

PHOTOCHEMICAL PROCESSES IN SUBSTITUTED 3,4-BENZOTROPILIDENES

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Abstract—The products and quantum yields from direct irradiation of 7-methyl-, 7,7-dimethyl-, 7,7-dicarbomethoxy-, and the unsubstituted 3,4-benzotropilidene have been determined. The major process of these excited 3,4-benzotropilidenes is formal 1,7-group migration to produce a benzonorcaradiene. In the case of the unsubstituted molecule and the 7,7-dimethyl derivative a minor process involving 1,3-hydrogen or methyl shift to produce a 1,2-benzotropilidene was characterized. The uniformly high quantum efficiencies for these reactions ($\Phi = 0.37\text{--}0.92$) indicate that group migration is the dominant process for decay of the 3,4-benzotropilidene excited states.

INTRODUCTION

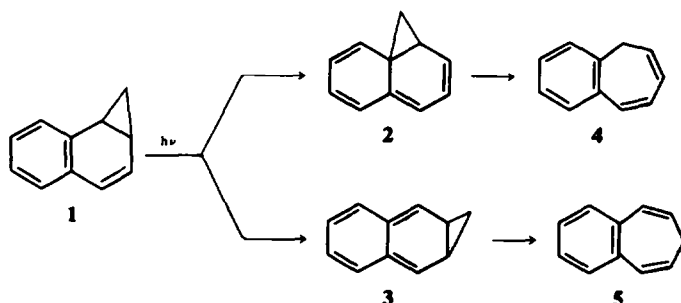
Investigations in the last several years have established the general nature of 1,5-sigmatropic shifts in norcaradiene derivatives¹ and homofulvene systems.² In the case of benzonorcaradienes, the initially formed products are 1,2- and 3,4-benzotropilidenes, compounds which show strong UV absorption in the region of irradiation of benzonorcaradienes. Thus, the eventual products obtained from benzonorcaradiene irradiation are often determined by the photochemical processes of initially formed benzotropilidenes. Due to the general interest in benzonorcaradiene photochemistry, it seemed advisable to learn more con-

cerning the reactive modes and quantum efficiencies of 1,2- and 3,4-benzotropilidenes.³ We wish to report here convenient syntheses for the unsubstituted-, 7-methyl-, 7,7-dimethyl-, and 7,7-dicarbomethoxy-3,4-benzotropilidenes and a detailed study of their photochemistry.

Syntheses of 3,4-benzotropilidenes

There appear in the literature several methods for producing 3,4-benzotropilidene itself. Unfortunately these published procedures often produced the compound in low yield and/or contaminated with the difficultly separable 1,2-benzotropilidene.^{4,5} We had initially hoped to utilize the procedure developed by Swenton and Madigan⁴ for the synthesis of the required compounds. Indeed, the synthesis of the 7,7-dicarbomethoxy benzotropilidene proceeded smoothly via this route as outlined below.

However, attempted utilization of this method for the 7-cyano-, 7,7-dicyano-, and the parent 3,4-benzotropilidene failed at the benzylic bromination step.‡ While no satisfactory route could be developed for the 7-cyano and 7,7-dicyano compounds,§ the sequence outlined below afforded the unsubstituted and 7-methyl-3,4-benzo-

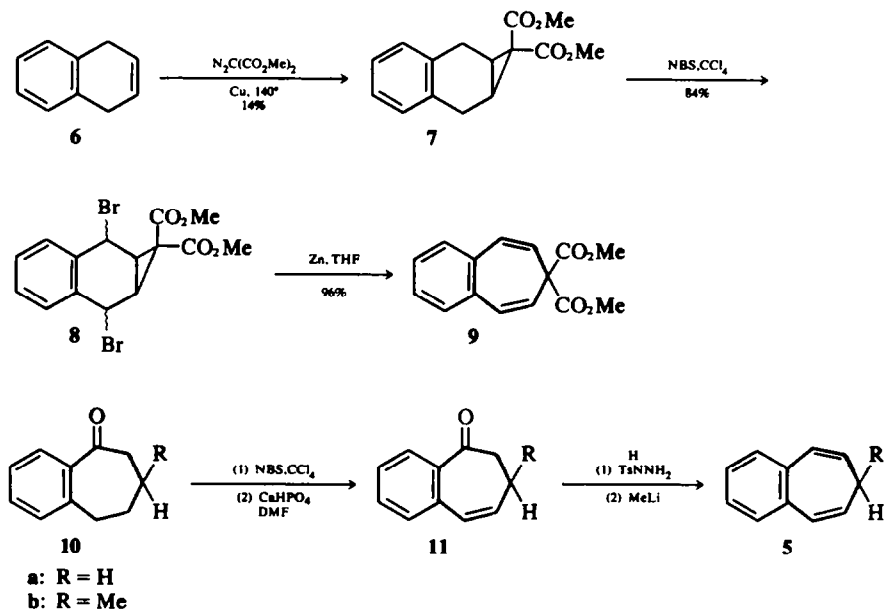


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‡Complex reaction mixtures were often produced in these NBS brominations. While all the products were not characterized, for the 7-cyano system the major process involved ring opening of the cyclopropane ring to produce a 1,2-dihydronaphthalene derivative.

§The 7,7-dicyano-3,4-benzotropilidene had been previously obtained in trace amounts from the decomposition of dicyanodiazomethane in naphthalene.^{1a}



tropolidene in reasonable yield and more importantly, completely free of the 1,2-isomer.

The 7,7-dimethyl-3,4-benzotropolidene, which is blocked from facile isomerization to the 1,2-isomer, was prepared as shown below.

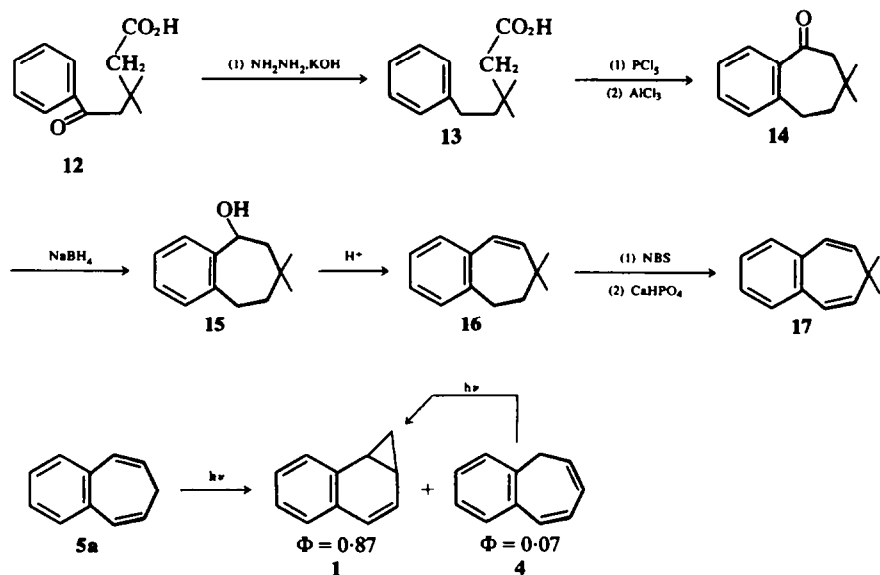
Irradiation of 3,4-benzotropolidene, 5a

The photochemistry of 5a had been previously studied by Pomerantz and Gruber^{3b} who showed by

*The failure to detect the minor product in the earlier study was apparently due to the use of 5a which contained $\pm 3\%$ of 4 as impurity.^{3b}

deuterium labeling that 1 was formed by a hydrogen shift process and not by di- π -methane rearrangement. However in our more detailed study, irradiation of 5a (>99.9% pure) at 350 nm through Pyrex gave at 10–15% conversion two products in a ca 10:1 ratio.* The amount of the minor product was maximized (4%) at 40% conversion of 5a and completely disappeared upon extended irradiation.

The major product from the reaction was isolated by preparative VPC and characterized as 1 by comparison of its spectroscopic properties with an authentic sample. The identity of the minor component was established as 4 by its VPC retention time



and its characteristic doublet at 7.02 τ in the NMR of the crude reaction mixture. The contention that **4** is a primary product from irradiation of **5a**, and not formed from secondary irradiation of **1**, is supported by the absence of naphthalene and 2,3-benzobicyclo[3.2.0]-hepta-2,6-diene even in the preparative irradiations of **5a**. It had been previously shown that irradiation of **1** produces the later products at a rate comparable to the production of **4**.^{1c}

To establish the efficiency of **5a** irradiation, quantum yield measurements were made. It proved possible to obtain only *ca* 80% separation of **1** from **5a** at low conversion by VPC; thus, the quantum yield ($\Phi = 0.87$) for appearance of **1** was determined by NMR. The quantum efficiency for **4** was then calculated from the 1:4 product ratio.

Irradiation of 7-methyl-3,4-benzotropilidene, **5b**

The ready availability of the 7-Me derivative, **5b**, prompted a brief investigation of its photochemistry to establish the migratory aptitude of Me vs H in the photochemical shift process. Irradiation of **5b** with 350 nm light afforded one major product in high yield (>90%) as well as high quantum efficiency ($\Phi = 0.93$). The identity of the major product as **18** was readily apparent from analytical and spectroscopic data, the singularly most informative property being its NMR spectrum: 2.90 (m, 4H), 3.85 (d, $J = 10$ Hz, 1H), 3.99 (d, $J = 10$ Hz, 1H), 7.85 (d of d, $J = 10$ Hz, $J = 5$ Hz, 1H), 8.68 (s, 3H), 8.84 (obscured d of d, 1H), and 10.17 (d of d, $J = 5$ Hz, $J = 3.5$ Hz, 1H) τ .

Careful VPC analysis of the reaction mixture showed a second component present at low conversion amounting to $\sim 1\%$ of the major product.

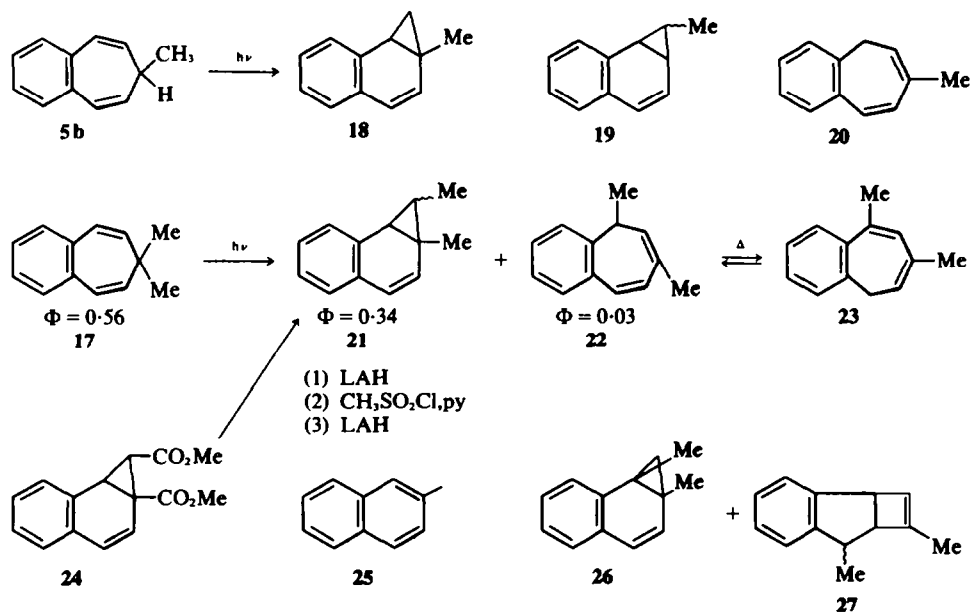
While this material had a VPC retention time corresponding to **20**, conclusive identification could not be made. Furthermore, no production of the methyl migrated product **19**, was found under conditions in which 0.1% could have been detected.

Irradiation of 7,7-dimethyl-3,4-benzotropilidene, **17**

The photochemistry of **17** appeared instructive for two reasons. First, from analogy with radical migrations and the results of **5b** irradiation, it could be surmised that excited **17** would undergo Me migrations quite slowly. Second, the geminal substitution in **17** would be expected to facilitate⁶ the potential but heretofore unobserved di- π -methane reaction in these systems. Thus, **17** appeared to afford the maximum possibility for departure from the photochemical shift process.

When the irradiation of **17** at 350 nm was carried out to 8–15% conversion, two new peaks (*ca* 10:1) were observed on the VPC. These materials were isolated by preparative VPC and the structure of the major product established as **21** by authentic synthesis. Examination of the NMR spectrum of the minor peak suggested that this material was a 1:2 mixture of 5,7-dimethyl- and 3,5-dimethyl-1,2-benzotropilidenes, **22** and **23**. This hypothesis was substantiated by independent preparation of **23** and its observed thermal isomerization to **22**. The NMR signals exhibited by the minor peak isolated by preparative VPC were entirely accounted for by the absorptions of **22** and **23**. Since **23** was not detected in the NMR of the crude irradiation mixture, the minor material formed is exclusively **22**, the product of photochemical 1,3-Me migration.

While the low conversion irradiations of **17** were reasonably clean, in contrast to the other systems



studied, extended irradiation produced in addition to **21** and **22**: **25**, **26**, and **27**. These products most reasonably arise from secondary irradiation of the major product **21**. While the structure of **25** was established by comparison with authentic 2-methylnaphthalene and that of **26** is reasonably established from its NMR spectrum, the structure assigned to **27** must be considered tentative. Of special interest is the failure to detect any product arising from di- π -methane rearrangement of this geminal dimethyl substituted system. Thus, in contrast to other studies which have shown central di-substitution to be beneficial to di- π -methane reactivity,⁶ in the 3,4-benzotropolilidene systems it is not sufficiently important to overcome photochemical group migration.

7,7-Dicarbomethoxy-3,4-benzotropolilidene, **9**

Our initial interest in this system derived from possible chemical transformation of one of the ester functions into another group, thus allowing photochemical migratory aptitude studies. However, the need for a rigorous structure proof for the Me migrated product from **17** prompted us to establish the product(s) from, and the efficiency for, the irradiation of **9**.

Irradiation of **9** at 350 nm led to a rapid reaction which produced one product which was homogeneous on a variety of VPC columns. Purification of this material by preparative VPC or distillation yielded a clear oil which gave combustion analysis and spectroscopic properties in agreement with **24** (Experimental).^{*} The formation of **24** from **9** by a carbomethoxy migration has ample precedent in the 1,7-carbomethoxy migration in 7-carbomethoxy-3,4-benzotropolilidene.¹⁴

^{*}Despite various methods of purification, the NMR spectrum of **24** showed a sharp ring singlet at δ 6.65 τ , and an apparent AB pattern of two doublets at 6.66 and 7.21 τ with $J = 10\text{ Hz}$ in a ratio of 3:1:1. This constituted *ca* 5% of the reaction mixture and may be due to a small amount of the 7-*endo* carbomethoxy group.

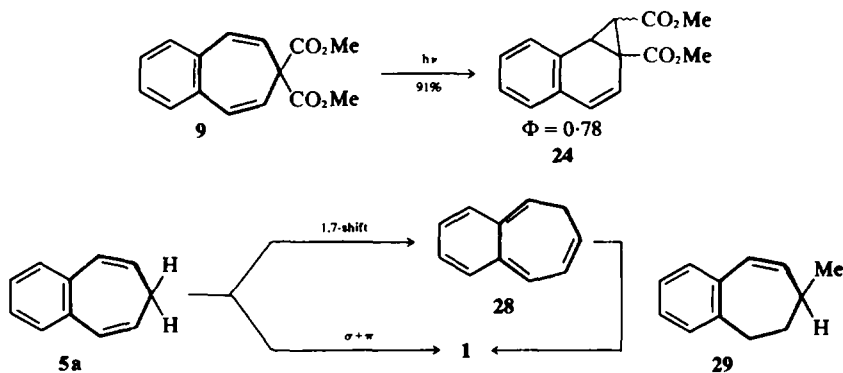
[†]Unpublished results of K. Burdett at 2537 Å have shown that at *ca* 20% conversion of **5b** to **18**, less than 0.5% of the analogous product from **29** was formed.

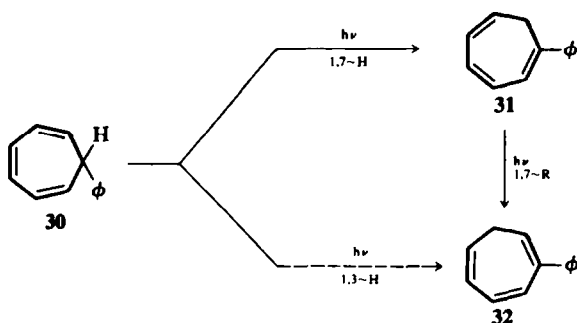
DISCUSSION

The major process observed in the photochemistry of 3,4-benzotropolilidenes is benzonorcaradiene formation. As noted previously,^{3b} these products may arise via either a 1,7-sigmatropic shift followed by valence isomerization or a $\sigma + \pi$ cycloaddition (either a $\pi_{2s} + \sigma_{2s}$ or a $\pi_{2s} + \sigma_{2s}$ route is photochemically allowed). Some evidence favoring the 1,7-shift route derives from the photostability of **29** under conditions where **5b** is reactive.[†] Thus, **29** which has available the $\sigma + \pi$ route, but not the 1,7-shift process, does not undergo hydrogen shift with great facility. Unfortunately, the comparison is not exact since the σ -bonds in **5b** and **29** may possess different bond energies. While no rigorous basis for choosing between the two processes is presently available, subsequent discussion will treat the process as a 1,7-photochemical shift.

A minor process for 3,4-benzotropolilidenes noted here for **5a** and **17** is formal photochemical 1,3-H and Me migrations. The importance of 1,3-shifts in cycloheptatriene derivatives has been examined both theoretically⁷⁻⁹ and experimentally.⁹⁻¹¹ Anastassiou⁸ has proposed that all suprafacial hydrogen shifts, 1,3-, 1,5-, and 1,7-, are allowed in excited cycloheptatriene, while more recently it has been proposed that only 1,7-shifts can occur.⁹ Regardless of the theoretical prediction, only 1,7-migrations appear to have been observed photochemically. The case of 7-phenylcycloheptatriene irradiation to 2-phenylcycloheptatriene,¹⁰ which was the strongest case for a possible 1,3-H migration, has been subsequently shown to occur *via* two consecutive 1,7-hydrogen migrations.⁹

The formation of 1,2-benzotropolilidenes from 3,4-benzotropolilidene irradiation can be accounted for by two mechanisms. One of these is direct 1,3-migration (path a) while the second process would involve a photochemical 1,7-shift in the intermediate **33** (path b). While we cannot rigorously exclude path b, we favor path a as this most readily accounts for the production of **22** from **17**. Had path b been operative then the higher photochemical migratory aptitude of H *vs* Me should have afforded 5,6-dimethyl-1,2-benzotropolilidene in the





second step instead of 22. Assuming path a is correct, these are to our knowledge the first examples of 1,3-shifts in these systems. Perhaps the closer competition between 1,3- and 1,7-shifts in the benzo system relative to cycloheptatriene results from the 1,3-photochemical shift not disrupting the aromatic system.

A third point concerns the high quantum efficiencies ($\Phi = 0.38 - 0.92$) for group migrations and the near complete absence of a competing di- π -methane process. Even in the case of 17, in which geminal Me substitution should have made the di- π -methane reaction more favorable, no di- π -methane product could be detected. Seemingly group migrations serve as a major pathway for excited state decay even in the case of alkyl shifts. The high quantum efficiencies for migration of hydrogen, carbomethoxy, and methyl moieties indicate that either the rates of migration for these groups are similar, or the rates for migration, while varying with the migrating group, are much faster than the rates of excited state decay to ground state.

A final point concerns the relative migratory aptitude of H *vs* Me of >1000 . While the higher preference for H *vs* Me migration seems reasonable, how meaningful this is in general may be open to question. The main problem concerns the conformation of the excited benzotropilidene and the stereoelectronic requirement for group migration. The essence of this problem has been discussed for thermal 1,7-shifts^{11,12} and will not be repeated here.

However, suffice it to say that the high preference for H migration in 5a noted here could arise predominately from a better overlap of the axial-like position in the benzotropilidene with the remainder of the π -system. Thus, the migratory aptitudes observed here should not be extrapolated to other photochemical systems.

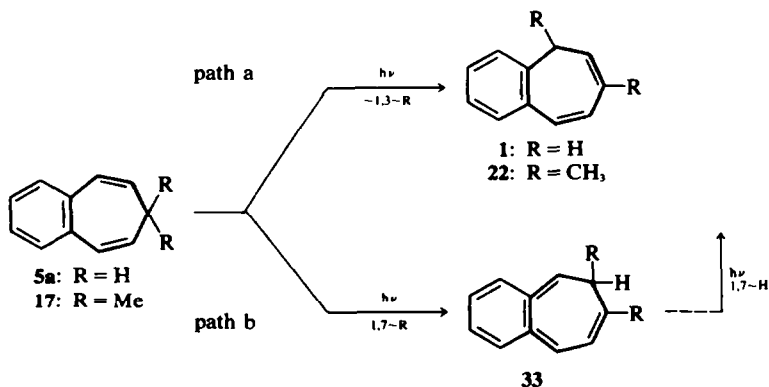
CONCLUSION

The photochemistry of 3,4-benzotropilidenes gives rise to one major process, a formal 1,7-group migration, and for certain systems a minor (*ca* 10%) formal 1,3-group migration. The quantum yields for the 1,7-shift are uniformly high ($\Phi = 0.37 - 0.92$) and thus serve as the major process for the excited singlet state of 3,4-benzotropilidenes.

EXPERIMENTAL

IR spectra were recorded with a Perkin-Elmer Infrared Model 137 spectrometer. UV spectra were determined with a Cary 14 recording spectrometer. The mass spectra were measured with an AEI MS-9 mass spectrometer. NMR spectra were measured at 60 MHz using TMS as internal standard. All elemental analyses were determined by Scandinavian Microanalytical Laboratory, Herlev, Denmark. All photolyses were carried out in an atmosphere of purified N₂.

7,7-Dicarbomethoxy-3,4-benzobicyclo[4.1.0]heptene, 7. A mixture of 25 g (0.19 m) 1,4-dihydronaphthalene and 8 g copper bronze was stirred at 140° while a mixture of 21 g



(0.13 mol) diazomalonate^{13*} and 25 g (0.19 mol) 1,4-dihydronaphthalene was added dropwise over 8 hr. After addition was complete, the excess dihydronaphthalene was removed *in vacuo* and the dark residue titrated with ether. The resulting dark solid was recrystallized from hexane-methylene chloride to afford 1.05 g of 7, m.p. 106–108°. The mother liquors were combined and chromatographed on Silica Gel (5 × 80 cm column slurry-packed with 8% ether-hexane). Elution proceeded as follows: 11, 8% ether-hexane, recovered dihydronaphthalene; 41, 8% ether-hexane, unidentified oil, ca 0.5 g; 41, 10% ether-hexane, unidentified oil, ca 1 g; 31, 10% ether-hexane, light yellow oily solid, 4.6 g. Recrystallization of the latter fraction gave 3.8 g pure diester for a combined yield of 4.85 g (14%). In one run a yield of 27% was realized; however, this could not be repeated. The analytical sample recrystallized from ether-hexane showed: m.p. 108–110°; IR (KBr), 3.30(w), 3.38(w), 3.52(w), 5.80(s), 7.04(s), 7.58(s), 7.98(s), 8.30(s), 9.08(s), 9.90(m), 10.28(m), 13.00(m), and 13.34(m) μ ; NMR (CCL₄), 3.10(m, 4H), 6.37 (s, 3H), 6.82 (m, 4H), 7.08 (s, 3H), and 7.89 (m, 2H) τ . (Found: C, 68.99; H, 6.16. Calcd. for C₁₅H₁₆O₂: C, 69.22; H, 6.20%).

7, 7-Dicarbomethoxy-2, 5-dibromo-3, 4-benzobicyclo [4.1.0]heptene, 8. A soln of 3.1 g (12 mmol) of 7 in 125 ml CCL₄ was refluxed with 4.29 g (0.024 moles) N-bromosuccinimide and a trace of dibenzoyl peroxide for 30 min. The succinimide was filtered immediately from the hot soln and the solvent removed under vacuum to give a faintly yellow solid. The solid was washed with a minimum amount of ether to yield 4.23 g (84%) of white, powdery dibromide 8: m.p. 133–136°; IR (KBr), 3.38(w), 5.74(s), 5.78(s), 7.01(m), 7.58(m), 8.00(s), 8.34 (w), 8.72(m), 9.12(w), 10.02(w), 10.98(w), 13.11(w), 13.38(w) μ ; NMR (CDCl₃), 2.77(s, 4H), 4.27(broad s, 2H), 6.27(s, 3H), 7.00(s, 3H), and 7.03(broad s, 2H) τ .

7, 7-Dicarbomethoxy-3, 4-benzotropilidene, 9. A soln of 6.00 g (0.014 mol) of 8, in 100 ml THF and 0.1 ml glacial AcOH was refluxed with 0.939 g (0.014 mol) powdered Zn for 2 hr at which time the mixture had turned from grey to white. The soln was filtered, the solvent removed from the filtrate under vacuum, and the oily residue dissolved in 60 ml ether. The ether soln was washed with sat NH₄Cl aq (2 × 60 ml) and dried over CaSO₄. Removal of solvent under vacuum gave 3.7 g crude tropilidene diester which was recrystallized from ether-hexane to yield 3.56 g (96%) of 9: m.p. 98–99°; IR (KBr), 3.35(w), 5.68(m), 5.75(s), 5.86(w), 6.96(m), 7.93(s), 8.11(s), 8.33(s), 9.31(s), 10.40(w), 10.51(w), 11.94(m), 12.45(s), 12.65(m), 13.19(m) μ ; NMR (CCL₄), 2.80(s, 4H), 3.32(d, 2H, J = 11 cs), 4.00(d, 2H, J = 11 cs), 6.40(s, 6H) τ . (Found: C, 69.49; H, 5.49. Calcd. for C₁₅H₁₆O₂: C, 69.74; H, 5.47%).

Irradiation of 7, 7-dicarbomethoxy-3, 4-benzotropilidene, 9. A soln of 1.00 g (4.09 mmol) of 9 in 200 ml cyclohexane and 50 ml EtOAc was degassed and irradiated at RT under N₂ with sixteen RPR-3500 Å lamps. The reaction was followed by VPC (9 × 1/8", 10% PDEAS on 60/80 Chrm W at 170°). After 2 hr the VPC indicated complete conversion of starting material to one symmetrical product peak. After removal of solvent, molecular distillation yielded 0.91 g (91%) of 24 as a

colorless liquid: IR (KBr), 3.26(w), 3.34(m), 5.76(s), 6.98(s), 7.22(m), 7.50(s), 7.75(s), 8.08(s), 8.39(s), 8.58(s), 8.83(s), 12.74(s), 13.17(m), 13.36(m), and 13.88(m) μ ; NMR (CCL₄) 2.5–3.0(m, 4H), 3.63(m, 2H), 6.33(s, 3H), 6.36(s, 3H), a one proton signal is concealed under the OMe signals at ~6.36, and 8.78(d, 1H, J = 6Hz) τ . (Found: C, 69.86; H, 5.50. Calcd. for C₁₅H₁₆O₂: C, 69.74; H, 5.47%).

2, 3-Benzocyclohepta-2, 4-dienone, 11. A mixture of 41.6 g (0.26 m) of 10, 54 g (0.30 m) N-bromosuccinimide and 0.1 g azobisisobutyronitrile in 750 ml CCL₄ was refluxed for 0.5 hr with stirring. The cooled mixture was filtered and the filtrate concentrated *in vacuo* to afford 75.0 g yellow oil. The mixture of crude bromo compound and 10.0 g (0.074 m) calcium hydrogen phosphate in 650 ml N,N-dimethylformamide was heated at 80° under N₂ for 14 hr. The cooled mixture was then poured into 11 water and the organic material extracted with ether (4 × 125 ml). The combined ether phases were washed with water (4 × 100 ml), sat brine soln (100 ml), and dried over CaSO₄. After removal of solvent *in vacuo* and a rapid vacuum distillation there was obtained 34.6 g of 11 contaminated with 10. Spinning band distillation using 10 g of di-n-butyl phthalate as chaser yielded the following results: (fraction, bp/pressure mmol, wt (g), % 11a) 1, 79–81°/0.06, 1.9, 20%; 2, 81–89°/0.07, 1.6, 60%; 3, 87–89°/0.07, 2.1, 88%; 4, 87–89°/2.0, 95%; 5, 77–80°/0.07–0.06, 18.9 g, >99%. If the crude debromination product was carried through the reaction sequence, the 3,4-benzotropilidene produced was contaminated with 3,4-benzocycloheptadiene.

3, 4-Benzotropilidene, 5a. In a typical preparation 4.33 g (27.4 mmol) of 11a and 5.9 g (32.8 mmol) tosylhydrazide in 100 ml abs MeOH containing 1 ml conc HCl was refluxed for 2 hr. Removal of the solvent *in vacuo* afforded a yellow oil which crystallized upon trituration with ether to yield 8.12 g (90%) of the tosyl hydrazide, m.p. 154–155.7°. To a magnetically stirred soln of 3.13 g (9.6 mmol) tosyl hydrazide in 100 ml abs ether at 0°, 9.2 ml 2.2 M MeLi was added dropwise during 0.5 hr. The reaction was then allowed to warm to RT during a 1 hr period and the deep red mixture quenched with 25 ml water. The organic phase was separated, washed with water (30 ml), sat brine soln (30 ml), and dried over CaSO₄. Removal of the ether yielded a dark oil which was passed through neutral alumina column (2% ether-hexane). After distillation of the solvent, the residual clear oil was molecularly distilled to afford 0.75 g (54%) of 5a as a colorless oil homogeneous by VPC and TLC.⁵

6-Methyl-2,3-benzocyclohepta-2,4-dienone, 11b. A mixture of 7.10 g (0.041 m) 6-methyl-2,3-benzocyclohepta-2-enone, 7.84 g (0.044 m) N-bromosuccinimide, and 0.1 g azobisisobutyronitrile in 130 ml CCL₄ was refluxed for 1 hr with stirring. The cooled mixture was filtered, and solvent removed *in vacuo* to yield 10.0 g yellow oil. The crude bromo compound and 60 g (0.044 m) calcium hydrogen phosphate in 200 ml N,N-dimethylformamide was heated at 80° under N₂ for 10 hr. The cooled mixture was poured into 500 ml water which was extracted with 3 × 100 ml portions ether. Then the combined ether phases were washed with water (50 ml), sat brine soln (50 ml), decolorized with 1 g activated charcoal, and dried over Na₂SO₄. Solvent removal *in vacuo* followed by distillation yielded 5.86 g (84%) crude 6-methyl-2,3-benzocyclohepta-2,4-dienone; b.p. 90° at 0.6 mm to 91° at 0.3 mm. Spinning band distillation of 11.9 g crude 11b at 0.05 mm using 10 g di-n-butyl phthalate as chaser yielded the following re-

*We obtained the substantially higher yields of the diazo compound (93 vs 43%) by using longer reaction times (26 hr) for the reaction of dimethyl malonate and tosyl axide in methylene chloride.

sults: fraction number, b.p., weight (g), % 6-methyl-2,3-benzocyclohepta-2,4-dienone; 1, 74–75°, 0.9, 40%; 2, 75–75.5°, 1.8, 58%; 3, 75.5–77°, 2.3, 87%; 4, 77–78°, 5.7, 99%.

7-Methyl-3, 4-benzotropilidene, 5b. In a manner analogous to that employed for **5a**, 4.53 g (26.4 mmol of **11b**, 5.1 g tosyl hydrazine, and 1 ml conc HCl in 100 ml EtOH yielded 7.88 g (88%) of the respective tosyl hydrazone, m.p., 138.5–140.5°. Reaction of 3 g (8.8 mm) of the tosyl hydrazone with 8.5 ml 2.2 M MeLi and workup in the manner described for **5a** yielded 0.63 g (47%) of **5b** as a colorless oil homogeneous by VPC and TLC.

3, 3-Dimethyl-5-phenylpentanoic acid, 13. Standard Wolf–Kishner reduction of 45 g (0.225 m) **3**, 3-dimethyl-4-benzoylbutanoic acid with 60 g (1.83 m) hydrazine, 31.5 g KOH, and 675 ml triethylene glycol afforded after distillation, b.p. 129–131°/2 mm, 34 g (73%) of **13** which solidified on cooling: m.p. 50–52°; IR (KBr) 3.35 (broad, s), 5.9(s), 7.65(s), 10.65(broad, m), 13.3(s), and 14.4(s) μ ; NMR (CCl₄) 2.85(s, 5H), 7.4(m, 2H), 7.65(m, 2H), 8.3(m, 2H), and 8.85(s, 6H) τ . (Found: C, 75.76; H, 8.80. Calcd. for C₁₅H₁₆O₂: C, 75.72%; H, 8.74%).

6,6-Dimethyl-2,3-benzocycloheptenone, 14. To a stirred soln of 64 g (0.34 m) of **13**, in 600 ml chlorobenzene was added 64 g (0.34 m) PCl₅, portionwise being careful to keep the system dry. After heating for 0.5 hr on a steam bath the POCl₃ produced was removed by vacuum distillation. Then to the cooled soln was added 40 g (0.34 m) AlCl₃, over 0.5 hr followed by heating the mixture at ca 40° for 0.5 hr and ca 60° for 0.5 hr. The mixture was quenched by the addition of conc HCl and the organic phase was consecutively washed with 5% HCl, water, 5% NaOHaq, and dried over CaSO₄. Fractionation of the slightly yellow oil resulting from *in vacuo* removal of solvent yielded 45 g (78%) of a colorless liquid b.p. 86–89°/0.2 mm, which solidified upon standing. Low temp recrystallization of the solidified material from hexane gave colorless plates: m.p. 54–54.5°; IR (KBr) 3.4(m), 6.0(s), 6.9(m), 7.30(s), 8.12(s), 12.65(s), 13.25(s), and 13.65(s) μ ; NMR (CCl₄) 2.3(m, 1H), 2.78(m, 3H), 7.4(m, 2H), 8.29(m, 2H), 7.9(s, 2H), and 8.9(s, 6H) τ . (Found: C, 82.92; H, 8.61. Calcd. for C₁₅H₁₆O: C, 83.00; H, 8.50%).

6, 6-Dimethyl-2, 3-benzocycloheptenol, 15. To a soln of 44 g (0.23 m) 6,6-dimethyl-2,3-benzocycloheptenone in MeOH was cautiously added 22.5 g (0.59 m) NaBH₄. The soln was stirred for 0.5 hr after which time 200 ml water was added, resulting in the separation of white crystals. The soln was refluxed for 0.5 hr and then cooled. The resulting solid which formed was collected, washed with water, and recrystallized from MeOH-water to give a quantitative yield of long colorless needles: m.p. 97.5–98.5°; IR (KBr) 3.0(s), 3.45(s), 7.3–7.4(s, doublet), 9.4(s), 9.6(s), 10.2(s), 13.25(s), 13.4(s), and 13.7(w) μ ; NMR (CCl₄) 2.65(m, 1H), 3.0(m, 3H), 5.2(m, 1H), 7.4(m, 2H), 7.7(s, 1H), 8.5(m, 4H), 8.8(s, 3H), and 9.1(s, 3H) τ . (Found: C, 82.01; H, 9.57. Calcd. for C₁₅H₁₆O: C, 82.10; H, 9.50%).

5, 5-Dimethyl-1, 2-benzocyclohepta-1, 3-diene, 16. To a soln of 44 g (0.23 m) 6,6-dimethyl-2,3-benzocycloheptenol in 600 ml dry benzene was added 4.5 g *p*-toluenesulfonic acid. The soln was refluxed until the water produced was completely azeotroped from the mixture and then the benzene was distilled off. The remaining oil was taken up

in ether, washed with 5% NaOHaq (200 ml), sat NaCl aq (200 ml), and dried over CaSO₄. After the solvent was removed *in vacuo*, fractionation of the remaining oil gave 34 g (85%) of a clear liquid b.p. 137–139°/17.5 mm: IR (neat) 3.45(s), 6.75(s), 6.9(broad, m), 11.75(s), 12.65(s), and 13.5(s) μ ; NMR (CCl₄) 3.0(s, 4H), 3.88(d, 1H, J = 12 cs), 4.55(d, 1H, J = 12 cs), 7.25(m, 2H), 8.25(m, 2H), and 8.89(s, 6H) τ . (Found: C, 90.60; H, 9.18. Calcd. for C₁₅H₁₆: C, 90.70; H, 9.0%).

7, 7-Dimethyl-3, 4-benzotropilidene, 17. To a soln of 10 g (0.058 m) **5**, 5-dimethyl-1, 2-benzocyclohepta-1, 3-diene in 135 ml CCl₄ was added 10 g (0.058 m) *N*-bromosuccinimide. The soln was heated to reflux at which time 0.1 g dibenzoyl peroxide was added. After 4 hr reaction the succinimide by-product was filtered off and the filtrate concentrated *in vacuo*. Attempted vacuum distillation of the bromo compound resulted in HBr evolution and a yield of 5.4 g (54%) of a clear liquid was obtained. Inspection of the distillate by VPC (15' \times 1/4", 20% Apiezon J on 60/80 Chromosorb W at 200°) showed the presence of two components in a ratio of 8:1. The pure tropilidene was obtained in 30% yield by preparative VPC: IR (neat) 3.45(s), 6.0(s), 6.8, 6.9, 7.0(s, triplet), 7.35, 7.45(m, doublet), 8.5(s), 10.6(s), 11.9(s), 13.0(s, broad), and 14.2(s) μ ; NMR (CCl₄) 2.65(s, 4H), 3.5(d, 2H), 4.4(d, 2H), (AB quartet centered at 3.5 and 4.4, J = 11 cs), and 8.85(s, 6H) τ . (Found: C, 91.51; H, 8.32. Calcd. for C₁₅H₁₄: C, 91.85; H, 8.24%).

Preparative irradiation of 7,7-dimethyl-3,4-benzotropilidene. A soln of 0.212 g (0.125 mmol) of **17** in 225 ml purified cyclohexane was irradiated at 3500 Å for 4 hr under a N₂. Analysis by VPC (15' \times 1/4", 20% Apiezon J on 60/80 Chromosorb W at 200°) showed the presence of 6 peaks in the ratio of 21:10:95:10:10:2. Peaks 1, 2, 3, 4, and 5 were isolated and purified by VPC.

Peak 1 was a colorless liquid, 2,3-benzobicyclo [3.2.0]-4,6-dimethylhepta-2,6-diene, **27**. IR (neat) 3.2(m), 3.35(s, doublet), 6.1(w), 6.8(s), 6.9(s), 9.85(m), 11.4(m), 11.85(m), 12.5(s), and 13.3(s, broad) μ ; NMR (CCl₄) 3.0(s, 4H), 4.05(m, 1H), 6.0(m, 1H), 7.0(m, 2H), 8.3(s, 3H), and 8.8(d, 3H, J = 7 Hz) τ . (Found: C, 91.54; H, 8.35. Calcd. for C₁₅H₁₄: C, 91.85; H, 8.24%).

Peak 2 was a white solid, 2-methylnaphthalene, **25**, identified by IR and NMR comparison with a known sample.

Peak 3 was a colorless liquid, 6,7-dimethyl-2,3-benzonorcaradiene, **21**. This material was a 2:1 mixture of *endo* and *exo* isomers and showed spectroscopic properties identical with synthesized compound.

Peak 4 was a colorless liquid assigned as **26**, on the basis of its NMR spectrum: NMR (CCl₄) 2.38–2.98(m, 4H), 3.92(center of AB quartet, J = 9 Hz), 8.42(s, 3H), 8.59(s, 3H), 8.94(d, J = 4 Hz), and 9.92(d, J = 4 Hz) τ .

Peak 5 was a mixture of **22**, and its 1, 5-shift isomer **23**. Inspection of the crude irradiation mixture prior to photolysis indicated the latter compound was not initially present and thus arose via thermal 1,5-hydrogen shift on the VPC column.

6,7-Dimethyl-2,3-benzonorcaradiene, 21.* To a refluxing soln of 0.8 g of LAH in 30 ml anhyd ether was added 0.7 g (2.0 mmol) of **24** in 30 ml anhydrous ether. After 5 hr at reflux the excess hydride was decomposed by cautious addition of 2.4 ml water, and then 30 ml 5% HCl added to the 0° soln to dissolve the aluminum salts. The organic phase was then separated and dried over CaSO₄. Removal of the solvent afforded 0.5 g of crude alcohol which was utilized without further purification.

*The low yield of **21** in this sequence undoubtedly arises from the extreme thermal lability of the ditosylate.

To an ice-cooled soln of 0.5 g (2.5 mmol) crude oil in 10 ml dry pyridine was added 1 ml methane sulfonyl chloride over 0.2 hr. The soln was stirred for 3 hr at 0° at which time the soln was poured into 20 g ice: 20 ml water and extracted with 50 ml ether. The organic layer was washed with 30 ml cold 5% HCl and dried over CaSO₄. The ethereal layer was added to a soln of 0.5 g (13 mmol) LAH in 20 ml anhyd ether at 0° over 0.1 hr. The soln was stirred for 3 hr at 0° at which time 2.0 ml water was cautiously added. The soln was filtered and the white ppt washed thoroughly with ether. VPC analysis (12' × 1/8", 20% Apiezon J on 60/80 Chromosorb W at 180°) showed the presence of two peaks in the ratio of 40:60. Peak 1 was identified as **21** by VPC retention time and IR spectrum.

Preparative VPC afforded 13.5 mg (3.4%) of **21**: IR (neat) 3.35(m), 6.7(m), 6.85(m), 12.55(s), 12.65(w), 13.0(w), 13.2(s), and 13.8(m) μ ; (Found: C, 91.74; H, 8.55. Calcd. for C₁₅H₁₄: C, 91.85; H, 8.24%).

Preparation of 5,7-dimethyl- and 3,5-dimethyl-1,2-benzotropolidene, 22 and 23. To an ethereal soln of 1 g (5.8 mm) 6-methyl-2,3-benzocyclohepta-2,4-dienone was added two equivs of MeLi in ether (5 ml, 2.2 M). The mixture was stirred for 1 hr, quenched with water and the organic phase separated. VPC analysis (11' × 1/8", 5% Carbowax on 60/80 Chrm G at 171°) indicated 50% alcohol and 50% unreacted ketone. This process was repeated 4 times after which a 93% conversion to alcohol had been effected. This crude alcohol mixture was then dehydrated

by stirring it at RT in 50 ml of benzene containing 0.8 g of *p*-toluenesulfonic acid for 1 hr. The mixture was then quenched with water and worked up in the usual fashion to afford a yellow oil which was chromatographed on alumina (2 × 25 cm column, hexane elution). Elution proceeded as follows: 50 ml, nil; 250 ml, 453 mg (46%) of a 60:40 mixture of 2,7-dimethyl-3,4-benzotropolidene and **23**. When this latter compound was collected by preparative VPC (12' × 1/4", 4% Apiezon H on 60/80 Chrm G at 160°) isomerization to a *ca* 1:6 mixture of **22** and **23** resulted. Except for relative amounts of the two compounds, the NMR of this material was identical with peak 5 obtained from the preparative VPC of the **17** irradiation. Analysis of the mixture yielded the following results: Found: C, 91.38; H, 8.44. Calcd. for C₁₅H₁₄: C, 91.76; H, 8.24%.

Quantum yield measurements. The quantum yields were determined with 330 nm light from a Bausch and Lomb high intensity monochromator (front and back slits at 5 mm) and a 200-watt mercury super-pressure lamp in the double cell apparatus previously described.^{13*}

The quantum yield measurements themselves consisted of three irradiations. The first was performed with potassium ferrioxalate in both front and back cells followed by measurement of the total light output. The second irradiation was done with the sample in the first compartment and fresh actinometer in the back cell. Analysis of the back cell gave the light transmitted by the photolysis soln. The third irradiation was identical to the first and was averaged with the first to give the light output for the quantum yield. In a typical determination 200–300 mg of the tropilidene was dissolved in 65 ml of purified cyclohexane, degassed with purified N₂, sealed and irradiated.

3, 4-Benzotropolidene, 5a. The solvent from the sample irradiation was removed *in vacuo* and the residue diluted with a known volume of a stock soln of fluorene in CDCl₃. The analysis for product involved integrating the methylene group of fluorene *vs* the *endo* cyclopropyl proton of benzonorcaradiene. The slight difference in sensitivity of the integrator in the two different regions of the spectrum was corrected using a known mixture of

*Unless otherwise noted, VPC analyses were performed on a Varian Model 1200 flame ionization gas chromatograph and relative areas measured with a Hewlett-Packard 3370 Å Integrator. Immediately prior to analysis the VPC was calibrated with known mixtures of the compounds. The peak areas in the quantum yield measurements were then corrected for VPC sensitivity employing the relationship:

$$\frac{\text{wt. standard}}{\text{wt. compound}} = F \cdot \frac{\text{area standard}}{\text{area compound}}$$

Table 1. Quantum yields for 3,4-benzotropolidenes

Compound	Light absorbed (mE)	Conc. M × 10 ⁻³	% Conv.	*Disappearance	*Appearance
5a ^b	0.255	22.1	15	— ^a	0.84
5a	0.255	22.3	12	— ^a	0.67
5a	0.290	22.8	23	— ^a	1.10
5b	0.171	24.2	10	0.92	1.00
5b	0.146	24.2	11	0.94	0.86
17	0.395	22.1	11	0.48	0.32
17	0.316	22.3	15	0.65 ^c	0.39
17	0.280	22.8	16	— ^a	0.33
9	0.119	10.2	13	0.77	0.83
9	0.107	10.2	10	0.76	0.84
9	0.098	10.2	11	0.78	0.82

^a Value not determined.

^b The lower precision for these numbers is due to the less accurate method of analysis and difficulty with lamp stability during these runs.

^c Some polymerization occurred during this run.

benzonorcaradiene and fluorine. The results of these measurements are recorded in Table 1.

7-Methyl-3,4-benzotropilidene, 5b. In a typical determination, a stock soln of 0.3019 g of **5b** and 0.02956 g dodecane in 80 ml purified cyclohexane was prepared and a 65 ml portion irradiated. The irradiated soln was analyzed for disappearance of starting material and appearance of product by VPC (13' × 1/8", 5% SE-30 on 60/80 Chrm G at 122°). After one of the quantum yield determinations, the material was irradiated to complete conversion and the product collected by preparative VPC. The colorless oil showed: IR (neat) 6.75(m), 6.85(m), 12.42(s), 12.85(s), 13.09(s), 13.55(s), and 14.0(m) μ ; NMR (see text). (Found: C, 92.33; H, 7.80. Calcd. for C₁₂H₁₄: C, 92.23; H, 7.67%).

7,7-Dimethyl-3,4-benzotropilidene, 17. In a typical measurement, a stock soln of 0.31005 g of **17** and 0.03224 g dodecane in 80 ml purified cyclohexane was formed and a 65 ml portion irradiated. The analysis for disappearance of starting material and product was made by using a calibration solution of **17**, **21**, and dodecane closely approximating the irradiation mixture. In the case of this analysis the VPC separation of product from starting material was only 80–90% complete under optimized conditions (25' × 1/8", 15% Apiezon M on 60/80 Chrm W at 180°). The results of these determinations are presented in Table 1.

7,7-Dicarbomethoxy-3,4-benzotropilidene, 9. The irradiation of **9** was carried out in cyclohexane: (55:15) using di-n-butyl phthalate as internal standard and the irradiation solution analyzed as in the preparative irradiation.

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