Triplet-Sensitized Photoisomerization of 1,4-Disubstituted Benzonorbornadienes. Intramolecular Competition by Electronically Diverse Bridgehead Functionality

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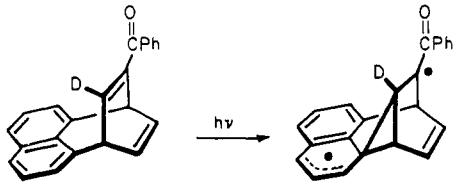
Abstract: A general synthetic route to 1-methoxy-4-X-benzonorbornadienes has been devised. Acetophenone-sensitized photoisomerization of six derivatives has been carried out. When X represents groups that are powerfully electron withdrawing, a single reaction channel is followed leading to **23**. Only when X = $NHCOCH_3$ or CH_3 is leveling encountered. The observed control of regioselectivity points to operation of a direct 1,2-aryl shift pathway without the intervention of a cyclopropyldicarbinyl species. Under these circumstances, the aromatic sextet is not transiently interrupted and product composition can be traced directly to the relative ability of a bridgehead substituent to stabilize a free radical center.

In the preceding paper,[1] we suggested guidelines for distinguishing those doubly channeled di-π-methane systems that undergo photoisomerization by a bridging mechanism from those that follow a concerted 1,2-aryl shift pathway. The available data indicate that fused aromatic systems are particularly prone to engage in the rebonding process by neighboring-group participation if low levels of aromatic delocalization are lost or if the second radical center is stabilized to a significant degree. The naphthobarrelene **1** constitutes a relevant example.[2] Irradiation



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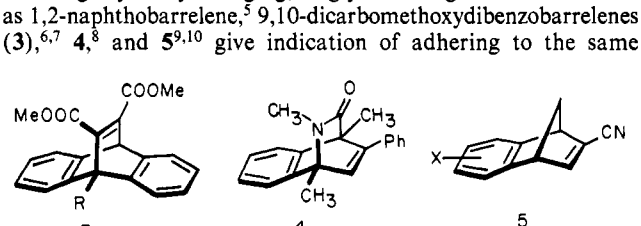
of **1** in a 2-methyltetrahydrofuran matrix at 77 K produces an ESR spectrum consistent with generation of the triplet state of **1**. A second species, identified also by ESR spectroscopy, has been assigned as **2**.[3] This direct evidence for the existence of **2** establishes that aryl–vinyl bridging can compete favorably in this instance with the customarily more prevalent vinyl–vinyl bridging.[4]

Although **1** embodies both criteria apparently necessary for inducing aryl–vinyl bridging, singly advantaged substrates such as 1,2-naphthobarrelene,[5] 9,10-dicarbomethoxydibenzobarrelenes (**3**),[6,7] **4**,[8] and **5**[9,10] give indication of adhering to the same



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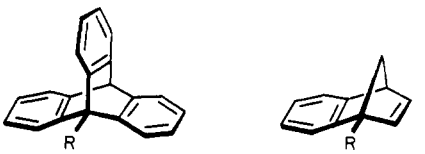
mechanistic profile.[1] Substitution of a bridgehead site by groups of varied electronic character has proven to be particularly controlling of product formation. Where **3** is concerned, *distal* rebonding operates in a wide range of examples, except when R is phenyl.[7] The latter anomaly has been rationalized.[1] It is therefore clear that within the triplet excited state of **3** electron-withdrawing and -donating groups share the common property of diverting the isomerization pathway to the alternate surface of the molecule. The latent potential of many of the substituents to stabilize odd-electron character is never realized.

In contrast, experiments conducted on bridgehead-substituted triptycenes (**6**)[7] and benzonorbornadienes (**7**)[1,10] disclose that



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photoisomerization proceeds with a marked preference for *proximal* rebonding. The observed product regioselectivities suggest that these systems take advantage of the stabilizing properties of R where such do exist. These experimental results are most plausibly interpreted in terms of a concerted 1,2-aryl migration.[1,10]

Substitution of a deuterium atom for R in **3**, **6**, and **7** leads to positive k_H/k_D values in all cases.[1,11,12] However, the fractionation factors do not differ adequately to be otherwise informative of detailed mechanism. For this reason and because the influence of larger bridgehead substituents is unquestionably substantial, we have been led to examine intramolecular competition experiments made possible by the attachment of electronically divergent functional groups to the two bridgehead sites in benzonorbornadiene. An unprecedented study of this type was expected to provide added insight into those factors that influence product development control in doubly connected di-π-methane rearrangements.

Results

Synthetic Protocol. In furtherance of a synthesis of 1,4-difunctional benzonorbornadienes, we sought rapid access to one member of the series that could be readily modified chemically. Retrosynthetic analysis prompted consideration of the 1-meth-

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(2) Demuth, M.; Bender, C. O.; Braslavsky, S. E.; Görner, H.; Burger, U.; Amrein, W.; Schaffner, K. *Helv. Chim. Acta* **1979**, *62*, 847.
(3) Demuth, M.; Lemmer, D.; Schaffner, K. *J. Am. Chem. Soc.* **1980**, *102*, 5407.
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(9) (a) Paquette, L. A.; Ku, A. Y.; Santiago, C.; Rozeboom, M. D.; Houk, K. N. *J. Am. Chem. Soc.* **1979**, *101*, 5972. (b) Ku, A. Y.; Paquette, L. A.; Rozeboom, M. D.; Houk, K. N. *Ibid.* **1979**, *101*, 5981.
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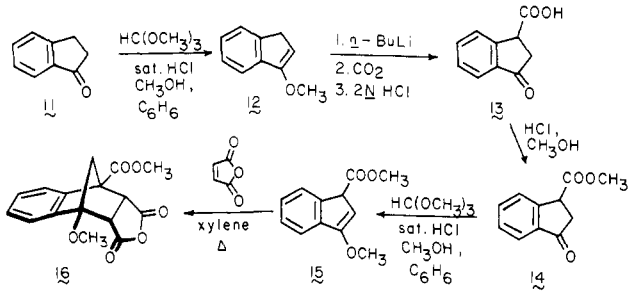
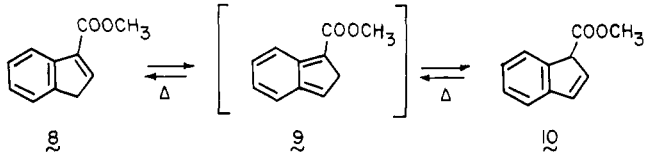
Scheme I



oxy-4-carbomethoxy derivative **17** for several reasons. First, ester **8** is recognized to be particularly responsive to [1,5]-hydrogen sigmatropy in refluxing xylene.[13] Evidently, the energetic costs



of disrupting benzenoid aromaticity are somewhat offset by the simultaneous evolution of extended conjugation at the ester site. The resulting isoindene **9** is notably reactive toward ethylenic dienophiles giving 1:1 Diels–Alder adducts.[13] Other substituents are not as accommodating.[14] Placement of the carbomethoxy group as in **10** was not expected to deter the conversion to **9**.

The ultimate success of this scenario rested on our ability to introduce a second substituent in a 1,3 relationship to the ester function. Also mandated was a comparable level of diene reactivity in the disubstituted isoindene despite the added steric encumbrance at a bonding center. Further refinement of our plan was dictated by the knowledge that 3-methoxy-1*H*-indenes can be deprotonated and carboxylated at C-1.[15]

Well aware of the potential complications associated with the conversion of 1-indanones to 3-methoxy-1*H*-indenes,[16] we allowed **11** to react with trimethyl orthoformate in methanol saturated with hydrogen chloride for a maximum of 15–30 min. Careful control of conditions afforded **12** in 59% yield (Scheme I). Longer reaction times led to self-condensation. Deprotonation of **12** with *n*-butyllithium followed by treatment with dry carbon dioxide and acid hydrolysis gave keto acid **13**, which was directly esterified. Conversion of **14** to enol ether **15** demanded the same close attention to detail previously applied to **11**. Without purification, **15** was heated in xylene solution with maleic anhydride. The desired [1,5]-hydrogen migration and [4 + 2] cycloaddition ensued to deliver **16** in 40.5% purified yield.

This adduct could be decarboxylated in refluxing diglyme by bis(triphenylphosphine)nickel dicarbonyl.[15,17] That 1,4-disubstituted benzonorbornadiene **17** had indeed been obtained was confirmed by the ^{1}H NMR spectrum, which displays inter alia two well-separated doublet pairs. The more downfield set (δ 6.85 and 6.73, J = 5.5 Hz) due to the vinyl protons is complemented by the more shielded methano proton signals at δ 2.83 and 2.68 (J_{AB} = 6.2 Hz). The missing bridgehead proton absorptions are supplanted by singlets of area 3 at δ 3.58 and 3.90 due to the methoxy and carbomethoxy groups, respectively.

With **17** in hand, the subsequent elaboration of **18–22** (Scheme II) followed conventional wisdom. Other equally precedented protocols were examined in certain cases but were abandoned when they failed completely or afforded poor yields of desired product.

Photoisomerization Studies. All six substrates were found to undergo rapid and efficient photorearrangement from their triplet excited states. The isomerizations were conducted in dilute, deoxygenated benzene solution with acetophenone as sensitizer under conditions where both starting materials and products absorbed insignificant levels of the incident 3500-Å radiation. The resulting reaction mixtures were subjected to ^{1}H NMR analysis prior to and following chromatographic removal of the acetophenone. The results are compiled in Table I.

Scheme II

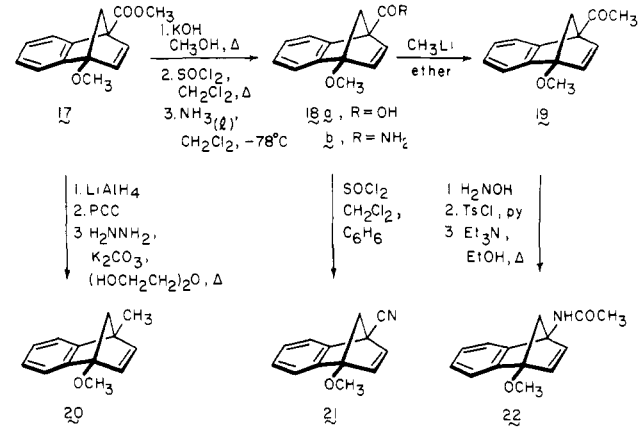
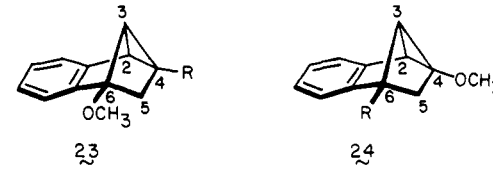


Table I. Product Regioselectivities for 1,4-Disubstituted Benzonorbornadienes

R	**23**,[a] %	**24**,[a] %
17, $COOCH_3$	100	0
18b, $CONH_2$	100	0
19, $COCH_3$	100	0
21, CN	100	0
22, $NHCOCH_3$[b]	62	38
20, CH_3	44	56

[a] The limits of detection are considered to be ±3%. [b] A small amount of an unidentified companion decomposition product inseparable from **24**-$NHCOCH_3$ is also formed. Since the relative proportion of this substance is folded into the 38% figure, this value must be regarded as a higher limit.

Carbomethoxy derivative **17** gave rise to a single photoproduct (100%), which was identified as **23**-$COOCH_3$. For the structural



assignment, advantage was again taken of the fact that the tetracyclo[5.4.0.0^{2,4}.0^{3,6}]undeca-1(7),8,10-triene ring system causes its aliphatic protons to possess very characteristic coupling constants and appear within well-defined chemical shift regions. Since the 4- and 6-positions in the present photoproducts are necessarily both substituted as in **23** and **24**, a distinction between these isomers becomes somewhat more cumbersome than when only one functional group is present. ^{1}H NMR chemical shift correlations with monosubstituted analogues prepared earlier[1,10] proved to be particularly helpful (Table II). In these systems, the proton at C-2 was noted to be particularly sensitive to the nature of the C-4 substituent. For example, whereas a 4-carbomethoxy group exerts a deshielding effect at this site (δ 3.32), an alkoxy group such as *tert*-butoxy causes H-2 to appear at substantially higher field. On this basis, the formation of **23**-$COOCH_3$ was clearly indicated by the appearance of its H-2 signal at δ 3.38.

Amide **18b** and ketone **19** followed a completely analogous reaction course. Nitrile **21**, the fourth benzonorbornadiene to carry a powerful electron-withdrawing group, afforded only **23**-CN and therefore is subject to the same product-determinative influences. The exceptionally close similarity of the H-2 chemical shift in **23**-CN (δ 3.23) to that in the 4-cyanotetracycloundecatriene (δ

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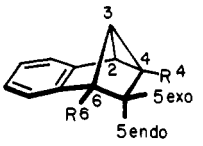
(17) Trost, B. M.; Chen, F. *Tetrahedron Lett.* **1971**, 2603.

Table II. Chemical Shifts of the Aliphatic Protons in Representative Tetracyclo[5.4.0.0^{2,4}.0^{3,6}]undeca-1(7),8,10-trienes (300 MHz, $CDCl_3$ Solution, δ)



compd	H_2	H_3	H_4	$H_{3\,exo}$	$H_{3\,endo}$	H_6	other
R_4 = $COOCH_3$, R_6 = H	3.32 (d, J = 5.4 Hz)	3.80 (ddd, J = 5.4, 3.4, 1.8 Hz)		3.02 (dd, J = 9.2, 7.8 Hz)	1.02 (dd, J = 9.2, 1.8 Hz)	3.34 (dd, J = 7.8, 3.4 Hz)	$COOCH_3$ (3.71, s)
R_4 = $OC(CH_3)_3$, R_6 = H	2.52 (ddd, J = 5.6, 3.9, 2.2 Hz)	3.64 (ddd, J = 5.6, 3.9, 2.2 Hz)		2.92 (dd, J = 8.2, 8.2 Hz)	1.39 (dd, J = 8.2, 2.2 Hz)	3.28 (dd, J = 8.2, 3.9 Hz)	$OC(CH_3)_3$ (1.28, s)
R_4 = $COOCH_3$, R_6 = OCH_3	3.38 (d, J = 5.6 Hz)	4.02 (dd, J = 5.6, 1.8 Hz)		2.97 (d, J = 9.0 Hz)	1.44 (dd, J = 9.0, 1.8 Hz)		$COOCH_3$ (3.73, s) OCH_3 (3.44, s)
R_4 = CN, R_6 = H	3.18 (d, J = 5.6 Hz)	3.85 (ddd, J = 5.6, 2.9, 1.8 Hz)		3.06 (dd, J = 8.4, 7.7 Hz)	1.07 (dd, J = 8.4, 1.8 Hz)	3.44 (dd, J = 7.7, 2.9 Hz)	
R_4 = CN, R_6 = OCH_3	3.23 (d, J = 5.7 Hz)	4.07 (dd, J = 6.0, 1.9 Hz)		2.98 (d, J = 8.9 Hz)	1.47 (dd, J = 8.9, 1.9 Hz)		OCH_3 (3.44, s)
R_4 = $NHCOCH_3$, R_6 = H	2.90 (d, J = 5.5 Hz)	3.88 (ddd, J = 5.5, 3.4, 2.4 Hz)		3.20 (dd, J = 8.2, 7.9 Hz)	1.17 (dd, J = 8.2, 2.4 Hz)	3.43, (dd, J = 7.9, 3.4 Hz)	$NHCOCH_3$ (1.98, s) $NHCOCH_3$ (6.14, br s)
R_4 = $NHCOCH_3$, R_6 = OCH_3	2.73 (d, J = 5.7 Hz)	4.05 (dd, J = 5.7, 2.2 Hz)		3.15 (d, J = 8.3 Hz)	1.57 (dd, J = 8, 2.2 Hz)		$NHCOCH_3$ (1.99, s) $NHCOCH_3$ (6.10, br s) OCH_3 (3.50, s)
R_4 = OCH_3, R = $NHCOCH_3$	2.77 (d, J = 5.6 Hz)	4.11 (dd, J = 5.9, 2.4 Hz)		3.06 (d, J = 8.3 Hz)	1.75 (dd, J = 8.3, 2.4 Hz)		$NHCOCH_3$ (2.10, s) $NHCOCH_3$ (2.10, s)
R_4 = CH_3, R_6 = H	2.24 (d, J = 4.9 Hz)	3.18 (ddd, J = 4.9, 2.9, 2.9 Hz)		2.54 (dd, J = 8.8, 8.3 Hz)	0.92 (dd, J = 8.8, 2.9 Hz)	3.28 (dd, J = 8.3, 2.9 Hz)	CH_3 (1.39, s)
R_4 = H, R_6 = CH_3	2.50 (dd, J = 5.4, 5.4 Hz)	3.06 (ddd, J = 5.4, 4.4, 2.8 Hz)	1.95 (ddd, J = 5.4, 4.4, 3.4 Hz)	2.39 (dd, J = 8.8, 3.4 Hz)	0.90 (dd, J = 8.8, 2.8 Hz)		CH_3 (1.49, s)
R_4 = CH_3, R_6 = OCH_3	2.34 (d, J = 5.4 Hz)	3.40 (dd, J = 5.7, 2.6 Hz)		2.47 (d, J = 8.6 Hz)	1.35 (dd, J = 8.6, 2.6 Hz)		CH_3 (1.44, s) OCH_3 (3.42, s)
R_4 = OCH_3, R_4 = CH_3	2.58 (d, J = 5.7 Hz)	3.64 (dd, J = 5.7, 2.7 Hz)		2.45 (d, J = 8.2 Hz)	1.52 (dd, J = 8.2, 2.7 Hz)		CH_3 (1.52, s) OCH_3 (3.42, s)

3.18) leaves no doubt as to the correctness of the structural assignment. In actuality, H-5 constitutes an additional informative spectral probe (Table II). When one of the powerful electron-withdrawing groups is positioned at C-4, H-5_{endo} is found at δ 1.0–1.1. By comparison, a 4-alkoxy group deshields this proton significantly, although less so than when it is bonded to C-6.

The full complement of substituent effects was revealed in the product mixture that results from irradiation of **20**. In this instance, the less prevalent isomer (44%) was identified as **23**-CH_3 on the strength of the chemical shifts of H-2 (δ 2.34) and H-5_{endo} (δ 1.35). For major isomer **24**-CH_3 (56%), the comparable protons are seen at v 2.58 and 1.22, respectively. The $\Delta\delta$ for H-2 (0.24 ppm) is closely similar to the $\Delta\delta$ determined for the 4-*tert*-butoxy- and 4-methyltetracycloundecatrienes (0.28 ppm) and lies in the same direction. Additionally, direct attachment of the methyl group to the cyclopropane ring in **23**-CH_3 can be inferred from the appearance of the singlet at δ 1.44 and the instability of **24**-CH_3 in solution. The magnetic anisotropy effect is maintained in the 4-methyl derivative (δ 1.39) but of course cannot operate when the alkyl group is attached to the C-6 site as in the simple hydrocarbon (δ 1.49) or **24**-CH_3 (δ 1.52, see Table II).

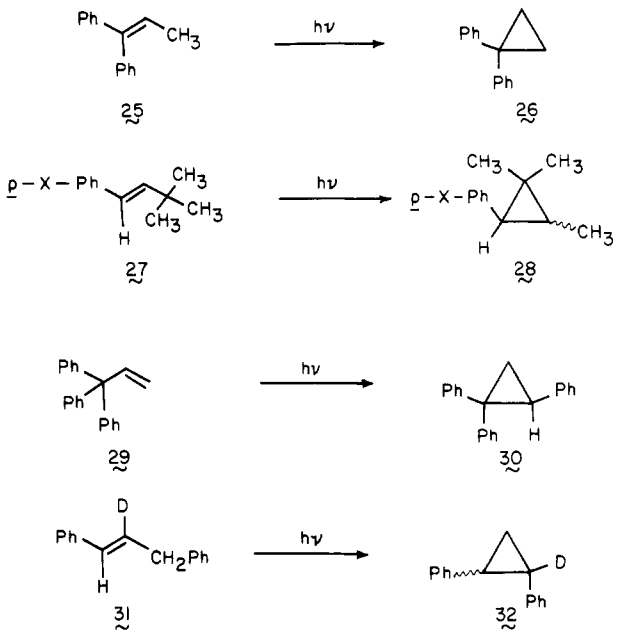
When acetamido derivative **22** was irradiated under the same conditions, two isomeric photoproducts resulted. A small amount of a third component was also formed. Although the ^1H NMR signals of the major photoisomer (**23**-$NHCOCH_3$, 62%) were well separated, those of the less dominant regioisomer overlapped in part with absorptions due to its decomposition product. Accordingly, the 38% yield assigned to **24**-$NHCOCH_3$ should be regarded as an upper limit. In this instance, the chemical shifts of H-2 proved to be too similar to be reliably diagnostic of structure. Fortunately, however, H-5_{endo} was adequately responsive to the C-4 and C-6 substitution plans. In **24**-$NHCOCH_3$, this doublet of doublets appears at δ 1.75, approximately 0.18 ppm *downfield* of that in **23**-$NHCOCH_3$. The greater deshielding capability of an acetamido function has been observed elsewhere; for example, in the simpler 4-substituted derivatives, the flanking acetamido group shifts H-2 downfield by 0.38 ppm relative to *tert*-butoxy (Table II). Further confirmation of our assignments could be derived from the acetamido shifts proper. Appropriately, the three-proton singlet due to this substituent in **23**-$NHCOCH_3$ (δ 1.99) is upfield of that in **24**-$NHCOCH_3$ as a direct consequence of its proximity to the three-membered ring. The latter substance also slowly decomposes on standing in solution.

Discussion

Origins of the Aryl Bridging Concept. In his pioneering work concerning the photochemical rearrangement of arylpropenes to cyclopropanes, Griffin demonstrated that the migratory group could be hydrogen (**25** → **26**),[18] alkyl (**27**-H → **28**-H),[19] or aryl

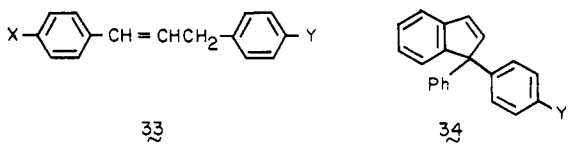
(18) Griffin, G. W.; Marcantonio, A. F.; Kristinsson, H.; Petterson, R. C.; Irving, C. S. *Tetrahedron Lett.* **1965**, 2951.

(**29** → **30**).[18] Subsequent studies by Hixson established on the



basis of the conversion of **31** to **32** that 1,2-phenyl shifting dominates heavily over hydrogen migration in this system.[20] At this point, the migrations of hydrogen and alkyl were classified as σ^2s + π^2s cycloadditions. In contrast, the greater efficiency of π–π interaction relative to σ–π interaction was taken to mean that aryl groups rearrange differently. Bridged radicals were invoked.

When the para substituent in **27** is cyano, a 3-fold increase in rearrangement rate is observed; in contrast, *p*-methoxy retards the photoisomerization.[21] Comparable electronic perturbations at X in **33** (Y = H) have the same effect (k_H = 1; k_{CN} = 41; k_{OCH_3}



≤ 0.04).[22] Substitution of Y in **33**[22] and **34**[23] by groups such as bromo, cyano, and methoxy dramatically induces favored migration of all three *p*-X-phenyl groups relative to phenyl. These findings conform to Ruchardt's earlier experiments where it was shown that a *p*-cyanophenyl group exhibits a much higher migratory aptitude to a free radical center than other aryl substituents.[24] Kinetic measurements denote that the effect does not arise by imposition of a retarding influence on phenyl shifting.[23] For *p*-anisyl, Ruchardt noted more ready migration in one case[25] but not another where it was marginally slower.

A few years earlier, Zimmerman and co-workers were carefully extending observations dealing with photochemical migratory aptitudes in 4,4-disubstituted 2-cyclohexenones[26] to the structurally related 1-methylene derivatives.[27] This change in substrate was necessary to guarantee that aryl migration was occurring from a diene $\pi \rightarrow \pi^*$ excited state rather than a triplet $n \rightarrow \pi^*$ state. Whereas direct irradiation of **35** led principally to **36**, **37** underwent no methyl migration when photoactivated (Scheme III).[28] Chiefly for this reason, an aryl bridging mechanism was advanced for **35**.[27,28]

Following upon this, a more extensive investigation was made of open-chain dienes of type **38**. When X = H and Y = CN, photoisomerization proceeds with full regioselectivity to deliver only **39**;[29] when Y = NMe_2, **40** results.[30] These reaction pathways were attributed to maintenance of maximum electron delocalization along the reaction coordinate. When the discovery was made that dianisyl diene **38** (X = H, Y = OCH_3) rearranges more slowly than the tetraphenyl derivative with an unexpected crossover in regioselectivity (**40**/**39** = 3.3:1), it was argued that ionic factors may dominate over odd-electron stabilization in the control of regioselectivity.[30] Although the trend is that electron-donating groups tend to appear on the product vinyl group whereas electron-withdrawing groups tend to appear on the cyclopropane ring, more intricate substitution plans[31] gave results that led to development of a sophisticated theoretical treatment (the ΔP matrix) of the data.[31,32] The core issue was correlation of the striking, though seemingly anomalous, rate inhibition caused by Y = OCH_3 and NMe_2 in **38** (X = H) with the established ability of these groups to stabilize radical centers.

When only bridgehead substituents are involved as in benzonorbornadienes **17**–**22** and electronic excitation is concentrated in a single aromatic chromophore, our ability to evaluate the details of those photochemical processes leading to **23** and/or **24** should be enhanced. A particularly relevant objective is clarification of whether aryl–vinyl bridging does or does not operate. Since this mechanistic pathway is mediated by cyclopropane ring formation, it becomes relevant to examine briefly the effects of substituents on cyclopropane structure.

The Case against Aryl–Vinyl Bridging. Much current work in structural chemistry has focused on the influence that substituents exert on the bond lengths in cyclopropane.[33] The coherent picture that has emerged for π-acceptor substituents, viz., shortening of the opposite and lengthening of the adjacent bonds,[34–37] nicely conforms to Hoffmann's pioneering molecular orbital rationalization.[38] On the other hand, structural changes wrought in three-membered rings by substituents having lone pairs are less regular.[39–44] These observations have fostered a number of theoretical studies aimed at explaining the different effects.[43,45–48]

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(22) Hixson, S. S. *J. Am. Chem. Soc.* **1972**, *94*, 2507.
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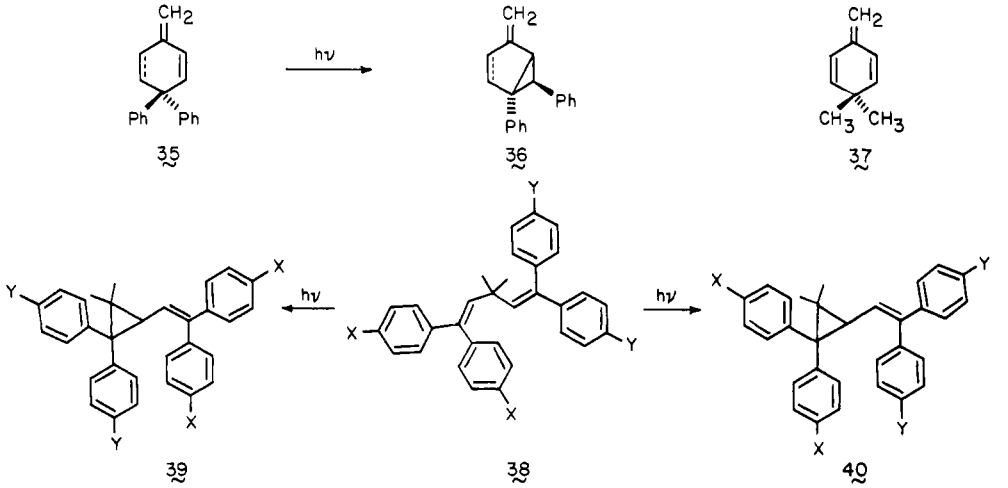
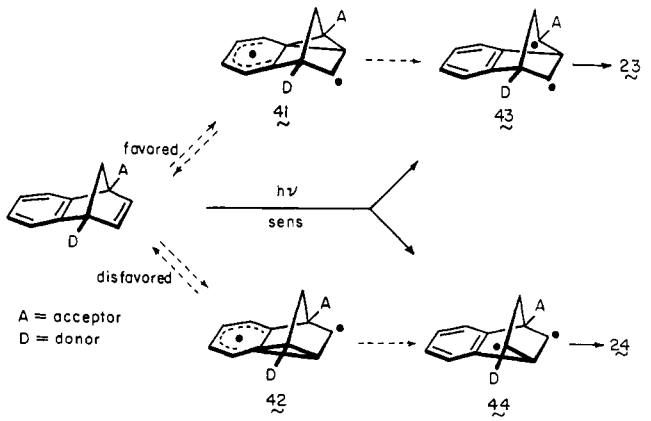
Scheme III



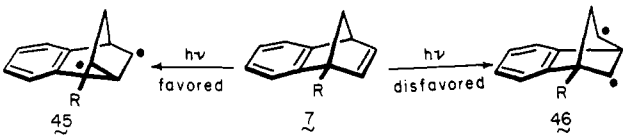
Much of the chemical individuality appears to arise neither from π donation of the lone pair nor the electronegativity of X. Instead, differentiation in ring bond lengths may be caused by local hybridization changes[47,49,50] which act to increase ring strain to varying degrees and by steric effects.[48] The greater the increase in ring strain, the more the donor substituent commands a structural response akin to that of a π-acceptor group. Clearly, this combination of effects cannot explain the regioselective excited-state behavior of 1,4-disubstituted benzonorbornadienes.

1-Substituted benzonorbornadienes undergo preferential bond reorganization proximal to the bridgehead substituent irrespective of its π-acceptor or π-donor nature.[1,10] The principal exception is deuterium. A greater than unity k_H/k_D likewise discounts the possibility that bridging rate differences constitute the source of di-π-methane regioselectivity. On the other hand, the entire spectrum of observations becomes internally consistent if aryl-bridged biradicals are bypassed in favor of a direct 1,2-aryl shift process.[1,10] Our earlier MO rationale for regioselectivity in the rearrangement of aryl- and vinyl-substituted benzonorbornadienes[9] is also in agreement with this conclusion.

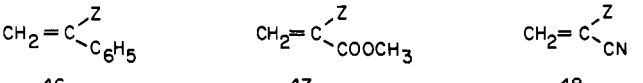
When 2-fold bridgehead substitution is introduced, the excited-state response is characterized by a strong bias for rebonding in the proximity of the π-acceptor group (A). The preference for delivery of **23** is consistent with the intervention of **41** but does



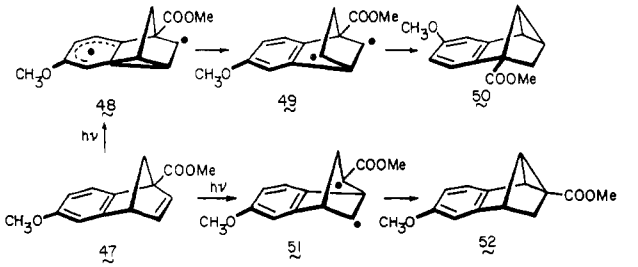
not require its direct involvement. In actual fact, the invoking of **41** and **42** only beclouds the true mechanistic issue. Our findings reflect the superior stabilizing capabilities (relative to OCH_3) of $COOCH_3$, $CONH_2$, $COCH_3$, and CN. This ordering of radical-stabilizing capabilities is likely to be seen to the extent noted herein only with operation of the concerted 1,2-aryl migration pathway. Most substituents, including alkoxy and alkyl, are well recognized to stabilize radical centers. Consequently, product ratios in the case of **7** are similarly determined by direct passage to the more stable 1,2-migrated (nonbridged) biradical **45**.



Concluding Remarks. We have arrived at the conclusion that regioselectivity in di-π-methane rearrangements of doubly connected substrates is governed by the level of stability that a bridgehead substituent can provide to a directly-formed 1,2-aryl shifted biradical. A reasonable extrapolation of this proposal can have interesting consequences when applied to a system such as **47**. If photoexcitation is to proceed with aryl bridging under full



control of the methoxy group, the meta rebonding option depicted in **48** should be determinative of product structure and **50** should



result.[51] In contrast, if the controlling influence lies in the bridgehead carbomethoxy group, rebonding as in **51** should take place since added stabilization is provided to one odd-electron center by this substituent and aromaticity is not disrupted. Preliminary experiments have indicated that the reaction channel that delivers **52** operates exclusively.[52] More complete details will follow in due course.

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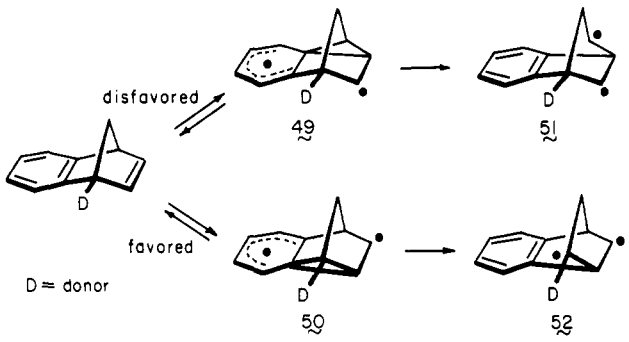

Experimental Section

3-Methoxy-1*H*-indene (12). To a magnetically stirred solution of 1-indanone (**11**) (10.0 g, 0.08 mmol), trimethyl orthoformate (10 mL), absolute methanol (10 mL), and benzene (150 mL) was added 1 mL of methanol saturated with dry hydrogen chloride. After 30 min at room temperature, the reaction mixture was filtered and immediately concentrated on a rotary evaporator. The residual oil was rapidly vacuum distilled (short path) to give 6.5 g (59%) of **12** as a colorless oil: bp 64 °C (8 torr) [lit. bp 101–104 °C (15 torr);[53] bp 116–117 °C (20 torr)[54]]; ^{1}H NMR ($CDCl_3$) δ 7.3 (m, 4 H), 5.23 (t, J = 2 Hz, 1 H) 3.83 (s, 3 H), 3.30 (d, J = 2 Hz, 2 H).

3-Carbomethoxy-1-indanone (14). A solution of **12** (6.5 g, 0.045 mol) in anhydrous tetrahydrofuran (40 mL) was cooled to −78 °C under a nitrogen atmosphere and treated slowly with *n*-butyllithium (30 mL, 1.6 M in hexane) via syringe. The anion was stirred for 2 h before dry carbon dioxide gas was introduced during an additional 2 h. The reaction mixture was allowed to warm to room temperature, poured into water, and extracted with ether. The aqueous phase was made acidic with 2 N hydrochloric acid, and the product was taken up in chloroform (3 × 250 mL), dried, and concentrated. This material was dissolved in methanol saturated with hydrogen chloride (100 mL), stirred for 1 h, and concentrated. There was obtained 7.7 g (91%) of **14** as a colorless oil; IR (neat, cm^{-1}) 3020, 2950, 1740, 1720, 1600, 1460, 1430, 1315, 1235, 1200, 1160, 1035, 750; ^{1}H NMR ($CDCl_3$) δ 7.8–7.2 (m, 4 H), 4.30 (dd, J = 7 and 4 Hz, 1 H), 3.75 (s, 3 H, 3.05 (d, J = 4 Hz, 1 H), 2.95 (d, J = 7 Hz, 1 H); mass spectrum, m/z (M^+) calcd 190.0630, obsd 190.0634.

1-Carbomethoxy-3-methoxy-1*H*-indene (15). A solution of **14** (7.55 g, 39.7 mmol), trimethyl orthoformate (7.55 mL), methanol (7.55 mL), benzene (110 mL), and hydrogen chloride saturated methanol (0.75 mL) was stirred at room temperature for 30 min and immediately processed as described above. There was obtained 8.0 g (99%) of **15** as a colorless oil, which, because it decomposed on attempted distillation, was used without further purification: ^{1}H NMR ($CDCl_3$) δ 7.7–7.05 (m, 4 H), 5.30 (d, J = 3 Hz, 1 H), 4.35 (d, J = 3 Hz, 1 H), 3.88 (s, 3 H), 3.75 (s, 3 H).

Diels–Alder Addition of Maleic Anhydride to 15. A mixture of **15** (8.6 g, 42.2 mmol), maleic anhydride (6.2 g, 0.632 mol), and xylene (10 mL) was heated at reflux under nitrogen for 6 h. Concentration in vacuo followed by HPLC purification (Waters Prep 500, silica gel, elution with ethyl acetate–petroleum ether, 1:1) afforded 5.16 g (40.5%) of **16** as a colorless solid: mp 159.5–160.5 °C (from ether); IR ($CHCl_3$, cm^{-1}) 3030, 2960, 1865, 1790, 1735; ^{1}H NMR ($CDCl_3$) δ 7.47–7.37 (m, 4 H), 4.35 (d, J = 9.3 Hz, 1 H), 3.95 (s, 3 H), 3.94 (d, 1 H), 3.60 (s, 3 H), 2.58 (d, J = 8.6 Hz, 1 H), 2.43 (d, J = 8.3 Hz, 1 H); mass spectrum, m/z ($M^+ - C_4O_3$) calcd 206.0943, obsd 206.0900.

Anal. Calcd for $C_{16}H_{14}O_6$: C, 63.57; H, 4.67. Found: C, 63.44; H, 4.79.

1-Methoxy-4-carbomethoxybenzonorbornadiene (17). A mixture of **16** (760 mg, 2.52 mmol) and bis(triphenylphosphine)nickel dicarbonyl (2.46 g, 3.85 mmol) in anhydrous diglyme (15 mL) was heated to vigorous reflux under argon for 12 h. The solvent was distilled off under vacuum and the residual black solid was leached with boiling ether. The combined organic extracts were filtered and evaporated. Most of the triphenylphosphine was removed by repeated recrystallization from petroleum ether. Final purification was accomplished by MPLC on silica gel (elution with 17% ethyl acetate in petroleum ether). Pure **17** was isolated as a faintly yellow oil (290 mg, 50%): ^{1}H NMR ($CDCl_3$) δ 7.29 (m, 2 H), 7.04 (m, 2 H), 6.85 (d, J = 5.5 Hz, 1 H), 6.73 (d, J = 5.5 Hz, 1 H), 3.90 (s, 3 H), 3.58 (s, 3 H), 2.83 (d, J = 6.2 Hz, 1 H), 2.68 (d, J = 6.2 Hz, 1 H); ^{13}C NMR (ppm, $CDCl_3$) 171.68, 148.37, 148.07, 143.58, 141.45, 125.31, 125.01, 121.06, 120.09, 94.91, 72.88, 61.11, 54.19, 52.19; mass spectrum, m/z (M^+) calcd 230.0943, obsd 230.0920.

1-Methoxybenzonorbornadiene-4-carboxylic Acid (18a). A solution of **17** (100 mg, 0.43 mmol) and potassium hydroxide (80 mg, 1.43 mmol) in 95% ethanol (5 mL) was heated at reflux for 6 h, cooled, and evaporated. The solid was dissolved in water and extracted twice with ether. The aqueous phase was acidified with 10% hydrochloric acid, and the precipitated acid was extracted into ether. The combined organic layers were dried, filtered, and evaporated to give **18a** (90 mg, 97.6%) as a colorless solid: mp 108–110 °C; IR (KBr, cm^{-1}) 3080, 2950, 1710; ^{1}H NMR ($CDCl_3$) δ 11.46 (br s, 1 H), 7.40 (dd, J = 7.5 and 6.9 Hz, 2 H), 7.09 (m, 2 H), 6.92 (d, J = 5.5 Hz, 1 H), 6.81 (d, J = 5.5 Hz, 1 H), 3.63 (s, 3 H), 2.93 (d, J = 6.5 Hz, 1 H), 2.77 (d, J = 6.0 Hz, 1 H); mass spectrum, m/z (M^+) calcd 216.0786, obsd 216.0784.

1-Methoxybenzonorbornadiene-4-carboxamide (18b). A solution of **18a** (140 mg, 0.65 mmol) and thionyl chloride (1 mL) in dichloromethane (5 mL) was heated at reflux for 5 h and freed of solvent. The crude acid chloride (148 mg, 97%) was obtained as a pale brown oil.

A solution of the acid chloride (284 mg, 1.21 mmol) in dry dichloromethane (3 mL) was added dropwise to dry liquid ammonia (7 mL) at −78 °C. The mixture was stirred at this temperature for 4 h and allowed to warm gradually overnight. The amide was obtained as a colorless solid (227 mg, 87%): mp 134–136 °C (from ether); IR ($CHCl_3$, cm^{-1}) 3520, 3490, 3415, 3020, 1685, 1595; ^{1}H NMR ($CDCl_3$) δ 7.32 (m, 2 H), 7.05 (m, 2 H), 6.91 (d, J = 5.8 Hz, 1 H), 6.75 (d, J = 5.5 Hz, 1 H), 6.43 (br s, 1 H), 5.87 (br s, 1 H), 3.57 (s, 3 H), 2.83 (d, J = 5.9 Hz, 1 H), 2.62 (d, J = 5.9 Hz, 1 H); mass spectrum, m/z (M^+) calcd 215.0946, obsd 215.0976.

1-Acetyl-4-methoxybenzonorbornadiene (19). A cold (−78 °C), nitrogen-blanketed solution of **18a** (75 mg, 0.35 mmol) in ether (3 mL) was treated slowly with methyllithium (0.51 mL of 1.5 M, 0.764 mmol). After 15 min, the reaction mixture was warmed to 0 °C, stirred for 3 h, and quenched by the addition of water. The ether phase was separated, washed with water, dried, and evaporated. The resulting solid was purified by spinning-plate chromatography (silica gel, elution with 5% ethyl acetate in petroleum ether) to give 55 mg (74%) of **19** as colorless crystals: mp 67–69 °C (from petroleum ether); IR (CCl_4, cm^{-1}) 2950, 1710; ^{1}H NMR ($CDCl_3$) δ 7.32 (d, J = 6.9 Hz, 1 H), 7.17 (d, J = 7.1 Hz, 1 H), 7.10–6.98 (m, 2 H), 6.93 (d, J = 5.5 Hz, 1 H), 6.75 (d, J = 5.6 Hz, 1 H), 3.59 (s, 3 H), 2.78 (d, J = 6 Hz, 1 H), 2.72 (d, J = 6 Hz, 1 H), 2.39 (s, 3 H); ^{13}C NMR (ppm, $CDCl_3$) 206.28, 149.10, 148.59, 143.93, 140.74, 125.40, 125.15, 121.06, 120.38, 95.19, 73.85, 72.45, 67.85, 54.18, 28.24.

Anal. Calcd $C_{14}H_{14}O_2$: C, 78.48; H, 6.59. Found: C, 78.34; H, 6.64.

1-Methoxy-4-(hydroxymethyl)benzonorbornadiene. A stirred slurry of lithium aluminum hydride (40.5 mg, 1.07 mmol) in ether (5 mL) was treated dropwise with a solution of **17** (250 mg, 1.07 mmol) in the same solvent (2 mL). The reaction mixture was stirred at room temperature for 20 min before being treated dropwise with ethyl acetate (2 mL) followed by water (5 mL). The white suspension was filtered through Celite (with thorough rinsing), and the organic layer of the filtrate was separated after shaking, dried, and evaporated. There was isolated 216 mg (98%) of the alcohol, which was used without additional purification: IR (neat, cm^{-1}) 3410, 2940; ^{1}H NMR ($CDCl_3$) δ 7.30 (m, 1 H), 7.18 (m, 1 H), 7.03 (m, 2 H), 6.77 (d, J = 5.5 Hz, 1 H), 6.62 (d, J = 5.5 Hz, 1 H), 4.31 (d, J = 1.9 Hz, 2 H), 3.58 (s, 3 H), 2.64 (d, J = 6 Hz, 1 H), 2.38 (d, J = 6 Hz, 1 H), 2.11 (br s, 1 H); mass spectrum, m/z (M^+) calcd 202.0994, obsd 202.0999.

1-Methoxybenzonorbornadiene-4-carboxaldehyde. The above carbinol (216 mg, 1.07 mmol) was dissolved in dichloromethane (5 mL) and treated with pyridinium chlorochromate (461 mg, 2.14 mmol). The dark slurry was stirred under an argon atmosphere for 3 h at room temperature and diluted with ether (100 mL). The supernatant liquid was passed through silica gel, the solvent was evaporated, and the product was purified by spinning plate chromatography (silica gel, elution with 10% ethyl acetate in petroleum ether). The aldehyde was obtained as a colorless oil (172 mg, 81%): IR (neat, cm^{-1}) 2950, 1725; ^{1}H NMR ($CDCl_3$) δ 10.23 (s, 1 H), 7.33 (d, J = 7 Hz, 1 H), 7.26 (d, J = 7 Hz, 1 H), 7.06 (m, 2 H), 6.88 (d, J = 5.7 Hz, 1 H), 6.80 (d, J = 5.5 Hz, 1 H), 3.58 (s, 3 H), 2.78 (d, J = 6 Hz, 1 H); mass spectrum, m/z (M^+) calcd 200.0837, obsd 200.0869.

1-Methoxy-4-methylbenzonorbornadiene (20). A mixture of the aldehyde (60 mg, 0.3 mmol), hydrazine hydrate (30 mg, 0.6 mmol), potassium carbonate (33 mg, 0.24 mmol), and diethylene glycol (26.1 mg, 0.25 mmol) was heated at the reflux temperature (180 °C) under an argon atmosphere for 2 h. The reflux condenser was replaced by a short-path distillation head holding a receiving flask and the volatile liquids were allowed to distil under argon during 1.5 h. After cooling, the inner surfaces of the equipment were washed with a mixture of ether and water. The combined washings were shaken and the ethereal layer was extracted with 10% hydrochloric acid prior to drying and solvent

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evaporation. Purification of the resulting brown oil by spinning plate chromatography (silica gel, elution with 2.5% ethyl acetate in petroleum ether) afforded 40 mg (72%) of **20** as a colorless oil: IR (neat, cm^{-1}) 2940; ^1H NMR ($CDCl_3$) δ 7.24 (m, 1 H), 7.11 (m, 1 H), 7.0 (m, 2 H), 6.67 (d, J = 5 Hz, 1 H), 6.45 (d, J = 5 Hz, 1 H), 3.55 (s, 3 H), 2.52 (d, J = 6 Hz, 1 H), 2.31 (d, J = 6 Hz, 1 H), 1.65 (s, 3 H); ^{13}C NMR (ppm, $CDCl_3$) 152.96, 150.3, 146.6, 143.8, 124.5, 124.3, 119.4, 119.2, 95.3, 75.9, 65.8, 52.6, 15.3; mass spectrum, m/z calcd 186.1044, obsd 186.1042.

1-Cyano-4-methoxybenzonorbornadiene (21). A solution of **18b** (120 mg, 0.56 mmol) was dissolved in the minimum amount of dichloromethane, thionyl chloride (1 mL) and benzene (3 mL) were added, and the solution was refluxed under argon for 6 h. Evaporation of the solvents gave a yellow solid, which was treated with ether and filtered to remove insoluble material. The filtrate was subjected to spinning plate chromatography (silica gel, elution with 5% ethyl acetate in petroleum ether). There was isolated 50 mg (49.3%) of **21**: IR (neat, cm^{-1}) 2970, 2270; ^1H NMR ($CDCl_3$) δ 7.43 (m, 1 H), 7.33 (m, 1 H), 7.11 (m, 2 H), 6.81 (d, J = 5.5 Hz, 1 H), 6.74 (d, J = 5.5 Hz, 1 H), 3.57 (s, 3 H), 2.98 (d, J = 6.2 Hz, 1 H), 2.72 (d, J = 6.2 Hz, 1 H); ^{13}C NMR (ppm, $CDCl_3$) 146.17, 145.57, 144.05, 140.04, 126.29, 125.57, 120.63, 120.53, 118.43, 94.58, 74.80, 54.36, 46.27; mass spectrum, m/z (M^+) calcd 197.0840, obsd 197.0814.

1-Acetamido-4-methoxybenzonorbornadiene (22). A mixture of **19** (70.1 mg, 0.328 mmol), hydroxylamine hydrochloride (114 mg, 1.64 mmol), and anhydrous sodium acetate (269 mg, 3.28 mmol) in methanol (10 mL) was stirred overnight at room temperature. Water (50 mL) was added and the white precipitate was taken up in ether. After drying and solvent evaporation, there was obtained 75 mg (100%) of the oxime as a white solid: mp 147.5–149.5 °C; IR (CCl_4, cm^{-1}) 3590, 3380 (br), 2940; ^1H NMR ($CDCl_3$) δ 7.31 (dd, J = 6.4 and 1.0 Hz, 1 H), 7.07 (dd, J = 6.4 and 1 Hz, 1 H), 7.05 (m, 2 H), 6.89 (d, J = 5.5 Hz, 1 H), 6.76 (d, J = 5.5 Hz, 1 H), 3.58 (s, 3 H), 2.68 (d, J = 6.1 Hz, 1 H), 2.67 (br s, 1 H), 2.64 (d, J = 6.1 Hz, 1 H), 2.13 (s, 3 H); mass spectrum, m/z (M^+) calcd 229.1103, obsd 229.1111.

A solution of the oxime (134.8 mg, 0.58 mmol) and *p*-toluenesulfonyl chloride (224.3 mg, 1.18 mmol) in anhydrous pyridine (3 mL) was stirred at ambient temperature for 3 days, diluted with water (50 mL), and extracted with ether. The combined organic layers were washed with water, saturated sodium bicarbonate solution, water, 10% hydrochloric acid, and water. Drying and concentration yielded the oxime tosylate as an off-white solid (155 mg, 93%): mp 128–129.5 °C dec (from ether); IR ($CHCl_3$, cm^{-1}) 3020, 1375, 1305, 1190, 1180; ^1H NMR ($CDCl_3$) δ 7.89 (d, J = 8.2 Hz, 2 H), 7.33 (d, J = 8.2 Hz, 2 H), 7.28 (d, J = 7.2 Hz, 1 H), 7.03 (dt, J = 7.1 and 1.5 Hz, 1 H), 6.91 (m, 2 H), 6.77 (d, J = 7.6 Hz, 1 H), 6.72 (d, J = 5.6 Hz, 1 H), 3.55 (s, 3 H), 2.65 (d, J = 6.1 Hz, 1 H), 2.56 (d, J = 6.1 Hz, 1 H), 2.44 (s, 3 H), 2.15 (s, 3 H); mass spectrum, m/z (M^+) calcd 383.1193, obsd 383.1243.

A solution of the oxime tosylate (119 mg, 0.42 mmol) and triethylamine (42.5 mg, 0.42 mmol) in 80% aqueous ethanol (10 mL) was heated at reflux for 8 h, diluted with water, saturated with sodium chloride, and extracted 4 times with ether. The combined ether layers were washed with water, dried, and concentrated to leave a pale yellow oil (59.7 mg). Purification by spinning plate chromatography (silica gel, elution with ethyl acetate) returned 18.6 mg of starting material and gave 39.6 mg (66% corrected) of **22**, colorless solid: mp 143.5–144.5 °C (from ether); IR ($CHCl_3$, cm^{-1}) 3440, 3010, 1680, 1520; ^1H NMR ($CDCl_3$) δ 7.29 (m, 1 H), 7.15 (m, 1 H), 7.04 (m, 2 H), 6.82 (d, J = 5.8 Hz, 1 H), 6.68 (d, J = 5.6 Hz, 1 H), 6.22 (br s, 1 H), 3.56 (s, 3 H), 3.08 (d, J = 5.6 Hz, 1 H), 2.66 (d, J = 5.6 Hz, 1 H), 2.16 (s, 3 H); ^{13}C NMR (ppm, $CDCl_3$) 170.26, 148.29, 143.26, 141.88, 125.27, 124.83, 119.80, 118.98, 92.90, 74.91, 68.35, 54.19, 23.80.

Photoisomerization of 17. General Procedure. A solution of **17** (85 mg, 0.37 mmol) and acetophenone (1 drop) in benzene (40 mL) was deoxygenated by bubbling nitrogen into the reaction mixture for 20 min. Irradiation was carried out in a Rayonet reactor equipped with 3500-Å lamps for 75 min, the solvent was removed in vacuo, and the product was purified by spinning plate chromatography (elution with 5% ethyl acetate in petroleum ether). Ester **23**-$COOCH_3$, a colorless oil, was the only product formed (85 mg, 100%): IR (neat, cm^{-1}) 2990, 2950, 2835, 1735; ^1H NMR, see Table II; ^{13}C NMR (ppm, $CDCl_3$) 171.59, 145.31, 138.24, 127.01, 126.09, 124.00, 118.86, 55.35, 53.73, 51.89, 36.57, 36.19, 26.91; mass spectrum, m/e (M^+) calcd 230.0943, obsd 200.0906.

Photoisomerization of 18b. From 21.8 mg (0.095 mmol) of **18b**, there was isolated 18.4 mg (84.4%) of **23**-$CONH_2$, a colorless solid: mp 172–176 °C, as the only observable product; IR ($CHCl_3$, cm^{-1}) 3530, 3490, 3415, 3020, 1670, 1590; ^1H NMR ($CDCl_3$) δ 7.42 (m, 1 H), 7.20 (m, 2 H), 7.15 (m, 1 H), 5.94 (br s, 1 H), 5.66 (br s, 1 H), 4.01 (dd, J = 5.5 and 1.6 Hz, 1 H), 3.44 (s, 3 H), 3.37 (d, J = 5.5 Hz, 1 H), 2.82 (d, J = 8.1 Hz, 1 H), 1.50 (dd, J = 8.1 and 1.7 Hz, 1 H); ^{13}C NMR (ppm, $CDCl_3$) 171.23, 144.97, 138.64, 127.07, 125.88, 124.00, 118.86, 86.68, 77.21, 54.47, 53.72, 36.65, 36.08; mass spectrum, m/z (M^+) calcd 215.0946, obsd 215.0961.

Photoisomerization of 19. From 65 mg (0.30 mmol) of **19**, there was obtained 60 mg (92%) of **23**-$COCH_3$ as a colorless oil. No other product was observed. IR (neat, cm^{-1}) 3052, 2935, 2825, 1683; ^1H NMR ($CDCl_3$) δ 7.4 (m, 1 H), 7.22 (m, 2 H), 7.15 (m, 1 H), 4.09 (dd, J = 6.5 and 1.8 Hz, 1 H), 3.43 (s, 3 H), 3.42 (partially hidden d, 1 h), 2.94 (d, J = 8.8 Hz, 1 H), 2.19 (s, 3 H), 1.53 (dd, J = 8.8 and 1.8 Hz, 1 H); mass spectrum, m/z (M^+) calcd 214.0993, obsd 214.0947.

Photoisomerization of 20. Two runs (72.1 and 65.1 mg) were made and the product mixtures were analyzed by ^1H NMR. Identical 56:44 ratios were obtained. The samples were combined and subjected to chromatography. The less polar material proved to be **23**-CH_3 (44%): ^1H NMR, see Table II; ^{13}C NMR (ppm, $CDCl_3$) 141.45, 126.58, 126.36, 124.78, 123.19, 118.65, 88.25, 53.54, 51.41, 41.35, 35.17, 25.82, 18.38; mass spectrum, m/z ($M^+ - C_2H_2$) calcd 160.0888, obsd 160.0870.

24-CH_3: ^1H NMR, see Table II; mass spectrum, m/z ($M^+ - C_2H_2$) calcd 160.0888, obsd 160.0972.

Photoisomerization of 21. Irradiation of a 48.9-mg sample of the nitrile led to isolation of 40.7 mg (83.2%) of **23**-CN. No other isomer was observed. IR (CCl_4, cm^{-1}) 2935, 2225; ^1H NMR, see Table II; ^{13}C NMR (ppm, $CDCl_3$) 144.2, 136.2, 127.7, 127.0, 124.5, 119.1, 87.9, 53.9, 52.8, 37.6, 36.0, 11.0; mass spectrum, m/z (M^+) calcd 197.0840, obsd 197.0849.

Photoisomerization of 22. Two runs (47 and 44.6 mg) were made and the product mixtures were analyzed by ^1H NMR. In addition to the presence of two photoisomers (62 and 38%), a third unknown decomposition product was present in small amounts. The mixture as a whole was purified by spinning plate chromatography.

23-$NHCOCH_3$: IR ($CHCl_3$, cm^{-1}) 3440, 3020, 1680; ^1H NMR, see Table II; ^{13}C NMR (ppm, $CDCl_3$) 170.91, 146.04, 139.37, 126.63, 125.54, 123.57, 118.93, 86.40, 53.70, 42.27, 40.03, 34.95, 29.65, 23.47; mass spectrum, m/z (M^+) calcd 229.1103, obsd 229.1083.

24-$NHCOCH_3$: IR ($CHCl_3$, cm^{-1}) 3440, 3020, 1680; ^1H NMR, see Table II; mass spectrum, m/z (M^+) calcd 229.1103, obsd 229.1083.

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