References and Notes

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Control by Meta Substituents of Benzo–Vinyl Bonding Options during Triplet Sensitized Photorearrangement of Benzonorbornadienes and *anti*-7,8-Benzotricyclo[4.2.2.$0^{2,5}$]deca-3,7,9-trienes

Leo A. Paquette,* Denise M. Cottrell, and Robert A. Snow

Contribution from the Evans Chemical Laboratories, The Ohio State University, Columbus, Ohio 43210.

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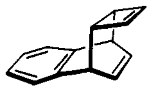
Abstract: A variety of meta-substituted benzonorbornadienes and *anti*-7,8-benzotricyclo[4.2.2.$0^{2,5}$]deca-3,7,9-trienes were synthesized. Triplet sensitized photoisomerization of the benzonorbornadienes afforded one or both possible tetracyclo[5.4.0.$0^{2,4}$.$0^{3,6}$]undeca-1(7),8-10-trienes. For R = NO_2, $COOC_2H_5$, CN, and $COCH_3$, benzo-vinyl bridging to the para position of the aryl ring was followed exclusively. When the substituent groups were OCH_3, F, and NH_2, the di-π-methane rearrangement proceeded chiefly by meta aryl bonding (78, 91, and 70% respectively). This crossover in bonding preferences was also seen in the benzotricyclodecatriene series. In these latter systems, competitive $[_{\pi}2 + _{\pi}2]$ intramolecular cycloaddition is also possible. When R = CN, only the di-π-methane rearrangement pathway is followed. In contrast, the methoxy derivative afforded 55% of the related benzobasketene and the *o,o′*-dimethoxy example gave rise to approximately 10% of bishomocubyl derivative. Accordingly, acceptor groups favor aryl-vinyl bonding while donor groups promote variable levels of $[_{\pi}2 + _{\pi}2]$ bonding. It is concluded that this reactivity pattern is dictated by the nature and relative energy level of the higher singly occupied molecular orbital. The di-π-methane regioselectivity is shown not to be in harmony with the reactivity patterns expected from radical or electrophilic attack on the aromatic ring. Rather, the observed bridging regioselectivity is seen to conform to the substituent perturbations upon the electronic distributions of the triplet excited states, in full agreement with theoretical assessments of the question.

That benzenoid excited states differ from parent ground states both in electronic structure and reactivity is now a well-recognized fact.[1] During $\pi \rightarrow \pi^*$ excitation, an electron is promoted from one molecular orbital to a higher energy MO of the same π system. The resultant change in electron distribution is intimately related not only to the nature of the ring substituent(s), but also to the multiplicity of that excited state which is utilized. Although molecular orbital treatments of $S_{1\pi\pi^*}$ excited states abound,[2] quantum mechanical descriptions of $T_{1\pi\pi^*}$ electronic distributions, particularly as these are affected by electron-donating and -withdrawing groups, are almost entirely lacking.[3] Since the number of aromatic photochemical rearrangements which proceed via triplet states continues to grow, knowledge of substituent influences on the various bonding options gains considerable importance. Expectations that the elucidation of reactivity patterns would serve a predictive role in future experimental undertakings and act as an important link with theoretical calculations provided the impetus for the present study.

The striking features of the triplet-sensitized di-π-methane photoisomerizations of meta-substituted benzonorbornadiene (**1**) and *anti*-7,8-benzotricyclo[4.2.2.$0^{2,5}$]deca-3,7,9-triene (**2**)


1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systems comprise the subject of this paper,[4] while the remarkably different control upon regioselectivity exhibited by their ortho counterparts is described in the accompanying contribution.[5] As noted above, little basis currently exists for predicting which course a $\pi \rightarrow \pi^*$ rearrangement will take when electron-withdrawing or -donating substituents are introduced.[6] The selection of ring systems **1** and **2** was predicated on three factors: (1) the established predilection of the parent hydrocarbons for triplet sensitized skeletal photoisomerization;[7,8] (2) the capability of their less symmetrical monosubstituted derivatives to react by more than one photochemical pathway, thus providing the opportunity for suitably delineating electronic effects on excited state reactivity; and (3) the structurally inflexible nature of these molecules which fixes the nonconjugated π systems in close proximity such that insight into intramolecular interactions not available from binary mixed solutions may be gained. Theoretical calculations are also thereby simplified.[9]

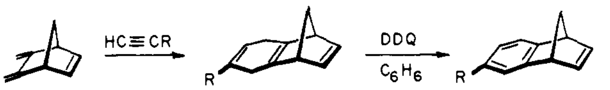
Benzonorbornadiene Syntheses. The 6-methoxy- (**4a**), 6-fluoro- (**4b**), and 6-nitrobenzonorbornadienes (**4c**), obtained in low yield by aprotic diazotization of anthranilic acids **3a–c** in 1,2-dichloroethane solution or decomposition of their diazonium carboxylate hydrochlorides with propylene oxide in the presence of cyclopentadiene, exhibited ^{1}H NMR spectra identical with those previously described for these molecules as prepared by other methods.[10-12] The preferred route to **4c** (86.3%) consisted of nitrating **1** with acetyl nitrate at −5 to −15 °C by a modification of Terabe and Konaka's procedure.[13] Aluminum amalgam reduction of **4c** readily afforded **5**.[14] Application of the Schiemann reaction to **5** provided an alternate route to **4b**.

3a, R=H, R'=OCH$_3$
b, R=H, R'=F
c, R=NO$_2$, R'=H

4a, R = OCH$_3$
b, R = F
c, R = NO$_2$

5

To bypass the need for preparing other benzyne precursors and with a view to achieving higher yields of cycloaddition products, the possibility of an alternative synthetic entry by Diels-Alder addition to 5,6-dimethylenebicyclo[2.2.1]hept-2-ene (**6**)[15] was examined. Heating of **6** with ethyl propiolate in a Carius tube at 80 °C for 3 days followed by direct dehydrogenation of the resulting **7a** with DDQ in benzene furnished **8a** in 86% yield. Using propiolonitrile, the ready synthesis of **8b** was similarly accomplished. Structural assignment to **8b** was confirmed by its independent synthesis involving *m*-iodobenzyne addition to cyclopentadiene and cyanide displacement of the halogen in 6-iodobenzonorbornadiene with sodium dicyanocuprate.[12] Saponification of **8a** provided carboxylic acid **8c**, treatment of which with methyllithium gave the 6-acetyl derivative **8d**.

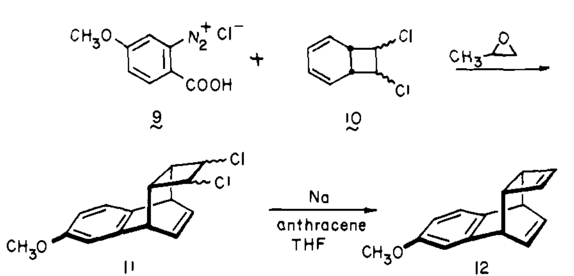


6

7a, R= COOC$_2$H$_5$
b, R= CN

8a, R= COOC$_2$H$_5$
b, R= CN
c, R= COOH
d, R= COCH$_3$

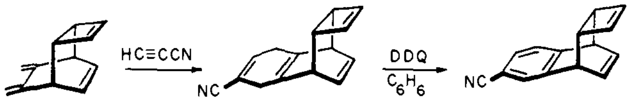
Preparation of the *anti*-7,8-Benzotricyclo[4.2.2.0^{2,5}]deca-3,7,9-trienes. Access to *m*-methoxy derivative **12** was gained by a modification of the procedure employed in the synthesis of parent hydrocarbon **2**.[8b] Decomposition of diazonium carboxylate hydrochloride **9** with propylene oxide in the presence of a mixture of *cis*- and *trans*-7,8-dichlorobicyclo[4.2.0]octa-2,4-diene (**10**) afforded adduct **11** in 65% yield. Direct dechlorination of **11** with sodium anthracenide in tetrahydrofuran led efficiently to **12** whose anti stereochemistry follows from existing precedent[16] and photochemical behavior (vide infra).



9 **10**

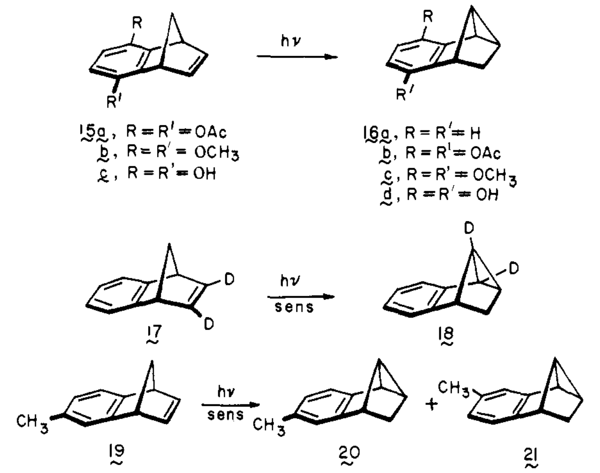
11 **12**

m-Cyano compound **14** was prepared by a modification of the methodology used to synthesize **8b**. Starting with known tetraene **13**,[15] we prepared **14** in 70% overall yield by initial treatment with propiolonitrile in refluxing benzene and subsequent dehydrogenation of the resulting adduct with DDQ. In this case, the method of synthesis uniquely defines the adduct stereochemistry. The exceedingly close correspondence of the pair of olefinic proton signals for **2**,[8b] **12**, and **14** (see Experimental Section) attests further to their common structural features.



13 **14**

Photorearrangement of the Benzonorbornadienes. Edman's study of the sensitized photoisomerization of **1**, **15a**, **17**, and **18** demonstrated their efficient conversion to the products indicated.[7a,b] In later investigations,[7c,d] it was discovered that **15b** and **15c** experience comparable rearrangement under both direct and sensitized conditions. These two systems are accordingly capable of reasonably efficient intersystem crossing (for **15c**, $\Phi_{\mathrm{ISC}} = 0.62$).[7c]



15a, R=R'=OAc
b, R=R'= OCH$_3$
c, R=R'=OH

16a, R=R'=H
b, R=R'=OAc
c, R=R'=OCH$_3$
d, R=R'=OH

17 **18**

19 **20** **21**

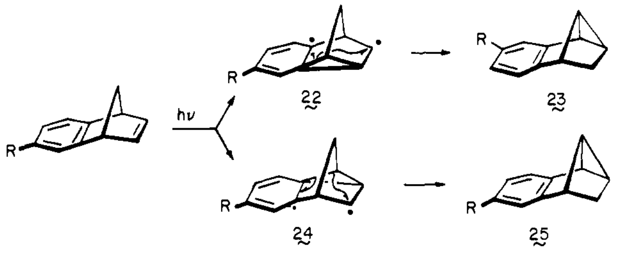
As regards the 6-substituted benzonorbornadienes, sensitized irradiation of **4a**, **4b**, **5**, and **8b** in dilute benzene solution at 3500 Å through Pyrex resulted in ready photoisomerization to tetracyclo[5.4.0.0^{2,4}.0^{3,6}]undeca-1(7),8,10-triene derivatives. Sensitizers ranging in triplet energy from 73.6 (acetophenone, see Table I) to 65.5 kcal/mol (thioxanthone) were utilized with equivalent success. Direct irradiation of these compounds at 2537 Å (cyclohexane solutions) or 3500 Å (benzene solutions) proved generally ineffective, although in certain instances there were observed low levels of photoisomerization at the shorter wavelength (**4a**, **4b**) and polymer formation (**4a**, **5**, **8b**). Not unexpectedly, nitro derivative **4c** and ketone **8d** were isomerized with nearly equal efficiency

Table I. Product Distributions from Sensitized (Acetophenone) Irradiations of 6-Substituted Benzonorbornadienes[a]

		Products (%)	
Compd	R		
4a	$-OCH_3$	78	22
4b	$-F$	91	9
4c	$-NO_2$	0	100
5	$-NH_2$	70	30
8a	$-COOC_2H_5$	0	100
8b	$-CN$	0	100
8d	$-COCH_3$[b]	0	100

[a] At 3500 Å through Pyrex in dilute benzene solution. [b] Direct irradiation under otherwise identical conditions.

Chart I



upon direct irradiation (C_6H_6, 3500 Å). These data suggest that the present reactions are likely proceeding through the respective T_1 states[7] and that the rates of intersystem crossing in all but **4c** and **8d** (**8a** was not studied in this respect) are quite slow.

The pair of mechanistic options available for di-π-methane rearrangement of a 6-substituted benzonorbornadiene are formally depicted in qualitative valence bond terms in Chart I. Initial benzo-vinyl bridging can occur either meta or para to the R group with formation of 1,3-biradicals **22** and/or **24**. Either of these intermediates can now proceed to product by a simple electronic reorganization. We have not concerned ourselves presently with the simultaneity or stepwise nature of these steps. Rather, the perspective has been to assess as accurately as possible the bonding preferences promoted by the various ring substituents. For this purpose, two problems had to be resolved. The first was to find conditions of analysis which would enable the detection and accurate quantitative determination of all photoproducts. The second was to isolate and fully characterize these products in unequivocal fashion. Difficulties in separation have previously proved insurmountable in prior studies of similar compounds[7a,11] and found to be comparably troublesome in the present methoxy, amino, and fluoro cases. As will be discussed, however, these experimental perplexities have been resolved satisfactorily through combined utilization of VPC, ^{1}H NMR, and ^{13}C NMR analysis, in tandem with functional group interconversions where possible and appropriate.

The photoisomerizations of those 6-substituted benzonorbornadienes bearing electron-withdrawing substituents (CN, $COCH_3$, NO_2, $COOC_2H_5$) proceeded with complete regiospecificity to provide a single tetracycloundecatriene in each instance (Table I). In no case were indications of minor product formation found. The gross structures of these photoisomers were easily deduced to be **23** or **25** by their ^{1}H NMR spectra which showed three aromatic hydrogens, two distinctively different benzylic protons, a methylene group having rigidly oriented exo and endo hydrogens, and a final pair of dissimilar cyclopropyl protons. Unambiguous assignment of the para-substituted formulation of **25**-CN to the cyano compound follows from direct spectral comparison with the homologous nitriles **30**-CN and **33a** whose structure elucidation has been achieved by single-crystal x-ray analysis (vide infra). That entirely comparable substitution plans were present in the acetyl and carbethoxy examples was determined by treatment of **25**-CN with methylmagnesium iodide and by sequential saponification and reaction with methyllithium of the photoisomerized ester. From these independent experiments, pure samples of **25**-$COCH_3$ were obtained which proved identical in all respects with the original ketone photoproduct. On the basis of these interconversions, all three tetracycloundecatrienes must share the same absolute positional assignment.

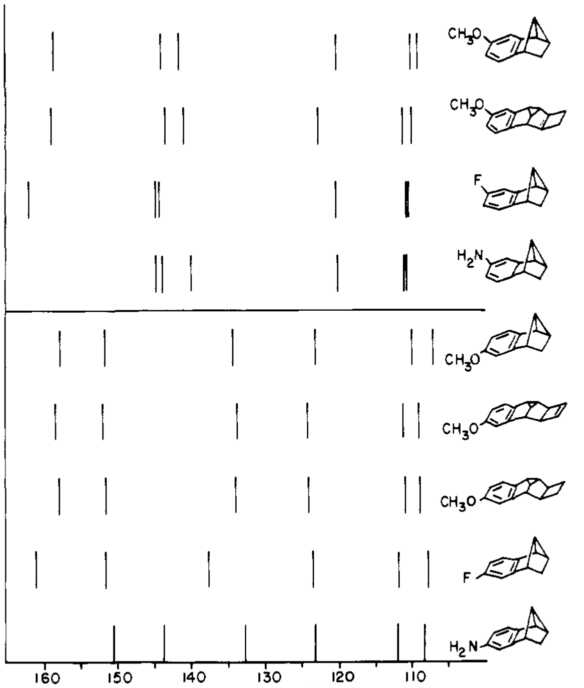


Figure 1. Schematic bar graph of ^{13}C chemical shifts for the aromatic carbons in selected photoproducts.

The structure of the nitro photoproduct was determined in a less direct manner. Its treatment with aluminum amalgam in an ether/ethanol/water mixture yielded the corresponding amine, mp 70.0–70.5 °C, which corresponded to the minor photoproduct formed from **5**. The latter was demonstrated subsequently to be **25**-NH_2 by ^{13}C NMR spectroscopy. Unfortunately, repeated attempts to effect further chemical transformations of this amine (e.g., $NH_2 \rightarrow N_2^+ \rightarrow CN$, OCH_3, I, OH) met with no success owing to the lability of the ring system under the varied conditions employed for diazotization. Notwithstanding, the available data do identify the substitution in the nitro photoisomer as **25**-NO_2.[17]

Turning attention to the electron-donating substituents (OCH_3, NH_2), we noted with the aid of uniquely suitable VPC conditions[18] that **4a** undergoes photorearrangement to two products. The minor component (22%) was unequivocally shown to be **25**-OCH_3 by Baeyer–Villiger oxidation of **25**-$COCH_3$, hydrolysis, and methylation with alkali and dimethyl sulfate. The ^{1}H and ^{13}C NMR spectra of **25**-OCH_3 differ notably from those of **23**-OCH_3 (78%), particularly in their downfield sectors. Thus, whereas **25**-OCH_3 exhibits two widely separated aromatic proton multiplets at 7.22–7.02 (1 H) and 6.55–6.35 ppm (2 H), **23**-OCH_3 exhibits a more closely spaced and more highly structured aromatic pattern (6.92–6.30 ppm, 3 H). The ^{13}C data are fully compiled in Table II and presented schematically (aryl carbons only) in Figure 1.

Table II. ^{13}C NMR Data of Selected Photoproducts ($CDCl_3$, 22.625 MHz, Me_4Si)

Compd	Chemical shifts, ppm: Aromatic carbons	Methoxyl	Aliphatic carbons
23-OCH_3	158.54,[a] 144.22,[a] 141.60,[a] 120.21, 110.15, 109.31	55.44	45.48, 42.70, 29.89,[b] 2900, 19.32
25-OCH_3	157.79,[a] 151.15,[a] 134.64.[a] 123.23, 110.04, 107.18	55.48	44.38, 43.59, 29.70,[b] 28.51, 19.23
23-NH_2	144.68,[a] 144.06,[a] 139.90,[a] 120.34, 111.33, 111.14		44.86, 42.73, 30.08,[b] 29.43, 19.61
25-NH_2	150.90,[a] 143.81,[a] 132.65,[a] 123.28, 111.98, 108.26		43.46, 43.41, 29.73,[b] 28.46, 19.23
29-OCH_3	158.78,[a] 143.41.[a] 142.33,[a] 140.93,[c] 137.10,[c] 122.85, 111.09, 122.85, 111.09,	55.36	62.75, 48.94, 48.13, 36.09, 34.53, 33.34
30-OCH_3	158.62,[a] 152.20,[a] 141.20,[c] 136.90,[c] 133.75,[a] 124.25, 111.14, 124.25, 111.14,	55.41	62.642, 49.15, 48.77, 35.82, 34.04, 32.53
34	158.14,[a] 151.72,[a] 134.13,[a] 124.25, 110.87, 108.99	55.41	54.98, 54.71, 36.58, 39.06, 36.15, 30.91, 24.22, 23.90
23-F	161.95 (d, J = 240.5),[a,d] 144.79 (d, J = 8.5),[a,d] 144.65 (d, J = 2.4),[d] 120.45 (d, J = 8.5),[d] 110.85 (d, J = 23.2),[d] 110.85		46.18, 42.79, 29.62,[b] 29.51, 19.59
25-F	161.25 (d, J = 240.5),[a,d] 151.53 (d, J = 8.6 Hz),[a,d] 137.74 (d, J = 2.4),[d] 123.53 (d, J = 8.5),[d] 111.66 (d, J = 23.2),[d]		45.21, 43.43, 29.62,[b] 28.70, 19.10

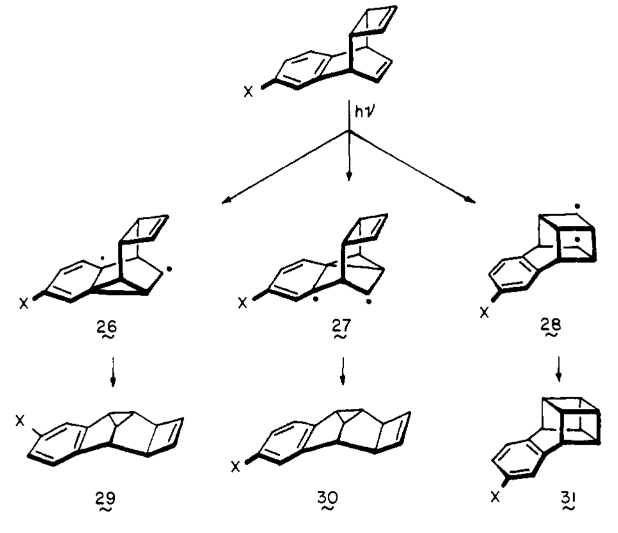
[a] Quaternary aromatic carbons. [b] Methylene carbons. [c] Olefinic carbons. [d] $J_{^{13}C^{19}F}$ values in hertz.

Sensitized irradiation of **5** afforded a product mixture which could not be separated gas chromatographically. Its ^{13}C NMR spectrum, on the other hand, clearly revealed the presence of two components. By relative integration of the pairs of signals, the product composition was deduced to be 70:30, the minor component having already been prepared by reduction of **25**-NO_2. In spite of the electronegativity differences between oxygen (as methoxy) and nitrogen (as amino), useful comparisons of the aryl carbon chemical shifts can be made. As illustrated in Figure 1, the spacings between signals in the major methoxy and amino photoproducts are more similar to each other and to **29**-OCH_3 than to those displayed by the minor isomers, **30**-OCH_3, and **34**. Since the substitution plans in **23**-OCH_3, **25**-NO_2, and **30**-CN (see below) have been defined without ambiguity, we consider the regioselectivity during photorearrangement of **4a** and **5** also to be established.

The excited state bonding preference of *m*-fluoro derivative **4b** was next assessed. Comparable sensitized photorearrangement gave rise to two products (91:9 ratio) which could be efficiently separated on the Bentone-34 column. The individual components were identified as **23**-F and **25**-F, respectively, chiefly on the basis of their ^{13}C NMR spectra. The proton data for the major component (see Experimental Section), while uniquely explicable in terms of a tetracyclo[5.4.0.$0^{2,4}$.$0^{3,6}$]undeca-1(7),8,10-triene formulation, did not permit unequivocal assignment of the particular fluorine substitution plan. For this purpose, recourse was made to ^{13}C data. As seen in Figure 1, the "fingerprint" evidence provided by the aromatic ring carbons defines convincingly the site of halogen substitution. Consequently, meta bonding is vastly preferred by the excited triplet state of **4b**.

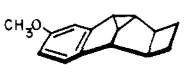
Photorearrangement of the *anti*-7,8-Benzotricyclo[4.2.2.$0^{2,5}$]deca-3,7,9-trienes. As concerns the triplet photochemistry of hydrocarbon **2** (E_T = 69-74 kcal/mol), the experimental data[4,8] indicate a slight preference (1.2:1) for isomerization along the di-π-methane rearrangement channel instead of the closely competitive [$_{\pi}2$ + $_{\pi}2$] cycloaddition pathway (Chart II). Skeletal rearrangement proceeds by initial benzo-vinyl bridging, but when X = H the meta (**26**-H) and para (**27**-H) bonding schemes are equivalent (in actuality, enantiomeric). However, when X is other than hydrogen, the pair of C-C bond forming steps in the di-π-methane manifold lose their identity and varying degrees of bridging regioselectivity can be expected depending upon the level of interaction between X and the π framework.

Chart II



As with the hydrocarbon, ether **12** was unreactive to sensitization by benzophenone (E_T = 69 kcal/mol); however, this was not the case with nitrile **14**, a finding which signaled the lower triplet energy of this diene. Direct irradiation failed to promote these isomerizations in both instances.

Triplet excitation of **14** was found to give rise efficiently to **30**-CN exclusively. Structure elucidation of this crystalline nitrile was achieved by single crystal x-ray analysis.[14,19] The para orientation of its cyclopropyl and cyano groups was thereby conclusively established. The photoisomerization of **12** at 3500 Å using acetophenone as sensitizer was followed by VPC on a 1.75% Bentone-34/5% SF-96/Chromosorb W column. Only by analysis on this column could the formation of three photoproducts be unequivocally demonstrated. Through an involved combination of elution and vapor phase chromatography, these components were separated and identified as **29**-OCH_3 (36%), **30**-OCH_3 (9%), and **31**-OCH_3 (55%). To establish the structures of the di-π-methane products, **29**-OCH_3 was subjected to diimide reduction. Saturation of the cyclobutene double bond in this manner gave oily ether **32** whose properties, most especially the aryl region of its ^1H NMR spectrum, suggested the methoxy group to be meta oriented relative to the cyclopropane ring. Comparable saturation of the double bond in **30**-CN produced nitrile **33a**, treatment of which with methylmagnesium iodide afforded ketone **33b**. Subsequent Baeyer-Villiger oxidation and sa-



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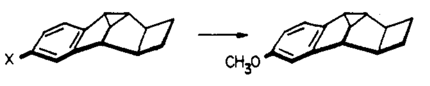
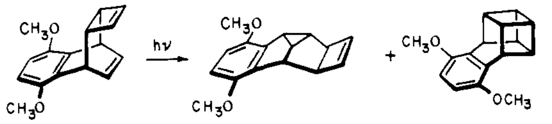


33a, X = CN
b, X = $COCH_3$
c, X = OH

34

ponification led to the phenol **33c**, whose methylation gave **34** and not **32**. As with the simpler benzonorbornadienes, therefore, the effect of methoxyl substitution is to direct C–C bond formation *chiefly* to the meta position. For the cyano example, para bonding is seen to operate *exclusively*.

In the case of anisole derivative **12**, 55% of the product mixture consists of the benzobasketene **31**-OCH_3. No comparable intramolecular cycloaddition was evident with cyano as substituent. For comparison purposes, dimethoxy diene **35**,



35 36 37

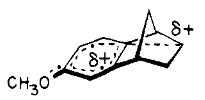
which has the benefit of symmetrical placement of its two functional groups, has also been studied. In this instance, the observed ratio of **36**:**37** (sensitized or direct irradiation; intersystem crossing now operates) was 10:1. Accordingly, electron-withdrawing substituents impede the [$_\pi 2 + {}_\pi 2$] bonding process.

Discussion

Note should first be taken of the fact that Zimmerman's earlier generalization[20] regarding the preference for triplet reactivity in rigid bicyclic systems where rotation about π bonds cannot operate is adhered to throughout the present series, with singlet states being unreactive. In the two benzonorbornadiene cases (**4c** and **8d**) where direct irradiation did result in photoisomerization, precedent in aryl ketone[21] and nitroarene photochemistry[22] decidely implicates intersystem crossing and involvement of the respective triplet states in bond relocation. Filipescu has previously established the capability of **15b** for intersystem crossing,[7c] in agreement with our findings with **35**. No clear distinction between $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ triplets can be made where this dichotomy exists, and it is conceivable that one or the other may be favored by a given substituent. Importantly, the gross reaction course follows the basic di-π-methane rearrangement route over the full range of substituents examined. That this state of affairs prevails, despite extensive alterations in the relative energy levels of the aryl and vinyl chromophores and in the location of triplet energy localization (see below), is viewed as remarkable.

The most striking results, however, are the full rearrangement regiospecificity encountered in several examples and the crossover in benzo-vinyl bonding preference seen in progressing from electron-withdrawing to donor aryl substituents. To the extent that the di-π-methane rearrangements of benzonorbornadienes and *anti*-7,8-benzotricyclo[4.2.2.0^{2,5}]deca-3,7,9-trienes can be considered to involve attack by a mildly electrophilic ethylenic π bond on the aromatic ring, it is of interest to compare the observed bridging regioselectivities with the course of hydrogen atom additions (in practice, T·) to monosubstituted benzenes in their S_0 state.[23] The hydrogen atom is recognized to be sterically nondemanding and relatively nonpolar, but with some electrophilic character.[24] The available data[23] would predict that methyl, cyano, and acetyl (meta dominant) should channel benzonorbornadiene photoisomerization toward **22**, while nitro, amino, carbomethoxy, and methoxy should promote bridging predominantly at the para carbon as in **24**.[25] Such is clearly not in agreement with our findings, a likely consequence of the excited state character of the aromatic moieties in the present work.

The capability of **4a** for extensive π stabilization via intermediates such as **38** has been well established. For example, treatment with formic acid and subsequent saponification gives 75% of **39**-OH[26] while HCl addition provides nearly exclusively **39**-Cl.[27] The methoxy group in **40**-OBs has little influence on the rate of solvolysis, whereas that in **39**-OBs increases the rate by a factor of 210, "the largest rate acceleration yet observed for a *p*-anisyl group."[28] These findings are opposite in direction to the bonding preference exhibited by triplet **4a** during di-π-methane rearrangement.



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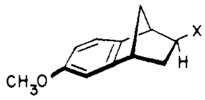

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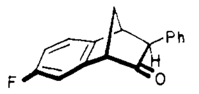
Carbalumination studies on **4b** reveal electrophilic attack to occur from the exo direction without skeletal rearrangement.[11] However, the regioisomeric ratio of **41**:**42** (30:70) obtained after hydrolysis and oxidation again contrasts with those observed upon sensitized irradiation of **4b**.



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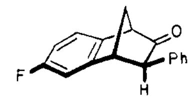
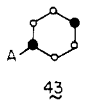


42

We emphasize that di-π-methane rearrangements involve both bond-making and bond-breaking steps. All that can be evaluated directly is the overall result, viz., that para bridging proceeds more rapidly than meta bridging, or the reverse. Hahn and Johnson[29] have concluded from their parallel study of the photochemistry of *m*-nitro derivative **4c** that the bridging step is the source of the stereospecificity. This is very likely also true in the other cases examined here, but there exists no quantitative supportive documentation. On the other hand, it would seem unlikely that biradical **22** would experience triplet decay more rapidly than **24**.[5,30] In any event, it is not possible through reasoning based upon radical or electrophilic addition reactions to predict the bridging regioselectivity of a triplet benzonorbornadiene molecule based upon its ground state structure.

A more reasonable explanation of bonding regioselectivity is based upon the concept of substituent perturbation of electronic distributions in triplet excited states. Although little data of this type are directly available, information gleaned from ESR experiments can be applied to triplet phenomena, given the generally accepted assumption that spin distributions in radical anions and lowest triplet states are quite similar.[31] In this connection, both Hirota's group[31a,32] and deJong and MacLean[31c] have found that electron spin density in triplet benzonitrile is concentrated largely at the para position. Wagner has recently reinforced the conclusion that the benzonitrile triplet is essentially a 1,4 diradical.[33] Substituted acetophenones and benzaldehydes behave comparably;[34,35] for all such strongly mesomeric groups, in fact, the electron spin density order is seen to be $P_4 > P_1 \gg P_2 \sim P_3$. In molecular orbital terms,[9] this sequencing arises because the acceptor substituent splits the degenerate $\psi_4\psi_5$ pair of benzene in a fashion which causes that orbital which is half occupied by the odd electron to have the configuration given by **43**. Wagner has further pointed out explicitly that one must consider not only the occupied π^* but the vacated π orbital in predicting electronic distribution in a triplet.[33]



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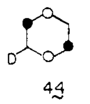

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In Terabe and Konaka's evaluation of long-range interactions in the 6-nitrobenzonorbornadiene radical anion and related molecules,[13,36] it was deduced that the hyperfine splittings were "mainly affected by the spin density at the para and meta positions". In particular, the hyperfine splittings of the exo-C_2 (homo-para-exo) hydrogen in **45** was very large, indicative of considerable unpaired electron density at the para aryl carbon. The relatively small homo-meta-exo hyperfine splitting reflects in turn a small unpaired electron density at the meta site. Although these findings conform to the pattern exhibited by the other electron-withdrawing substituents, the situation does not appear to be completely straightforward. Firstly, the magnitudes of these long-range interactions were not exactly proportional to the spin densities at the aryl carbons. Secondly, the hyperfine splitting due to the vinyl homo-para hydrogen in **46** is only slightly larger than that due to its homo-meta counterpart. This would appear to reflect operation of an additional through-space interaction mechanism, as expected.[34]

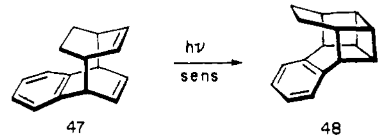
45

46

A case for electron-donating substituents can be similarly derived. For example, aromatic amines in their singlet and triplet states are known to exhibit significantly reduced basicity.[37] At the experimental level, the radical anions of toluene and anisole are well known to have low electron densities at the ortho and meta positions. As pointed out by Santiago and Houk,[9] electron donor groups on the aromatic ring also lead to alteration of the relative energies of ψ_4 and ψ_5 (formerly degenerate). In such cases, however, the lower lying of these two antibonding MOs (singly occupied in the triplet stage) has the configuration depicted in **44** which lacks a large coefficient at the site of substitution and the para position.[38] It follows on this basis that the preferential meta bridging in **4a** and **5** results from the larger singly occupied MO density at the meta position and its resulting more favorable interaction with the vacant LUMO of the ethylenic moiety.

The fluoro substituent in **4b** would appear to be exerting its customary anomalous effect.[39] However, photoelectron spectroscopic data on **4b** and the remainder of the benzonorbornadienes herein studied show this halogen not to be entirely paradoxical.[40]

The final point is the intriguing competition between di-π-methane rearrangement and $[{}_\pi 2 + {}_\pi 2]$ intramolecular cycloaddition to which the *anti*-7,8-benzotricyclo[4.2.2.0^{2,5}]deca-3,7,9-trienes are subject. Looking first to precedent, we note that Zimmerman's group has determined benzobarrelene,[41] 2,3-naphthobarrelene,[42] and 2,3-anthrabarrelene[43] to undergo vinyl-vinyl bridging exclusively under sensitized conditions with formation of aryl fused semibullvalenes. In contrast, 1,2-naphthobarrelene prefers to react by naphtho-vinyl bridging from its triplet state[42] and an interpretation based upon excited state energetics has been advanced. In yet another study, Yang and Libman observed that **47** undergoes xanthone-sensitized photorearrangement to give only **48**, the product expected from vinyl-vinyl interaction.[44]



47 **48**

As concerns hydrocarbon **2**, we see that its triplet state differs in reactivity from the above examples in that benzo-vinyl and vinyl-vinyl bonding are almost equally competitive. As donor groups are attached to the aryl ring, vinyl-vinyl bonding gains preference; acceptor substituents exert the opposite effect. This pattern is that expected if triplet energy becomes progressively more heavily localized in the aryl chromophore as aryl electron density is depleted.

Experimental Section

Proton magnetic resonance spectra were recorded with Varian T-60, A-60A, and HA-100 instruments, while carbon magnetic resonance spectra were obtained with a Bruker 90 spectrometer. Apparent splittings are given in all cases. Infrared spectra were recorded on Perkin-Elmer Model 137 and 467 spectrometers, whereas mass spectra were obtained with an AEI-MS9 instrument at an ionizing potential of 70 eV. Elemental analyses were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark.

6-Methoxybenzonorbornadiene (4a). To a stirred solution of 5-methoxyanthranilic acid (**3a**, 26.07 g, 0.156 mol) in 95% ethanol (300 mL) cooled to 0 °C was added dropwise 15.3 mL of concentrated hydrochloric acid during 5 min. Isoamyl nitrite (36.2 g, 0.31 mol) was introduced by dropwise addition during 20 min, whereupon the mixture was swirled for 20 min, treated with 225 mL of ether, and swirled for another 5 min. The resulting precipitate was separated by suction filtration, washed with anhydrous ether (3 × 100 mL), and cautiously air dried. This material (29.98 g, 89.9%) was transferred to a 1-L three-necked flask into which had been placed propylene oxide (18 g, 0.3 mol) and freshly cracked cyclopentadiene (48 g, 0.727 mol) dissolved in 500 mL of 1,2-dichloroethane. This mixture was heated with stirring at the reflux temperature for 3.5 h, allowed to cool overnight, filtered through a pad of Celite, and evaporated to a viscous brown oil. This substance was dissolved in benzene (50 mL) and passed through a column of alumina (activity grade 1, 3 × 20 cm) using benzene as eluent. The eluate was evaporated to leave an orange oil which was rechromatographed on alumina (elution with 10% benzene in hexane). All fractions containing the desired product were combined and fractionally distilled three times to give 1.75 g (7.3%) of pure **4a**, bp 65 °C (0.6 mm). The ^{1}H NMR spectrum was identical with that reproduced:[10] λ_{max} (cyclohexane) 248.5 nm (ϵ 2130), 283.5 (1790), and 289.0 sh (1610).

6-Fluorobenzonorbornadiene (4b). A solution of 5-fluoroanthranilic acid[45] (21.4 g, 0.138 mol) and 200 mL of freshly cracked cyclopentadiene in acetone (250 mL) at 5 °C and a solution of isoamyl nitrite (32.32 g, 0.276 mol) in 1,2-dichloroethane (15 mL) were added simultaneously to 1,2-dichloroethane (500 mL) maintained at gentle reflux and stirred mechanically. Heating was maintained for 5 h and the mixture was stirred overnight while cooling. The solvent was removed under reduced pressure and the residue was taken up in ether (300 mL), filtered through Celite, washed with saturated sodium bicarbonate solution (2 × 100 mL) and water (3 × 100 mL), dried, and evaporated. The volatile components of the residue were vacuum transferred at 0.05 mm. Pure **4b** was isolated by preparative VPC on column A[46] to give 1.66 g (7.5%) of colorless oil: δ_{Me_4Si} (CCl_4) 7.06-6.28 (m, 5), 3.75 (m, 2) and 2.22 (m, 2); *m/e* 160.0691 (calcd, 160.0688).

Anal. Calcd for $C_{11}H_9F$: C, 82.47; H, 5.66. Found: C, 82.55; H, 5.73.

Subsequent to completion of this work, Eisch and Burlinson described an independent synthesis of **4b**.[11]

6-Nitrobenzonorbornadiene (4c). A. From 4-Nitroanthranilic Acid. To 1,2-dichloroethane (500 mL) continuously stirred and maintained at reflux was added simultaneously, dropwise, and in equal proportions as to volume (a) a solution of isoamyl nitrite (15.6 g, 0.133 mol) in 25 mL of 1,2-dichloroethane and (b) a solution of freshly cracked cyclopentadiene (105 g, 1.59 mol) and 4-nitroanthranilic acid (19.7 g, 0.108 mol) in 350 mL of acetone. The reaction mixture was heated at reflux for 5 h after completion of the additions, allowed to cool overnight, filtered to remove a small amount of black precipitate, and evaporated. The residual brown oil was taken up in ether (500 mL), filtered through Celite, washed twice with equal volumes of saturated sodium bicarbonate solution and water, dried, and evaporated after removal of the desiccant. The resulting oil was dissolved in benzene (50 mL) and passed down a column of basic alumina (activity grade, 4 × 2 in.) with benzene elution. The solvent was removed and the residue fractionally distilled to give initially dicyclopentadiene and then **4c** (1.90 g, 9.4%), bp 199 °C (0.2 mm), the spectral properties of which were consistent with the structural assignment.

B. Nitration of Benzonorbornadiene. Acetic anhydride (200 mL) contained in a 500-mL three-necked flask fitted with a pressureequalizing addition funnel, low temperature thermometer, and rubber septum was stirred under nitrogen while cooled in ice. Nitric acid (18.8 mL of 70% solution) was added dropwise at 15–25 °C. The solution was then cooled to −10 °C while benzonorbornadiene (17.12 g, 0.12 mol) was introduced slowly by syringe. The reaction mixture was stirred for 40 min at −10 °C and then poured onto 800 g of ice and water with good stirring. After 30 min, the organic material was extracted into ether (4 × 50 mL) and the combined ether phases were washed with water, 5% sodium bicarbonate solution, and water before drying and evaporation. Distillation of the residual brown oil gave 19.43 g (8633%) of **4c**, bp 130 °C (0.3 mm), identical with the above sample.

6-Aminobenzonorbornadiene (5). A solution of **4c** (0.4112 g, 2.197 mmol) in ethanol 15 mL), water (7 mL), and ether (40 mL) was treated with 0.475 g (17.6 mg-atoms) of freshly prepared aluminum amalgam under nitrogen. The reaction mixture was stirred with initial gentle reflux due to heat of reaction. After 12 h at ambient temperature, the mixture was treated with Celite, filtered, and evaporated. The residue was taken up in ether (25 mL), washed with water (3 × 15 mL), dried, filtered, evaporated, and molecularly distilled (88 °C, 0.01 mm) to give 0.2567 g (74.3%) of **5**:[13] $\nu_{\max}$ (neat) 3430, 3350, 3210, 3065, 2985, 2935, 2865, 1613, 1471, 1349, 1303, 1250, 1115, and 820 cm^{-1}; $\delta_{\text{Me}_4\text{Si}}$ ($CDCl_3$) 7.01–6.52 (m, 4), 6.12 (m, 1), 3.69 (m, 2), 3.34 (s, 2), and 2.16 (m, 2); *m/e* 157.0894 (calcd, 157.0891).

Alternate Synthesis of 4b from 5. To a mechanically stirred solution of **5** (3.13 g, 19.9 mmol) in 20 mL of tetrahydrofuran cooled to −24 °C under nitrogen were added 7.0 mL (9.4 g) of a 50% aqueous solution of fluoroboric acid, 6.5 g of solid sodium fluoroborate, and 3.0 mL of water. After 20 min, a solution of sodium nitrate (1.57 g, 22.75 mmol) in 6 mL of water was added dropwise. The reaction mixture was stirred at −24 °C for 0.5 h, and then rapidly filtered. The precipitate was washed successively with cold water (10 mL), cold methanol (10 mL), and cold ether (10 mL) before drying (first in air for 2 h, and then at 25 °C (30 mm) for 12 h) to afford 4.94 g (96.8%) of a slightly yellow diazonium tetrafluoroborate which decomposed at 98–105 °C with the evolution of BF_3. This material (4.94 g) was suspended in 80 g of light mineral oil in a 500-mL flask equipped with Claisen head and vacuum take-off adapter into an ice-cooled receiver. The suspension was stirred and heated to 105 °C for 5 h while a reduced pressure of 30 mm was applied to remove evolved BF_3. After cooling to ambient temperature, the reaction mixture and distillate (trace) were taken up in ether (250 mL), washed with 1 N potassium hydroxide solution (100 mL) and water (2 × 100 mL), dried, filtered, and evaporated at 30 mm. The remaining volatiles were removed at 170 °C (0.3 mm) to give 0.81 g of material which was molecularly distilled at 60 °C (1 mm) to give 0.65 g of **4b** (10%) which was almost free of mineral oil impurities. A pure sample isolated by VPC proved identical with the earlier sample.

6-Carbethoxybenzonorbornadiene (8a). A sealed (under vacuum) Carius tube containing 3.70 g (0.031 mol) of 5,6-dimethylenebicyclo[2.2.1]hept-2-ene (**6**),[15] 6.16 g (0.063 mol) of ethyl propiolate, and 40 mg of hydroquinone was heated at 80 °C for 3 days. The resulting product was directly dissolved in 15 mL of benzene and this solution was added dropwise to DDQ (7.15 g, 0.032 mol) in benzene (100 mL) cooled in an ice bath. The reaction mixture was stirred at ice bath temperature for 2 h and then at room temperature for 8 h. The precipitate was separated by filtration and washed well with benzene. The combined filtrates were concentrated to a volume of 20 mL and passed down a column (15 × 2.5 cm) of alumina with benzene elution (300 mL). The elute was evaporated and the residue distilled at 93 °C (0.06 mm) to give 5.81 g (86%) of **8a** as a colorless oil: $\nu_{\max}$ (neat) 1716 cm^{-1}; $\delta_{\text{Me}_4\text{Si}}$ (CCl_4) 7.78–7.12 (m, 3), 6.69 (m, 2), 4.24 (q, J = 7 Hz, 2), 3.82 (m, 2), 2.23 (m, 2) and 1.30 (t, J = 7 Hz, 3).

An analytical sample was obtained by preparative VPC on column B[46] at 165 °C.

Anal. Calcd for $C_{14}H_{14}O_2$: C, 78.48; H, 6.59. Found: C, 78.71; H, 6.65.

6-Cyanobenzonorbornadiene (8b). A mixture of triene **6** (2.40 g, 0.020 mol) and propiolonitrile (0.80 g, 0.016 mol) was sealed in a Carius tube at 0.02 mm while cooled at −78 °C. The tube was heated at 50 °C for 69 h, cooled to −78 °C, and opened. Residual starting material was vacuum transferred into a cold (−78 °C) receiver at 20 °C (0.02 mm). Crude adduct **7b** (1.4 g) exhibited the following ^1H NMR spectrum: $\delta_{\text{Me}_4\text{Si}}$ ($CDCl_3$) 6.75 (m, 2), 6.50 (m, 1), 3.30 (m, 2), 3.21–2.61 (m, 4), and 1.94 (m, 2).

Without further purification, this material was dissolved in 10 mL of benzene to which was added 2.5 g (0.011 mol) of DDQ. The reaction mixture was stirred overnight at room temperature, filtered, and passed down a 2 × 22 cm column of alumina (activity grade I) using benzene as eluent. After evaporation of the solvent, the product was sublimed, recrystallized from hexane, and resublimed (37 °C, 0.02 mm) to give 0.70 g (26%) of pure **8b**: mp 65.5–66.5 °C (lit.[12] mp 65–66 °C); $\delta_{\text{Me}_4\text{Si}}$ (CCl_4) 7.37 (m, 1), 7.17 (m, 2), 6.71 (m, 2), 3.90 (m, 2), and 2.45–2.04 (m, 2); $\lambda_{4\max}$ (cyclohexane) 231 nm (ϵ 5610), 252 (3990), 276.5 (1150), and 286 (920).

Alternative Synthesis of 8b from 5-Iodoanthranilic Acid. To a mechanically stirred and gently refluxing solution of isoamyl nitrite (13.0 g, 0.11 mol) in 100 mL of dry dichloromethane was added dropwise a solution of 5-iodoanthranilic acid[47] (16.01 g, 0.0609 mol) and cyclopentadiene (50 g, 0.75 mol) in 250 mL of anhydrous acetone. The reaction mixture was heated to reflux for 8 h, cooled, filtered, and freed of solvent under reduced pressure. The residue was dissolved in ether (200 mL), filtered, and washed with saturated sodium bicarbonate solution (3 × 100 mL) and water (2 × 100 mL) prior to drying and evaporation. A solution of the remaining reddish oil in ligroin (30–60 °C, 500 mL) was filtered to remove precipitated polymers and passed down a 20 × 2 cm column of basic alumina. After removal of solvent, fractional distillation of the residual oil gave 2.1 g (12.9%) of 6-iodobenzonorbornadiene (bp 68–74 °C, 0.02 mm): $\delta_{\text{Me}_4\text{Si}}$ (CCl_4) 7.46–6.73 (m, 3), 6.60 (m, 2), 3.70 (m, 2), and 2.12 (m, 2); *m/e* 267.9757 (calcd, 267.9751).

A composite of sodium cyanide (0.615 g, 12.55 mmol) and cuprous cyanide (1.15 g, 12.84 mmol) was added to a solution of 6-iodobenzonorbornadiene (0.60 g, 2.24 mmol) in 10 mL of dry dimethylformamide under nitrogen. The reaction mixture was stirred and heated at reflux for 9 h, cooled to ambient temperature, poured into 50 mL of saturated sodium cyanide solution, covered with 50 mL of ether, and stirred for 1 h. The ether phase was removed, and the aqueous layer was extracted with ether (3 × 15 mL). The combined ethereal solutions were washed with water (3 × 25 mL), dried, filtered, and evaporated to leave a pale yellow oil which solidified. Sublimation at 50 °C (0.1 mm) afforded 0.346 (92.5%) of **8b** which was identical in all respects with that prepared above.

Benzonorbornadiene-6-carboxylic Acid (8c). A solution of 1.0634 g (4.97 mmol) of **8a** in 20 mL of ethanol and 10 mL of water containing 1 mL of 10 N sodium hydroxide solution was heated at reflux for 4 h, cooled, and evaporated in vacuo. The solid was taken up in water (20 mL), the solution was acidified with 5 N hydrochloric acid, and the resulting precipitate was extracted into ether (3 × 25 mL). The combined organic phases were washed with water (20 mL), dried, filtered, and evaporated to leave 0.873 g (94.5%) of **8c**: mp 162–163 °C (from benzene); $\nu_{\max}$ (KBr) 1680 cm^{-1}; $\delta_{\text{Me}_4\text{Si}}$ ($CDCl_3$) 12.73 (br s, 1), 7.95–7.19 (series of m, 3), 6.76 (m, 2), 3.91 (m, 2), and 2.31 (m, 2).

Anal. Calcd for $C_{12}H_{10}O_2$: C, 77.40; H, 5.41. Found: C, 77.33; H, 5.56.

6-Acetylbenzonorbornadiene (8d). To a stirred solution of acid **8c** (450 mg, 2.42 mmol) in 25 mL of anhydrous ether cooled to 0 °C was added dropwise 5.5 mL of 1.1 M methyllithium in hexane. After 2 h at 0 °C and 8 h at room temperature, the ethereal suspension was poured into water (50 mL) with stirring and acidified with 2 N hydrochloric acid. The ether layer was separated, the aqueous phase was extracted with ether (3 × 10 mL), and the combined organic solution was washed with water, dried, and evaporated. The residual oil was purified by preparative VPC on column B[46] at 150 °C to give 347 mg (78%) of **8d**: mp 59.0–59.5 °C (from hexane); $\nu_{\max}$ (neat) 1678 cm^{-1}; $\delta_{\text{Me}_4\text{Si}}$ (CCl_4) 7.66–7.06 (m, 3), 6.69 (m, 2), 3.86 (m, 2), 2.42 (s, 3), and 2.25 (m, 2).

Anal. Calcd for $C_{13}H_{12}O$: C, 84.75; H, 6.57. Found: C, 84.83; H, 6.70.

3,4-Dichloro-12-methoxy-*anti*-7,8-benzotricyclo[4.2.2.$0^{2,5}$]deca-7,9-diene (11). A 9.65-g sample of 5-methoxybenzenediazonium carboxylate hydrochloride (prepared as described above) was transferred to a solution containing 8.74 g (0.05 mol) of **10** and 7.5 mL (6.0 g, 0.10 mol) of propylene oxide dissolved in 175 mL of 1,2-dichloroethane. This mixture was stirred at reflux until none of the salt **9** remained (3.5 h). Removal of the solvent in vacuo left a dark brown oil, chromatography of which on alumina (45 × 3.5 cm, elution with 10–75% methylene chloride in petroleum ether) afforded a total 9.12 g (65%) of **11** as a mixture of isomers. Recrystallization of an oily semisolid fraction from ethanol and then ether gave colorless crystals, mp 124–125.5 °C, which were sublimed (110–115 °C, 0.15 mm) before analysis: ν_{max} (CCl_4) 2958, 1608, 1482, 1285, 1181, 1142, 1114, 1040, 860, and 670 cm^{-1}; δ_{Me_4Si} ($CDCl_3$) 7.13–6.42 (m, 5), 4.19–3.94 (m, 4), 3.73 (s, 3), and 2.83–2.67 (m, 2).

Anal. Calcd for $C_{15}H_{14}Cl_2O$: C, 64.07; H, 5.02; Cl, 25.22. Found: C, 63.67; H, 4.93; Cl, 24.89.

12-Methoxy-*anti*-7,8-benzotricyclo[4.2.2.0^{2,5}]deca-3,7,9-triene (12). Sodium metal (3.46 g, 0.15 g-atom) cut into small pieces was added to a solution of anthracene (26.75 g, 0.15 mol) in anhydrous tetrahydrofuran under nitrogen and the mixture was stirred at room temperature for 18 h. With cooling of the resulting dark blue solution in ice, a solution of **11** (13.97 g, 0.05 mol) in 30 mL of tetrahydrofuran was added during 10 min. After 30 min at room temperature, water (2 mL) was introduced dropwise until the blue color was discharged. After solvent removal, the residue was chromatographed three times on alumina (3.5 × 40 cm, elution with 2% ether in petroleum ether); the order of elution was 9,10-dihydroanthracene, anthracene, and **12**. A final alumina chromatography using incrementally higher concentrations of carbon tetrachloride in petroleum ether gave fractions containing pure **12** which was further purified by molecular distillation at 96 °C (1.0 mm): λ_{max} (cyclohexane) 230 nm sh (ϵ 3465), 279 (2110), and 286 (2020); δ_{Me_4Si} ($CDCl_3$) 7.0 (d, J = 7.5 Hz, 1), 6.74 (d, J = 2.5 Hz, 1), 6.50 (q, J = 7.5 and 2.5 Hz, 1), 6.14 (m, 2), 5.98 (s, 2), 3.68 (s, 3), 3.80–3.52 (m, 2), and 2.62 (m, 2).

Anal. Calcd for $C_{15}H_{14}O$: C, 85.68; H, 6.71. Found: C, 85.53; H, 6.85.

12-Cyano-*anti*-7,8-benzotricyclo[4.2.2.0^{2,5}]deca-3,7,9-triene (14). To a solution of tetraene **13** (5.32 g, 0.034 mol)[15] in 40 mL of benzene was added 2.00 g (0.039 mol) of propiolonitrile. This reaction mixture was heated at reflux with magnetic stirring for 8 h. Solvent removal left a yellow oil which was chromatographed on Florisil (25 × 1.5 cm, elution with 1:1 benzene–hexane). There was isolated 6.34 g (90.0%) of the Diels–Alder adduct as a colorless oil which crystallized upon refrigeration.

A solution of this adduct (6.34 g, 0.0306 mol) in benzene (20 mL) was added to a stirred solution of DDQ (7.0 g, 0.0310 mol) in the same solvent (80 mL). After 30 min at room temperature, the precipitate was separated by filtration and the filtrate was evaporated to leave a dark brown, oily solid. Chromatography of this material on alumina (15 × 1.5 cm, elution with 1:1 ether–benzene) furnished a yellow oil which was rechromatographed (now benzene elution) on alumina. There was obtained 5.85 g of pale yellow oil which crystallized on standing (mp 86–89 °C). Recrystallization of this product from hexane–benzene (3:1) gave colorless, crystalline **14**, mp 88.5–89.5 °C, which was sublimed (52 °C, 1.0 mm) prior to analysis: λ_{max} (cyclohexane) 245 nm (ϵ 7550), 273 sh (955'), and 282 sh (805); δ_{Me_4Si} (CCl_4) 7.42–7.03 (m, 3), 6.13 (3 lines, 2), 5.93 (s, 2), 3.78 (m, 2), and 2.57 (m, 2).

Anal. Calcd for $C_{15}H_{11}N$: C, 87.80; H, 5.36. Found: C, 87.58; H, 5.34.

Generalized Sensitized Photoisomerizations of Benzonorbornadienes. A solution of **4a** (158 mg, 0.921 mmol), acetophenone (176 mg, 1.46 mmol), and dodecane (41 mg) in 50.0 mL of benzene was divided among three Kimax test tubes. Each was purged with nitrogen for 30 min, stoppered with a serum cap, and irradiated at 3500 Å in a Rayonet apparatus. Samples were withdrawn by syringe at various time intervals and analyzed by flame ionization VPC. It was assumed that the detector responses for **4a** and its photoisomers were identical for the purpose of this analysis. Some typical data follow: 0 min (100% of **4a**); 1 min (92.1% of **4a** remaining); 4 min (58.3%); 10 min (6.2%); 15 min (4.1%); and 25 min (0%). With *m*-methylacetophenone, benzophenone, and thioxanthone, comparable results were seen. In contrast, direct irradiation at 3500 Å led to no measurable change after 120 min. Direct irradiation at 2537 Å (quartz optics) did result in slow isomerization to products: 106 min, 93.0% of **4a** and 2.4% product; 160 min, 72.7% of **4a** and 5.5% product; 276 min, 48.2% of **4a** and 7.6% product.

In a typical preparative run, 0.3153 g (1.83 mmol) of **4a** and 0.300 g (1.92 mmol) of acetophenone in 100 mL of benzene was irradiated as above for 80 min. VPC analysis on column C[46] indicated the absence of starting material and the formation of two products in the ratio of 78:22. After evaporation of the solvent and silica gel chromatography (elution with petroleum ether) to remove the sensitizer, the products were isolated by preparative VPC on column D[53] at 140 °C. The major component, isolated in 51.4% yield, was characterized as **23**-OCH_3 on the basis of its spectra; ν_{max} (CCl_4) 3045, 3015, 2940, 2865, 2835, 1610, 1590, 1495, 1247, and 1138 cm^{-1}; δ_{Me_4Si} (CCl_4) 6.92–6.30 (m, 3), 3.70 (s, 3), 3.19 (m, 2), 2.75 (m, 1), 2.38 (m, 1), 1.88 (m, 1), and 0.74 (m, 1); ^{13}C NMR (see Table II).

Anal. Calcd for $C_{12}H_{12}O$: C, 83.69; H, 7.02. Found: C, 83.96; H, 7.13.

The minor component, isolated in 7.3% yield, was shown to be identical in all respects with the methoxy compound prepared by chemical transformation of **25**-CN (see below). Accordingly, it is assigned structure **25**-OCH_3.

Preparative Scale Irradiation of 8b. The reactivity of **8b** was initially established by irradiation of **8b** at suitable analytical levels in the above fashion: 2 min (88.5% remaining), 6 min (53.3%), 10 min (32.9%), 25 min (6.2%), 45 min (0.7%), 83 min (0.5%). A single product was detected by VPC. Benzophenone and thioxanthone produced comparable conversions, but direct irradiation at 2537 Å gave no volatile product, although some polymerization was noted.

A solution of **8b** (0.201 g, 1.203 mmol) and acetophenone (0.243 g, 2.02 mmol) in 50 mL of benzene was irradiated in the usual fashion for 2.5 h. Evaporation of the solvent left a colorless oil which was purified by preparative VPC on column B[46] at 155 °C. There was isolated 0.180 g (89.6%) of **25**-CN: ν_{max} (neat) 2230 cm^{-1}; δ_{Me_4Si} (CCl_4) 7.32 (br s, 2), 7.12 (br s, 1), 3.32 (m, 2), 2.85 (m, 1), 2.52 (m, 1), 2.06 (m, 1), and 0.70 (m, 1).

Anal. Calcd for $C_{12}H_9N$: C, 86.20; H, 5.43. Found: C, 86.36; H, 5.58.

9-Acetyltetracyclo[5.4.0.0^{2,4}.0^{3,6}]undeca-1(7),8,10-triene (25-$COCH_3$). To a stirred solution of methylmagnesium iodide (prepared from 63 mg (2.59 × 10^{-3} g-atom) of magnesium and 369 mg (2.60 mmol) of methyl iodide) in 3 mL of anhydrous ether was added dropwise under nitrogen a solution of **25**-CN (180 mg, 1.078 mmol) in 3 mL of dry benzene. This mixture was heated to remove the ether and refluxed for 3.5 h. After cooling, 5 mL of 2 N hydrochloric acid was added dropwise and the mixture was again heated at reflux for 1.25 h. The layers were separated and the aqueous phase extracted with ether (3 × 10 mL). The combined ether layers were washed with water (15 mL) and dilute sodium bicarbonate solution (10 mL) before drying and evaporation. The resulting greenish oil was purified by preparative VPC on column B[46] to give 126 mg (63.7%) of **25**-$COCH_3$: mp 59.0–59.5 °C (from hexane); ν_{max} (neat) 1678 cm^{-1}; δ_{Me_4Si} (CCl_4) 7.76–7.24 (m, 3), multiplets at 3.33 (2 H), 2.84 (1 H), 2.47 (1 H), 2.02 (1 H), and 0.72 (1 H), and a singlet at 2.43 (3 H).

Anal. Calcd for $C_{13}H_{12}O$: C, 84.75; H, 6.57. Found: C, 84.37; H, 6.59.

9-Acetoxytetracyclo[5.4.0.0^{2,4}.0^{3,6}]undeca-1(7),8,10-triene (25-OAc). A solution of **25**-$COCH_3$ (1.35 g, 7.34 mmol) and 85% *m*-chloroperbenzoic acid (2.95 g, 14.5 mmol) was stirred in the dark for 7 days at ambient temperature. Progress of the reaction was monitored by VPC. The solvent was evaporated and the residue was taken up in 100 mL of ether, washed with saturated sodium bicarbonate solution (3 × 50 mL) and water (2 × 50 mL), dried, filtered, and evaporated. A portion of the resulting oil (1.20 g) was purified by preparative VPC on column B:[46] ν_{max} (neat) 1759 cm^{-1}; δ_{Me_4Si} (CCl_4) 7.33–6.69 (m, 3), 3.22 (m, 2), 2.80 (m, 1), 2.43 (m, 1), 2.15 (s, 3), 1.90 (m, 1), and 0.80 (m, 1); *m/e* 200.0839 (calcd, 200.0837).

9-Methoxytetracyclo[5.4.0.0^{2,4}.0^{3,6}]undeca-1(7),8,10-triene (25-OCH_3). A solution of **25**-OAc (1.00 g, 5.00 mmol) in 10 mL of ethanol containing 3 mL of 1 N potassium hydroxide was heated at 50 °C for 3 h, cooled, and evaporated. The residue was taken up in 5 mL of water, covered with 10 mL of ether, and treated with excess 2 N hydrochloric acid. The organic layer was separated, the aqueous layer was extracted with ether (3 × 5 mL), and the combined organic phases were washed with water, dried, filtered, and evaporated.

The resulting oily phenol (570 mg) was dissolved in 25 mL of 1 N potassium hydroxide and treated with excess dimethyl sulfate. Stirring was continued for 6 h, at which time the product was extracted into ether and processed as above. Distillation at 70 °C (0.01 mm) gave 410 mg of **25**-OCH_3 which was purified further on column B:[46] ν_{max} (neat) 3040, 2990, 2950, 2930, 2855, 2835, 1610, 1588, 1480, 1291, 1245, 1232, 1180, 1132, and 1027 cm^{-1}; δ_{Me_4Si} (CCl_4) 7.22–7.02 (m, 1), 6.55–6.35 (m, 2), 3.65 (s, 3), 3.33–3.00 (m, 2), 2.74 (m, 1), 2.35 (m, 1), 1.84 (m, 1), and 0.74 (m, 1); *m/e* 172.0891 (calcd, 172.0888).

Anal. Calcd for $C_{12}H_{12}O$: C, 83.69; H, 7.02. Found: C, 83.31; H, 7.06.

Preparative Scale Photoisomerization of 8a. A solution of **8a** (860 mg, 4.02 mmol) and acetophenone (476 mg, 3.96 mmol) in 450 mL of benzene was irradiated for 3 h as previously described. VPC analysis indicated no remaining **8a** and formation of a single product. The solvent was evaporated and the residue was chromatographed on alumina (elution with 20% benzene in hexane) to give crude oily **25**-$COOC_2H_5$ which was molecularly distilled at 105 °C (0.02 mm). There was obtained 510 mg (59.3%) of colorless oil, an analytical sample of which was isolated from column B[46] at 165 °C: ν_{max} (neat) 1715 cm^{-1}; δ_{Me_4Si} (CCl_4) 7.85–7.22 (m, 3), 4.26 (q, J = 7 Hz, 2), 3.30 (m, 2), 2.81 (m, 1), 2.46 (m, 1), 2.02 (m, 1), 1.36 (t, J = 7 Hz, 3), and 0.76 (m, 1).

Anal. Calcd for $C_{14}H_{14}O_2$: C, 78.48; H, 6.59. Found: C, 78.56; H, 6.87.

Tetracyclo[5.4.0.0^{2,4}.0^{3,6}]undeca-1(7),8,10-triene-9-carboxylic Acid (25-COOH). A solution of **25**-$COOC_2H_5$ (1.9833 g, 9.27 mmol) in 20 mL of ethanol and 10 mL of water containing 1 mL of 10 N sodium hydroxide solution was heated at reflux for 4 h, cooled, and evaporated in vacuo. The solid residue was taken up in water (20 mL), acidified with 5 N hydrochloric acid, extracted into ether (3 × 25 mL), washed with water (20 mL), dried, and evaporated. There was obtained 1.40 g (81.2%) of **25**-COOH: mp 163.5–164.5 °C (from benzene); ν_{max} (KBr) 1674 cm^{-1}; δ_{Me_4Si} ($CDCl_3$) 12.45 (br s, 1), 8.02–7.38 (m, 3), 3.39 (m, 2), 2.89 (m, 1), 2.54 (m, 1), 2.08 (m, 1), and 0.76 (m, 1).

Anal. Calcd for $C_{12}H_{10}O_2$: C, 77.40; H, 5.41. Found: C, 77.14; H, 5.47.

Alternative Preparation of 25-COCH$_3$. To an ice-cooled solution of **25**-COOH (1.40 g, 7.53 mmol) in 120 mL of anhydrous ether was added 15.0 mL of 1.1 M methyllithium in hexane. The reaction mixture was stirred at 0 °C for 2 h and at room temperature for 12 h before pouring onto water (100 mL) subsequently acidified with 2 N hydrochloric acid. The usual workup and molecular distillation (123 °C, 0.2 mm) gave 1.35 g (97.5%) of **25**-$COCH_3$ identical in all respects with the earlier sample.

Direct Irradiation of 8d. A solution of **8d** (22.8 mg, 0.124 mmol) and dodecane (14.3 mg, internal standard) in 10.0 mL of benzene contained in a Kimax test tube was purged with nitrogen for 20 min and irradiated at 3500 Å for 1800 s: 300 s (49.4% remaining); 700 s (13.0%); 1500 s (2.8%); 1800 s (trace). The solvent was evaporated and the product collected by preparative VPC from column B[46] at 165 °C. There was isolated 19.3 mg (84.6%) of **25**-$COCH_3$ totally identical with the earlier samples.

Preparative Scale Photoisomerization of 4c. A solution of **4c** (10.91 g, 57.3 mmol), acetophenone (28.65 g, 0.183 mol), and tetradecane (35 mg) in 70 mL of benzene was irradiated in the predescribed fashion for 16 h, at which time approximately 34% of starting material remained. The solvent was evaporated and the mixture was separated by preparative HPLC on silica gel. There was obtained 2.51 g (23.0%) of recovered **4c** and 6.02 g (55.2%) of **25**-NO_2, mp 46.0–46.5 °C, as the only product: ν_{max} (neat) 3050, 2925, 2860, 1608, 1593, 1510, 1418, 1379, 1342, 1308, and 1248 cm^{-1}; δ_{Me_4Si} (CCl_4) 7.95–7.73 (m, 2), 7.42 (m, 1), 3.42 (m, 2), 2.92 (m, 1), 2.57 (m, 1), 2.11 (m, 1), and 0.76 (m, 1); *m/e* 187.0637 (calcd 187.0633).

Anal. Calcd for $C_{11}H_9NO_2$: C, 70.58; H, 4.85. Found: C, 70.58; H, 4.85.

Preparative Scale Irradiation of 5. A solution of **5** (3.29 g, 20.9 mmol) and 3.05 g (25.4 mmol) of acetophenone in 700 mL of benzene was irradiated at 3500 Å through Pyrex under nitrogen for 44 h. VPC analysis of the yellow-brown solution indicated 65% conversion of **5** to products. The volume of the solution was reduced to 200 mL and the amines were extracted into cold 2 N hydrochloric acid (3 × 50 mL). The combined acid layers were extracted with ether (3 × 30 mL) before basification with excess 10% sodium hydroxide solution and reextraction with ether (3 × 50 mL). The resulting oil was molecularly distilled at 85 °C (0.5 mm). The mixture of **23**-NH_2 and **25**-NH_2 was separated from unreacted **5** by preparative VPC on column E[46] at 165 °C. The ^{13}C NMR spectrum of this mixture indicated the two photoproducts to be present in a 7:3 ratio. The minor component proved identical with **25**-NH_2 as prepared below. The major product was assigned as **23**-NH_2 on the basis of its ^{13}C NMR data (Table II) and the ^1H NMR spectrum of the mixture. By subtraction of signals, the resonance for **23**-NH_2 could be assigned as follows: δ_{Me_4Si} ($CDCl_3$) 6.62 (m, 2), 6.45 (m, 1), 3.28 (s, 2), 3.13 (m, 2), 2.74 (m, 1), 2.32 (m, 1), 1.86 (m, 1), and 0.73 (m, 1).

9-Aminotetracyclo[5.4.0.0^{2,4}.0^{3,6}]undeca-1(7),8,10-triene (25-NH$_2$). To a mechanically stirred solution of **25**-NO_2 (3.00 g, 16.0 mmol) in ether (500 mL) containing 35 mL of water and 125 mL of ethanol contained in a 1-L three-necked flask under nitrogen was added aluminum amalgam (freshly prepared from 3.60 g (0.133 g-atom) of aluminum foil cut into 10 × 2 cm strips). The reaction mixture was stirred overnight at 35 °C, cooled, filtered through Celite, and reduced in volume to 100 mL. The solution was extracted with 1 N hydrochloric acid (2 × 100 mL) and the acid layer was extracted with ether (50 mL), rendered alkaline with excess 10% sodium hydroxide solution, and reextracted with ether (3 × 50 mL). These combined extracts were washed with water (2 × 100 mL), dried, filtered, and evaporated to leave a solid which was recrystallized from hexane and sublimed at 55 °C (0.1 mm); mp 70.0–70.5 °C; ν_{max} (KBr) 3415, 3330, 3030, 2985, 2930, 1622, 1587, 1486, and 1243 cm^{-1}; δ_{Me_4Si} ($CDCl_3$) 7.14 (m, 1), 6.40 (m, 2), 3.41 (s, 2), 3.35–2.97 (m, 2), 2.77 (m, 1), 2.38 (m, 1), 1.86 (m, 1), and 0.72 (m, 1); *m/e* 157.0894 (calcd, 157.0891).

Anal. Calcd for $C_{11}H_{11}N$: C, 84.04; H, 7.05. Found: C, 83.95; H, 7.12.

Preparative Scale Irradiation of 4b. A solution of **4b** (330 mg, 2.06 mmol) and acetophenone (373 mg, 3.10 mmol) in benzene was irradiated through Pyrex with 3500 Å lamps in a Rayonet reactor for 75 min. VPC analysis on column C[46] (110 °C) indicated the absence of **4b** and presence of two photoproducts in a 91:9 ratio. The solvent was removed by distillation at atmospheric pressure and the residual material was subjected to preparative VPC purification on column F[46] to give 279 mg (84.6%) of the **23**-F/**25**-F mixture. A pure sample of the major photoproduct (**23**-F), isolated by preparative VPC fractionation on column D,[46] exhibited the following spectral properties: δ_{Me_4Si} (CCl_4) 7.08–6.39 (m, 3), 3.22 (m, 2), 2.77 (m, 1), 2.38 (m, 1), 1.90 (m, 1), and 0.72 (m, 1); ^{13}C NMR (see Table II); *m/e* 160.0691 (calcd, 160.0688).

Anal. Calcd for $C_{11}H_9F$: C, 82.47; H, 5.66. Found: C, 82.66; H, 5.72.

Triplet-Sensitized Photoisomerization of 14. A solution of **14** (111 mg) and acetophenone (38 mg) in benzene (20 mL) was deoxygenated with nitrogen and irradiated in a stoppered Pyrex test tube with 3500 Å lamps for 2 h. Evaporation of solvent left a yellow oil, the components of which were separated by preparative VPC on column G[46] (180 °C). Under these conditions, 5.4 mg of **14** was recovered. There was also collected 51.2 mg of **30**-CN, the exclusive photoproduct (analytical VPC studies on numerous columns). The analytical sample was obtained as colorless crystals, mp 62–63.5 °C after recrystallization from hexane and sublimation (58 °C, 0.1 mm): ν_{max} (CCl_4) 3042, 2940, 2230, 1480, 1282, and 642 cm^{-1}; δ_{Me_4Si} ($CDCl_3$) 7.45–7.10 (m, 3), 6.24 (d, J = 2.25 Hz, 1), 5.99 (m, 1), 3.68 (d, J = 5.25 Hz, 1), 3.20–3.07 (br s, 1), 3.02–2.70 (m, 2), 2.40 (dd, J = 7.5 and 6.0 Hz, 1), and 2.10 (dd, J = 8.25 and 6.0 Hz, 1); ^{13}C NMR ($CDCl_3$) 151.36, 148.11, 141.25, 136.83, 130.92, 125.72, 124.58, 119.67, 109.24, 62.01, 48.98, 48.88, 37.21, 35.30, and 33.87 ppm.

Anal. Calcd for $C_{15}H_{11}N$: C, 87.80; H, 5.36. Found: C, 87.78; H, 5.36.

Triplet-Sensitized Photoisomerization of 12. A solution of **12** (740 mg) and acetophenone (97 mg) in 150 mL of benzene was prepared, transferred to eight Pyrex test tubes, deoxygenated (then stoppered), and irradiated as above for 5 h. The progress of the photolysis was monitored by VPC analysis on column C[53] (180 °C). At termination, three photoproducts were evident; their relative percentage composition as determined by this technique (uncalibrated) was 9:36:55%. Solvent was removed in vacuo and the residual yellow oil was subjected to alumina chromatography. Elution with ether–hexane mixtures furnished early fractions enriched in **31**-OCH_3 and later fractions enriched with respect to unreacted **12**, **29**-OCH_3, and **30**-OCH_3. The latter mixture was combined with that from a second identical experiment (total of 700 mg) and chromatographed on silica gel impregnated with silver nitrate (10%). Elution with hexane–ether (95:5) gave 400 mg of the combined di-π-methane photoproducts, while ether elution returned 280 mg of pure **12**. Pure **29**-OCH_3 (96 mg) and **30**-OCH_3 (15 mg) were obtained by preparative VPC on column H (160 °C).

The oily chromatography fractions containing **31**-OCH_3 were induced to crystallize by seeding with crystals obtained by preparative VPC purification of a small sample. Three recrystallizations from ethanol gave white crystals: mp 53–54 °C; ν_{max} (CCl_4) 2970, 2838, 1613, 1487, 1468, 1318, 1160, 1045, and 944 cm^{-1}; λ_{max} (cyclohexane) 270 nm (ϵ 1450), 275 (2060), 278 (2200), and 285 (2400); δ_{Me_4Si} (CCl_4) 7.12–6.49 (m, 3), 3.97 (m, 2), 3.68 (s, 3), 3.34 (m, 2), and 2.87 (m, 4).

Anal. Calcd for $C_{15}H_{14}O$: C, 85.68; H, 6.71. Found: C, 85.50; H, 6.66.

29-OCH_3 was obtained as a colorless oil: ν_{max} (CCl_4) 3040, 2939, 2830, 1603, 1481, 1465, 1434, 1331, 1281, 1172, 1141, 1095, 1089, and 1034 cm^{-1}; $\delta_{\mathrm{Me_4Si}}$ ($CDCl_3$) 6.93-6.72 (m, 2), 6.51 (dd, J = 8.25 and 2.25 Hz, 1), 6.20 (d, J = 2.85 Hz, 1), 5.94 (m, 1), 3.74 (s, 3), 3.50 (d, J = 5.25 Hz, 1), 3.16-3.02 (m, 1), 2.95 (d, J = 2.25 Hz, 1), 2.69 (dd with additional splitting, J = 12.0 and 6.0 Hz, 1), 2.31 (dd, J = 7.5 and 6.75 Hz, 1), and 2.07-1.83 (dd, J = 7.50 and 6.75 Hz, 1); *m/e* 210.1048 (calcd, 210.1044).

Anal. Calcd for $C_{15}H_{14}O$: C, 85.68; H, 6.71. Found: C, 85.74; H, 6.76.

30-OCH$_3$ also was isolated as a colorless oil: $\nu_{\max}$ (CCl_4) 3030, 2931, 2830, 1479, 1464, 1428, 1364, 1331, 1290, 1131, and 1030 cm^{-1}; $\delta_{\mathrm{Me_4Si}}$ ($CDCl_3$) 7.11 (d, J = 7.50 Hz, 1), 6.70-6.48 (m, 2), 6.22 (d, J = 2.25 Hz, 1), 5.98 (m, 1), 3.75 (s, 3), 3.51 (d, J = 6.0 Hz, 1), 3.13-2.95 (m, 2), 2.65 (dd with additional splitting, J = 12.0 and 6.0 Hz, 1), 2.30 (t, J = 6.0 Hz, 1), and 1.92 (dd, J = 8.25 and 6.25 Hz, 1); *m/e* 210.1048 (calcd, 210.1044).

Diimide Reduction of 29-OCH$_3$. A solution of **29**-OCH$_3$ (72 mg, 0.34 mmol) and potassium azodicarboxylate (1.12 g, 6.2 mmol) in 25 mL of methanol was treated dropwise with 1.0 mL (16 mmol) of acetic acid. The mixture was allowed to stir for 1 h before addition of water (50 mL) and ether extraction (3 × 50 mL). The combined organic layers were washed with sodium bicarbonate solution and brine, dried, and evaporated. Chromatography of the residual yellow oil on alumina (elution with hexane-ether, 9:1) afforded 73 mg (100%) of **32** as a colorless oil. Further purification was achieved by preparative VPC on column G[46] (185 °C) to give 43.5 mg of product: $\delta_{\mathrm{Me_4Si}}$ (CCl_4) 7.04 (d, J = 8.25 Hz, 1), 6.63-6.40 (m, 2), 3.72 (s, 3), 3.36 (d, J = 5.25 Hz, 1), 3.05-2.80 (dd, J = 12.0 and 6.0 Hz, 1), and 2.77-1.50 (series of m, 8).

Anal. Calcd for $C_{15}H_{16}O$: C, 84.90; H, 7.55. Found: C, 84.75; H, 762.

Diimide Reduction of 30-CN. A solution of **30**-CN (1.14 g, 5.56 mmol) and potassium azodicarboxylate (20.82 g, 114 mmol) in methanol (200 mL) was treated dropwise during 45 min with 20 mL (320 mmol) of acetic acid. After 1 h, workup as above gave 1.02 g (88.7%) of **33a** as a colorless oil: $\nu_{\max}$ (neat) 2930, 2224, 1605, 1478, 988, 834, and 610 cm^{-1}; $\delta_{\mathrm{Me_4Si}}$ (CCl_4) 7.23-7.03 (m, 3), 3.46 (d, J = 5.0 Hz, 1), 3.09 (dd, J = 12 and 6 Hz, 1) and 2.77-1.46 (m, 8).

Anal. Calcd for $C_{15}H_{13}N$: C, 86.96; H, 6.28. Found: C, 86.77; H, 6.66.

1,2,2a,2b,6b,6d,6e-Octahydro-5-acetylbenzo[*a*]cyclobuta[*f*]cyclopropa[*cd*]pentalene (33b). To a solution of methylmagnesium iodide (from 1.36 g of methyl iodide and 235 mg of magnesium turnings) in 35 mL of anhydrous ether was added 30 mL of dry benzene and the ether was removed by distillation. A 1.04-g (5.04 mmol) sample of **33a** was introduced and the mixture was refluxed under nitrogen for 3.5 h before hydrolysis at 0 °C with 20 mL of 2.9 N hydrochloric acid. A yellow precipitate separated. This mixture was refluxed for 30 min when an additional 10 mL of water was added and heating was resumed (90 min). Following dilution with water, the organic phase was separated and the aqueous layer was extracted with benzene-ether (1:1, 100 mL). The combined organic phases were washed with sodium bicarbonate solution and brine before drying and evaporation. The crystalline residue was chromatographed on Florisil (elution with hexane-chloroform 9:1 → 1:1) to give 1.09 g (97%) of **33b**: mp 91.5-92.5 °C (from hexane); $\nu_{\max}$ (CCl_4) 2935, 1682, 1605, 1421, 1354, 1293, and 1277 cm^{-1}; $\delta_{\mathrm{Me_4Si}}$ (CCl_4) 7.57 (dd, J = 7.5 and 1.5 Hz, 1), 7.38 (br s, 1), 7.13 (d, J = 7.5 Hz, 1), 3.44 (d, J = 5 Hz, 1), 3.03 (dd, J = 12 and 6 Hz, 1), 2.40 (s, 3), and 2.80-1.46 (series of m, 8).

Anal. Calcd for $C_{16}H_{16}O$: C, 85.71; H, 7.14. Found: C, 85.68; H, 7.29.

1,2,2a,2b,6b,6c,6d6e-Octahydro-5-hydroxybenzo[*a*]cyclobuta[*f*]cyclopropa[*cd*]pentalene (33c). A solution of **33b** (550 mg, 245 mmol) and *m*-chloroperbenzoic acid (85%, 658 mg, 4.07 mmol) in chloroform (40 mL) was heated at 53 °C with stirring for 20 h. An additional 200 mg of peracid was added and heating was continued for an additional 20 h. The cooled mixture was washed with saturated sodium bicarbonate solution and brine, dried, and evaporated. To the residual yellow oil was added 560 mg of potassium hydroxide in 5 mL of water and adequate ethanol to effect solution. This mixture was heated at 55 °C for 18 h, the ethanol was removed under reduced pressure, and the alkaline solution was extracted with dichloromethane (2 × 25 mL) to remove neutral compounds. The aqueous phase was acidified with hydrochloric acid and extracted with ether (2 × 50 mL). The combined ether layers were washed with sodium bicarbonate solution and water, dried, and evaporated prior to chromatography of the residual brown oil on silicic acid. Elution with dichloromethane gave 240 mg (49.4%) of **33c** as a white, crystalline solid: mp 122-123 °C (from carbon tetrachloride-hexane); $\nu_{\max}$ (CCl_4) 3615, 2930, 1487, 1310, and 1174 cm^{-1}; $\delta_{\mathrm{Me_4Si}}$ ($CDCl_3$) 7.16-6.13 (m, 3), 4.95 (br s, 1), 3.38 (d, J = 5 Hz, 1), and 3.17-1.56 (series of m, 9).

Anal. Calcd for $C_{14}H_{14}O$; C, 84.85; H, 7.07. Found: C, 84.51; H, 7.12.

1,2,2a,2b,6b,6c6d,6e-Octahydro-5-methoxybenzo[*a*]cyclobuta[*f*]cyclopropa[*cd*]pentalene (34). A mixture of **33c** (220 mg, 1.11 mmol), 1.11 N sodium hydroxide solution (1.4 mL), and water (5 mL) was warmed slightly to dissolve the phenol. Dimethyl sulfate (159 mg, 1.27 mmol) was added and the mixture was heated at 60-70 °C for 90 min with stirring. Another 1.4 mL of base and 159 mg of dimethyl sulfate were introduced and the process repeated. The cooled mixture was made basic and extracted with ether (2 × 50 mL). Subsequent to drying and evaporation of the combined organic layers, the residual yellow oil was chromatographed on alumina. Elution with hexane-ether (19:1) afforded 120 mg (50.5%) of **34** as a colorless oil. The analytical sample was obtained by preparative VPC on column G[46]: $\delta_{\mathrm{Me_4Si}}$ (CCl_4) 7.12-6.27 (m, 3), 3.66 (s, 3), 3.35 (d, J = 5 Hz, 1), and 3.10-1.50 (series of m, 9).

Anal. Calcd for $C_{15}H_{16}O$: C, 84.90; H. 7.55. Found: C, 84.65; H, 7.74.

Photoisomerization of 2a,3,8,8a-Tetrahydro-4,7-dimethoxy-3,8-ethenocyclobuta[*b*]naphthalene (35). The title compound was prepared as described by Reppe and co-workers.[48] A solution of **35** (632 mg) in purified cyclohexane (160 mL) was deoxygenated, transferred to eight Pyrex test tubes (stoppered with serum caps), and irradiated for 6 h in a Rayonet reactor with a bank of 16 3000-Å lamps. Removal of solvent in vacuo gave a yellow oil. The crude photolysate from two runs was purified by thick layer chromatography on alumina (elution with 90% cyclohexane-8% benzene-2% ether). There was obtained 1.14 g of **36** as a colorless, crystalline solid: mp 84-85 °C (from ethanol); $\nu_{\max}$ (CCl_4) 3040, 3000, 2940, 2830, 1492, 1465, 1439, 1278, 1254, 710, and 672 cm^{-1}; $\lambda_{\max}$ (cyclohexane) 288 nm (ϵ 3460), 296 (3260), and 298 nm (3140); $\delta_{\mathrm{Me_4Si}}$ ($CDCl_3$) 6.33 (br s, 2), 6.13 (d, J = 2.5 Hz, 1), 5.90 (m, 1), 3.65 (s, 3), 3.62 (s, 3), 3.73-3.46 (m, 1), 3.00 (m, 2), 2.43 (m, 2), and 1.87 (dd, J = 8 and 6 Hz, 1).

Anal. Calcd for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71. Found: C, 80.21; H, 6.76.

The remaining fractions were combined and subjected to thick layer chromatography on silica gel. There was isolated 185 mg of **37** as colorless crystals: mp 122-123 °C (from ethanol); $\nu_{\max}$ (CCl_4) 2975, 2837, 1490, 1465, 1440, 1320, 1271, 1255, 1172, 1153, 1104, 1090, 1032, 962, and 715 cm^{-1}; $\lambda_{\max}$ (cyclohexane) 288 nm (ϵ 4160), 292 sh (3750), 295 sh (3800), and 297 sh (3680); $\delta_{\mathrm{Me_4Si}}$ ($CDCl_3$) 6.66 (s, 2), 4.62 (m, 2), 3.77 (s, 6), 3.38 (m, 2), and 2.87 (m, 4).

Anal. Calcd for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71. Found: C, 80.04; H, 6.70.

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(17) Professor Roger Hahn and Dr. Richard P. Johnson have informed us (March 26, 1976) of their independent investigation of the photochemistry of **4c**. Their proof of the **25**-NO$_2$ assignment consisted in the nitration of **16a** and utilization of the directive influence of the cyclopropane ring for electrophilic attack at the para position.

(18) At the time of our preliminary communication where we reported conversion of **4a** exclusively to **23**-OCH$_3$,[4] several dozen columns had been used to analyze this photolysis mixture. Only one component was ever witnessed and smooth Gaussian curves were generally obtained. However, our suspicions were aroused when we later recorded the ^{13}C NMR spectrum and observed weak extraneous signals. Subsequent VPC work revealed that this mixture could indeed be separated on a combination column containing Benton-34 (1 part) and SF-96 (3 parts) on 60/80 mesh Chromosorb W. This state of affairs applies equally to the separation of **29**-OCH$_3$ and **30**-OCH$_3$.

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