Demonstration and Analysis of Bridging Regioselectivity Operative during Di-π-methane Photorearrangement of Ortho-Substituted Benzonorbornadienes and *anti*-7,8-Benzotricyclo[4.2.2.0^{2,5}]deca-3,7,9-trienes

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Abstract: The triplet-state photoisomerizations of a number of ortho-substituted benzonorbornadienes and *anti*-7,8-benzotricyclo[4.2.2.0^{2,5}]deca-3,7,9-trienes are reported. All of the examples studied underwent di-π-methane rearrangement with preferential benzo-vinyl bridging to the adjacent aryl carbon. For the nitro- and acetylbenzonorbornadienyl cases, the rearrangement was regiospecific. When the substituent group was cyano (96%), methoxy (89.3%), amino (82.6%), methyl (70%), or fluoro (50%), the bonding preference was somewhat less dramatic (degree of ortho bridging given in %). Sensitized irradiation of *o*-methoxybenzotricyclodecatriene **27** gave rise to a 66:10:24 mixture of **38**-OCH_3, **39**-OCH_3, and **40**-OCH_3. In contrast, cyano derivative **29** afforded an 84:8:8 mixture of **38**-CN, **39**-CN, and **40**-CN. The diminished level of vinyl-vinyl bonding in the latter case (11-12:1 vs. 3:1) denotes that concentration of triplet energy in the aromatic moiety promotes benzo-vinyl bridging. The observed regioselectivity is shown to conform to the magnitude of the relevant orbital coefficients as calculated by perturbation theory and supported by PE data.

In the preceding paper,[1] we delineated the striking control exerted by meta substituents on the directionality of benzo-vinyl bonding from the triplet excited states of benzonorbornadienes and *anti*-7,8-benzotricyclo[4.2.2.0^{2,5}]deca-3,7,9-trienes. In the case of an acceptor substituent, fully regiospecific para bridging was observed with ultimate formation of **2**. As concerns donor substituents, a marked predilection for

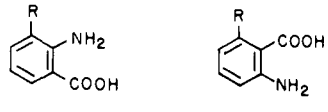
2 **1** **3**

meta bridging to give predominantly **3** was noted. This cross-over in product formation can be accounted for in terms of a simple MO model.[2] The level of sophistication of this treatment was such, however, that predictions concerning possible selectivity during di-π-methane rearrangement of the related ortho-substituted derivatives could not be made.

We now demonstrate that the latter substitution plan can indeed exert large directive effects and that the bonding preferences are now *all in the same direction* regardless of electronic character. Additionally, more extensive elaboration of the theoretical model is shown to provide a basis for understanding these contrasting directional effects.[3]

Results

Syntheses. Access to an ortho-substituted benzonorbornadiene can best be accomplished through Diels-Alder addition of the desired benzyne to cyclopentadiene. In this study, the requisite benzynes were generated by aprotic diazotization of anthranilic acid precursors. Owing to the requirement of ultimate ortho substitution, the anthranilic acids must necessarily carry three contiguous functional groups aligned as in A or B. Interestingly, little or no success has been realized in

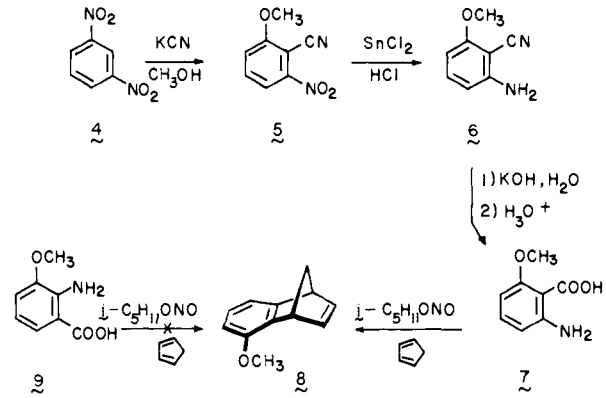


A **B**

attempts to utilize acids of type A in such reactions. In contrast, alternate substitution plan B has afforded high yields of products. Accordingly, one is advised under circumstances of this type to position the amino group which must experience diazotization at a peripheral position.

These points are nicely illustrated in the case of methoxy derivative **8** (Scheme I). The action of methanolic potassium

Scheme I

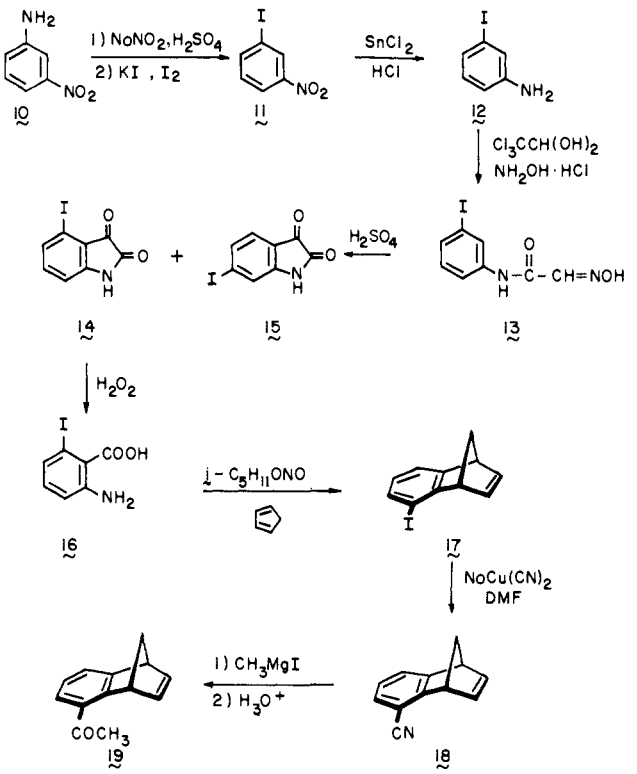


4 **5** **6** **9** **8** **7**

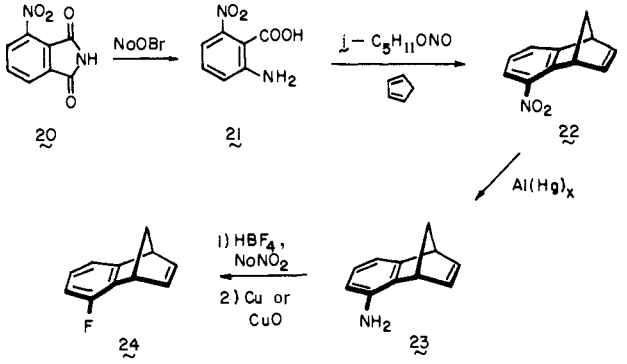
cyanide on *m*-dinitrobenzene (**4**) gave the previously described 2-nitro-6-methoxybenzonitrile (**5**)[4] which was reduced directly to **6** with stannous chloride in hydrochloric acid.[5] Subsequent saponification of **6** afforded 6-methoxyanthranilic acid (**7**)[6] in 17% overall yield. Exposure of **7** to isoamyl nitrite in the presence of cyclopentadiene resulted in the formation of **8** (57%). All attempts to prepare **8** from the more readily available 3-methoxyanthranilic acid (**9**)[7] failed to give more than a trace of **8** under similar conditions.

Successful synthesis of nitrile **18** was realized through the intermediacy of 5-iodobenzonorbornadiene (**17**, Scheme II). In the preferred sequence, the diazotization of *m*-nitroaniline (**10**) was followed by treatment with potassium iodide-iodine to give **11** (96.5%)[8] and reduction with stannous chloride to afford *m*-iodoaniline (**12**, 55%)[8] admixed with aniline (34%). Submission of **12** to the isatin synthesis led via intermediate **13** (93.5%) to a mixture of the desired 4-iodo derivative (**14**, 64%) and its 6-iodo isomer (**15**, 17%).[9] When oxidized with

Scheme II



Scheme III



alkaline hydrogen peroxide, **14** was converted to 6-iodoanthranilic acid (**16**, 65%) which gave **17** (59%) upon diazotization as before. Treatment of **17** with sodium dicyanocuprate in refluxing dimethylformamide yielded 88% of **18** as the only isolable product. The action of methylmagnesium iodide converted **18** into the acetyl derivative **19**.

Guided by the successful reactions of **7** and **16** together with the negative results encountered with **9**, we synthesized 6-nitroanthranilic acid (**21**) by oxidation of 3-nitrophthalimide (**20**) with sodium hypobromite.[10] After thorough drying, **21** was treated with isoamyl nitrite and cyclopentadiene in refluxing ethylene dichloride. The yield of crystalline **22** was 58%. While attempted reduction of **22** with sulfurated sodium borohydride failed to give **23**, the *o*-amino derivative was isolated in 91% yield upon aluminum amalgam reduction. The successful conversion of **23** to 5-fluorobenzonorbornadiene (**24**) was achieved through use of modified Schiemann procedures.[11,12] Thus, treatment of this aniline with aqueous fluoroboric acid and sodium nitrite at 0 °C, followed by Cu (or CuO) promoted decomposition at this temperature under conditions which evaded isolation, furnished **24** in 60% yield.

Synthesis of the *anti*-7,8-benzotricyclo[4.2.2.0^{2,5}]deca-

Scheme IV

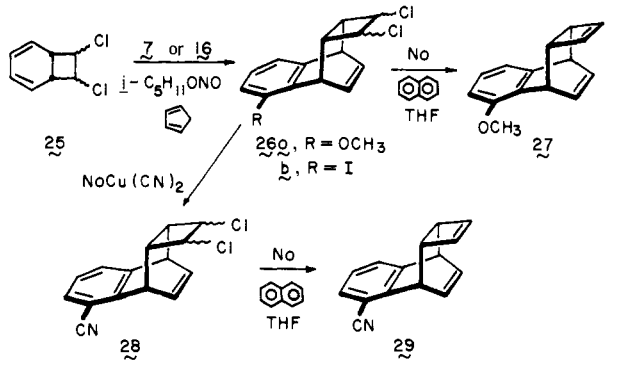
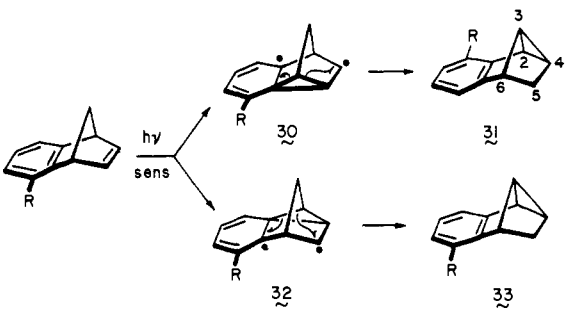


Chart I



3,7,9-trienes paralleled the scheme developed earlier for the parent hydrocarbon[13] and *m*-methoxy derivative[1] (Scheme IV). Thus, reaction of **25** with *o*-methoxy- and *o*-iodobenzyne gave **26a** and **26b** in 35 and 52% yields, respectively. Whereas the dechlorination of **26a** with sodium naphthalenide proceeded readily to furnish **27** (80%), this reagent acted on **26b** to effect reductive removal of the iodine atom as well. To bypass this difficulty, **26b** was first treated with sodium dicyanocuprate in dimethylformamide. Conventional isolation procedures afforded **28** in almost quantitative yield. The cyclobutyl chlorine atoms are therefore sufficiently inert toward this copper reagent to allow selective replacement of the aryl-iodine substituent. When submitted to reductive dechlorination, **28** was converted to the desired *o*-cyano derivative **29** (33%).

Benzonorbornadiene Photoisomerizations. At the inception of this study, only one example of ortho-substituted benzonorbornadiene photochemistry had appeared in the literature. The substance in question was the *o*-methyl derivative which Edman demonstrated was partitioned under triplet sensitized conditions to a 70:30 product mixture.[14] The major photoisomer was tentatively assigned structure **31**-CH_3 on the basis of ^{1}H NMR similarities of its aryl proton region with those of the parent tetracyclo[5.4.0.0^{2,4}.0^{3,6}]undeca-1(7),8,10-triene. It was noted that the *o*-methyl group exerted a real, though moderate, excited state directive effect which had been found during comparable rearrangement of the meta-substituted isomer.

As outlined in Chart I, di-π-methane rearrangement in this instance can proceed by benzo–vinyl bridging either ortho (cf. **30**) or meta (as in **32**) to the aryl substituent. In the first option, subsequent bond relocation has the effect of positioning R proximal to the cyclopropyl moiety (**31**). Alternatively, the substituent finds itself in a distal relationship to the three-membered ring (cf. **33**). Edman's early results suggested that mere alkyl substitution was adequate to direct bonding preferentially to that benzo position ortho to R. We now detail evidence which shows that this pathway predominates in all other cases except when R is fluoro, and can be made fully regiospecific when the electron-withdrawing capabilities of R become sufficiently elevated.

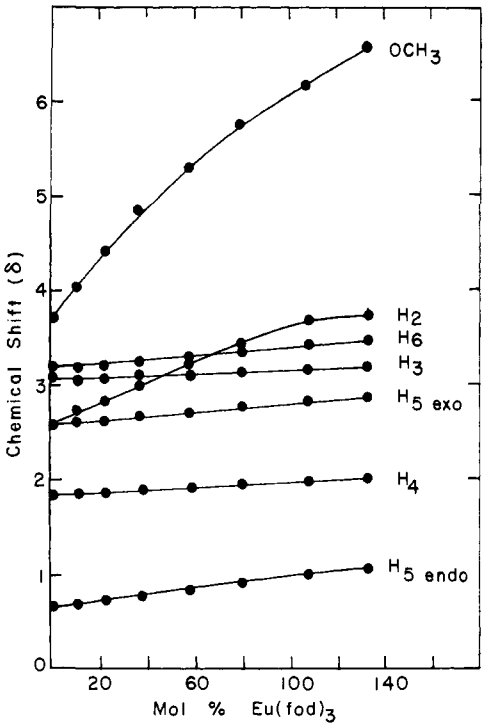


Figure 1. Plot of chemical shift dependence vs. mol % $Eu(fod)_3$ for **31**-OCH_3.

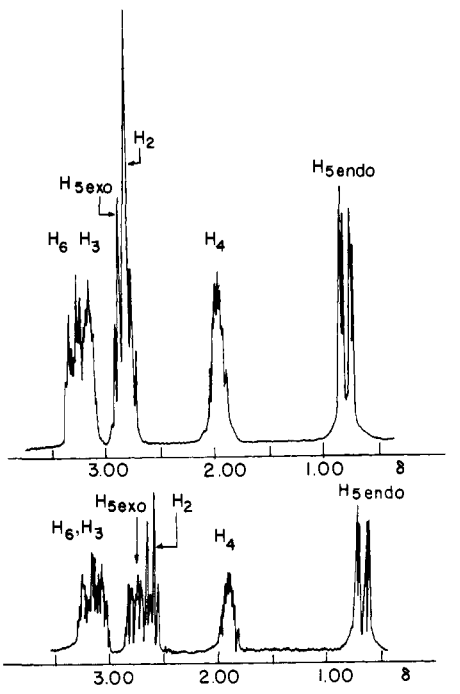
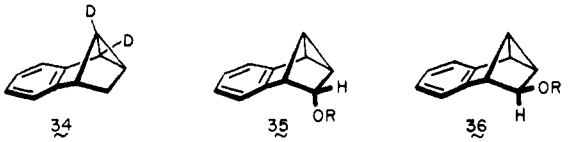


Figure 2. ^1H NMR spectra (100 MHz, $CDCl_3$ solution) of **31**-OCH_3 (bottom) and **33**-OCH_3 (top).

The acetophenone-sensitized irradiation of **8** promoted efficient conversion to a mixture of two difficultly separable isomers formed in an 89.3:10.7 ratio (VPC analysis). Separation of this pair of compounds eluded us for considerable time until the efficacy of Bentone-34 was recognized.[1] With the aid of a 5% Bentone-34/10% SF-96 combination column, we succeeded in isolating pure samples of **31**-OCH_3 and **33**-OCH_3. The major component was obtained in quantities sufficient to allow pursuit of lanthanide induced ^1H NMR pseudocontact shift experiments which convincingly showed the compound to be **31**-OCH_3. The data for the aliphatic protons are displayed graphically in Figure 1. Given the assumptions that Eu(III) coordinates exclusively with the methoxyl oxygen in this case and that pseudoaxial symmetry prevails at the site of complexation, then the benzylic bridgehead proton proximate to OCH_3 should experience the greatest deshielding (excluding OCH_3 itself).

The aliphatic region of the 100-MHz spectrum of **31**-OCH_3 in CCl_4 which is illustrated in Figure 2 is seen to be divided into five distinct regions. For proper assignment of the six protons, recourse was made to pertinent reference data. The ^1H NMR spectrum of **34** as detailed by Edman and Reddy[14,15] shows



34 **35** **36**

substantial reduction in the intensities of its δ 3.09 and 2.35 absorptions. Because the multiplicities of these signals are identical with those seen for the δ 3.05 and 2.58 multiplets in **31**-OCH_3, there is little doubt that these represent the two protons replaced by deuterium in **34**. From considerations of molecular models which show H_{5endo} to be proximate to and directly below the aryl π cloud, this proton should be shielded more than normal aliphatic protons because of benzene ring anisotropy. In line with this conclusion, the predictably less complex multiplicity of this signal (no coupling to the bridgehead proton, etc.), and clear agreement with the earlier assignment by Story for the parent tricyclic olefin,[16] the δ 0.67 multiplet is attributed to H_{5endo}. The two multiplets at δ 2.62 and 1.86 are readily assignable to H_{5exo} and H_4, respectively, since only the latter is a cyclopropyl proton and the former is subject to those higher levels of spin–spin coupling associated with exo protons.

From among the three remaining absorptions, that at lowest field (δ 3.17) can be unequivocally attributed to H_6, the benzylic proton which does not also possess cyclopropyl character. This conclusion follows from spin decoupling studies on **31**-H (H_6 appears at 3.18) which show $J_{5endo,6}$ and $J_{5exo,6}$ to be 0.4 and 7.6 Hz, respectively, in agreement with prevailing dihedral angles of ca. 100 and 0°.[15] Interestingly, both of these coupling constants are somewhat larger than those previously reported for benzonorbornene[17] and norbornene.[18]

Although a solution to the structural question was now in hand, we desired a distinction between H_2 and H_3 for completeness. In **31**-H, both protons are seen to couple weakly to H_{5exo} (0.2 Hz) and rather strongly to H_4 (5.0 and 4.2 Hz, respectively) as expected for such structural arrangements. The magnitudes of their spin interactions with H_6 require, however, that the δ 3.05 multiplet be assigned to H_3 ($J_{3,6}$ = 3.0 Hz) and the δ 2.58 absorption to H_2 ($J_{2,6}$ = 0.7 Hz). Long-range couplings between the bridgehead protons in norbornenes are known to attain a maximum of 1.0–1.5 Hz in certain cases.[19,20] In benzonorbornenes, the magnitudes of such interactions are generally somewhat smaller.[17] On this basis, a 3.0-Hz splitting cannot be reconciled with a W-plan arrangement between H_2 and H_6 and must be the vicinal interaction of H_3 with the benzylic proton (compare $J_{2,3}$ = 4.8 Hz).[15] Thus, the benzylic cyclopropyl proton appears *upfield* of its apical counterpart in the tetracyclo[5.4.0.0^{2,4}.0^{3,6}]undeca-1(7),8,10-trienes reported herein. The spectra of oxygenated derivatives **35** and **36** as reported by Tufariello and Rowe[21] also appear to follow this trend, although the data reported are not totally adequate to be conclusive.

Sensitized (acetophenone, benzophenone, 9-thioxanthone) irradiation of *o*-cyano derivative **18** in benzene solution yielded two products in a 96:4 ratio. Through combined use of HPLC and VPC techniques, the two components were obtained pure and identified as **31**-CN (major) and **33**-CN (minor). The

Table I. LIS Data on **31**-CN and **33**-CN (100 MHz, CCl_4, δ Values)

Compd	Eu(fod)$_3$, mol %	Chemical shifts[a] H_6	H_3	H_{5exo}	H_2	H_4	H_{5endo}
31-CN	0	3.44	3.36	2.98	2.79	2.11	0.71
	8.6	3.58	3.52	3.09	3.36	2.25	0.91
	34.4	4.2[b]	4.2[b]	3.56	5.61	2.78	1.69
	Total shift, ppm	0.76	0.84	0.58	2.82	0.67	0.98
33-CN	0	3.62	3.00	2.95	2.55	2.03	0.75
	15	4.19	3.14	3.10	2.68	2.13	1.03
	Total shift, ppm	0.57	0.14	0.15	0.13	0.10	0.28

[a] The chemical shifts given in some cases are for the most salient peak in the multiplet and not the midpoint. [b] Salient peaks not unambiguously discernible owing to overlapping signals.

Table II. LIS Data on **31**-NH_2 (100 MHz, $CDCl_3$, δ Values)

Eu(fod)$_3$, mol %	Chemical shifts H_6	H_3	H_{5exo}	H_2	H_4	H_{5endo}
0	3.34	3.16	2.78	2.34	1.98	0.74
3	3.51	3.23	2.98	2.92	2.07	1.00
6	*a*	*a*	3.14	3.61	2.27	1.34
10	3.91	3.57	3.30	4.21	2.42	1.64
Total shift, ppm	0.57	0.41	0.52	1.87	0.44	0.90

[a] Peaks overlap with other resonances and preclude reliable assignment.

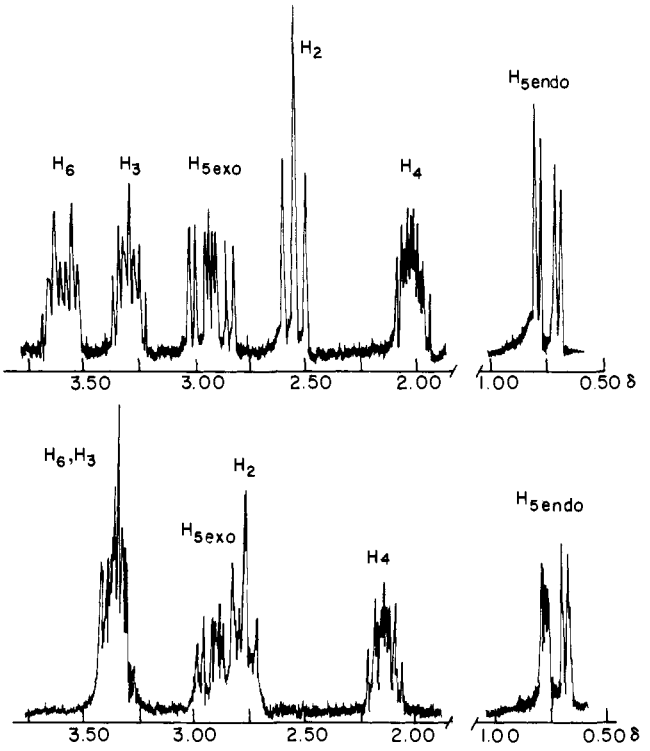
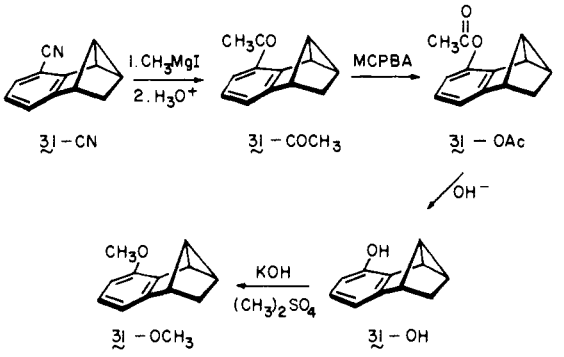


Figure 3. ^1H NMR spectra (100 MHz, $CDCl_3$ solution) of **31**-Cn)bottom) and **33**-CN (top).

Scheme V



aliphatic regions of their 100-MHz ^1H NMR spectra illustrated in Figure 3 reveal the dramatic influence of the differently positioned cyano groups on certain chemical shifts. Treatment with Eu(fod)$_3$ resulted in dramatic changes in both spectra. In the case of **31**-CN, for example, the apparent triplet centered at δ 2.79 appears at δ 5.61 after addition of 33.4 mol % shift reagent. This behavior parallels that observed previously for **31**-OCH_3. Relevant LIS data are presented in Table I. Our studies with **33**-CN were limited by small quantities of material and the attendant loss of resolution due to paramagnetic broadening when relatively high concentrations of Eu(fod)$_3$ are dissolved in a minimal volume of solvent. However, at the concentrations of lanthanide reagent indicated (Table I), the individual peaks were particularly well resolved such that double resonance experiments were feasible. As indicated in the Experimental Section, all coupling constants proved entirely comparable to those determined earlier for the parent hydrocarbon.

These findings suggested that **8** and **18** had experienced isomerization from their triplet states to give predominantly photoproducts with the *identical* substitution plan. This important point was established unequivocally by the series of chemical interconversions outlined in Scheme V. Furthermore, **31**-OCH_3 as prepared therein proved to be identical with the sole photoisomer obtained by direct irradiation (3500 Å) of **19**. Accordingly, the acetyl derivative likewise exhibits the same bridging regioselectivity.

Details of the photochemical behavior of *o*-nitro derivative **22** were next investigated. Whether irradiated directly (3500 Å) or with acetophenone as sensitizer, **22** was converted to a mixture of three products in a ratio of 91.5:0.5:8. The major component, most conveniently isolated by HPLC on silica gel, was subsequently identified as **31**-NO_2 (see below). The minor constituent, although not yet isolated in pure form, is believed to be **33**-NO_2. The remaining substance (8%) was independently shown to arise from **31**-NO_2 on prolonged irradiation and is therefore of little consequence to the regioselectivity question. Aluminum amalgam reduction of **31**-NO_2 gave **31**-NH_2 which proved identical with the major component (86.2%) isolated from sensitized irradiation of **23**. In Table II are provided the results of Eu(fod)$_3$ experiments on **31**-NH_2 which conclusively establish the amino group to be proximal to H_2.

Further evidence for the identity of the preferred excited state pathways in all five systems examined so far was gained from examination of relevant ^{13}C spectra (Figure 4), particularly in the aliphatic region. The data reveal that two aliphatic carbons are quite sensitive to positional alterations on the aromatic moiety. These are, of course, the pair of benzylic carbons and the effect is one of steric compression which is shielding in nature. Comparison of the spectrum of the parent hydrocarbon with those of **31**-OCH_3 and **31**-NH_2 indicates that the 29.38 ppm absorption in **31**-H has been shifted upfield to 26.03 and 25.87 ppm, respectively. This signal remains relatively unaffected in the spectra of **33**-OCH_3 (29.09) and **33**-NH_2 (29.00). However, the latter pair of photoisomers exhibit peaks at 39.44 and 39.22, respectively, which correspond to that at 43.40 in **31**-H (Table III). These upfield shifts are not seen in the major isomers. Significantly, the spectrum of the 8,11-dimethoxy derivative (**37**)[1] shows shielding effects at both sites (Figure 4).

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

Compd	Chemical shifts, ppm: Aromatic carbons	Methoxyl	Aliphatic carbons
31-H	149.24,[a] 142.36,[a] 125.71, 124.71, 123.04, 119.83		45.24, 43.40, 29.54,[b] 29.38, 19.29
31-OCH_3	156.22,[a] 151.53,[a] 129.22,[a] 126.06, 113.09, 108.74	55.44	44.67, 43.78, 29.59,[b] 26.03, 19.29
31-NH_2	150.77,[a] 142.20,[a] 126.63,[a] 125.85, 113.65, 111.09		43.78, 43.65, 29.62,[b] 25.87, 19.32
37	150.83,[a] 147.35,[a] 138.18,[a] 131.65,[a] 109.61, 108.80	56.06	44.81, 40.03, 29.11,[b] 26.65, 19.48
33-OCH_3	152.58,[a] 144.73,[a] 135.75,[a] 127.20, 116.16, 107.96	55.44	45.11, 39.44, 29.86,[b] 29.08, 19.50
33-NH_2	143.73,[a] 138.72,[a] 126.95,[a] 114.25, 112.68, 111.09		44.51, 39.22, 29.81,[b] 29.00, 19.32
38-OCH_3	156.31,[a] 152.70,[a] 141.19,[c] 136.93,[c] 128.70,[a] 127.47, 115.28, 105.65	55.09	62.52, 55.40, 49.41, 49.02, 35.70, 33.71, 30.04
39-OCH_3	153.77,[a] 143.46,[a] 140.99,[c] 137.26,[c] 136.64,[a] 127.83, 116.55, 107.97	55.09	60.32, 55.09, 48.59, 45.96, 35.72, 33.77, 33.77
38-CN	151.59,[a] 146.86,[a] 141.32,[c] 136.74,[c] 129.59, 126.73, 126.60, 118.34,[d] 108.14[a]		61.92, 49.37, 49.11, 37.28, 35.23, 33.09
39-CN	154.26,[a] 143.27,[a] 141.19,[c] 137.03,[c] 129.03, 128.32, 127.08, 117.40,[d] 106.48[a]		61.04, 48.82, 48.82, 36.47 34.45, 33.54

[a] Quaternary aromatic carbons. [b] Methylene carbons. [c] Olefinic carbons. [d] Nitrile carbons.

Table IV. Product Distributions from Sensitized (Acetophenone) Irradiation of 5-Substituted Benzonorbornadienes[a]

Compd	R	Products, % **31**	**33**
8	OCH_3	89.3	10.7
18	CN	96	4
19	$COCH_3$[b]	>99	
22	NO_2	>99	Trace
23	NH_2	82.6	17.4
24	F	50	50
	CH_3[c]	70	30

[a] At 3500 Å through Pyrex in dilute benzene solution. [b] Direct irradiation under otherwise identical conditions. [c] See ref 14.

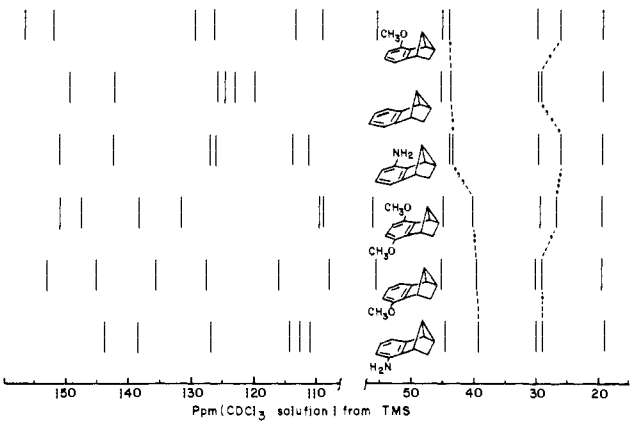
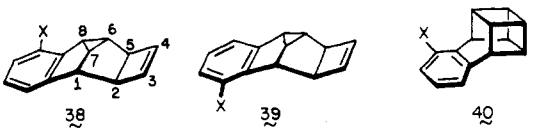


Figure 4. Schematic bar graph of ^{13}C chemical shifts of selected photoproducts.

With the knowledge obtained from the spin decoupling and LIS studies described above, it becomes possible to assign ^{13}C chemical shifts to all the aliphatic carbons in the tetracyclo[5.4.0.$0^{2,4}$.$0^{3,6}$]undeca-1(7),8,10-triene system. Off-resonance decoupling studies indicate the carbon which gives rise to the 29.54 ppm signal in **31**-H to be coupled to two protons; it is therefore C_5. The identity of C_2 and C_6 was recognized above and C_4 is seen to be the most shielded carbon (19.29) by analogy with tricyclene[22] and static semibullvalene.[23] The remaining carbon (C_3) must therefore be the source of the 45.24 ppm absorption.

The photochemical isomerization of **24** does not proceed in the absence of a sensitizer. With acetophenone present, conversion to an approximately 50:50 mixture of **31**-F and **33**-F was realized. These isomers proved not to be separable. However, independent access to pure **31**-F was gained by submission of **31**-NH_2 to conditions of the Schiemann reaction. In view of these findings, the fluorine substituent is seen to stand alone as the one which does not dictate a preference for excited state benzo-vinyl bonding to the ortho position (Table IV). Rather, the two possible pathways (Chart I) appear to be statistically equivalent.

Excited State Behavior of the *anti*-7,8-Benzotricyclo[4.2.2.$0^{2,5}$]deca-3,5,7-trienes. Acetophenone sensitized irradiation of **27** resulted in rapid conversion to photoproducts. As progress of the reaction was monitored by VPC on a 1.75% Bentone-34/5% SF-96 column, only two components were observed to form at the expense of starting material. Preparative VPC isolation using 10% SF-96 on Chromosorb W efficiently separated unreacted **27**, di-π-methane product, and *o*-methoxybenzobasketene (**40**-OCH_3). However, the 90-MHz ^1H NMR spectrum of the second fraction revealed it to be



38-OCH_3 admixed with lesser amounts of **39**-OCH_3. The problem of their separation was resolved by initial column chromatography of the unpurified photolysate on alumina. By this procedure, an approximately equal mixture of **39**-OCH_3 and **40** was isolated together with pure **38**-OCH_3. This pair of compounds could then be separated by VPC on a 5% Bentone-34/5% SF-96 column at 180 °C. Under these conditions, **40**-OCH_3 was partially isomerized to *o*-methoxybenzosnoutene.[24] The ratio of **38**-OCH_3:**39**-OCH_3:**40**-OCH_3 was determined to be 66:10:24. Accordingly, di-π-methane rearrangement in this system is approximately three times more efficient than intramolecular cycloaddition.

The ^1H NMR spectrum ($CDCl_3$) of **38**-OCH_3, which consists of a highly structured aromatic pattern (δ 7.23–6.53, 3 H), a pair of olefinic protons (6.22, d, J = 3 Hz; 5.97 m), a benzylic methine proton (3.57, d, J = 4.5 Hz), two cyclobutyl hydrogens (3.14, m; 2.99, d, J = 3 Hz), and a trio of cyclopropyl protons (2.78–2.41, m, 2; 2.04, dd, J = 7.5 and 6 Hz), exhibited most pronounced downfield shifting of the high field (cyclopropyl) region (excluding the effect on OCH_3) when treated with 38.2 mol − eu(TFN)$_3$. The aromatic region is easily discerned to consist of a pattern having great similarity with that exhibited by **31**-OCH_3. In this same context, the rather different aryl absorptions of **39**-OCH_3 (δ 7.11 (d, J =

Table V. LIS Data on **38**-CN and **39**-CN (90 MHz, $CDCl_3$, δ Values)

Compd	$Eu(fod)_3$, mol %	Proton chemical shifts				
		Aryl	H_3, H_4	H_1	H_2, H_5	Cyclopropyl
38-CN	0	7.38–7.09	6.25, 5.98	3.67	3.18, 2.75	2.98–2.53, 2.18
	10.1	7.59–7.16	6.27, 6.01	3.73	3.25, 2.88	3.04–2.73, 2.25
	30.9	7.92–7.23	6.30, 6.05	3.82	3.37, 3.06	3.28–2.85, 2.33
	Total shift, ppm	0.54–0.14	0.05, 0.07	0.15	0.19, 0.31	0.30–0.32, 0.15
39-CN	0	7.47–7.05	6.24, 6.03	3.85	3.10, 3.10[a]	2.81, 2.43, 2.07
	11.1	7.55–7.12	6.27, 6.05	4.06	3.29, 3.19	2.84, 2.49, 2.12
	33.9	7.77–7.22	6.30, 6.08	4.33	3.53, 3.27	2.94, 2.55, 2.17
	Total shift, ppm	0.30–0.17	0.06, 0.05	0.48	0.43, 0.17	0.13, 0.12, 0.10

[a] Overlapping signals.

7.50 Hz, 1 H) and 6.70–6.48 (m, 2 H)) compare closely to those of **33**-OCH_3.

An equally convincing case for the structural assignments can be made by comparison of ^{13}C chemical shift data in the four compounds (Table III). Thus, the aromatic carbons in **31**-OCH_3 resonate at positions (156.22, 151.53, 129.22, 126.06, 113.09, and 108.74 ppm) closely similar to those in **38**-OCH_3 (156.31, 152.70, 128.70, 127.47, 115.28, and 105.65 ppm). These chemical shifts differ meaningfully from those observed for **33**-OCH_3 (152.58, 144.73, 135.75, 127.20, 116.16, and 107.96 ppm) and **39**-OCH_3 (153.77, 143.46, 136.64, 127.83, 116.55, and 107.97 ppm) which, however, share an unquestionable commonality.

The triplet sensitized photoisomerization of **29** (E_T = 69–74 kcal/mol) afforded **38**-CN, **39**-CN, and **40**-CN in a ratio of 84:8:8. Preliminary chromatography of this mixture on alumina furnished in later fractions a mixture of unreacted **29** and **38**-CN. By subsequent elution of this pair of compounds through silver nitrate impregnated silica gel, **38**-CN was obtained in a pure state since **29** complexes readily with silver ion.[25] Rechromatography of the other alumina fractions on silica gel furnished fractions enriched in **39**-CN and **40**-CN. Finally, these components were separated by VPC on a 5% FFAP column.

The 90-MHz ^1H NMR spectra of **38**-CN and **39**-CN showed them to be benzosemibullvalene derivatives. However, the major photoproduct exhibits its benzylic absorption (δ 3.67) upfield of the analogous doublet in the minor di-π-methane isomer (3.85). Since a cyano group deshields adjacent protons, these data suggest that the substituent in **39**-CN is proximal to this proton and meta to the cyclopropane ring. Conversely, the cyano group in **38**-CN is ortho to the three-membered cycle. These conclusions were supported by $Eu(fod)_3$ studies as before (see Experimental Section).

The 90-MHz ^1H NMR spectrum of **40**-CN confirmed it to be a benzobasketene derivative. Significantly, the two benzylic protons in this compound are seen at δ 4.61 and 4.21, a finding which confirms the fact that the cyano group strongly deshields peri hydrogens of this type (in benzobasketene itself, these protons appear at δ 4.17).[26]

The ratio of benzo-vinyl to vinyl-vinyl bonding in **29** is therefore on the order of 11–12:1. This ratio, when compared to those observed in the *o*-methoxy derivative (3:1) and parent hydrocarbon (1.2:1), denotes again as in the meta series a predilection for electron-withdrawing substituents to concentrate excited state reactivity into the aromatic ring.

Discussion

Our observations indicate that triplet di-π-methane rearrangements of ortho-substituted benzonorbornadienes (and *anti*-7,8-benzotricyclo[4.2.2.$0^{2,5}$]deca-3,7,9-trienes) proceed with a high preference for benzo–vinyl bridging to the ortho position except for the fluoro example (50% ortho, 50% meta). This regioselectivity denotes a preference for electronic reorganization via intermediate biradical **30** rather than **32**. On the basis of ground state analogy, electron-withdrawing groups could be expected to preferentially stabilize **30**, since odd electron density could be dissipated by resonance. However, for donor substituents comparable stabilization is not expected.[27] Notwithstanding, the amino and methoxy derivatives give rise to extensive amounts of **31** (89 and 83%) and **38** (66%). We thus conclude that biradical stability is of little consequence in the initial bonding step.

It must again be emphasized that these di-π-methane rearrangements are two-step processes and that only the overall result is directly observable. Intermediates **30** and **32** can experience decay to ground state biradicals or bond breaking to deliver product. Once triplet decay has occurred, return to starting material would be the likely event.[28] That great differences would exist in the triplet decay rates of **30** and **32** is rather unlikely. This conclusion is founded simply on the fact that acceptor groups which can interact strongly with an odd electron as in **30** (but not **32**) and thereby facilitate the requisite spin inversion would on this basis direct chemical reactivity into the opposite channel. Yet only minor (when R = CN, NO_2) or vanishing quantities (when R = $COCH_3$) of **33** were in evidence.

On the other hand, the further conversion of **30** and **32** to products by bond relocation is expected to be only slightly exothermic because of the reestablishment of aromatic character. And if biradical stability were to have an influence here, **30** should react more slowly than **32** when R is electron withdrawing. But this is contrary to our experimental findings.

Accordingly, we again regard the relative rates of benzo-vinyl bridging to be the source of the observed regioselectivity,[1] as do Hahn and Johnson.[29] On this basis, it would appear that the prevailing electronic distributions to the triplet states of the substrates might control the relative rates of initial bond making. But electron densities at the ortho and meta positions of a monosubstituted aromatic triplet (as gleaned from available ESR data) are commonly closely balanced and therefore unreliable for predictive purposes.

Rather, the parallel regioselectivity noted for the ortho-substituted benzonorbornadienes can be phenomenologically accounted for in terms of frontier orbital polarization caused by the donor and acceptor groups. As discussed briefly elsewhere,[3] perturbation theory discloses that such a substitution plan causes not only a split in the degeneracy of the benzenoid HOMOs and LUMOs, but leads also to further mixing of higher orbitals into those at the frontier levels. The extent of this mixing is intimately related to the difference in the various orbital energies and is best unraveled by numerical calculation. The magnitude of the coefficients are, of course, directly affected by such mixing. The net result, namely, that LUMO (a_2*) polarization in acceptor cases and HOMO (b_1) polarization in donor examples serve to control regioselectivity, is seen to be promotion of ortho benzo–vinyl bridging in either case.[3] These conclusions have recently received additional

experimental support in the form of photoelectron spectral analysis.[30]

In summary, therefore, we can say that the first and decisive part of the bond-making process is dictated throughout by electron density considerations, with that carbon atom carrying the higher density (i.e., having the larger orbital coefficient) engaging the π electrons of the nearby nonconjugated double bond and engendering preferential reaction. Although the ordering of electron transmission to the different aryl carbons cannot always be estimated qualitatively (e.g., from ground state reactivity considerations), the present study constitutes an initial set of experimentally based guidelines, extrapolation from which may prove serviceable for other excited state processes.

As a final matter of interest, we see that decline of triplet energy localization in the aromatic portion of the *o*-methoxy compounds again results in a greater level of vinyl-vinyl bonding in **27** relative to nitrile **29**.

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.

2-Amino-6-methoxybenzonitrile (6). To a 5-L three-necked flask fitted with a thermometer, mechanical stirrer, and condenser were placed 1347 g of stannous chloride dihydrate and 2 L of concentrated hydrochloric acid. With external cooling, 263 g of **5**[4] was added portionwise so as to maintain the reaction temperature between 20 and 30 °C. The mixture was stirred for an additional 30 min at 25 °C before being heated to 65 °C while 500 mL of solvent was removed under reduced pressure. The solution was then cooled, made strongly basic with excess 40% sodium hydroxide solution, and continuously extracted with ether in a 10-L flask. There was obtained 186 g (85%) of **6**, mp 125–138 °C (lit.[5] mp 141 °C), which was used without further purification.

6-Methoxyanthranilic Acid (7). A mixture of unpurified **6** (186 g) and 20% sodium hydroxide solution (400 mL) was stirred at the reflux temperature for 3 days, filtered, and acidified to pH 4. The resulting tan precipitate was collected by filtration to give 74.6 g (35.6%) of **7**, mp 71–75 °C. This material was suitable for direct utilization in the benzyne generation step.

5-Methoxybenzonorbornadiene (8). Into a 1-L three-necked flask equipped with a mechanical stirrer, addition funnel, and condenser topped with a mineral oil bubbler were placed 100 mL of methylene chloride and 10.80 g (0.092 mol) of isoamyl nitrite. This solution was held at gentle reflux while a solution of **7** (14.0 g, 0.084 mol) and freshly cracked cyclopentadiene (70 g, 1.06 mol) in 60 mL of acetone was slowly introduced. The reaction mixture was heated at reflux overnight (12 h), cooled to 25 °C, filtered through a pad of Celite, and evaporated. The resulting brown oil upon distillation gave 7.82 g (54.2%) of **8**: bp 70 °C (0.02 mm); ν_{max} (neat) 3070, 2980, 2945, 2870, 2840, 1612, 1594, 1483, 1307, 1264, 1112, 1063, 811, 787, 757, 738, and 725 cm^{-1}; λ_{max} (cyclohexane) 285.5 nm (ϵ 1270), 282 sh (1260), 277.5 (1300), and 213 (23 000); δ_{Me_4Si} (CCl_4) 6.96–6.31 (m, 5), 4.16 (m, 1), 3.82 (m, 1), 3.74 (s, 3) and 2.18 (m, 2). The analytical sample was isolated by preparative VPC on column A[31] (150 °C).

Anal. Calcd for $C_{12}H_{12}O$: C, 83.69; H, 7.02. Found: C, 83.82; H, 7.25.

3-Iodonitrobenzene (11). A solution of **10** (100 g, 0.71 mol) in aqueous sulfuric acid (350 g of concentrated H_2SO_4 in 1 L of water) contained in a 2-L flask equipped with a mechanical stirrer was maintained at 5 °C in an ice–salt bath while sodium nitrite (51.7 g, 0.75 mol) dissolved in 110 mL of water was introduced by means of an addition funnel whose stem was immersed below the acid solution. The cold reaction mixture was then siphoned slowly into a cold (5 °C), mechanically stirred solution of potassium iodide (200 g, 1.21 mol) and iodine (200 g, 0.79 mol) in 200 mL of water contained in a 5-L flask. After 2 h at 5 °C, the resulting solution was allowed to stand overnight before heating on a steam bath for 30 min and cooling. The excess iodine was destroyed with sodium bisulfite solution before extraction with chloroform (500 and 100 mL). The combined extracts were filtered through a pad of Celite, washed with water, and evaporated. The crude product was crystallized from ethanol to give **11** as golden crystals, mp 34–35 °C. From two preparative runs (347.1 g of **10**), the combined yield of **11** was 445.7 g (71.2%).

3-Iodoaniline (12). To a cooled (20 °C) stirred solution of stannous chloride dihydrate (854.5 g), methanol (1460 mL), and concentrated hydrochloric acid (965 mL) was added portionwise 229.0 g (0.920 mol) of **11**. The mixture was stirred at ambient temperature for 8 h, freed of methanol by distillation below 45 °C at reduced pressure, and filtered to remove precipitated salts. After the addition of excess 40% sodium hydroxide solution, the liberated amine was steam distilled, and the crude distillate was extracted with ether (3 × 100 mL). The combined dried extracts were evaporated and fractionally distilled to give aniline (29.1 g, 34%), bp 49 °C (0.5 mm), and *m*-iodoaniline (**12**, 110.0 g, 55%), bp 122 °C (0.5 mm) (lit.[8] bp 142–143 °C (12 mm)).

***m*-Iodoisonitrosoacetanilide (13).** Into a 12-L three-necked flask equipped with a mechanical stirrer, thermometer, and condenser were placed, in order, 138.7 g (0.839 mol) of chloral hydrate, 1800 mL of water, 2 kg of sodium sulfate, a solution of **12** (168.4 g, 0.769 mol) in 3 L of water containing 66.4 mL of concentrated hydrochloric acid, and a solution of hydroxylamine hydrochloride (138.7 g) in 500 mL of water. This mixture was heated slowly to gentle reflux during 45 min and cooled rapidly to 0 °C. The tan-colored precipitate was filtered and air dried to give 204.6 g (91.8%) of **13**, mp 154–156 °C (lit.[9] mp 157 °C).

4-Iodoisatin (14). To 600 g of concentrated sulfuric acid heated to 50 °C was added with stirring 133 g (0.459 mol) of **13** in portions so that the temperature was maintained between 55 and 65 °C. An ice bath was used to assist in temperature moderation. The mixture was then heated to 80 °C for 10 min, cooled to 25 °C, poured onto 4 kg of crushed ice, and allowed to stand for 30 min. The resulting precipitate was filtered, washed well with water, dissolved in 2 N sodium hydroxide solution, filtered, and acidified with glacial acetic acid at 0 °C. The resulting red precipitate (80 g) was filtered and recrystallized from glacial acetic acid to give 59.1 g (47.2%) of pure **14**, mp 260 °C (lit.[10] mp 260 °C).

6-Iodoanthranilic Acid (16). To a mechanically stirred solution of **14** (59.1 g, 0.216 mol) in 1.5 N sodium hydroxide solution (500 mL) heated to 50 °C was added 30% hydrogen peroxide (54 mL) during 1 h (45–65 °C). After standing overnight at room temperature, the reaction mixture was carefully neutralized with 12 N hydrochloric acid, treated with charcoal, and filtered through a pad of Celite. The volume was reduced to 400 mL in vacuo and acidified to pH 4. The resulting precipitate was collected by filtration to give 37.1 g (65.2%) of **16**, mp 147–148 °C (lit.[9] mp 149 °C).

5-Iodobenzonorbornadiene (17). Treatment of **16** (10.84 g, 41.2 mmol) with isoamyl nitrite (5.35 g, 45.7 mmol) and cyclopentadiene (32.3 g, 0.489 mol) as predescribed gave 6.55 g (59.4%) of **17**, bp 90 °C (0.02 mm). An analytical sample was obtained by preparative VPC on column A[31] (155 °C): ν_{max} (neat) 2980, 2940, 1565, 1447, 1410, 1301, 1131, 1067, 883, 840, 785, 765, 752, and 716 cm^{-1}; δ_{Me_4Si} (CCl_4) 7.40–6.46 (m, 5), 4.02 (m, 2) and 2.27 (m, 2).

Anal. Calcd for $C_{11}H_9I$: C, 49.28; H, 3.38. Found: C, 49.27; H, 3.51.

5-Cyanobenzonorbornadiene (18). To a solution of **17** (5.38 g, 20 mmol) in dry dimethylformamide (40 mL) were added sodium cyanide (2.20 g, 45 mmol) and cuprous cyanide (3.95 g). The mixture was heated at reflux for 4 h with stirring, cooled, poured into saturated sodium cyanide solution (200 mL), covered with ether (200 mL), and stirred for 30 min. The organic phase was separated, washed with water (2 × 100 mL), dried, filtered, and evaporated. The residual oil was distilled to give 2.94 g (88%) of **18** which was further purified by preparative VPC on column A[31] (150 °C): ν_{max} (neat) 2985, 2940, 2235, 1465, 1419, 1304, 1226, 810, 790, 766, 740, and 725 cm^{-1}; λ_{max} (cyclohexane) 212 nm (ϵ 26 000), 284 (2060), and 292 (2160); δ_{Me_4Si} (CCl_4) 7.42–6.62 (m, 5), 4.07 (m, 1), 3.88 (m, 1), and 2.18 (m, 2).

Anal. Calcd for $C_{12}H_9N$: C, 86.20; H, 5.43. Found: C, 86.08; H, 5.54.

5-Acetylbenzonorbornadiene (19). To a refluxing solution of methylmagnesium iodide (prepared from 187 mg (7.70 mg-atoms) of magnesium and 1.084 g (7.64 mmol) of methyl iodide) in 20 mL of ether was added under nitrogen a solution of **18** (493 mg, 2.95

mmol) in 5 mL of anhydrous benzene. A further 10 mL of benzene was added and the ether was displaced in large part by distillation. The mixture was heated at reflux for 5 h, cooled, and treated carefully with 2 N hydrochloric acid (15 mL). Hydrolysis was effected by heating at the reflux temperature for 4 h. Cooling, separation of the layers, and extraction of the aqueous phase with ether (3 × 15 mL) gave a combined organic solution which was washed with an equal volume of water, dried, filtered, and evaporated. Molecular distillation of the residue at 110 °C (0.02 mm) and preparative VPC purification on column A[31] afforded 410 mg (75.7%) of **19**: ν_{max} (neat) 1679 cm^{-1}; δ_{Me_4Si} (CCl_4) 7.33-6.55 (m, 5), 4.74 (m, 1), 3.79 (m, 1), 2.44 (s, 3), and 2.20 (m, 2).

Anal. Calcd for $C_{13}H_{12}O$: C, 84.75; H, 6.57. Found: C, 84.60; H, 6.59.

6-Nitroanthranilic Acid (21). To a solution of **20** (9.6 g, 0.05 mol) in 1 N potassium hydroxide solution (50 mL) cooled to 5 °C was added an ice-cooled solution of bromine (2.5 mL, 0.05 mol) dissolved in 100 mL of 1 N potassium hydroxide followed by an additional 150 mL of the alkali. The mixture was heated with stirring on a steam bath for 80 min, cooled, and treated with 2 N hydrochloric acid (100 mL). After frothing had subsided, the precipitate was collected by filtration, washed with cold water, and dried in vacuo at 50 °C for 24 h: 7.8 g (85.7%), mp 176 °C (lit.[10] mp 180 °C).

5-Nitrobenzonorbornadiene (22). Treatment of **21** (18.2 g, 0.10 mol) with isoamyl nitrite (20.7 g, 0.177 mol) and cyclopentadiene (120 g, 1.82 mol) as before gave 10.8 g (57.8%) of **22**, bp 105 °C (0.1 mm), as a pale yellow liquid which solidified on standing. Repeated recrystallization (charcoal decolorization) from hexane gave pure **22**: mp 59.0-60.0 °C; ν_{max} (neat) 2965, 2935, 2860, 1582, 1520, 1450, 1351, 1303, 1227, 1217, 1200, 1166, 1160, 1139, 1048, 1007, 874, 815, 806, 761, 745, and 725 cm^{-1}; δ_{Me_4Si} (CCl_4) 7.72-6.71 (m, 5), 4.85 (m, 1), 3.96 (m, 1), and 2.31 (m, 2).

Anal. Calcd for $C_{11}H_9NO_2$: C, 70.58; H, 4.85. Found: C, 70.58; H, 4.88.

5-Aminobenzonorbornadiene (23). A solution of **22** (3.12 g, 16.7 mmol) in 15 mL of ethanol, 7 mL of water, and 40 mL of ether was treated with 3.60 g (0.133 g-atom) of freshly prepared aluminum amalgam under nitrogen. The 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 (72 °C, 0.01 mm) to give 2.39 g (91.2%) of 23: ν_{max} (neat) 3430, 3350, 3240, 2970, 2935, 1616, 1474, 1302, and 718 cm^{-1}; δ_{Me_4Si} ($CDCl_3$) 6.87-6.54 and 6.39-6.08 (m, 5), 3.78 (m, 2), 3.39 (s, 2), and 2.16 (m, 2); *m/e* 157.0894 (calcd, 157.0891).

Anal. Calcd for $C_{11}H_{11}N$: C, 84.04; H, 7.05. Found: C, 83.84; H, 7.05.

5-Fluorobenzonorbornadiene (24). To a stirred solution of **23** (1.157 g, 7.37 mmol) in 6 mL of tetrahydrofuran cooled to 0 °C with an ice-salt bath was added 2.6 mL of 50% fluoroboric acid dropwise, followed by 2.0 g of sodium fluoroborate. Benzene (5 mL) was introduced and sodium nitrite (622 mg, 9.01 mmol) dissolved in 3 mL of water was added during 15 min at 5 °C with continued stirring. A yellow precipitate which formed after addition of a few drops of this solution slowly decomposed with nitrogen evolution. After 15 min at 0 °C, cupric oxide powder (0.2 g) was added, the ice bath was removed, and the mixture was stirred at 25 °C for 12 h. The organic phase was separated and the aqueous layer was washed with ether (3 × 10 mL). The combined organic layers were washed with water (3 × 20 mL), dried, filtered, evaporated, and flash distilled into a trap cooled to −78 °C. Pure **24** was isolated from this transferred material by preparative VPC on column B;[31] yield 470 mg (39.8%); ν_{max} (neat) 2980, 2935, 1630, 1593, 1421, 1305, 1265, 1236, 971, 811, 784, 757, and 722 cm^{-1}; δ_{Me_4Si} (CCl_4) 6.95-6.39 (m, 5), 4.11 (m, 1), 3.81 (m, 1), and 2.20 (m, 2); *m/e* 160.0690 (calcd, 160.0688).

Anal. Calcd for $C_{11}H_9F$: C, 82.47; H, 5.66. Found: C, 82.54; H, 5.86.

3,4-Dichloro-11-methoxy-*anti*-7,8-benzotricyclo[4.2.2.0^{2,5}]-deca-7,9-diene (26a). A suspension of **7** (16.7 g, 0.10 mol) in absolute ethanol (200 mL) was cooled to 0 °C prior to addition of concentrated hydrochloric acid (10 mL) which precipitated the hydrochloride salt. Isoamyl nitrite (23.4 g, 0.199 mol) was added during 40 min to the stirred suspension maintained at −5 to 0 °C. Absolute ether (450 mL) was added to the dark red solution, and it was stirred at the same temperature for an additional 1 h. The rust-colored diazonium carboxylate was filtered, washed with ether (4 × 50 mL), and air dried for 10 min.

This salt (18.0 g, 84.2%) was added to a stirred mixture of **25** (33.78 g, 0.194 mol) and propylene oxide (12.89 g, 0.222 mol) in 1,2-dichloroethane (400 mL) which was heated at reflux for 4 h. Solvent removal in vacuo left a viscous black oil which was subjected to chromatography on alumina. Elution with dichloromethane (5 → 60%) in petroleum ether gave 9.85 g (35.1%) of **26a** as a colorless oil which partially crystallized on standing. The crystalline isomer was obtained as a white solid: mp 111.5-113 °C (from ethanol); ν_{max} ($CHCl_3$) 2945, 2845, 1588, 1467, 1087, 996, and 897 cm^{-1}; δ_{Me_4Si} ($CDCl_3$) 7.24-6.56 (m, 5), 4.66 (m, 1), 4.11 (m, 3), 3.80 (s, 3), and 2.74 (m, 2).

Anal. Calcd for $C_{15}H_{14}Cl_2O$: C, 64.07; H, 5.06. Found: C, 64.30; H, 5.06.

11-Methoxy-*anti*-7,8-benzotricyclo[4.2.2.0^{2,5}]deca-3,7,9-triene (27). Into a solution of sodium naphthalenide (from 1.72 g of sodium and 9.60 g of naphthalene) in 100 mL of tetrahydrofuran cooled to 0 °C was introduced 7.02 g (25.0 mmol) of **26a** dissolved in 50 mL of the same solvent during 15 min. The ice bath was removed and the mixture was stirred for 30 min before the addition of water to discharge the dark green color. The reaction mixture was filtered, evaporated, and chromatographed on alumina. Elution with hexane-ether (98:2) gave a group of fractions, rechromatography of which under the same conditions gave 4.23 g (80%) of **27**: mp 48.5-49.5 °C (from ethanol); ν_{max} ($CHCl_3$) 2930, 2842, 1589, 1467, 1304, 1085, 999, and 969 cm^{-1}; δ_{Me_4Si} ($CDCl_3$) 7.22-6.53 (m, 3), 6.20 (m, 2), 6.04 (m, 2), 4.27 (m, 1), 3.92-3.62 (m, 1), 3.77 (s, 3), and 2.62 (m, 2).

Anal. Calcd for $C_{15}H_{14}O$: C, 85.68; H, 6.71. Found: C, 85.77; H, 6.61.

3,4-Dichloro-11-iodo-*anti*-7,8-benzotricyclo[4.2.2.0^{2,5}]deca-7,9-diene (26b). A 51.5-g (0.196 mol) sample of **16** was treated in the above manner with 23.6 mL of concentrated hydrochloric acid, 53.0 g (0.454 mol) of isoamyl nitrite, 34.5 g (0.020 mol) of **25**, and 46.4 g (0.80 mol) of propylene oxide. Chromatography of the resulting dark brown oil on alumina (including rechromatography of satellite fractions) gave 38.3 g (51.8%) of **26b** based upon **16**. The white, crystalline solid melted at 135-137 °C; δ_{max} (CCl_4) 3060, 2965, 1446, 1428, 1172, 1155, 1120, 877, and 670 cm^{-1}; δ_{Me_4Si} ($CDCl_3$) 7.68-6.54 (m, 5), 4.64-4.32 (m, 1), 4.13-3.93 (m, 3), and 2.85-2.58 (m, 2).

Anal. Calcd for $C_{14}H_{11}Cl_2I$: C, 44.60; H, 2.92. Found: C, 44.59; H, 3.05.

3,4-Dichloro-11-cyano-*anti*-7,8-benzotricyclo[4.2.2.0^{2,5}]deca-7,9-diene (28). A mixture of **26b** (27.08 g, 0.073 mol), cuprous cyanide (13.1 g, 0.146 mol), and sodium cyanide (7.15 g, 0.146 mol) in freshly distilled dry dimethylformamide (360 mL) was refluxed with stirring under nitrogen for 8 h. The dark reaction mixture was cooled and transferred to a separatory funnel with 500 mL of saturated sodium cyanide solution and 1 L of ether. The layers were separated and the aqueous phase extracted with ether (3 × 200 mL) prior to washing of the combined ether layers with water (2 × 300 mL) and brine (3 × 250 mL). The dried solution was evaporated and the residue (19.43 g) recrystallized from chloroform-ethanol to give 6.78 g of **28**, mp 172-173 °C. The mother liquors, when subjected to chromatography on alumina (elution with benzene-ether mixtures), afforded an additional 12.20 g of the oily lower melting isomers of the cyano dichloride which partially crystallized on standing (total 18.98 g, 95%). The crystalline isomer was sublimed at 93 °C (0.05 mm) before analysis: mp 172-173 °C; ν_{max} ($CHCl_3$) 2228, 1350, 952, and 897 cm^{-1}; δ_{Me_4Si} ($CDCl_3$) 7.53-7.02 (m, 3), 6.87-6.59 (m, 2), 4.87-4.50 (m, 1), 4.40-4.00 (m, 3), and 2.92-2.63 (m, 2).

Anal. Calcd for $C_{15}H_{11}Cl_2N$: C, 65.22; H, 3.99; N, 5.07. Found: C, 65.11; H, 4.00; N, 4.78.

11-Cyano-*anti*-7,8-benzotricyclo[4.2.2.0^{2,5}]deca-3,7,9-triene (29). Reaction of **28** (2.01 g, 7.3 mmol) with sodium naphthalenide (from 0.50 g of sodium and 2.80 g of naphthalene) in dry tetrahydrofuran (total of 130 mL) under nitrogen for 4.5 h, followed by the predescribed workup and alumina chromatography (elution with 1 → 80% dichloromethane in petroleum ether), separated naphthalenic materials from a dark yellow oil. This crude product was rechromatographed on silica gel (elution with 1% ether in pentane) to give 1.06 g of **29** as a light yellow oil which crystallized on standing. Recrystallization from hexane and hexane-benzene (4:1) furnished 0.50 g (33%) of colorless, crystalline solid: mp 82.5-83.5 °C; ν_{max} (CCl_4) 3050, 2942, 225, 1438, 1402, 1349, 1290, and 1166 cm^{-1}; λ_{max} (cy-

clohexane) 216 nm (ε 11 240), 277 (2190), and 287 (2485); δ_{Me_4Si} ($CDCl_3$) 7.55–6.96 (m, 3), 6.23 (m, 2), 6.06 (s, 2), 4.25 (m, 1), 3.87 (m, 1), and 2.63 (m, 2).

Anal. Calcd for $C_{15}H_{11}N$: C, 87.80; H, 5.36. Found: C, 87.65; H, 5.38.

Generalized Sensitized Photoisomerizations of Benzonorbornadienes. The procedure described in the preceding paper[1] was followed in this study.

Irradiation of 8. A solution of **8** (460 mg, 2.67 mmol) and acetophenone (587 mg, 3.75 mmol) in benzene (400 mL) was irradiated through Pyrex under nitrogen with a bank of 3500 Å lamps in a Rayonet reactor for 2 h. VPC analysis on column C[31] showed two products to be present in a ratio of 89.3:10.7. The solvent was evaporated, the residue was chromatographed on silica gel (petroleum ether elution) to remove the sensitizer, and the eluate was separated into its two components on column D[31] (150 °C). Major component **31**-OCH_3, isolated in 53% yield, solidified: mp 38.5–39.0 °C (from hexane); ν_{max} (neat) 3040, 2990, 2950, 2925, 2855, 2835, 1609, 1588, 1481, 1283, 1260, 1092, and 757 cm^{-1}; δ_{Me_4Si} (CCl_4) 6.97–6.44 (m, 3), 3.82 (s, 3), 3.24 (m, 2), 2.79 (m, 2), 1.98 (m, 1), and 0.81 (m, 1).

Anal. Calcd for $C_{12}H_{12}O$: C, 83.69; H, 7.02. Found: C, 83.64; H, 7.02.

Minor component **33**-OCH_3, isolated pure in 0.83% yield after repeated passes through column D,[31] was a colorless liquid: δ_{Me_4Si} (CCl_4) 6.97–6.34 (m, 3), 3.66 (s, 3), 3.51 (m, 1), 3.12 (m, 1), 2.76 (m, 1), 2.38 (m, 1), 1.88 (m, 1), and 0.68 (m, 1); *m/e* 172.0891 (calcd, 172.0888).

General Procedure for Eu(III) LIS Studies. Recourse was made to the dilution technique of Shapiro and Johnston.[32] A stock solution of **31**-OCH_3 (205 mg, 1.19 mmol) in 2.0 mL of carbon tetrachloride containing 5% (v/v) Me_4Si was prepared. Two hundred microliters of this solution was transferred via syringe to a dried, thin-walled 5-mm o.d. ^1H NMR tube into which had been placed 53.1 mg (0.051 mmol) of Eu(fod)$_3$. After recording of the 100-MHz spectrum, an additional 100 μL of stock solution was added, and so on to 1200 μL. Two hundred microliters of this solution was then transferred to a second tube containing 156.4 mg (0.151 mmol) of Eu(fod)$_3$, and the process was repeated using 50-μL aliquots of the first Eu(III)-containing solution. The results are plotted in Figure 1.

Preparative Scale Irradiation of 18. A solution of **18** (1.063 g, 6.36 mmol) and acetophenone (771 mg, 6.42 mmol) in benzene (130 mL) was irradiated as above for 4 h. VPC analysis indicated that two products were present in a 24:1 ratio. The solvent was evaporated, the residual oil was molecularly distilled (90 °C, 0.05 mm), and the distillate was subjected to high-pressure liquid chromatography (HPLC) on silica gel (elution with 85% hexane–10% ether–5% benzene). The fractions containing pure major component were again distilled (90 °C, 0.05 mm) to give 747 mg (70.3%) of **31**-CN: ν_{max} (neat) 3050, 2975, 2925, 2860, 2230, 1469, 1438, 1308, 1277, 1247, 1224, 1210, 1171, 1160, 1039, 980, 945, 898, 844, 802, 758, and 693 cm^{-1}; δ_{Me_4Si} (CCl_4) 7.48–6.96 (m, 3), 3.45 (m, 2), 3.15–2.72 (m, 2), 2.18 (m, 1), and 0.75 (m, 1).

Anal. Calcd for $C_{12}H_9N$: C, 86.20; H, 5.43. Found: C, 86.37; H, 5.59.

The fractions enriched in the minor component were combined and subjected to preparative VPC on column E[31] (155 °C). The 11 mg of pure **33**-CN so obtained exhibited the following properties: ν_{max} (neat) 3055, 2925, 2860, 2235, 1470, 1438, 1314, 1269, 1245, 1163, 1028, 990, 954, 823, 802, 773, and 754 cm^{-1}; δ_{Me_4Si} (CCl_4) 7.59–6.93 (m, 3), 3.62 (m, 1), 3.30 (m, 1), 2.95 (m, 1), 2.55 (m, 1), 2.03 (m, 1), and 0.75 (m, 1); *m/e* 167.0738 (calcd, 167.0735).

Spin decoupling studies on **31**-CN subsequent to the addition of Eu(fod)$_3$ elucidated the following coupling constants: $J_{3,5endo} = 2.5$; $J_{5exo,5endo} = 9.0$; $J_{5exo,6} = 8.0$; $J_{4,5exo} = 3.0$; $J_{2,3} = 4.7$; $J_{2,4} = 4.7$; $J_{3,6} = 3.0$; and $J_{4,6} = 2.5$ Hz.

11-Acetyltetracyclo[5.4.0.0^{2,4}.0^{3,6}]undeca-1(7),8,10-triene (31-$COCH_3$). To a stirred solution of methylmagnesium iodide (from 367 mg (15.1 mg-atoms) of magnesium and 2.20 g (15.5 mmol) of methyl iodide) in 20 mL of anhydrous ether was added under nitrogen a solution of **31**-CN (1.10 g, 6.58 mmol) in 20 mL of dry benzene. Most of the ether was displaced by heating and the residual solution was heated at reflux for 3.5 h. After being cooled to 0 °C, the mixture was treated dropwise with 2 N hydrochloric acid (30 mL) and heated again at reflux for 1.25 h. The layers were separated and the aqueous layer extracted with ether (3 × 50 mL). The combined organic phases were washed with water (75 mL) and dilute sodium bicarbonate solution (75 mL) prior to drying, filtration, and evaporation. Distillation of the residue gave 918 mg (75.5%) of **31**-$COCH_3$: bp 71 °C (0.3 mm); ν_{max} (neat) 3045, 2925, 2860, 1678, 1581, 1432, 1355, 1260, 1240, 1125, and 766 cm^{-1}; δ_{Me_4Si} (CCl_4) 7.61–6.90 (m, 3), 3.49 (m, 1), 3.26 (m, 2), 2.81 (m, 1), 2.54 (s, 3), 2.09 (m, 1), and 0.72 (m, 1); *m/e* 184.0891 (calcd, 184.0888).

Anal. Calcd for $C_{13}H_{12}O$: C, 84.75; H, 6.57. Found: C, 84.82; H, 6.68.

11-Acetoxytetracyclo[5.4.0.0^{2,4}.0^{3,6}]undeca-1(7),8,10-triene (31-OAc). A solution of **31**-$COCH_3$ (801 mg, 4.35 mmol) and *m*-chloroperbenzoic acid (1.58 g, 9.16 mmol) in chloroform (75 mL) was stirred at 30 °C for 6 days. The solvent was evaporated and the residue was taken up in ether (75 mL) before washing with saturated sodium bicarbonate solution (3 × 100 mL) and water (equal volume). The ether solution was dried, filtered, and evaporated to leave a waxy solid (830 mg) which was purified by preparative VPC on column A.[31] Pure **31**-OAc exhibited mp 73 °C; ν_{max} (film) 1765, 1588, 1470, 1369, 1242, 1214, 1202, and 1162 cm^{-1}; δ_{Me_4Si} (CCl_4) 7.06–6.05 (m, 3), 3.41–3.01 (m, 2), 2.75 (m, 1), 2.37 (m, 1), 2.17 (s, 3), 1.93 (m, 1), and 0.76 (m, 1); *m/e* 200.0839 (calcd, 200.0837).

11-Hydroxytetracyclo[5.4.0.0^{2,4}.0^{3,6}]undeca-1(7),8,10-triene (31-OH). A solution of **31**-OAc (740 mg) 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 ether (10 mL), and treated with excess 2 N hydrochloric acid. The organic phase was separated and the aqueous layer extracted with ether (3 × 5 mL). The combined ether portions were washed with water (15 mL), dried, filtered, and evaporated. Distillation at 100 °C (0.01 mm) gave 332 mg (57%) of **31**-OH: ν_{max} (neat) 3360, 3045, 2990, 2960, 2925, 2860, 1592, 1482, 1465, 1276, 1241, 1215, 1195, 1155, 1073, 937, and 760 cm^{-1}; δ_{Me_4Si} ($CDCl_3$) 7.04–6.43 (m, 3), 5.24 (s, 1), 3.48–2.95 (m, 2), 2.95–2.47 (m, 2), 1.96 (m, 1), and 0.72 (m, 1); *m/e* 158.0734 (calcd, 158.0732).

Methylation of 31-OH. To a stirred solution of **31**-OH (1.00 g, 0.63 mmol) in 10 mL of 1 N potassium hydroxide was added 1 mL of dimethyl sulfate. The reaction mixture was stirred at ambient temperature for 6 h and extracted with ether (2 × 15 mL). The combined organic layers were washed with water (10 mL), dried, filtered, and evaporated. The residual oil was purified by preparative VPC on column A[31] to give 866 mg (79.5%) of **31**-OCH_3 which proved identical in all respects with the major photoproduct from **8**.

Irradiation of 5-Acetylbenzonorbornadiene (19). A solution of **19** (33.9 mg, 0.18 mmol) and dodecane (24.2 mg) in 10 mL of benzene was irradiated under nitrogen at 3500 Å through Pyrex for 1.67 h. Progress of the reaction was as usual followed by VPC. Only one product was observed after complete disappearance of **19**. This product was isolated by preparative VPC on column A[31] to give 22.6 mg (67%) of **31**-$COCH_3$ indistinguishable from the ketone prepared above.

Preparative Scale Photoisomerization of 22. A stirred solution of **22** (2.65 g, 14.2 mmol) and acetophenone (3.40 g, 28.3 mmol) in benzene (600 mL) contained in a Pyrex vessel was sparged with nitrogen for 30 min and irradiated with 3500 Å lamps in a Rayonet reactor. VPC analysis showed formation of three products in a 91.5:0.5:8 ratio after 37 h. The solvent was evaporated and the sensitizer removed by elution through silica gel with ether–benzene (1:1). The oily eluate was subjected to HPLC on silica gel using 5% ether in hexane as solvent. Fractions containing the major photoproduct were combined, evaporated, and molecularly distilled (72 °C, 0.02 mm) to give 1.07 g (40.4%) of **31**-NO_2: mp 53.0–53.5 °C; ν_{max} (film) 3050, 2990, 2965, 2930, 2865, 1620, 1583, 1522, 1407, 1348, 1310, and 1243 cm^{-1}; δ_{Me_4Si} (CCl_4) 8.02–7.64 and 7.30–6.93 (m, 3), 3.61–3.17 (m, 3), 2.90 (m, 1), 2.18 (m, 1), and 0.72 (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, 70.51; H, 4.88.

Control Experiments Concerning Lability of 31-NO_2 to 3500-Å Light. A. Without Sensitizer. A solution of **31**-NO_2 (33.7 mg) and *n*-tetradecane (25.5 mg) in 10 mL of benzene was irradiated in the usual fashion. After 13.5 h, only 75.4% of starting material remained. This was accompanied by ca. 8% of the second major photoproduct seen during photoisomerization of **22**. The solution had become dark and opaque.

B. Acetophenone Sensitization. A solution of **31**-NO_2 (34.3 mg), acetophenone (26.5 mg), and *n*-tetradecane (22.8 mg) in 10 mL of

benzene was irradiated as above for 13.5 h. At this point, 83.7% of **31**-NO_2 remained and ca. 6% of the secondary photoproduct had formed. Again, the solution had become brown and opaque. No attempt was made in either experiment to characterize the new substance.

11-Aminotetracyclo[5.4.0.0^{2,4}.0^{3,6}]undeca-1(7),8,10-triene (31-NH_2). A. By Photoisomerization of 23. A solution of **23** (602 mg, 3.83 mmol) and acetophenone (1.06 g, 8.84 mmol) in 150 mL of benzene was prepared and irradiated as before for 40 h. At this point, VPC analysis on column C[31] (170 °C) indicated almost complete conversion to two photoproducts in an 82.6:17.4 ratio. The volume of solution was reduced to 30 mL and the amines were extracted into 1 N hydrochloric acid (3 × 50 mL). The combined acidic layers were extracted with ether (2 × 50 mL), basified with 20% potassium hydroxide solution, and reextracted with ether (3 × 40 mL). The latter extracts were washed with water, dried, filtered, and evaporated. The residue was molecularly distilled (85 °C, 0.01 mm) to give 470 mg (78%) of a mixture of two amines. A sample of the major component could be obtained in pure form by preparative VPC on column F[31] (155 °C): ν_{max} (neat) 3440, 3360, 3215, 3040, 2985, 2980, 2915, 1617, 1594, 1478, 1295, and 1239 cm^{-1}; δ_{Me_4Si} ($CDCl_3$) 7.03–6.30 (m, 3), 3.54 (s, 2), 3.37–2.90 (m, 2), 2.73 (m, 1), 2.27 (m, 1), 1.92 (m, 1), and 0.69 (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, 83.84; H, 7.22.

The minor component could not be isolated in this manner, but satisfactory ^{13}C data could be obtained from the mixture of two amines. It should be noted that the ratio of the major and minor components as assessed by VPC was identical with the value (82.75:17.25) determined by measurement of the averaged intensities of the aliphatic carbon resonances.

B. By Reduction of 31-NO_2. The aluminum amalgam reduction utilized to prepare **23** was employed to convert 436 mg (2.33 mmol) of **31**-NO_2 into 342 mg (93.4%) of **31**-NH_2 after distillation at 90 °C (0.02 mm). The two samples of this amine were identical in all respects.

Sensitized Irradiation of 24. A solution of **24** (283 mg, 1.76 mmol) and acetophenone (293 mg, 2.42 mmol) in benzene (50 mL) was prepared and irradiated in the usual fashion at 3500 Å through Pyrex for 1 h. VPC analysis on column C[31] indicated the absence of any starting material and the presence of two new components in a 1:1 ratio. All attempts to separate these isomers on a preparative scale were unsuccessful. The mixture of **31**-F and **33**-F was isolated in 87.5% yield by preparative VPC on column B:[31] δ_{Me_4Si} (CCl_4) 7.11–6.52 (m, 3), 3.53 (m, 0.5), 3.20 (m, 1.5), 2.59–2.94 (m, 1.5), 2.46 (m, 0.5), 1.93 (m, 1), and 0.74 (m, 1). Compare the spectrum of pure **31**-F described below.

11-Fluorotetracyclo[5.4.0.0^{2,4}.0^{3,6}]undeca-1(7),8,10-triene (31-F). A 710-mg (4.52 mmol) sample of **31**-NH_2 dissolved in 10 mL of tetrahydrofuran and 10 mL of benzene was treated with 2.0 mL of 50% fluoroboric acid solution and 1.5 g (13.7 mmol) of sodium fluoroborate. This mixture was cooled to 0 °C and solid sodium nitrite (390 mg, 5.65 mmol) was slowly added with stirring. The contents were held at 0 °C for 1 h and then stirred at 35 °C for 12 h. Water (50 mL) was added, the organic phase was separated, and the aqueous phase was extracted with ether (2 × 20 mL). The combined organic layers were washed with water (3 × 50 mL), dried, filtered, and carefully evaporated. VPC analysis of the resudie on column C[31] revealed the presence of **31**-F and parent hydrocarbon in approximately equal amounts. The desired **31**-F was isolated in 37.5% yield by preparative VPC on column D:[31] ν_{max} (neat) 3065, 3055, 2995, 2970, 2935, 2865, 1629, 1588, 1477, 1288, 1278, 1248, 1238, 1168, 1076, 1045, 991, 939, 913, 800, and 758 cm^{-1}; δ_{Me_4Si} (CCl_4) 7.03–6.59 (m, 3), 3.25 (m, 2), 2.78 (m, 1), 2.66 (m, 1), 1.98 (m, 1), and 0.74 (m, 1); *m/e* 160.0691 (calcd, 160.0688).

Anal. Calcd for $C_{11}H_9F$: C, 82.47; H, 5.66. Found: C, 82.37; H, 5.68.

Sensitized Irradiation of 27. A solution of **27** (640 mg) and acetophenone (640 mg) in benzene (160 mL) was deoxygenated by bubbling nitrogen through the solution for 1 h and irradiated as predescribed for 5.5 h. A portion of the resulting mixture was subjected to preparative VPC on column G[31] (180 °C). There was collected 3.3 mg of unreacted **27**, 21.6 mg of a mixture of **38**-OCH_3 and **39**-OCH_3 (solid, mp 57–60 °C), and 8.0 mg of **40**-OCH_3 (oil). The 90-MHz ^1H NMR spectrum of the solid showed it to consist of a major and minor component (previously unrecognized on all VPC columns employed).

The reaction mixtures from four such irradiations were combined and this yellow oil was chromatographed on alumina. Elution with ether (1%) in petroleum ether afforded 1.95 g of mixture free of sensitizer. Rechromatography on alumina as before gave 970 mg of an oily mixture of unreacted **27**, **38**-OCH_3, **39**-OCH_3, and **40**-OCH_3, together with 870 mg of a two-component mixture containing only **27** and **38**-OCH_3. The first of these fractions was again subjected to alumina chromatography as before. Under these conditions, a pure sample of **40**-OCH_3 was obtained (190 mg) as a colorless, crystalline solid: mp 92–93 °C (from hexane); ν_{max} (CCl_4) 2970, 1478, 1335, 1294, 1259, 1172, and 1097 cm^{-1}; δ_{Me_4Si} ($CDCl_3$) 7.28–6.64 (m, 3), 4.64 (m, 1), 4.08 (m, 1), 3.78 (s, 3), 3.37 (m, 2), and 2.94 (m, 4).

Anal. Calcd for $C_{15}H_{14}O$: C, 85.68; H, 6.71. Found: C, 85.84; H, 6.78.

Fractions 28–39 of the first chromatography, fractions 30–46 from the second chromatography, and fractions 45–54 from the third were combined to give 1.54 g of a mixture containing very little **40**-OCH_3. Chromatography on silica gel impregnated with silver nitrate (10%) and elution with 1% ether in petroleum ether returned 880 mg of **38**-OCH_3 as a colorless solid: mp 64–65.5 °C (from hexane); ν_{max} (CCl_4) 3044, 2939, 1482, 1467, 1280, 1258, and 1083 cm^{-1}; δ_{Me_4Si} ($CDCl_3$) 7.23–6.53 (m, 3), 6.22 (d, J = 3 Hz, 1), 5.97 (m, 1), 3.83 (s, 3), 3.57 (d, J = 4.5 Hz, 1), 3.14 (m, 1), 2.99 (d, J = 3 Hz, 1), 2.78–2.41 (m, 2), and 2.04 (dd, J = 7.5 and 6 Hz, 1).

Anal. Calcd for $C_{15}H_{14}O$: C, 85.68; H, 6.71. Found: C, 85.69; H, 6.74.

Fractions 41–44 from the third alumina chromatography were combined with the mother liquors from recrystallization of **38**-OCH_3 (total 280 mg). Preparative VPC separation on column H[31] (180 °C) led to collection of 35 mg of **39**-OCH_3 (colorless oil), 9.3 mg of *o*-methoxybenzosnoutene (colorless solid, mp 120.5–122 °C), and 36 mg of a mixture of the snoutene and **40**-OCH_3.

For **39**-OCH_3: ν_{max} (CCl_4) 3031, 2932, 2833, 1473, 1465, 1438, 1310, 1276, 1255, 1114, 1078, and 665 cm^{-1}; δ_{Me_4Si} ($CDCl_3$) 7.20–6.77 (m, 2), 6.70–6.57 (d with additional splitting, J = 8.25 Hz, 1), 6.26 (d, J = 2.25 Hz, 1), 6.05 (m, 1), 3.78 (s, 3), 3.72 (d, J = 5.25 Hz, 1), 3.08 (br s, 2), 2.65 (dd, J = 12.0 and 6.0 Hz, 1), 2.36 (dd, J = 7.50 and 6.45 Hz, 1), and 1.96 (dd, J = 9.0 and 6.75 Hz, 1); *m/e* 210.1048 (calcd, 210.1045).

For the *o*-methoxybenzosnoutene: δ_{Me_4Si} ($CDCl_3$) 7.24–6.69 (m, 3), 4.12 (m, 1), 3.85 (s, 3), 3.60 (m, 1), 2.32 (m, 2), and 1.67 (m, 4).

Photoisomerization of 29. In a typical run, a solution of **29** (617 mg) and acetophenone (308 mg) in benzene (155 mL) was prepared and irradiated in the usual fashion for 3 h. The product mixtures from two such runs (1.01 g) were chromatographed on alumina (elution with 5% ether in petroleum ether). Fractions 33–62 (0.57 g) (containing 66% of **29**, 24% of **38**-CN, and 10% of **39**-CN) were rechromatographed on silica gel impregnated wih silver nitrate (10%). Elution with ether (1 → 10%) in petroleum ether gave several fractions containing only **38**-CN (95%) and **39**-CN (5%) (300 mg, oil) and other fractions containing essentially pure **29** (210 mg). The oil was sublimed to give a white solid, mp 38–40 °C, recrystallization of which from hexane–benzene (9:1) gave pure **38**-CN: mp 50–52 °C; ν_{max} (CCl_4) 3050, 2940, 2238, 1471, 1448, 1295, 1284, 1186, 1151, and 669 cm^{-1}; δ_{Me_4Si} ($CDCl_3$) 7.38–7.09 (m, 3), 6.25 (d, J = 3 Hz, 1), 5.98 (m, 1), 3.67 (d, J = 5 Hz, 1); 3.18 (br s, 1), 2.98–2.53 (m, 3), and 2.18 (dd, J = 8 and 6 Hz, 1)

Anal. Calcd for $C_{15}H_{11}N$: C, 87.80; H, 5.36. Found: C, 87.65; H, 5.38.

Fractions 18–32 of the original alumina chromatography (150 mg) were rechromatographed on silica gel (elution with 2% benzene in petroleum ether). Fractions 16–23 obtained in this manner (110 mg) were rechromatographed on silica gel under identical conditions. This led to an oil (49 mg) highly enriched with respect to **39**-CN and **40**-CN. Preparative scale VPC of this mixture on column E[31] (190 °C) gave 13 mg of **39**-CN and 11.4 mg of **40**-CN.

For **39**-CN, a colorless oil: ν_{max} (CCl_4) 3055, 2945, 2239, 1471, 1447, 1298, 1285, 1184, 1150, 684, and 666 cm^{-1}; δ_{Me_4Si} ($CDCl_3$) 7.47–7.05 (m, 3), 6.24 (d, J = 5 Hz, 1), 6.06–6.0 (m, 1), 3.84 (d, J = 5 Hz, 1), 3.10 (br s, 2), 2.81 (dd, J = 12 and 6 Hz, 1), 2.43 (dd, J = 8 and 6 Hz, 1), and 2.07 (dd, J = 8 and 7 Hz, 1); *m/e* 205.089 (calcd, 205.089).

For **40**-CN, a colorless solid: mp 109–112 °C; ν_{max} (CCl_4) 2980, 2239, 1457, 1346, 1266, 1194, 1176, and 947 cm^{-1}; δ_{Me_4Si} ($CDCl_3$)

7.62-7.21 (m, 3), 4.61 (m, 1), 4.21 (m, 1), 3.49 (m, 2), and 2.98 (m, 4); *m/e* 205.089 (calcd, 205.089).

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Spectroscopy of Radical Cations. The McLafferty Rearrangement Product in Fragmentation of *n*-Butylbenzene and 2-Phenylethanol Ions

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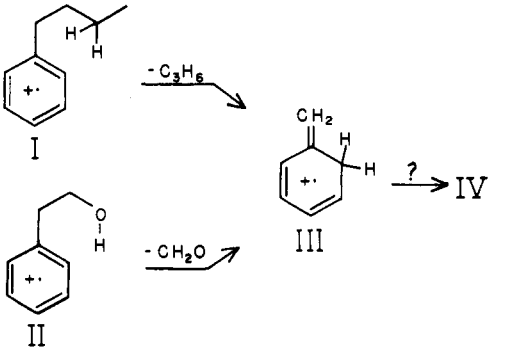
Abstract: Photodissociation spectroscopy was applied to the question of the structure of the ultimate *m/e* 92 ion resulting from fragmentation of *n*-butylbenzene and 2-phenylethanol parent ions. Identical spectra were obtained for *m/e* 92 derived from these two precursors, and ruled out either the toluene or cycloheptatriene structure. Exhaustive photodissociation using the time-resolved photodissociation method indicated that the *m/e* 92 population consisted of at least 75% of a single structure, and that the fragmentations to give *m/e* 92 yield less than 10% of the toluene structure and less than 20% of the cycloheptatriene structure. Comparison with theory and with the known 1,3,5-hexatriene spectrum was consistent with and suggestive of retention of the methylenecyclohexadiene structure predicted by the McLafferty fragmentation mechanism.

Optical spectroscopy of gas-phase ions can be conveniently investigated taking advantage of the fragmentation processes which frequently follow photon absorption. This approach has been termed photodissociation spectroscopy, and has proven to be of value in determining structures of gas-phase ions[1] and in elucidating electronic properties of radical cations.[1,2] The obvious possibilities of this technique for spectroscopic study of interesting ions resulting from rearrangement fragmentation of larger parent ions have as yet not been pursued, and the present experiments were undertaken to bring this approach to bear on the product ion of one such electron impact induced fragmentation reaction.

The McLafferty rearrangement process yielding $C_7H_8^+$ from *n*-butylbenzene (I) and 2-phenylethanol (II) parent ions is well understood in principle.[3,4] The McLafferty mechanism



leads to the initial formation of III. An abundance of evidence (recently summarized by Levsen, McLafferty, and Jerina[4]) indicates that the rearrangement does follow this path, and it may be assumed without much question that III is formed

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