylic Acid (39). A mixture of 1.42 g (8.0 mmol) of anthracene in 10 ml of anhydrous tetrahydrofuran was placed in a dry 50-ml three-necked flask equipped with a glass-covered stirring bar. Sodium metal (0.184 g, 8.0 mmol) cut into small pieces was added, and the mixture was stirred under nitrogen at room temperature for 5 hr, after which time no undissolved sodium or anthracene could be detected, and the solution was a very dark blue.[18] A solution of 0.450 g (1.75 mmol) of the crude epimeric mixture of **38** in 10 ml of dry tetrahydrofuran was added dropwise over 5 min. The reaction mixture was stirred for 20 min with a few drops of water being added at the end to discharge any remaining color. The solvent was removed in vacuo and the residue taken up in 50 ml of ether and 50 ml of 5% sodium hydroxide. All the anthracene did not dissolve. The ether layer was separated and the base layer washed with ether (5 × 30 ml). The combined ether layers were then extracted with 5% sodium hydroxide (2 × 50 ml). The combined base layers were acidified with concentrated sulfuric acid, and the precipitate was extracted into ether (3 × 50 ml). The combined ether layers were washed with water (50 ml) and saturated sodium chloride solution (50 ml). After drying over anhydrous calcium sulfate, the ether was removed in vacuo to give a solid residue which was sublimed [55° (0.5 mm)] to give **39** as fine white needles: mp 123–125°; ir (KBr) 5.86 (s) and 13.4 μ (m); NMR[19] ($CDCl_3$, 100 MHz) τ 2.84 (s, 4 H), 3.50 (d of d, $J = 2.9$, $J = 2.2$ Hz, 1 H), 3.79 (d of d, $J = 2.9$, $J = 1.2$ Hz, 1 H), 5.50 (m, $J = 2.9$, $J = 1.2$, $J = 1.8$ Hz, 1 H), 6.42 (d, $J = -17.1$ Hz, 1 H), and 6.94 (d of d, $J = -17.1$, $J = 1.8$ Hz, 1 H); mass spectrum *m/e* (relative intensity) 186 (M, 37), 187 (M + 1, 3), 63 (9), 115 (33), (14), 139 (9), 140 (10), 141 (B, 100), 142 (20), 160 (5), and 168 (5).

Anal. Calcd for $C_{12}H_{10}O_2$: C, 77.40; H, 5.41. Found: C, 77.10; H, 5.47.

1,4-Dihydro-1-naphthoic Acid (40). Liquid ammonia (25 ml) was condensed into a 100-ml flask, equipped with an overhead stirrer and maintained at −78°, containing 2 g (0.012 mol) of 1-naphthoic acid, and 1.56 g (0.034 mol) of absolute ethanol. Diced sodium, 0.786 g (0.034 mol), was added in a single portion to the reaction, at which time the suspension cleared, followed immediately by formation of a precipitate. Liquid ammonia was added during the reduction to keep the suspension mobile. When the reaction was complete, the ammonia was pumped off at −78° and replaced with 60 ml of dry hexane. The reaction was then filtered, the solid pressed dry and immediately added to a two-phase hydrolysis mixture (175 ml, 30% HCl–50 ml of ethyl ether). The ether layer was separated and washed with water (3 × 30 ml) until the washings were neutral followed by a saturated brine wash and finally dried over calcium sulfate. The solvent was removed, yielding 1.06 g (52%) of a clear oil which crystallized on standing, 90% pure by VPC. One recrystallization from chloroform–hexane (1:8) yielded 1,4-dihydronaphthoic acid melting at 79–81° (lit.[20] mp 88.5–90.5°). This material was 99% pure by VPC when analyzed as the methyl ester.

2-Carbomethoxy-3,4-benzobicyclo[4.1.0]hept-3-ene (41). To 50 ml (0.045 mol) of ethyl zinc iodide solution, prepared by the procedure of Sawada and Inouye,[21] was added 12 g (0.045 mol) of methylene iodide and the solution refluxed for 1 hr, at which time 2 g (0.0106 mol) of **40** was added and reflux continued for 48 hr. The reaction was decomposed with 5% hydrochloric acid, and the organic layer was separated, washed with water, saturated sodium thiosulfate solution, water again, and dried over calcium sulfate. Concentration afforded a pale-yellow oil which was chromatographed on the TLC grade silica gel column (1 × 43 in.) with 3% ether–petroleum ether. There was obtained 1.1 g (51%) of a colorless oil containing an 80:20 ratio of isomers. The isomers were separated by preparative VPC on a column (column G at 190°) and their structures assigned by NMR (CCl_4, 100 MHz). Major isomer, trans: τ 3.1 (m, 4 H), 6.05 (broad d, $J = 3$ Hz, 1 H), 6.32 (s, 3 H), 7.04 (broad s, 2 H), 8.7 (m, 2 H), and 9.6 (m, 2 H); ir (neat) 5.76 (s), 7.0 (m), 7.55 (m), 7.85 (m), 8.05 (s), 8.5 (s), 8.67 (s), 9.8 (m), and 13.55 μ (s); exact mass (calcd *m/e* 202.09937) 202.09964 (difference 0.0003).

Anal. Calcd for $C_{13}H_{14}O_2$, trans isomer: C, 77.25; H, 6.93; O, 15.82. Found: C, 76.85; H, 6.91; O, 16.24.

Minor isomer, cis: nmr (CCl_4, 100 MHz): τ 3.04 (m, 4 H), 6.10 (broad s, 1 H), 6.46 (s, 3 H), 6.74 (broad d, $J = 14$ Hz, 1 H), 7.16 (broad d, $J = 14$ Hz, 1 H), 8.64 (m, 2 H), 9.64 (m, 1 H), and 9.94 (m, 1 H); ir (neat) 5.78 (s), 7.02 (m), 7.85 (m), 8.19 (s), 8.42 (s), 8.69 (s), 9.73 (m), 13.3 (s), and 13.69 μ (s); exact mass (calcd *m/e* 202.09937) 202.09965 (difference 0.0003).

2-Carbomethoxy-3,4-benzotropilidene (42). To a refluxing mixture of 0.37 g (2 mmol) of *N*-bromosuccinimide in 13 ml of carbon tetrachloride containing 0.191 g (9 mmol) of the **41** isomer mixture was added ~10 mg of azobisisobutyronitrile. After 30 min, the reaction was complete, and the mixture was filtered hot. The filtrate was concentrated and dissolved in 12 ml of dry tetrahydrofuran containing a drop of concentrated hydrochloric acid. The solution was heated to near reflux at which time 0.0618 g (9 mmol) of zinc dust was added. After the initial foaming stopped, the reaction was refluxed for an additional 10 min then concentrated in vacuo. The residue was dissolved in saturated sodium chloride solution and extracted with ether; the ether layer was washed with water, saturated brine, dried over calcium sulfate, and removed, yielding a yellow oil which was chromatographed on silica gel (2 × 30 cm column 3% ether–petroleum ether). One 500-ml fraction was taken which yielded the crude product as a colorless oil. This oil was chromatographed on the TLC grade silica gel column (1 × 43 in.) as follows: 0.8 l., petroleum ether, nil; 0.9 l., 2% ether–petroleum ether, nil; 0.8 l., 3% ether–petroleum ether, 36 mg (13%) of **42**: NMR (CCl_4, 100 MHz) τ 2.5 (m, 1 H), 2.84 (m), 3.08 (t, J

= 7.5 Hz, 4 H), 3.8 (d, J = 10 Hz, 1 H), 4.16 (d of t, J = 10, J = 7.5 Hz, 1 H), 6.36 (s, 3 H), and 7.71 (t, J = 7.5 Hz, 2 H); ir (neat) 5.84 (s), 7.02 (m), 8.05 (m), 8.41 (s), 8.55 (m), 9.65 (m), 12.65 (m), 12.76 (m), and 13.25 μ (m); mass spec, exact mass (calcd m/e 200.08372) 200.08394 (difference 0.0002).

Irradiation of 2-Carbomethoxy-3,4-benzotropilidene (42). A solution of 0.0030 g of **42** and 0.0600 g of octadecane in 2 ml of purified cyclohexane was degassed with nitrogen and irradiated 93 min with 350-nm light in the Rayonet apparatus. The irradiation was followed by VPC (column C at 160°) with the following results. The starting material concentration had decreased 40% with the formation of one unidentified product in ca. 3% yield.

Preparative Irradiation of 1-Cyano-2,3-benzonorcaradiene (30). A solution of 0.456 g of **30** in 30 ml of dry ether was irradiated for 5 hr with source II (ca. 20% conversion). Analysis of VPC showed the presence of three products in order of increasing retention time with the ratio 1:17:4. The starting material and the last two peaks were isolated by preparative VPC (column G at 170°). The starting material peak showed ir and NMR spectra identical with those of **30**.

The major peak was a colorless oil (**47**) which showed: ir (neat) 4.5 (m), 6.7 (m), 6.93 (m), 11.5 (m), 12.8 (s), and 13.3 μ (s); NMR (see text).

Anal. Calcd for $C_{12}H_9N$: C, 86.23; H, 5.40; N, 8.38. Found: C, 86.10; H, 5.18; N, 8.15.

The last peak was obtained as a colorless liquid and identified as **48**: ir (neat) 4.5 (m), 6.72 (m), 6.9 (s), 11.4 (m), 13.2 (s), and 13.75 μ (m); NMR (See text); exact mass (calcd for $C_{12}H_9N$, 167.07349) 167.07375 (difference 0.0003).

Irradiation of 6-Carbomethoxy-1,2-benzotropilidene (44). A degassed solution of 0.21 g (1 mmol) of **44** in 20 ml of dry ether was irradiated with source II for 2 hr. The solvent was removed in vacuo and the residual clear oil chromatographed on silica gel (1.5 × 45 cm column slurry packed in 3% ether–hexane). Elution proceeded as follows: 140 ml, nil; 200 ml, 0.168 g (80%) of a clear oil which crystallized on standing. Three recrystallizations from 90:10 methanol–water yielded material: mp 40–40.5°; ir (KBr) 5.76 (s), 8.01 (s), 9.48 (m), 13.31 (m), and 13.52 μ (m); NMR (CCl_4) τ 2.92 (s, 4 H), 3.6 (d, J = 2.5 Hz, 1 H), 3.9 (d, J = 2.5 Hz, 1 H), 5.62 (br. s, 1 H), 6.32 (br. s, 1 H), 6.59 (d, J = 17 Hz, 1 H), and 7.02 (d of d, J = 17, J = 2 Hz, 1 H).

Quantum-Yield Determinations and Irradiations at 260–280 nm. Quantum-yield measurements were performed as previously described[9a] using a Bausch and Lomb monochrometer and a double-compartment irradiation cell. The results are compiled in Table I. Irradiations in this range were in the range of 1–6% conversion. Product identity was established in these cases by the products' VPC retention, ir, or NMR spectra. Because of the low output of the 200-W super-pressure lamps in this region, preparative irradiations were not performed. Errors in the determinations of these values could be as high as 25% in some cases because of the difficulty of VPC analysis at these low conversion levels.

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