Triplet-State Benzonorbornadiene Di-π-methane Photorearrangements. Competition between Bridgehead and Vinyl Substituents for Control of the Product-Determining 1,2-Aryl Shift Step

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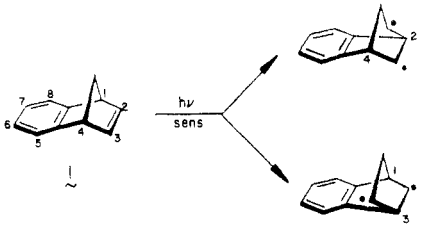
A group of four 1,2-disubstituted benzonorbornadienes has been synthesized and subjected to triplet-sensitized di-π-methane photoisomerization. Comparison has also been made with the excited-state behavior of the 1-bromo-3-methyl derivative. In the 1,2-dimethyl and 1,2-bis(trimethylsilyl) derivatives, both of the available reaction channels are utilized to a comparable extent, thereby signaling that bridgehead Me and Me_3Si substituents are capable of essentially leveling the otherwise strong directive effect of their vinylic counterparts. Bridgehead cyano substitution overwhelms any potential contribution of a vinyl methyl group. When bromine occupies the bridgehead site, the impact of 2- or 3-methyl substitution is clearly additive. These observations are discussed in the context of the mechanistic details of the rearrangement.

A fundamental property of benzonorbornadienes relates to the pair of competitive 1,2-aryl migrations that materialize upon triplet-state photoexcitation. The symmetry of the parent hydrocarbon (1) ensures that its two possible isomerizations are enantiomerically related and hence isoenergetic.[2] However, monosubstitution of any position not in the symmetry plane, viz., C-1 to C-8, makes possible direct evaluation of the capabilities of that group to control the regioselectivity of the rebonding process.

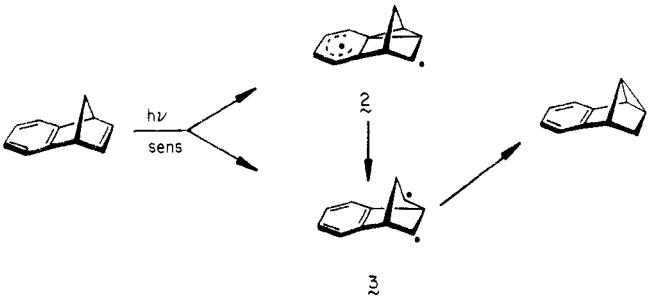


1

Extensive studies by Paquette and co-workers of this class of compounds have revealed a number of pronounced excited-state substituent effects. For example, reaction of systems with C-5 aryl substitution is recognized to proceed exclusively by utilization of the ortho carbon atom irrespective of the electronic character of R.[3] In contrast, the ultimate fate of substrates carrying the R group at C-6 is inextricably linked to the electron-acceptor (migration of the para carbon) or electron-donor characteristics (predominant meta carbon shift) of the substituent.[4] When a bridgehead site is occupied, migration of the proximal aryl center is strongly favored in all cases except when R is bromine (heavy atom effect) or deuterium (isotopic control).[5] A cyano[6] or trimethylsilyl group[7] attached to a vinylic carbon overwhelmingly enhances the migratory ability of the benzenoid carbon atom most remote from it; the vinyl methyl effect is in the same direction but less pronounced.[8]

Appropriate disubstitution of the benzonorbornadiene framework can provide valuable information on the relative extent to which a group at some location in 1 can enhance, neutralize, or override the directive capabilities of the other. In the 1-methoxy-4-R series, exclusive use of that reaction channel involving the aryl carbon proximal to R is observed; only when the 4-substituent is $NHCOCH_3$ or CH_3 is leveling encountered.[9] The triplet photoisomerization of 1-R-6-methoxybenzonorbornadienes results in overwhelming control by the bridgehead substituent (migration of nearby C-8a) when it is strongly electron-withdrawing.[7] As the electronic character of R is modified, the extent of proximal di-π-methane rearrangement falls off, but the pathway normally favored by the *m*-methoxy group never dominates.

The present effort seeks as its goal an experimental resolution of the question whether the powerful controlling effect of a bridgehead substituent is adequate to outweigh the likewise pronounced influence of a vinyl R group. This issue holds considerable importance in our assessment of the actual reaction profile of the 1,2-aryl shift. The relative ease with which phenyl and vinyl groups migrate in general under di-π-methane conditions points up their intrinsic ability to undergo rebonding by use of an appropriate pπ orbital. Where benzonorbornadienes are concerned, the so-called aryl–vinyl bridged species 2 results.[10] Continued electronic reorganization gives rise to the aryl-migrated 1,3-biradical 3. Although Zimmerman's mechanistic



2 3

analysis of the di-π-methane process left open the possibility that either 2 or 3 could serve as a true reaction

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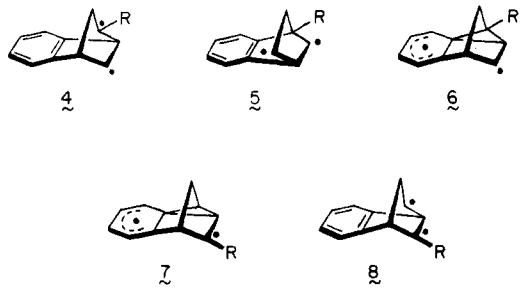
intermediate,[11] the cyclopropyldicarbinyl species **2** has virtually without exception been considered the crucial saddle point, despite the obvious disruption of aromaticity associated with this structural type. Molecular orbital calculations have recently been advanced in support of this claim.[12] However, many of the findings described above and an appreciable number of observations made in other laboratories[13] can be rationalized more succintly in terms of **2** as a fleeting transition-state entity, with "direct" 1,2-aryl migration to intermediate **3** being product-determining. The basis of this interpretation resides predominantly in the strong directive effects provided *at the intramolecular competition level* by various bridgehead substituents and the proviso that there is no reversibility (or revertibility) in these systems.

Thus, if bridgehead R can stabilize a radical center, the involvement of **4** should be appreciably more thermodynamically favored than the arrangement in **5**, and bridgehead substituents have indeed been noted to favor proximal rebonding strongly. Regiochemical control by bridgehead R at the cyclopropyldicarbinyl stage (**6**) has been generally considered to be much less significant, although a gradient of mechanism has not at all been ruled out.[7]

Quantum yield data relating to the benzonorbornadienes carrying methyl and trimethylsilyl substituents show these photoisomerizations to be particularly efficient.[7] At least for these derivatives, there appears to be minimal or no opportunity for reversion to the respective benzonorbornadiene ground states via one or another energy-wasting process. Accordingly, we were especially attracted to the utilization of these groups as probes of bridgehead/vinyl control.

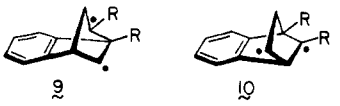


4 **5** **6** **7** **8**

It is to be noted that when the R group happens to be positioned on the etheno bridge, the odd electron that is to materialize can be stabilized in either reactive species (see **7** and **8**), provided that the aryl migration occurs on the distal side of the benzonorbornadiene framework. All of the vinyl-substituted derivatives examined to date respond in the expected fashion. How will bridgehead and vinyl substituents fare when allowed to vie in antagonist fashion within **1**?

Results

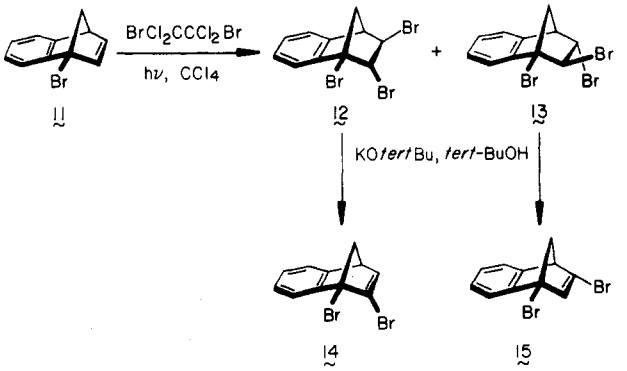
Synthetic Considerations. Inspection of the specific rebonding schemes favored by bridgehead and vinylic substituents shows that opposition to the usual preferences would be realized if combined in a 1,2-relationship. Thus, operation of that rebonding pathway proximal to C-1 as in **9** effectively insulates the vinylic R group from possible stabilization of the 1,3-biradical species. Use of the alternative reaction channel delivers an intermediate (**10**) which takes direct advantage of the stabilization inherent in overlap of vinylic R with one of the free radical centers;



9 **10**

under these circumstances, however, the bridgehead substituent is precluded from making a comparable contribution. Since arrival at **9** or **10** constitutes an irreversible commitment to product formation,[14] the inherent relative controlling capability of one or the other substituent becomes clearly reflected in the product distribution. It must be explicitly noted, of course, that it is the transition-state differences that determine reaction-rate ratios and not the differences between the products themselves, except as the latter affect transition states.

At the beginning of this study, we were aware of only one simple benzonorbornadiene derivative substituted in a 1,2-manner, the dimethyl example.[15a] Because of the specificity of the earlier route, a more general synthetic protocol was developed. Free radical bromination of the known **11**[15b,c] produced in a 3:1 ratio and 82% combined yield the chromatographically separable tribromides **12** and **13**. The NMR spectra of these isomers, although similar, reveal sufficient information to allow tentative assignments to be made. Compound **12** exhibits a singlet bridgehead proton adsorption at δ 3.50, indicating that the vicinal proton must be oriented endo.[16] Since this C*H*Br resonance appears as a doublet (J = 2.8 Hz), a trans relationship to the neighboring C*H*Br is called for. The exo stereochemical assignment to the latter proton is supported by its triplet nature, a reflection of added W-plan coupling to the methylene proton syn to the benzene ring.[17] The spin–spin interactions in **13** are more extensive and not as amenable to first-order analysis at 300 MHz.



11 **12** **13** **14** **15**

The stage was now set for the critical dehydrobromination of each tribromide. In line with precedent,[18] treatment of **12** with potassium *tert*-butoxide proceeded with abstraction of the exo CHBr proton and cis elimination to give **14** (90%). Entirely analogous reactivity was

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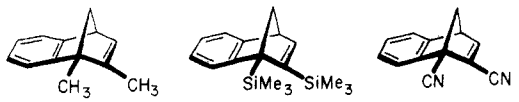
Table I. Product Distributions Realized from Triplet-State Photoisomerization of 1,2-Disubstituted Benzonorbornadienes[a]

compd	R_1	R_2	series	bridgehead control 23, %	vinylic control 24, %
16	CH_3	CH_3	a	42	58
17	$SiMe_3$	$SiMe_3$	b	45	55
21	CN	CH_3	c	100	
20	Br	CH_3	d	10	90

[a] The limits of detection are considered to be better than ±3%.

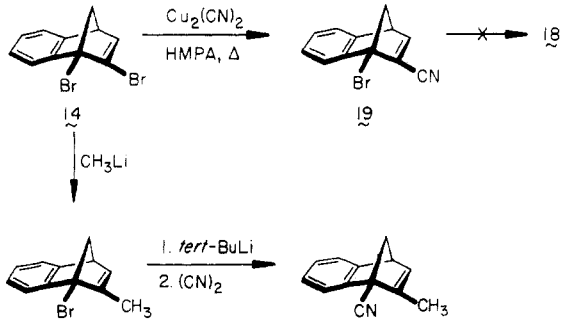
exhibited by **13**; dibromide **15** was formed exclusively (89% isolated). Structural assignment to **14** was achieved by means of off-resonance and 2D-INADEQUATE ^{13}C NMR techniques. The observed ^{13}C–^{13}C connectivities unambiguously define the specific location of the two bromine atoms. Parallel measurements in the case of **15** confirmed the 1,3-substitution plan and ruled out operation of any adventitious skeletal rearrangement.

Since the practicalities of mechanistic interpretation would be well served if the two pendant groups were identical, we set out to determine first if **14** could be effectively dimetalated. When this dibromide was treated at −78 °C with an excess of *tert*-butyllithium followed by dimethyl sulfate, the 1,2-dimethyl derivative **16** was produced. While an entirely comparable process made access to the bis(trimethylsilyl) analogue **17** practical, a successful route to the dinitrile **18** (cyanogen quench)[5] could not be defined.



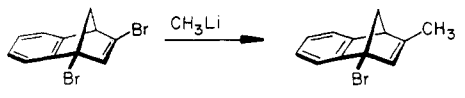
16 17 18

In an attempt to realize an alternative route to **18**, **14** was heated with cuprous cyanide in hexamethylphosphoramide (HMPA) at 125 °C for several hours. The vinylic bromine atom was selectively replaced in low yield (14%). Numerous attempts to transform **19** into **18** proved uniformly unsuccessful. It can be argued that the reason underlying our failure to obtain the dinitrile resides in the sensitivity of the vinyl cyano functionality in **19** to chemical modification at the nearby bridgehead site. This postulate receives some support from the finding that **20**, the product of direct methylation of **14** with methyllithium, did undergo conversion to **21** as indicated below.



14 19 20 21

With a practical route to **20** having been achieved, the 1,3-disubstituted analogue **22** was identically prepared from **15** in order that the bridgehead bromine heavy atom effect[5,9] could be compared in both series.

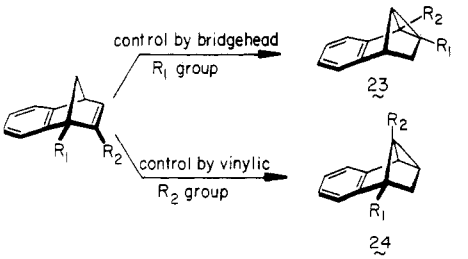


15 22

Photoisomerizations. In all the examples studied herein, triplet sensitization was effected with acetophenone (E_T = 73.6 kcal/mol) on dilute benzene solutions. The photorearrangements were conducted at room temperature with a full bank of 350-nm lights in a Rayonet reactor. Progress of the reactions was monitored by capillary gas chromoatography (GC). Once starting material was consumed, the solvent was removed in vacuo and product composition was again evaluated by quantitative ^1H NMR integration. When mixtures resulted, the components were subsequently separated by medium-pressure liquid chromatography (MPLC) or preparative GC.

The pair of options available to **16**, **17**, and **20–22** are illustrated below. Proper structural assignment to either tetracyclo[5.4.0.0^{2,4}.0^{3,6}]undeca-1(7),8,10-triene is greatly facilitated by the fact that all six of the aliphatic protons in the parent hydrocarbon appear at well-spaced chemical shifts and have distinctively different multiplicities. The particular substitution plan normally follows directly from first-order analysis of 300-MHz ^1H NMR spectra (see Experimental Section).

The response of **16** to the predescribed photochemical conditions was to deliver the photoisomers **23a** and **24a** in a 42:58 ratio (Table I). On the premise that perfect additivity may operate within **16**, the predicted ratio for bridgehead/vinyl control would be (90/10) × (19/81) or 68:32. The discrepancy between calculated and experimental values implies that the vinyl methyl group in **16** is exerting a more powerful directing influence than it does when present alone. This phenomenon has been observed previously during photoisomerization of 2-methylbenzonorbornadienes carrying aryl substituents such as methoxy and cyano.[8] The effect may arise as the result of modestly greater vinyl π orbital contribution to the dominant excited-state configuration in **16** relative to the 2-methyl example.



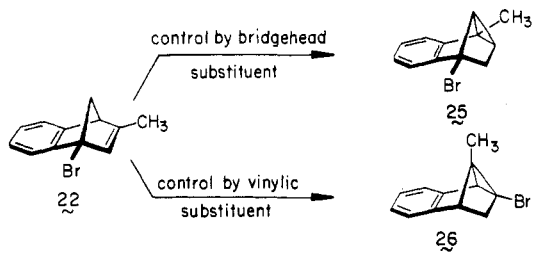
The bis(trimethylsilyl) derivative **17** was seen to afford a very closely comparable 45:55 mixture of two photoproducts which were separated and characterized as **23b** and **24b**. This product distribution discloses that bridgehead Me_3Si is capable of almost completely leveling the otherwise overwhelming domination by vinylic Me_3Si for control of the two available rebonding pathways. The significance of this finding is discussed below.

Where the bridgehead cyano/vinylic methyl combination is concerned as in **21**, a single excited-state process occurs to give **23c**. Reactions conducted to 10–50% conversion likewise gave no indication of the presence of the second isomer. On this basis, it is clear that the regiospecificity

is the direct result of kinetic factors that come under the complete control of the cyano functionality.

Sensitized irradiation of **19** yielded the photoproducts **23d** and **24d** in a 10:90 ratio. Since additivity in this instance (50/50) × (19/81) leads to a closely similar prediction for the isomer distribution, the competing reactions appear to be operating normally, except for a modicum of additional vinyl methyl control as before.

Comparable handling of **22** promoted efficient conversion to an 18:82 mixture of **25** and **26**. Since bridgehead bromine is regioneutral (50:50) in its directive capabilities, the issue here as in **19** is whether methyl is capable of exerting its influence in the presence of the heavy atom. When methyl is present by itself on the etheno bridge, distal rebonding is favored to the extent of 81%. The product distribution determined for **22** is considered to be identical within experimental error.



22 25 26

Discussion

The present observations indicate that as aryl migration begins in a triplet benzonorbornadiene system, a bridged intermediate is not required as much as is completion of the 1,2-phenyl shift. With substituents present exclusively on the aromatic ring, this important mechanistic claim is not self-evident, although it is already clear that the observed excited-state regiochemical preferences conform in direction to expectations based primarily upon differences in electron densities within the SOMO.[6,8,19] Attachment of a pendant group to a vinylic position understandably fosters regiochemical control in that direction which provides transient stabilization for one of the odd-electron centers. As noted earlier, however, these findings do not permit a distinction between the relative importance of transient biradicals **7** and **8**.

Additional mechanistically significant information began to surface when consideration was given to bridgehead monosubstituted benzonorbornadienes and related molecules.[5] Because the R group is now too remote from and orthogonal to the clouds of the olefinic double bond and flanking aromatic ring, regioselectivity predictions cannot now be advanced solely on the basis of vacant orbital energies and shapes. Nevertheless, impressively high levels of regiocontrol are observed. This can be construed to be a reflection of the pivotal role played by biradicals **4** and/or **6** in the operation of the di-π-methane rearrangement.

The experiments most revealing of mechanistic detail happen to involve substrates where intramolecular competition between bridgehead and aryl or vinyl substituents can operate. As usual, regioselectivity control is heavily localized in the competitive formation of two possible intermediates; now, however, only one of these species can be electronically stabilized by the bridgehead R group. If it is assumed that the two intermediates differ little in the rates at which they leave their hypersurfaces and cut across those of the various geometric forms that lead to the product options, then their structures can be construed to be those depicted in **9** and **10**. Although bridged species such as **6** cannot provide comparable opportunity to R for electronic stabilization, these structures must be transversed early in the photoisomerization trajectory. Scenarios may well exist where bridged species are more stable than their 1,2-aryl shifted counterparts. For the present examples, however, no evidence has surfaced to require that they be regarded as mandatory resting points.

A key observation is that the various substrates examined invariably choose to take maximum advantage of the radical stabilizing properties of bridgehead R and to an extent closely comparable to that of a vinylic substituent. This parallelism is particularly impressive when it is recognized that no hybridization change need occur at C-2; a mere uncoupling of the π-bond electrons operates at that site. On the other hand, C-1 has to experience considerable modification of its electronic character in order to become a full-fledged radical center. The magnitude to which this occurs would appear to be best accommodated by the "direct" 1,2-aryl shift scheme and not by forming a stable bridged intermediate.

For the preceding conclusion to be correct, these di-π-methane rearrangements must have no significant reversible component. We[5,9] and others[20] have previously given attention to this specific question. For dibenzobarrelenes, small levels of an intermediate quenchable back to starting material were detected and caused some difficulty in assessing regiochemistry results.[20] Although a similar phenomenon has not been uncovered for benzonorbornadienes, let us assume reversibility to be a component of these excited-state reactions. Under these circumstances, biradicals **6** and **7** would not now be transition states but intermediates and would not necessarily have the same $k_{forward}/k_{reverse}$ reaction rate ratios. Consideration would now also have to be given to the possible equilibration of, for example, **6** with **7** through the olefin triplet and to when these structures might undergo intersystem-crossing to ground-state singlets.

The two definitive pieces of evidence available are as follows: (1) substituents on the bridgehead carbon strongly accelerate proximal rebonding, necessarily by stabilization of one radical center; (2) the quantum efficiencies observed for select benzonorbornadienes are high, suggesting the energy-wasting return to starting material is hardly rampant and may operate only to a modest degree or not at all.

Are *both* of these phenomena consistent with a tendency (rate) for dicyclopropyl–dicarbinyl radical partitioning? Without doubt, scenarios that would lead to identical regiochemical distributions might be arrived at by this scheme. As a result, the regiochemical consequences of substitution do not by themselves unequivocally resolve such a complex issue; more detailed photophysical investigations are necessary. For the present, however, analysis based on the direct 1,2-aryl pathway is simpler, more direct, and in agreement with the available Φ values for CH_3 and Me_3Si derivatives in particular. Also, since the reaction-rate ratios are already realized in the transition-state differences, the appreciable levels of stabilization available, for example, to **4** and **9**, must already be impacting on the relative energetics. The strong regiodirecting influence of bridgehead substituents could implicate **6** and its congeners to be late transition states. If this were so and bond breaking to the bridgehead site were substantively ad-

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vanced, these activated complexes would closely resemble **4**, **9**, and related 1,2-aryl-migrated biradical intermediates and become less distinguishable.

Experimental Section

Radical Bromination of 1-Bromobenzonorbornadiene. A carbon tetrachloride solution (100 mL) of **11** (9.0 g, 40.7 mmol) and 1,2-dibromo-1,1,2,2-tetrachloroethane (16.0 g, 49 mmol) was irradiated with a 275-W sunlamp. The progress of reaction was monitored by gas chromatography and shown to be >95% after 1.75 h. The two resulting products were formed in a 4.1:1 ratio. The reaction mixture was concentrated, and the tribromide isomers were separated by chromatography on silica gel (elution with petroleum ether) using a Waters Prep 500 high-pressure liquid chromatograph. While tribromide **12** (9.24 g) was obtained as a colorless oil, tribromide **13** (3.51 g) slowly crystallized on standing, mp 60–62 °C. The combined yield was 82%.

For **12**: IR (neat, cm^{-1}) 3075, 3950, 2985, 2950, 1460, 1275, 1180, 1025, 965, 915, 850, 765, 650; ^1H NMR (300 MHz, $CDCl_3$) δ 7.27 (m, 4 H), 4.70 (d, J = 2.8 Hz, 1 H), 3.79 (dd, J = 2.8, 2.2 Hz, 1 H), 3.50 (s, 1 H), 2.92 (d, J = 9.7 Hz, 1 H), 2.56 (dt, J = 9.7, 2.2 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) 142.6, 140.8, 128.4, 127.4, 124.2, 121.4, 65.4, 64.0, 55.4, 54.7, 51.3 ppm; MS, m/z (M^+ – Br) calcd 300.9050, obsd 300.9084.

For **13**: IR (neat, cm^{-1}) 2995, 1465, 1280, 1270, 1190, 985, 970, 915, 765, 735, 640; ^1H NMR (300 MHz, $CDCl_3$) δ 7.40 (d, J = 6.7 Hz, 1 H), 7.24 (m, 3 H), 4.74 (br s, 1 H), 3.88 (br s, 1 H), 3.40 (br s, 1 H), 2.80 (d, J = 9.9 Hz, 1 H), 2.48 (d, J = 9.9 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) 142.9, 141.6, 127.91, 127.87, 122.2, 66.3, 62.3, 57.6, 54.7, 49.8 ppm; MS, m/z (M^+) 379.8233, obsd 379.8212.

Anal. Calcd for $C_{11}H_9Br_3$: C, 34.69; H, 2.38. Found: C, 34.38, H, 2.47.

1,2-Dibromobenzonorbornadiene (14). To 100 mL of freshly distilled *tert*-butyl alcohol was added freshly cut potassium metal (1.05 g, 26.9 mmol), and heating at the reflux temperature was maintained for 6 h. A solution of **12** (8.91 g, 23 mmol) in 20 mL of the same solvent was introduced and heating was continued for an additional 11 h. After cooling, the reaction mixture was concentrated in vacuo, dissolved in ether, and poured into water. The aqueous phase was extracted with petroleum ether, and the combined organic layers were washed with brine, dried, and evaporated to leave 6.55 g of impure **14**. Purification on a Waters Prep 500 HPLC (silica gel, elution with petroleum ether) afforded 6.33 g (90%) of pure **14** as a colorless oil, which quickly discolors on standing at room temperature: IR (neat, cm^{-1}) 3070, 3050, 2990, 2950, 1565, 1455, 1265, 1220, 1175, 1080, 1025, 1010, 915, 860, 810, 800, 760, 645; ^1H NMR (300 MHz, $CDCl_3$) δ 7.5 (m, 1 H), 7.19 (dd, J = 2.0, 5.7 Hz, 1 H), 7.05 (m, 2 H), 6.81 (dd, J = 0.9, 3.6 Hz, 1 H), 3.93 (br s, 1 H), 2.97 (dd, J = 1.7, 7.0 Hz, 1 H), 2.77 (ddd, J = 1.1, 1.8, 7.0 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) 148.5, 147.2, 140.8, 138.5, 126.0, 125.0, 121.7, 121.3, 76.6, 70.7, 49.5 ppm; MS, m/z (M^+) calcd 299.8973, obsd 299.8974.

1,3-Dibromobenzonorbornadiene (15). Heating tribromide **13** (1.10 g, 2.9 mmol) with potassium *tert*-butoxide [from 220 mg (5 mmol) of potassium metal] in *tert*-butyl alcohol (45 mL total) for 10 h and workup in the predescribed manner yielded 850 mg of crude dibromide. Purification by MPLC on silica gel (elution with petroleum ether) gave 770 mg (89%) of **15** as a colorless oil; IR (neat, cm^{-1}) 2995, 2950, 1555, 1455, 1270, 1195, 1165, 940, 905, 885, 805, 760, 630; ^1H NMR (300 MHz, $CDCl_3$) δ 7.39 (d, J = 7.4 Hz, 1 H), 7.31 (d, J = 7.1 Hz, 1 H), 7.13 (dt, J = 7.4, 1.2 Hz, 1 H), 7.05 (dt, J = 7.3, 1.1 Hz, 1 H), 6.70 (s, 1 H), 3.83 (s, 1 H), 3.0 (dd, J = 1.8, 6.9 Hz, 1 H), 2.72 (dt, J = 1.2, 6.9 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) 148.7, 146.6, 143.0, 135.8, 125.9, 125.6, 121.8, 121.4, 77.8, 64.6, 57.1 ppm; MS m/z (M^+) calcd 299.8972, obsd 299.8979.

Anal. Calcd for $C_{11}H_8Br_2$: C, 44.04; H, 2.61. Found: C, 44.09; H, 2.74.

1,2-Dimethylbenzonorbornadiene (16). To a cold (–100 °C), magnetically stirred pentane solution (15 mL) of *tert*-butyllithium (3.2 mL, 5.5 mmol) was added a pentane solution (2 mL) of **14** (0.40 g, 1.3 mmol) followed by 1 mL of tetrahydrofuran. After 10 min, an excess of dimethyl sulfate was introduced, the cooling bath was removed, and the contents were allowed to warm to room temperature. The crude product was isolated by partitioning between water and pentane followed by drying and evaporation of the organic phase. Gas chromatography of this material (0.30 g) revealed the mixture to consist of 43% monomethylated and 50% dimethylated material. MPLC on silica gel (elution with petroleum ether) returned 180 mg of mixture which was ultimately purified by preparative GC. A total of 90 mg (40%) of **16** was isolated; IR (neat, cm^{-1}) 3065, 2960, 2930, 2860, 1485, 1470, 1385, 1305, 1015, 810, 790, 765, 755; ^1H NMR (300 MHz, $CDCl_3$) δ 7.23 (m, 2 H), 7.03 (m, 2 H), 6.36 (s, 1 H), 3.79 (s, 1 H), 2.33 (dd, J = 1.4, 6.8 Hz, 1 H), 2.25 (d, J = 6.8 Hz, 1 H), 1.79 (d, J = 1.7 Hz, 3 H), 1.65 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) 154.4, 154.1, 153.4, 136.2, 124.0, 123.7, 120.5, 119.1, 73.6, 57.4, 48.3, 13.8, 13.4 ppm; MS, m/z (M^+) calcd 170.1095, obsd 170.1099.

1,2-Bis(trimethylsilyl)benzonorbornadiene (17). To a cold (–78 °C), magnetically stirred pentane solution (15 mL) of *tert*-butyllithium (4.4 mL, 7.0 mmol) was added a pentane solution (1.5 mL) of **14** (0.40 g, 1.33 mmol) and tetrahydrofuran (0.5 mL). After 10 min, chlorotrimethylsilane (0.76 g, 7.0 mmol) was introduced, the cooling bath was removed, and the reaction mixture was allowed to come to room temperature, where it was stirred for 1 h before being poured into ice–water. The product was extracted with pentane. Capillary gas chromatography revealed the mixture to consist of ca 60% monosilylated and 40% disilylated product. Pure **17** was isolated by preparative GC of the concentrate: 78.5 mg (20%) of colorless oil; IR (neat, cm^{-1}) 3070, 2960, 2930, 2900, 1535, 1265, 1255, 935, 910, 845, 755, 700; ^1H NMR (300 MHz, $CDCl_3$) δ 7.24 (m, 3 H), 6.89 (m, 2 H), 3.89 (br s, 1 H), 2.15 (m, 2 H), 0.58 (s, 9 H), 0.07 (s, 9 H); ^{13}C NMR (75 MHz, $CDCl_3$) 158.0, 157.2, 154.3, 153.6, 123.8, 123.5, 122.5, 121.2, 68.2, 53.7, 51.2, –0.3, –0.8 ppm; MS, m/z (M^+) calcd 286.1573, obsd 286.1576.

Anal. Calcd for $C_{17}H_{26}Si_2$: C, 71.25; H, 9.15. Found: C, 71.57; H, 9.21.

1-Bromo-2-cyanobenzonorbornadiene (19). To a solution of **14** (700 mg, 2.3 mmol) in hexamethylphosphoramide (12 mL) was added cuprous cyanide (800 mg), and the magnetically stirred mixture was heated at 115–125 °C for 3 h. The cooled reaction mixture was poured into an aqueous ferric sulfate/ammonium sulfate solution and extracted with petroleum ether. The combined organic layers were dried and concentrated, and the residue was subjected to MPLC purification (silica gel, elution with 8% ethyl acetate in petroleum ether). There was obtained 80 mg (14%) of **19** as a colorless oil: ^1H NMR (300 MHz, $CDCl_3$) δ 7.62 (d, J = 3.6 Hz, 1 H), 7.47 (d, J = 7.1 Hz, 1 H), 7.28 (d, J = 7.0 Hz, 1 H), 7.12 (m, 2 H), 4.11 (t, J = 1.8 Hz, 1 H), 2.93 (dd, J = 1.6, 7.5 Hz, 1 H), 2.80 (d, J = 7.5 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) 158.4, 147.6, 145.1, 131.3, 126.6, 126.1, 122.5, 122.4, 113.9, 78.0, 64.1, 49.9 ppm; MS, m/z (M^+) calcd 246.9820, obsd 246.9824.

1-Bromo-2-methylbenzonorbornadiene (20). A cold (–78 °C), magnetically stirred solution of **14** (840 mg, 2.8 mmol) in pentane (20 mL) was treated with methyllithium (3.3 mL, 3.0 mmol). Following the addition of 1 mL of tetrahydrofuran, the reaction mixture was allowed to warm to 0 °C, and dimethyl sulfate (380 mg, 3.0 mmol) was added. After 5 min, the reaction mixture was poured onto ice and water and extracted with pentane. Concentration of the combined organic layers followed by MPLC on silica gel (elution with petroleum ether) furnished 460 mg (71%) of **20**: IR (neat, cm^{-1}) 3070, 2995, 2945, 1460, 1440, 1280, 1245, 1175, 1025, 985, 950, 790, 755; ^1H NMR (300 MHz, $CDCl_3$) δ 7.38 (d, J = 6.5 Hz, 1 H), 7.18 (dd, J = 1.9, 5.7 Hz, 1 H), 7.04 (m, 2 H), 6.31 (s, 1 H), 3.80 (s, 1 H), 2.82 (dd, J = 1.7, 6.6 Hz, 1 H), 2.67 (d, J = 6.6 Hz, 1 H), 1.84 (d, J = 1.7 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) 152.5, 150.2, 149.6, 134.8, 125.4, 124.6, 121.1, 120.7, 77.4, 71.1, 47.8, 15.4 ppm; MS, m/z (M^+) calcd 236.0014, obsd 236.0007.

Anal. Calcd for $C_{12}H_{11}Br$: C, 61.29; H, 4.72. Found: C. 61.30; H, 4.82.

1-Cyano-2-methylbenzonorbornadiene (21). A cold (–78 °C), magnetically stirred solution of **20** (0.20 g, 0.85 mmol) in pentane (2 mL) was treated in turn with *tert*-butyllithium (1.87 mmol in pentane) and with tetrahydrofuran (0.2 mL). The reaction mixture was stirred at this temperature for 10 min, an ether solution containing excess cyanogen was added, and the contents were allowed to warm to room temperature. The product was partitioned between water and petroleum ether, and the combined organic layers were dried and concentrated. Purification by MPLC

on silica gel (elution with 3% ethyl acetate in petroleum ether) gave 30 mg (20%) of **21**: IR (neat, cm^{-1}) 3070, 2990, 2945, 2245, 1455, 1445, 1285, 1135, 1030, 1015, 1005, 865, 800, 760; ^1H NMR (300 MHz, $CDCl_3$) δ 7.44 (dd, J = 3.3, 5.2 Hz, 1 H), 7.20 (m, 1 H), 7.03 (m, 2 H), 6.33 (s, 1 H), 3.85 (s, 1 H), 2.70 (dd, J = 1.6, 6.9 Hz, 1 H), 2.57 (d, J = 6.9 Hz, 1 H), 1.91 (d, J = 1.7 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) 149.8, 149.2, 146.7, 135.8, 126.0, 124.8, 121.6, 120.3, 118.6, 72.1, 53.6, 49.0, 14.4 ppm; MS, m/z (M^+) calcd 181.0892, obsd 181.0883.

Anal. Calcd for $C_{13}H_{11}N$: C, 86.16; H, 6.12. Found: C, 86.31; H, 6.36.

1-Bromo-3-methylbenzonorbornadiene (22). Methyllithium (2.0 mL, 2.4 mmol) was added to a cold (−78 °C) pentane solution (12 mL) of **15** (0.42 g, 1.4 mmol) followed by 0.5 mL of tetrahydrofuran. After warming to 0 °C, excess dimethyl sulfate was introduced, and the reaction mixture was poured into ice–water. The product was extracted into pentane, and the combined organic extracts were dried and concentrated. Purification of the residue by MPLC on silica gel (elution with petroleum ether) gave 0.29 g (88%) of **22** as a colorless oil; IR (neat, cm^{-1}) 3070, 3050, 2980, 2940, 2810, 1455, 1440, 1280, 1245, 1210, 1185, 1170, 1010, 960, 900, 890, 785, 755, 740; ^1H NMR (300 MHz, $CDCl_3$) δ 7.33 (d, J = 7.3 Hz, 1 H), 7.21 (d, J = 6.8 Hz, 1 H), 7.06 (dt, J = 7.4, 1.1 Hz, 1 H), 6.98 (dt, J = 7.4, 1.2 Hz, 1 H), 6.2 (s, 1 H), 3.53 (s, 1 H), 2.80 (dd, J = 1.7, 6.6 Hz, 1 H), 2.64 (dd, J = 1.2, 6.6 Hz, 1 H), 1.83 (d, J = 1.8 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) 153.7, 150.7, 148.4, 138.2, 125.0, 124.9, 120.9, 120.6, 77.5, 65.3, 53.4, 15.9 ppm; MS, m/z (M^+) calcd 234.0044, obsd 234.0030.

Anal. Calcd for $C_{12}H_{11}Br$: C, 61.29; H, 4.72. Found: C, 61.33; H, 4.78.

Photoisomerization of 1,2-Dimethylbenzonorbornadiene. A benzene-d_6 solution (1 mL) of freshly purified **16** (70 mg) and acetophenone (20 μL) was transferred to an NMR tube, purged with nitrogen for 30 min, and irradiated at 350 nm in a Rayonet reactor. The isomerization was complete in 4 h yielding **23a** and **24a** in a 42:58 ratio. The two photoproducts were separated in pure condition by sequential HPLC and GC. A total of 61 mg (87%) of these compounds was isolated.

For **23a**: IR (neat, cm^{-1}) 3025, 2975, 2950, 2925, 2860, 1425, 1390, 1070, 1035, 1025, 760; ^1H NMR (300 MHz, $CDCl_3$) δ 7.30 (d, J = 7.2 Hz, 1 H), 7.15 (dt, J = 7.2, 1.5 Hz, 1 H), 7.03 (m, 2 H), 3.25 (dd, J = 7.7, 2.8 Hz, 1 H), 2.85 (t, J = 2.8 Hz, 1 H), 2.57 (t, J = 8.2 Hz, 1 H), 1.50 (s, 3 H), 1.42 (s, 3 H), 0.97 (dd, J = 8.7, 2.8 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) 150.2, 146.3, 125.4, 124.4, 121.9, 119.4, 55.1, 40.5, 37.4, 30.6, 15.1, 13.2 ppm; MS, m/z (M^+) calcd 170.1095, obsd 170.1091.

For **24a**: IR (neat, cm^{-1}) 3025, 2950, 2960, 1470, 1205, 1020, 755; ^1H NMR (300 MHz, $CDCl_3$) δ 7.39 (dd, J = 7.0, 1.5 Hz, 1 H), 7.12 (m, 2 H), 6.98 (d, J = 6.7 Hz, 1 H), 2.30 (dd, J = 8.8, 3.2 Hz, 1 H), 2.28 (d, J = 5.4 Hz, 1 H), 1.19 (dd, J = 5.4, 3.3 Hz, 1 H), 1.45 (s, 3 H), 1.34 (s, 3 H), 0.84 (d, J = 8.8 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) 151.3, 142.3, 125.6, 124.3, 122.8, 118.0, 56.5, 50.0, 34.7, 34.5, 22.5, 15.6, 12.1 ppm; MS, m/z (M^+) calcd 170.1095, obsd 170.1100.

Photoisomerization of 1,2-Bis(trimethylsilyl)benzonorbornadiene. A solution of freshly purified **17** (49 mg) and acetophenone (40 μL) in benzene (7 mL) was purged with purified nitrogen for 30 min and subsequently irradiated at 350 nm in a Rayonet reactor for 1 h at ambient temperature under nitrogen. Capillary gas chromatography showed two photoproducts to be present in a 45:55 ratio. The isomers were separated by a combination of MPLC and GC. A total of 90% of **23b** and **24b** was isolated.

For **23b**: IR (neat, cm^{-1}) 2960, 1470, 1255, 1170, 970, 925, 840, 755; ^1H NMR (300 MHz, $CDCl_3$) δ 7.43 (d, J = 7.3 Hz, 1 H), 7.10 (dt, J = 7.3, 1.7 Hz, 1 H), 7.02 (dt, J = 7.2, 1.1 Hz, 1 H), 6.98 (dd, J = 7.8, 1.2 Hz, 1 H), 3.23 (dd, J = 7.4, 2.5 Hz, 1 H), 2.97 (t, J = 2.6 Hz, 1 H), 2.74 (dd, J = 9.2, 7.5 Hz, 1 H), 0.55 (dd, J = 9.1, 2.8 Hz, 1 H), 0.16 (s, 9 H), 0.13 (s, 9 H); ^{13}C NMR (75 MHz, $CDCl_3$) 152.4, 143.7, 125.13, 125.11, 124.5, 118.9, 50.2, 42.7, 34.3, 33.2, 22.7, 0.12, 0.02 ppm; MS, m/z (M^+) calcd 286.1573, obsd 286.1568.

For **24b**: IR (neat, cm^{-1}) 3020, 2950, 2910, 1460, 1255, 1105, 910, 895, 845, 755; ^1H NMR (300 MHz, $CDCl_3$) δ 7.39 (d, J = 7.2 Hz, 1 H), 7.08 (m, 1 H), 6.98 (m, 2 H), 2.71 (dd, J = 9.3, 3.4 Hz, 1 H), 2.41 (d, J = 5.3 Hz, 1 H), 2.07 (dd, J = 5.2, 3.4 Hz, 1 H), 0.91 (d, J = 9.2 Hz, 1 H), 0.23 (s, 9 H), −0.03 (s, 9 H); ^{13}C NMR (75 MHz, $CDCl_3$) 151.9, 144.4, 125.2, 124.1, 122.7, 120.4, 50.0, 45.1, 35.7, 31.3, 23.8, −0.8, −1.7 ppm; MS, m/z (M^+) calcd 286.1573, obsd 286.1586.

Photoisomerization of 1-Cyano-2-methylbenzonorbornadiene. A benzene solution (7 mL) of freshly purified **21** (17.3 mg) and acetophenone (10 μL) was purged with nitrogen (30 min) and irradiated with 350-nm light (1 h). The lone photoproduct was separated from acetophenone by preparative GC. There was isolated 9.5 mg (52%) of **34c**: IR (neat, cm^{-1}) 3050, 2970, 2930, 2870, 2225, 1480, 1465, 1455, 1395, 1000, 760; ^1H NMR (300 MHz, $CDCl_3$) δ 7.42 (d, J = 7.5 Hz, 1 H), 7.26 (dt, J = 7.4, 1.2 Hz, 1 H), 7.18 (dt, J = 7.3, 1.1 Hz, 1 H), 7.06 (d, J = 7.2 Hz, 1 H), 3.61 (t, J = 2.7 Hz, 1 H), 3.41 (dd, J = 8.0, 3.2 Hz, 1 H), 3.07 (t, J = 8.5 Hz, 1 H), 1.13 (dd, J = 9.0, 2.1 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) 147.9, 141.0, 126.7, 123.0, 120.2, 119.7, 56.6, 41.8, 40.6, 32.9, 18.2, 13.4 ppm; MS, m/z (M^+) calcd 181.0892, obsd 181.0890.

Photoisomerization of 1-Bromo-2-methylbenzonorbornadiene. A solution of **19** (67 mg) and acetophenone (55 μL) in benzene was purged with nitrogen (45 min) and irradiated at 350 nm in a Rayonet reactor (2 h). The two photoproducts **24d** and **24d**, formed in a 10:90 ratio, were obtained pure by MPLC on silica gel. A total of 64 mg (96%) of the purified isomers was recovered.

For **23d**: IR (neat, cm^{-1}) 3045, 3025, 2985, 2935, 1465, 1460, 1385, 1240, 1115, 1055, 1020, 995, 935, 870, 805, 755; ^1H NMR (300 MHz, $CDCl_3$) δ 7.36 (d, J = 7.24 Hz, 1 H), 7.19 (dt, J = 7.3, 1.1, Hz, 1 H), 7.10 (dt, J = 7.2, 1.0 Hz, 1 H)8 7.01 (d, J = 7.1 Hz, 1 H), 3.53 (dd, J = 8.1, 3.6 Hz, 1 H), 3.43 (t, J = 2.9 Hz, 1 H), 3.11 (t, J = 8.4 Hz, 1 H), 1.66 (s, 3 H), 1.51 (dd, J = 8.8, 2.3 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) 148.6, 143.5, 126.1, 125.7, 122.7, 119.9, 58.0, 42.8, 41.8, 41.3, 39.2, 15.3 ppm; MS, m/z (M^+) 234.0044, obsd 234.0019.

For **24d**: IR (neat, cm^{-1}) 3040, 2950, 2920, 1460, 1240, 1200, 1045, 1025, 990, 945, 760; ^1H NMR (300 MHz, $CDCl_3$) δ 7.39 (dd, J = 5.8, 1.9 Hz, 1 H), 7.24 (m, 3 H), 3.05 (dd, J = 9.3, 3.6 Hz, 1 H), 2.40 (d, J = 5.5 Hz, 1 H), 2.17 (dd, J = 5.5, 3.7 Hz, 1 H), 1.51 (s, 3 H), 1.47 (d, J = 9.3 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) 147.5, 139.1, 127.3, 125.3, 122.9, 120.4, 64.3, 60.1, 40.4, 33.2, 24.6, 13.4 ppm; MS, m/z (M^+) calcd 234.0044, obsd 234.0046.

Photoisomerization of 1-Bromo-3-methylbenzonorbornadiene. A solution of **22** (99 mg) and acetophenone (80 μL) in benzene (15 mL) was purged with nitrogen (30 min) and irradiated as above for 2.7 h. Two photoproducts were formed in an 82:18 ratio. MPLC of the mixture on silica gel (elution with petroleum ether) yielded pure **26** (77 mg) and pure **25** (18 mg, total 96% yield).

For **25**: IR (neat, cm^{-1}) 3045, 2955, 2925, 2865, 1465, 1375, 1235, 1205, 1055, 1050, 940, 875, 815, 755; ^1H NMR (300 MHz, $CDCl_3$) δ 7.24 (m, 4 H), 3.56 (dd, J = 4.8, 2.2 Hz, 1 H), 3.15 (dd, J = 9.0, 3.8 Hz, 1 H), 2.05 (dd, J = 4.7, 3.9 Hz, 1 H), 1.56 (dd, J = 8.9, 2.0 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) 147.7, 142.1, 127.2, 125.5, 121.7, 119.9, 59.7, 58.8, 43.8, 34.5, 26.8, 14.7 ppm; MS, m/z (M^+) calcd 234.0044, obsd 234.0021.

For **26**: IR (neat, cm^{-1}) 3045, 3025, 2950, 2860, 1465, 1255, 1225, 1150, 1135, 1105, 1065, 1025, 985, 785, 755, 690; ^1H NMR (300 MHz, $CDCl_3$) δ 7.45 (d, J = 6.6 Hz, 1 H), 7.14 (m, 3 H), 3.38 (d, J = 8.0 Hz, 1 H), 3.02 (t, J = 8.3 Hz, 1 H), 2.57 (s, 1 H), 1.52 (s, 3 H), 1.42 (d, J = 8.8 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) 147.3, 141.0, 126.1, 125.5, 123.7, 120.7, 60.7, 47.6, 42.6, 37.61, 37.55, 12.4 ppm; MS, m/z (M^+) calcd 234.0044, obsd 234.0034.

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