fraction nor the crude reaction mixture showed the presence of isomer **1a**. Early blank fractions through all fractions showing the slower eluting isomer **1b** were combined and analyzed by 250-MHz $^1$H NMR. The NMR spectrum of recovered oxaziridine was indistinguishable from that of pure starting isomer **1b** (vide supra). The ratio of isomers **1a/1b** is easily determined by high-field $^1$H NMR by measurement of the methyl absorptions at $\delta$ 1.511 and 1.414, respectively. The chromatographed oxaziridine from the isomerization experiment showed no isomerization, **1b** $\rightleftarrows$ **1a**, within the limits of FT NMR detection (<1% isomer **1a** present).

In a control run performed as above but omitting brucine, isomer **1b** was shown to be stable (TLC, $^1$H NMR) in refluxing acetonitrile over the period (1 h) of the isomerization experiment.

**Methyl Ethyl Ketone Trapping Experiment.** Oxaziridines **1a,b** were fragmented by the action of brucine dihydrate in refluxing acetonitrile in the presence of 5.0, 10.0, and 70.4 equiv of methyl ethyl ketone. The experiment performed with 10.0 equiv of trapping ketone is representative. Oxaziridines **1a,b** (15.8 mg, 0.10 mmol), brucine dihydrate (50.0 mg, 0.116 mmol), methyl ethyl ketone (72.1 mg, 1.00 mmol), and dodecane (8.0 $\mu$L) were refluxed in acetonitrile (1.3 mL). The reaction was monitored for 2 h through the point of 60% conversion of **1a,b** into products (GLC vs. dodecane internal standard). No 2-*n*-propyl-3-methyl-3-ethyloxaziridine (**12**, $R_1$ = Me, $R_2$ = Et; Scheme III) was detected.[18]

**Reaction of Oxaziridines 1a,b with Dimethylamine.** A stock solution of oxaziridines **1a,b** (51.4 mg, 0.33 mmol) and dideuterio oxaziridines **1a,b** (52.5 mg, 0.33 mmol) was prepared in $CDCl_3$ (1.2 mL). The molecular ion cluster in the low-resolution mass spectrum of the mixture was measured and averaged over 10 consecutive scans. The ratio of the *m/e* 157 to *m/e* 159 mass peaks ($M^+$, oxaziridine-$d_0$/$M^+$, oxaziridine-$d_2$) for the stock solution was 1.18 ± 0.04 (see Table I).

Two 5-mm NMR tubes were charged with the stock solution (0.5 mL) of oxaziridines and cooled to 0 °C. Dimethylamine (0.3–0.5 mL) was added to each tube, and the tubes were sealed and warmed to ambient temperature. The fragmentation in each tube was monitored by $^1$H NMR. The first tube was opened after 8 h (45% conversion) and the second after 24 h (60% conversion). The ratio of remaining **1a,b** to dideuterio **1a,b** was determined by mass spectrometry (vide supra). The results are presented in Table I (see text).

Oxaziridines **1a,b** (250 mg, 1.59 mmol) in $CDCl_3$ (0.5 mL) were cooled to 0 °C. To this solution was added dimethylamine (approximately 0.6 mL) and the tube was sealed. The mixture was warmed to ambient temperature and monitored by $^1$H NMR. At approximately 50% reaction the tube was opened and the reaction mixture was analyzed by GLC. No 1,1-dimethyl-2-*n*-propylhydrazine[19] nor its air-oxidation product, *N,N*-dimethyl-*n*-propylhydrazone,[20] was detected.

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**Registry No.** **1a**, 80160-86-7; dideuterio-**1a**, 80160-87-8; **1b**, 80160-88-9; dideuterio-**1b**, 80160-89-0; **5**, 108-10-1; **14**, 107-10-8; **15**, 26524-34-5.

(18) An authentic sample of **12** for coinjection was prepared from *n*-butylamine and methyl ethyl ketone by the procedure used for **1a,b**.

(19) Made by $LiAlH_4$ reduction of *N,N*-dimethyl-*n*-propylhydrazone.

(20) Made by condensation of *N,N*-dimethylhydrazine and propionaldehyde. 1,1-Dimethyl-2-*n*-propylhydrazine was seen to revert slowly to the hydrazone upon standing (also see ref 9).

# Regioselectivities in the Di-$\pi$-methane Photorearrangement of 2-Methylbenzonorbornadienes Carrying Methoxy- and Cyanoaryl Substituents. The Vinyl Methyl Effect

Leo A. Paquette,* Elliott Bay, Audrey Yeh Ku, Nelson G. Rondan, and K. N. Houk*

*Departments of Chemistry, The Ohio State University, Columbus, Ohio 43210, and The University of Pittsburgh, Pittsburgh, Pennsylvania 15260*

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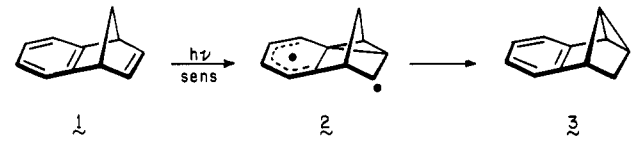
The triplet-state photoisomerizations of 2-methylbenzonorbornadiene and all eight possible aryl cyano- and methoxy-substituted derivatives have been investigated. The parent hydrocarbon underwent di-$\pi$-methane rearrangement with preferential (81%) benzo–vinyl bridging to C-3 ($\beta$ bridging). The 5-$CH_3O$, 6-$CH_3O$, 5-CN, and 7-CN examples represent cases where the substituent effects should work cooperatively, and a single photoproduct was formed in each instance. In the remaining four examples, the substituents are positioned to direct in an antagonist fashion. Interestingly, the product ratios for the 7-$CH_3O$ and 7-CN systems are within experimental error of those determined on the basis of perfect substituent additivity effects. As concerns the 8-$CH_3O$ and 8-CN derivatives, the apparent directing effect of methyl for $\beta/\alpha$ bridging is seen to be slightly higher (96:4) than usual. Probable causes for this phenomenon are presented. Because of its role as a moderate controller of excited-state regioselectivity, the methyl substituent has proven to be a useful probe of such reactions. Synthetic approaches to the alkyl-substituted benzonorbornadienes are also detailed.

Perhaps as a result of its preeminent position as the most widely encountered photoisomerization process,[1] the di-$\pi$-methane rearrangement is rapidly developing into a useful tool for the elucidation of excited-state substituent effects. The dramatic regioselectivities which have been observed to this time point up the need for further investigation, not only to determine their generality but also to gain information concerning their relative efficiencies. The latter phenomenon can be most easily studied by internal competition, where at least two substituents are made to vie for control of different bonding pathways. This technique has been applied in the present experimental undertaking.

(1) Hixson, S. S.; Mariano, P. S.; Zimmerman, H. E. *Chem. Rev.* **1973**, *73*, 531.

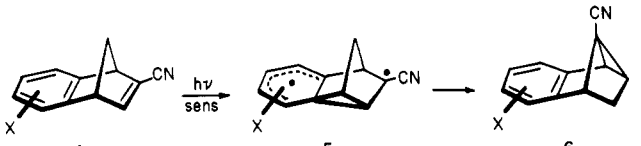
0022-3263/82/1947-0422$01.25/0 

As in our previous investigations,[2-5] use has been made of benzonorbornadiene derivatives. There are several important reasons underlying this choice. First, molecules such as 1 are "doubly connected"[6] di-π-methane systems, such that two regiochemically distinct aryl–vinyl bonding schemes materialize upon unsymmetrical substitution. Second, the conversion to biradical intermediates 2 is invariably a clean triplet process,[7] thereby providing direct insight into the distribution of electronic excitation in triplet biradicals of type 2. Third, drastic deviation from ground-state geometry is circumvented by confining the photoexcited di-π-methane system to a rigid framework. The degree of twisting of the double bond about its axis is thereby restricted, and the geometries of both ground and excited states can be considered not to be significantly different. Our work with benzonorbornadienes is complementary to that of the Zimmerman group which has been investigating polar substituent effects on the singlet-state photochemical behavior of 1,4-pentadienes (flexible singly bridged substrates)[8] and to that of Bender and co-workers which has dealt with benzobarrelenes (molecules capable of both singlet/triplet photoisomerization and vinyl–vinyl/aryl–vinyl bridging).[9]




1 2 3

We have earlier described the striking control of bonding options which operates during the photorearrangement of benzonorbornadienes substituted by electron donor and acceptor groups in the meta[2] and ortho positions.[3] In brief, meta acceptors induce regiospecific para bridging, while meta donors prefer meta bridging. Either type of ortho substituent promotes bridging to the adjacent (ortho) aryl carbon. However, the presence of a vinyl cyano group as in 4 totally dampens the normal bonding preferences of such aryl substituents and engenders fully regiospecific rearrangement via 5, such that 3-cyanotetracyclo[5.4.0.0$^{2,4}$.0$^{3,6}$]undeca-1(7),8,10-trienes (6) are isolated in isomerically pure form.[4,5]

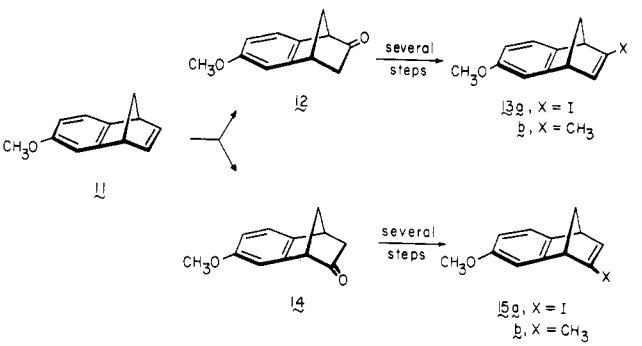



4 5 6

X = OCH$_3$, CN

Clearly, the vinyl cyano group is so all-controlling that no information is made available on the finer points of competitive substituent control. For this reason, we were led to investigate the extent of the influence available to a vinyl methyl group in dictating bridging regioselectivity. 2-Methylbenzonorbornadiene (**8a**) and its eight possible aryl cyano and methoxy derivatives have been synthesized and subjected to light-induced isomerization. The intriguing regioselectivity patterns which have been observed provide new insight into prevailing electronic distributions within triplet excited states.

Scheme I



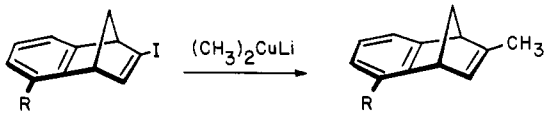

12 13a, X = I; b, X = CH$_3$

11

14 15a, X = I; b, X = CH$_3$

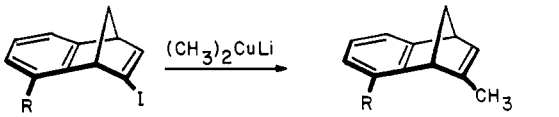
## Results

**Synthesis of Reactants.** The various 2-methylbenzonorbornadienes were made available by reaction of the corresponding 2-iodobenzonorbornadienes with lithium dimethylcuprate. Parent iodide **7a** and the two pairs of ortho isomers (**7b,c** and **9a,b**) were previously known,[4,5]




7 8

a, R = H; b, R = CN; c, R = OCH$_3$




9 10

a, R = CN; b, R = OCH$_3$

and their methyl-substituted counterparts are easily distinguished by their $^1$H NMR spectra. In both **8b** and **8c** the two benzylic protons appear at very different chemical shifts above and below δ 3.75, while in **10a** and **10b** these signals are merged into a multiplet near δ 3.85. Evidently, the shielding and deshielding experienced by H-4 in **8b** and **8c**, respectively, as a consequence of its proximity to the flanking aryl substituent,[4,5] is somewhat depressed when this proton is also proximal to the vinyl methyl group (the bridgehead protons in **8a** are seen at δ 3.76 and 3.42).

To arrive at the *m*-methoxy isomers **13b** and **15b**, we took advantage of the potential of the methoxyl group in 11 for long-range pπ aryl participation as demonstrated earlier by Tanida[10] and by Ku.[5] Subsequent conversion

(2) (a) Paquette, L. A.; Cottrell, D. M.; Snow, R. A.; Gifkins, K. B.; Clardy, J. *J. Am. Chem. Soc.* **1975**, *97*, 3275. (b) Paquette, L. A.; Cottrell, D. M.; Snow, R. A. *Ibid.* **1977**, *99*, 3723.

(3) (a) Santiago, C.; Houk, K. N.; Snow, R. A.; Paquette, L. A. *J. Am. Chem. Soc.* **1976**, *98*, 7443. (b) Snow, R. A.; Cottrell, D. M.; Paquette, L. A. *Ibid.* **1977**, *99*, 3734.

(4) Paquette, L. A.; Ku, A. Y.; Santiago, C.; Rozeboom, M. D.; Houk, K. N. *J. Am. Chem. Soc.* **1979**, *101*, 5972.

(5) Ku, A. Y.; Paquette, L. A.; Rozeboom, M. D.; Houk, K. N. *J. Am. Chem. Soc.* **1979**, *101*, 5981.

(6) Hahn, R. C.; Johnson, R. P. *J. Am. Chem. Soc.* **1977**, *99*, 1508.

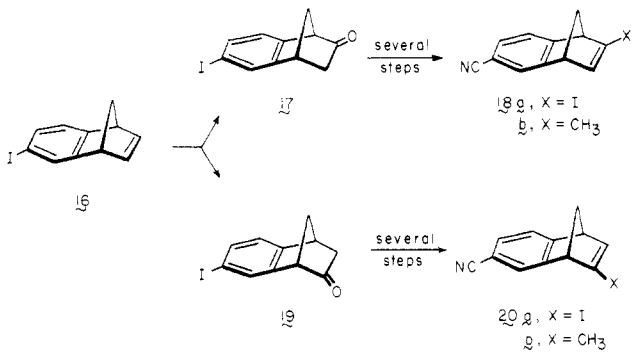
(7) The initial observation is due to: Edman, J. R. *J. Am. Chem. Soc.* **1969**, *91*, 7103.

(8) For recent developments, see: (a) Zimmerman, H. E.; Gruenbaum, W. T. *J. Org. Chem.* **1978**, *43*, 1997. (b) Zimmerman, H. E.; Welter, T. R. *J. Am. Chem. Soc.* **1978**, *100*, 4131. (c) Zimmerman, H. E.; Steinmetz, M. G.; Kreil, C. L. *Ibid.* **1978**, *100*, 4146. (d) Zimmerman, H. E.; Klun, R. T. *Tetrahedron* **1978**, *34*, 1775. (e) Zimmerman, H. E.; Armesto, D.; Amezua, M. G.; Gannett, T. P.; Johnson, R. P. *J. Am. Chem. Soc.* **1979**, *101*, 6367.

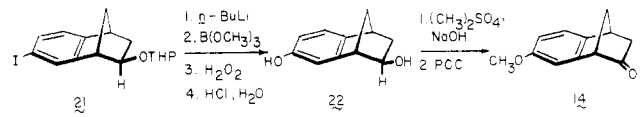
(9) (a) Bender, C. O.; Shugarman, S. S. *J. Chem. Soc., Chem. Commun.* **1974**, 934. (b) Bender, C. O.; Brooks, D. W. *Can. J. Chem.* **1975**, *53*, 1684. (c) Bender, C. O.; Wilson, J. *Helv. Chim. Acta* **1976**, *59*, 1469. (d) Bender, C. O.; King-Brown, E. H. *J. Chem. Soc., Chem. Commun.* **1976**, 878. (e) Demuth, M.; Bender, C. O.; Braslavsky, S. E.; Görner, H.; Burger, U.; Amrein, W.; Schaffner, K. *Helv. Chim. Acta* **1979**, *62*, 847. (f) Bender, C. O.; Brooks, D. W.; Cheng, W.; Dolman, D.; O'Shea, S. F.; Shugarman, S. S. *Can. J. Chem.* **1978**, *56*, 3027. (g) Bender, C. O.; O'Shea, S. F. *Ibid.* **1979**, *57*, 2804.

(10) Tanida, H.; Ishitobi, H.; Irie, T.; Tsushima, T. *J. Am. Chem. Soc.* **1969**, *91*, 4512.

Scheme II




Scheme III



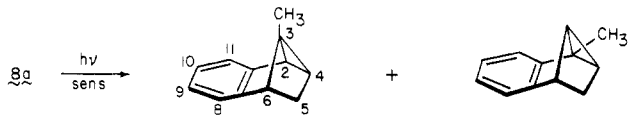

of the isomerically pure ketones **12** and **14** to the desired methyl-substituted benzonorbornadienes followed conventional methodology (Scheme I).

Access to the *m*-cyano-substituted derivatives **18b** and **20b** was necessarily achieved less directly via 6-iodobenzonorbornadiene (**16**).[2] Since an iodine atom is traditionally electron-withdrawing ($\sigma^*$ for *p*-I = 0.135) as compared to a methoxyl group ($\sigma^*$ for *p*-$OCH_3$ = –0.778),[11] homoconjugative interaction within **16** during electrophilic attack can be expected to disfavor homo-para cation generation. This effect has previously been encountered in the response of both 6-chloro-[12] and 6-fluorobenzonorbornadiene[13] to various electrophiles. We had earlier observed synthetically useful regioselectivities in certain hydroxylation reactions of **16**.[4] Hydroboration–oxidation, for example, provided a 14:1 mixture of benzonorbornadienone, while oxymercuration–demercuration and subsequent Jones oxidation led to a product mixture richer in the minor component formed earlier (ratio 1:1.5). In line with the expectation that electrophiles would preferentially attack $C_2$ in **16**, as delineated also by molecular orbital theory,[14] the major products of these reactions were designated as **17** and **19**, respectively (Scheme II).

While the confidence level in these structural assignments was adequate for the earlier study,[15] definitive proof of the validity of these assignments was mandated at this time (see below). Accordingly, an interconversion of the *m*-iodo and *m*-methoxy series was undertaken. For this purpose, the *minor* oxymercuration product of **16** (i.e., the *major* hydroboration isomer) was converted to its tetrahydropyranyl ether (**21**). Following halogen–metal exchange of **21** with *n*-butylithium,[16] the organometallic was condensed with trimethyl borate, and the organoborane intermediate was oxidized and hydrolyzed[17] (Scheme III).

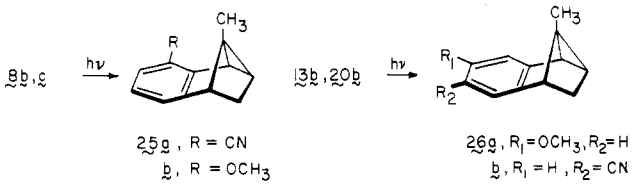
The resulting phenolic alcohol (**22**) was chemospecifically methylated and then oxidized. The ketone so produced proved to be identical in all respects with **14**. The major oxymercuration product is therefore **17** and the major hydroboration product **19**. Consequently, a reversal in the prior assignments to **17** and **19** is necessary, and the mechanistic aspects of the formation of these ketones requires reevaluation.[4] Perhaps the transmission of homoconjugative electronic interaction is substituent dependent. While powerful electron-releasing or -withdrawing groups could exert an effect which declines only rather slowly with distance, weaker substituents might be subject to a more significant drop-off in homoconjugative control. Although this question requires further study, the substitution patterns of our substrates were now securely established. As expected, the $^1H$ NMR spectra of **13b**/**15b** and **18b**/**20b** are strikingly similar and less easily distinguished.

**Photoisomerization Studies.** Irradiations were routinely carried out in a Rayonet reactor equipped with 3500-Å lamps on benzene solutions containing acetophenone as the sensitizer. In the case of **8a**, rearrangement




proceeded rapidly and cleanly to give the pair of photoproducts **23** (81%) and **24** (19%) in high yield. Because the aliphatic regions in the $^1H$ NMR spectra of tetracyclo[5.4.0.0$^{2,4}$.0$^{3,6}$]undeca-1(7),8,10-trienes are almost always divided into five distinct regions, each endowed with well-defined multiplicity unique to the particular proton,[2-7] structural assignments in this series can be confidently made on spectroscopic grounds alone. As concerns regioisomer **23**, for example, the signal due to H-6 at $\delta$ 3.2–3.0 is seen to be simplified to a doublet of doublets ($J_{5exo,6}$ = 7.8 Hz, $J_{4,6}$ = 2.8 Hz). Furthermore, H-$5_{endo}$ appears as a simple doublet at $\delta$ 0.66 ($J_{5endo,5exo}$ = 9.6 Hz) instead of its more customary doublet of doublet pattern which would result from additional W-plan coupling to H-3. Most telltale, of course, is the nondetectability of an absorption attributable to H-3. Turning to **24**, we see reinstatement of the multiplet due to H-3, return of the doublet multiplicity to H-$5_{endo}$, absence of the H-2 triplet, and loss of those spin–spin interactions normally produced by H-2. Comparable first-order techniques were employed to deduce the structures of all the additional photoproducts described herein (consult the Experimental Section).

With this result in hand, attention was next turned to those examples where the effects of the vinyl methyl and aryl substituents were expected to be reinforcing. This was desirable in order to establish whether regiospecificity would in fact be encountered. Indeed, sensitized irradiation of **8b** and **8c** in the predescribed manner produced uniquely the 3-methyl-substituted photoisomers **25a** and **25b**, respectively. Had the alternate bridging mode op-



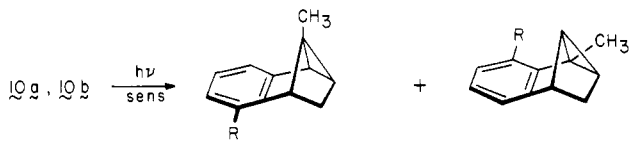

erated, the methyl group and the polar aryl functionality would have appeared at C-2 and C-7, respectively. The $^1H$ NMR spectra easily permit distinction between these options.

(11) Hine, J. "Physical Organic Chemistry", 2nd ed.; McGraw-Hill: New York, 1962; pp 87, 90.
(12) Uemura, S.; Miyoshi, H.; Okano, M.; Morishima, I.; Inubushi, T. *J. Organomet. Chem.* **1979**, *165*, 9.
(13) Eisch, J. J.; Burlinson, N. E. *J. Am. Chem. Soc.* **1976**, *98*, 753.
(14) Fujimoto, H.; Uemura, S.; Miyoshi, H. *Tetrahedron* **1981**, *37*, 55.
(15) Since the vinyl cyano substituent totally dominated product control in the dicyanobenzonorbornadienes,[4] a structural reversal in this pair of substrates would simply necessitate translocation of the aryl substituent in the photoproducts from one meta position to the other. None of the conclusions arrived at in the earlier paper would be vitiated.
(16) Schlosser, M.; Ladenberger, V. *J. Organomet. Chem.* **1967**, *8*, 193.
(17) Kidwell, R. L.; Murphy, M.; Darling, S. D. *Org. Synth.* **1969**, *49*, 90.

Since "meta" methoxy and "meta" cyano exert opposite directing influences, only **13b** and **20b** qualify as additional examples where the interplay of excited-state substituent effects should be additive. Again in these two cases, di-$\pi$-methane rearrangement provided isomerically pure products identified as **26a** and **26b**.

Although the preceding four observations reinforce our earlier discoveries of directed preference for electronic reorganization within triplet-excited benzonorbornadienes, they shed no light on the more intriguing question of competitive substituent control. On the other hand, the additional four substrates **10a,b**, **15b**, and **18b** are appropriately structured for this purpose and have given rise to informative differences in regioselectivity.

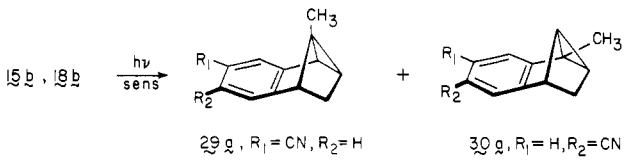
The *o*-cyano derivative **10a** was seen to afford a 50:50 mixture of two photoproducts which were separated chromatographically and characterized as **27a** and **28a**.



**27g**, R = CN; **b**, R = $OCH_3$ **28g**, R = CN; **b**, R = $OCH_3$

While a mixture of regioisomers **27b** and **28b** was also realized in the methoxy series, **27b** was found to predominate by a factor of 3:1. These product distributions disclose that while "ortho" cyano and vinyl methyl are quite evenly matched in their abilities to control regioselectivity, and alkyl group dominates over the "ortho" methoxy substituent to a level which has a meaningful impact on the product distribution.

Where the meta isomers **15b** and **18b** are concerned, the cyano derivative delivered a mixture of **29a** (12%) and **30a** (88%), and the methoxy compound afforded **29b** and **30b** in an inverted ratio (60:40). The significance of these findings is discussed below.



**29g**, $R_1$ = CN, $R_2$ = H; **b**, $R_1$ = H, $R_2$ = $OCH_3$ **30g**, $R_1$ = H, $R_2$ = CN; **b**, $R_1$ = $OCH_3$, $R_2$ = H

## Discussion

We have previously analyzed substituent control of regioselectivity during di-$\pi$-methane photorearrangement of benzonorbornadienes in terms of the donor–acceptor interactions which gain importance in the relevant frontier orbital.[3,18] As denoted by photoelectron spectroscopy,[19] donor substituents such as methoxyl raise the energies of occupied orbitals appreciably. In contrast, cyano and other acceptor substituents lower both filled and vacant orbital energies to a large extent. Some dependency of the locus of aryl substitution is evident, but this phenomenon has heretofore been considered relatively unimportant to the overall orbital energy picture.

Critical to our understanding of the excited-state behavior of these molecules is the realization that aryl donor substituents decrease the level of alkene contribution to the HOMO while increasing alkene contribution to the LUMO. Acceptors give rise to the opposite effect. Furthermore, while the HOMO is the controlling frontier molecular orbital involved in the "ortho" $OCH_3$ example, it is recognized to be the LUMO which is the discriminating factor where "meta" $OCH_3$ is concerned.[19]

Cyano and other acceptor substituents induce large LUMO polarization, with the result that the particular energy and shape of this vacant orbital dictate the bridging regioselectivity. In fact, substitution by cyano in this manner withdraws electron density more or less uniformly from all regions of the molecule. The initial product-determining aryl–vinyl bridging step is also dictated by electron density considerations, and acceptors enhance the level of alkene contribution to the HOMO.

Let us now compare the bridging ratios observed in the present study for the vinyl methyl derivatives with those previously determined for the corresponding systems lacking an alkene substituent. The product ratios are those of $\beta$ vs. $\alpha$ bridging, as defined in the drawing below:

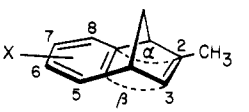


Table I. Comparison of Bridging Predicted from Monosubstituted Models and Observed Bridging Modes

| entry | benzonorbornadiene | $\beta/\alpha$ bridging ratio: predicted | obsd |
|---|---|---|---|
| 1 | 2-$CH_3$-5-$CH_3O$ (**8c**) | (81/19) × (89/11) = 97:3 | ~97:3[a] |
| 2 | 2-$CH_3$-6-$CH_3O$ (**13b**) | (81/19) × (78/22) = 94:6 | ~97:3[a] |
| 3 | 2-$CH_3$-7-$CH_3O$ (**15b**) | (81/19) × (22/78) = 55:45 | ~60:40 |
| 4 | 2-$CH_3$-8-$CH_3O$ (**10b**) | (81/19) × (11/89) = 34:66 | ~75:25 |
| 5 | 2-$CH_3$-5-CN (**8b**) | (81/19) × (96/4) = 97:3 | ~97:3[a] |
| 6 | 2-$CH_3$-6-CN (**18b**) | (81/19) × (3/97) = 11:89 | ~12:88 |
| 7 | 2-$CH_3$-7-CN (**20b**) | (81/19) × (97/3)[a] = 99:1 | ~97:3[a] |
| 8 | 2-$CH_3$-8-CN (**10a**) | (81/19) × (4/96) = 15:85 | ~50:50 |

[a] Ratios of 100:0 (only one regioisomer observed) were adjusted to ~97:3 to allow for possible detection limits.

On the basis of those product ratios observed in the parent monosubstituted cases, the degree of regiochemical control decreases in the following order (percent of major bridging mode in parentheses): *m*-CN (100% para) > *o*-CN (96% ortho) > *o*-$CH_3O$ (89% ortho) > vinyl $CH_3$ (81% $\beta$) > *m*-$CH_3O$ (78% meta).[2,3] In addition, studies of the compounds carrying both a vinyl cyano substituent and an aromatic methoxy or cyano group indicate that the vinyl–cyano segment is more strongly directing than either of the aromatic substituents.[4,5]

By use of the ratios of isomers formed from the monosubstituted compounds as an index of the preference for formation of one isomer, the predicted product ratios are compared to those found experimentally in Table I.

Entries 1, 2, 5, and 7 all represent cases where the substituent effects should be cooperative, $\beta$ to the vinyl methyl, ortho to an *o*-methoxy or cyano, para to a *m*-cyano, and meta to a *m*-methoxy substituent. Indeed, in all of these examples a single product is observed, in agreement with expectation.

Entries 3, 4, 6, and 8 represent cases where the two substituents are positioned to direct in an antagonist

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fashion: the vinyl methyl should promote $\beta$ bridging, while the aromatic substituents should promote $\alpha$ bridging. Where the 2-$CH_3$-7-X (X = $CH_3O$ or CN) examples are concerned, the predicted ratios, based on perfect additivity, are within experimental error of the observed ratios. On the other hand, the results for the 2-$CH_3$-8-X derivatives indicate that the vinyl methyl group is exerting a more powerful directing influence than it does when present alone in **8a**. In both instances, the apparent directing effect of methyl is 96:4 for $\beta/\alpha$ bridging, slightly higher than the basal preference of 81:19.

The vinyl methyl group causes an increased preference for $\beta$ bridging of about 1 kcal/mol in **10a** and **10b** as compared to the preference exerted by the methyl group is 2-methylnorbornadiene. Although the regiospecificity found in the other vinyl methyl, ortho-substituted compounds (**8a,b**) masks any enhanced methyl influence in these cases, the same phenomenon is most likely present in these molecules. This implies that the 2-methyl ortho-substituted species experience an anomalously high methyl-directing influence, while the 2-methyl meta-substituted compounds give additive substituent effects. Inspection of the MO's of the relevant molecules does not reveal any obvious explanation of this difference. The effect probably arises from a greater enhancement of vinyl $\pi$ orbital contribution to the dominant excited-state configuration in the ortho-substituted cases than in the meta-substituted examples and in **8a**. However, the multiconfigurational nature of the excited triplets makes it impossible to verify this hypothesis from inspection of ground-state orbitals. The refinement of our model to deal with subtle points of this type must await calculations on the triplet states of benzonorbornadienes.

In summary, we see that a vinyl methyl substituent is a moderate controller of triplet di-$\pi$-methane regioselectivity. As such, this group is useful as a tool for "fine tuning" our earlier predictions, as is made particularly evident with **10a** and **10b**. Otherwise, perfect additivity based upon the behavior of the individual monosubstituted examples is commonly realized. Although related studies are continuing, it now appears that enlargement of the scope of the di-$\pi$-methane rearrangement in a predictable, comprehensive fashion should be entirely possible. Note that no assumptions have been made concerning the question of whether initial bridging is reversible or not. We hope to be able to comment explicitly on this point in the near future.

## Experimental Section

Infrared spectra were recorded on a Perkin-Elmer Model 467 spectrophotometer. The $^1H$ NMR spectra were determined with Varian T-60, Varian EM-360, and Bruker HX-90 instruments, and apparent splittings are given in all cases. The $^{13}C$ spectra were also obtained with the Bruker spectrometer. Mass spectra were measured on an AEI-MS9 spectrometer at an ionizing energy of 70 eV. Preparative-scale VPC separations were performed on Varian Aerograph Model A-90-P3 instruments equipped with thermal-conductivity detectors. Microanalytical determinations were performed at the Scandinavian Microanalytical Laboratory.

**2-Methylbenzonorbornadiene (8a).** A 131-mg (0.49 mmol) sample of 2-iodobenzonorbornadiene[4] was added at −20 °C to a solution of lithium dimethylcuprate (from 10 equiv of methyllithium and 5 equiv of cuprous iodide). Stirring for 10 h at −20 °C followed by 1 h at room temperature preceded pouring of the reaction mixture onto ice. The product was extracted into ether and the combined extracts were dried and evaporated. VPC analysis (2 ft × 0.25 in. column, 10% SE-30, at 60 °C) revealed approximately 15% contamination by benzonorbornadiene. Pure **8a** was collected by preparative VPC: 42 mg (55%); $^1H$ NMR ($CDCl_3$) $\delta$, 7.3–6.65 (m, 4 H), 6.05 (7, 1 H), 3.76 (m, 1 H), 3.42 (m, 1 H) 2.4–2.0 (m, 2 H), 1.78 (d, $J$ = 1.5 Hz, 3 H); $^{13}C$ NMR ($CDCl_3$) 153.75, 152.64, 151.72, 134.77, 124.33, 123.90, 121.23, 120.89, 68.65, 55.15, 50.54, 16.36 ppm.

Anal. Calcd for $C_{12}H_{12}$: C, 92.26; H, 7.74. Found: C, 92.16; H, 7.77.

**2-Methyl-5-cyanobenzonorbornadiene (8b).** Treatment of 2-iodo-5-cyanobenzonorbornadiene[4] (890 mg, 3.04 mmol) with excess lithium dimethylcuprate (−78 °C for 12 h, room temperature for 2 h) as described above gave a pale yellow solid. Sublimation gave 500 mg (91%) of **8b** as a colorless solid: mp 49–50 °C: $^1H$ NMR ($CDCl_3$) $\delta$ 7.4–6.7 (m, 3 H), 6.15 (m, 1 H), 4.08 (m, 1 H), 3.58 (7, 1 H), 2.5–2.1 (m, 2 H), 1.82 (d, $J$ = 2.0 Hz, 3 H); $^{13}C$ NMR ($CDCl_3$) 158.03, 154.63, 153.12, 133.90, 126.81, 124.82, 105.59, 68.45, 55.25, 50.10, 16.31 ppm; mass spectrum, calcd $m/e$ 181.0891, found 181.0898.

Anal. Calcd for $C_{13}H_{11}N$: C, 86.14; H, 6.12. Found: C, 85.76; H, 6.07.

**2-Methyl-8-cyanobenzonorbornadiene (10a).** A 1.0-g sample (3.41 mmol) of 2-iodo-8-cyanobenzonorbornadiene[4] was treated with lithium dimethylcuprate in the manner described for **8b**. There was obtained 540 mg (88%) of **10a** as a pale yellow oil which was purified by chromatography on silica gel: $^1H$ NMR ($CDCl_3$) $\delta$ 7.37–6.7 (m, 3 H), 6.19 (m, 1 H), 3.82 (m, 2 H), 2.5–2.1 (m, 2 H), 1.93 (d, $J$ = 1.2 Hz, 3 H); mass spectrum, calcd $m/e$ 181.0891, found 181.0896.

Anal. Calcd for $C_{13}H_{11}N$: C, 86.14; H, 6.12. Found: C, 85.95; H, 6.14.

**2-Methyl-5-methoxybenzonorbornadiene (8c)** was obtained in 62% yield by reaction of 2-iodo-5-methoxynorbornadiene[5] with lithium dimethylcuprate as colorless liquid which was purified by preparative VPC: $^1H$ NMR ($CDCl_3$) $\delta$ 6.95–6.45 (m, 3 H), 6.1 (m, 1 H), 3.8 (m, 1 H), 3.77 (s, 3 H), 3.45 (m, 1 H), 2.2 (m, 2 H), 1.8 (d, $J$ = 2.1 Hz, 3 H); mass spectrum, calcd $m/e$ 186.1045, found 186.1048.

Anal. Calcd for $C_{13}H_{14}O$: C, 83.82; H, 7.58. Found: C, 84.17; H, 7.41.

**2-Methyl-8-methoxybenzonorbornadiene (10b)** was obtained in 73% yield by reaction of 2-iodo-8-methoxybenzonorbornadiene[5] (100 mg) with lithium dimethyl cuprate as a colorless liquid which was purified by preparative VPC: $^1H$ NMR ($CDCl_3$) $\delta$ 6.95–6.45 (m, 3 H), 6.17 (m, 1 H), 3.9–3.7 (m, 2 H), 3.85 (s, 3 H), 2.2 (7, 2 H), 1.85 (d, $J$ = 2.2 Hz, 3 H); mass spectrum calcd $m/e$ 186.1045, found 186.1048.

Anal. Calcd for $C_{13}H_{14}O$: C, 83.82; H, 7.58. Found: C, 83.78; H, 7.29.

**2-Methyl-6-methoxybenzonorbornadiene (13b)** was obtained in 68% yield by the procedure described above by beginning with **13a**:[5] $^1H$ NMR ($CDCl_3$) $\delta$ 7.0–6.7 (m, 2 H), 6.45–6.3 (m, 1 H), 6.07 (m, 1 H), 3.75 (s, 3 H), 3.73 (m, 1 H), 3.42 (m, 1 H), 2.20 (m, 2 H), 1.83 (d, $J$ = 2.0 Hz, 3 H); mass spectrum, calcd $m/e$ 186.1045, found 186.1048.

**2-Methyl-7-methoxybenzonorbornadiene (15b)** was obtained from **15a**[5] in 86% yield by using the predescribed method: $^1H$ NMR ($CDCl_3$) $\delta$ 7.2–6.65 (m, 3 H), 6.35 (dd, $J$ = 8, 2 Hz, 1 H), 6.17 (m, 1 H), 3.80 (s, 3 H), 3.9–3.7 (m, 1 H), 3.5 (m, 1 H), 2.27 (m, 2 H), 1.83 (d, $J$ = 2.1 Hz, 3 H); mass spectrum, calcd $m/e$ 186.1045, found 186.1048.

***exo*-2-(Tetrahydropyranyloxy)-7-iodobenzonorbornene (21).** To a magnetically stirred solution of *exo*-2-hydroxy-7-iodobenzonorbornene[4] (3.0 g, 10.5 mmol) and dihydropyran (1.44 mL, 15.8 mmol) in dichloromethane (40 mL) was added pyridinium tosylate (2.21 g, 8.2 mmol). The reaction mixture was stirred under nitrogen at room temperature for 24 h, poured into water, and extracted with dichloromethane. The combined organic extracts were dried and evaporated to leave 3.9 g of residual oil which was used without further purification: $^1H$ NMR ($CDCl_3$) $\delta$ 7.6–7.2 (m, 2 H), 6.8 (d, $J$ = 8 Hz, 1 H), 4.1–3.0 (series of m, 6 H), 2.0–1.3 (m, 10 H).

***exo*-2,7-Dihydroxybenzonorbornene (22).** The sample of **21** prepared above was dissolved in anhydrous ether (20 mL) with magnetic stirring under nitrogen. While being cooled to 0 °C in an ice bath, this solution was treated with *n*-butyllithium (7.3 mL of 1.6 M in hexane) via syringe over 15 min. After being stirred at 0 °C for 2.5 h, the reaction mixture was transferred by syringe to a magnetically stirred tetrahydrofuran solution (20 mL) of trimethyl borate (1.32 mL, 11.6 mmol) that was cooled to −20 °C.

Stirring was maintained at this temperature for 2 h, at which point chilled acetic acid (0.91 mL, 15.9 mmol) was added in one portion followed immediately by water (1.1 mL) and 30% hydrogen peroxide (1.2 mL). The dark solution was allowed to warm to room temperature, stirred for 1 h; transferred to a separatory funnel, and washed with saturated ferrous ammonium sulfate solution until the color of ferric ion was no longer produced. The organic layer was concentrated, and the residue was taken up in ether and extracted with 5% sodium hydroxide solution. The combined alkline phases were extracted with ether, acidified with concentrated hydrochloric acid, and extracted again with ether. The latter ether layers were washed with brine, dried, and evaporated to leave 1.17 g of **22**: $^1$H NMR ($CDCl_3$) $\delta$ 7.1–6.7 (m, 2 H), 6.53 (dd, $J$ = 7, 2 Hz, 1 H), 4.8 (s, 2 H), 4.8–3.7 (series of m, 3 H), 2.1–1.3 (m, 4 H).

**7-Methoxy-2-benzonorbornenone (14).** The unpurified phenol **22** was dissolved in water (5.5 mL) containing sodium hydroxide (0.54 g, 13.5 mmol). The resulting clear yellow solution was cooled to 0 °C, and dimethyl sulfate (1.28 mL, 13.5 mmol) was added slowly with stirring. The reaction mixture was stirred at room temperature for 2 h and extracted with ether. The combined extracts were washed with brine, dried, and concentrated to leave 1.1 g of oil. This material was dissolved in ether (20 mL) and shaken in a separatory funnel for 5 min with 15% hydrochloric acid (20 mL) to ensure complete hydrolysis of any remaining tetrahydropyranyl ether. Processing as before afforded 1.1 g of crude methoxy alcohol: $^1$H NMR ($CDCl_3$) $\delta$ 7.15–6.8 (m, 2 H), 6.61 (dd, $J$ = 7, 2 Hz, 1 H), 3.9 (s, 3 H), 3.8–3.5 (m, 3 H), 2.1–1.4 (m, 5 H).

This material in dichloromethane (150 mL) was stirred with pyridinium chlorochromate (4.97 g, 23.1 mmol) at room temperature for 4 h, poured into water, and extracted into ether. The combined organic layers were washed with water, 1 N hydrochloric acid, saturated sodium bicarbonate solution, and water. After the mixture was dried and concentrated, there was obtained a yellow oil which was purified by medium-pressure liquid chromatography on silica gel (elution with 20% ethyl acetate in petroleum ether) to give 230 mg (12% overall) of **14** identical in all respects with an authentic sample: $^1$H NMR ($CDCl_3$) $\delta$ 7.2–6.5 (m, 3 H), 3.72 (s, 3 H), 3.65–3.4 (m, 2 H), 2.7–1.75 (series of m, 4 H); $^{13}$C NMR ($CDCl_3$) 213.4, 158.8, 141.3, 140.7, 122.1, 112.3, 110.2, 58.4, 55.5, 50.8, 41.1, 40.8 ppm. For comparison, the $^{13}$C NMR data for **12** are as follows: 212.8, 159.5, 150.3, 131.4, 124.3, 111.2, 108.8, 56.9, 55.4, 50.3, 42.1, 40.4 ppm.

**2-Methyl-6-cyanobenzonorbornadiene (18b)** was prepared from **18a** as described above in 96% yield and was purified by preparative VPC: $^1$H NMR ($CDCl_3$) $\delta$ 7.35–7.1 (m, 3 H), 6.15 (m, 1 H), 3.80 (m, 1 H), 3.55 (m, 1 H), 2.5–2.1 (m, 2 H), 1.82 (d, $J$ = 2.1 Hz, 3 H); $^{13}$C NMR ($CDCl_3$) 157.8, 153.9, 153.5, 134.8, 129.6, 123.5, 121.6, 117.8, 107.9, 68.4, 55.3, 50.2, 16.3 ppm; mass spectrum, calcd $m/e$ 181.0891, found 181.0896.

Anal. Calcd for $C_{13}H_{11}N$: C, 86.14; H, 6.12. Found: C, 85.86; H, 6.15.

**2-Methyl-7-cyanobenzonorbornadiene (20b)** was prepared in the predescribed manner from the corresponding vinyl iodide in 82% yield and was purified by preparative VPC: $^1$H NMR ($CDCl_3$) $\delta$ 7.32–7.07 (m, 3 H), 6.10 (m, 1 H), 3.78 (m, 1 H), 3.54 (s, 1 H), 2.45–2.0 (m, 2 H), 1.82 (d, $J$ = 2.1 Hz, 3 H); $^{13}$C NMR ($CDCl_3$) 158.6, 154.0, 153.0, 134.2, 130.1, 123.8, 121.4, 120.1, 107.4, 68.3, 54.8, 50.8, 16.3; mass spectrum, calcd $m/e$ 181.0891, found 181.0896.

Anal. Calcd for $C_{13}H_{11}N$: C, 86.14; H, 6.12. Found: C, 85.78; H, 6.12.

**General Photoisomerization Procedure.** The mono- or disubstituted benzonorbornadiene was dissolved in benzene (50 mL) containing 2 or 3 drops of acetophenone, and the solution was deoxygenated by bubbling nitrogen through the sample of 20 min. After being placed under a nitrogen atmosphere, the reaction mixture was irradiated with 3500-Å light in a Rayonet reactor for 20–40 min. The solvent and acetophenone were removed in vacuo, and the residue was purified as indicated.

**2- and 3-Methyltetracyclo[5.4.0.0$^{2,4}$.0$^{3,6}$]undeca-1(7),8,10-triene (23 and 24).** The photolysate obtained from **8a** was subjected to preparative VPC purification (10% Carbowax 30M, 100 °C). Major component **23** (81%) was obtained as a colorless oil; $^1$H NMR ($CDCl_3$) $\delta$ 7.4–6.9 (m, 4 H), 3.2–3.0 (dd, $J$ = 7.8, 2.8 Hz, 1 H), 2.9–2.55 (ddd, $J$ = 9.6, 7.8, 3.0 Hz, 1 H), 2.23 (d, $J$ = 5.7 Hz, 1 H), 1.8 (ddd, $J$ = 5.7, 3.0, 2.8 Hz, 1 H), 1.41 (s, 3 H), 0.66 (d, $J$ = 9.6 Hz, 1 H); $^{13}$C NMR ($CDCl_3$) 148.85, 142.49, 125.64, 124.53, 123.02, 120.21, 55.01, 46.61, 34.47, 27.24, 23.30, 15.05 ppm.

Minor component **24** (19%) was also indicated as a colorless oil: $^1$H NMR ($CDCl_3$) $\delta$ 7.3–6.93 (m, 4 H), 3.33–3.08 (m, 1 H), 3.03–2.50 (m, 2 H), 1.86–1.65 (m, 1 H), 1.43 (s, 3 H), 0.76 (dd, $J$ = 8.5, 2.2 Hz, 1 H).

**3-Methyl-11-cyanotetracyclo[5.4.0$^{2,4}$.0$^{3,6}$]undeca-1(7),8,10-triene (25a).** The photoisomerization of **8b** led exclusively to **25a** which was purified by silica gel chromatography and isolated as a colorless oil: $^1$H NMR ($CDCl_3$) $\delta$ 7.37–6.95 (m, 3 H), 3.17 (dd, $J$ = 7.3, 2.8 Hz, 1 H), 2.78 (ddd, $J$ = 9.5, 7.3, 3.0 Hz, 1 H), 2.45 (d, $J$ = 5.7 Hz, 1 H), 2.13–1.95 (ddd, $J$ = 5.7, 3.0, 2.8 Hz, 1 H), 1.40 (s, 3 H), 0.60 (d, $J$ = 9.5 Hz, 1 H); mass spectrum, calcd $m/e$ 181.0891, found 181.0896.

**3-Methyl-11-methoxytetracyclo[5.4.0$^{2,4}$.0$^{3,6}$]undeca-1(7),8,10-triene (25b).** The photoisomerization of **8c** afforded a single product identified as **25b**. Purification by preparative VPC led to isolation of a colorless oil: $^1$H NMR ($CDCl_3$) $\delta$ 7.1–6.5 (m, 3 H), 3.87 (s, 3 H), 3.08 (dd, $J$ = 7.4, 2.8 Hz, 1 H), 2.81 (ddd, $J$ = 9.5, 7.4, 3.4 Hz, 1 H), 2.40 (d, $J$ = 5.8 Hz, 1 H), 1.97 (ddd, $J$ = 5.8, 3.4, 2.8 Hz, 1 H), 1.40 (s, 3 H), 0.58 (d, $J$ = 9.5 Hz, 1 H); mass spectrum, calcd $m/e$ 186.1045, found 186.1050.

**3-Methyl-10-methoxytetracyclo[5.4.0.0$^{2,4}$.0$^{3,6}$]undeca-1(7),8,10-triene (26a).** The photolysate obtained from **13b** contained a single rearrangement product which was obtained as a colorless oil by preparative VPC and characterized as **26a**: $^1$H NMR ($CDCl_3$) $\delta$, 7.3–6.3 (m, 3 H), 3.7 (s, 3 H), 2.97 (dd, $J$ = 7.3, 2.8 Hz, 1 H), 2.75 (ddd, $J$ = 9.6, 7.3, 3.4 Hz, 1 H), 2.5 (d, $J$ = 5.7 Hz, 1 H), 2.05 (ddd, $J$ = 5.7, 3.4, 2.8 Hz, 1 H), 1.38 (s, 3 H), 0.60 (d, $J$ = 9.6 Hz, 1 H); mass spectrum, calcd $m/e$ 186.1045, found 186.1050.

**3-Methyl-9-cyanotetracyclo[5.4.0.0$^{2,4}$.0$^{3,6}$]undeca-1(7),8,10-triene (26b).** Photoisomerization of **20b** furnished isomerically pure **26b**: $^1$H NMR ($CDCl_3$) $\delta$ 7.5–7.0 (m, 3 H), 3.3–2.7 (overlapping m, 2 H), 1.9 (m, 1 H), 1.47 (s, 3 H), 0.77 (dd, $J$ = 9.4, 2.3 Hz, 1 H); $^{13}$C NMR ($CDCl_3$) 149.4, 148.4, 130.5, 123.7, 123.5, 121.3, 107.8, 57.2, 46.2, 35.1, 26.8, 24.6, 14.9 mass spectrum, calcd $m/e$ 181.0891, found 181.0896.

**3-Methyl-8-cyano- and 2-Methyl-11-cyanotetracyclo-[5.4.0.0$^{2,4}$.0$^{3,6}$]undeca-1(7),8,10-triene (27a and 28a).** Sensitized irradiation of **10a** afforded a colorless oil which was determined to be a 50:50 mixture of **27a** and **28a** by appropriate integration of VPC and $^1$H NMR data. The isomers were separated by preparative VPC.

For **27a**: $^1$H NMR ($CDCl_3$) $\delta$ 7.65–7.0 (m, 3 H), 3.88 (dd, $J$ = 7.5, 2.4 Hz, 1 H), 3.1–2.6 (m, 1 H), 2.34 (d, $J$ = 5.3 Hz, 1 H), 2.0 (m, 1 H), 1.43 (s, 3 H), 0.63 (d, $J$ = 9.3 Hz, 1 H); mass spectrum, calcd $m/e$ 181.0891, found 181.0896.

For **28a**: $^1$H NMR ($CDCl_3$) $\delta$ 7.4–7.17 (m, 3 H), 3.45–2.75 (m, 2 H), 1.80 (m, 1 H), 1.71 (s, 3 H), 0.77 (dd, $J$ = 9.3, 2.3 Hz, 1 H); mass spectrum, calcd $m/e$ 181.0891, found 181.0896.

**3-Methyl-8-methoxy- and 2-Methyl-11-methoxytetracyclo[5.4.0.0$^{2,4}$.0$^{3,6}$]undeca-1(7),8,10-triene (27b and 28b).** Upon sensitized irradiation, **10b** was transformed into a colorless, oil mixture of **27b** and **28b** (ratio 3:1) which were separated by preparative VPC.

For **27b**: $^1$H NMR ($CDCl_3$) $\delta$ 7.17–6.52 (m, 3 H), 3.77 (s, 3 H), 3.26 (dd, $J$ = 7.6, 2.8 Hz, 1 H), 2.87–2.70 (ddd, $J$ = 9.2, 7.6, 3.4 Hz, 1 H), 2.17 (d, $J$ = 5.8 Hz, 1 H), 1.87–1.70 (ddd, $J$ = 5.8, 3.4, 2.8 Hz 1.37 (s, 3 H), 0.57 (d, $J$ = 9.2 Hz, 1 H); mass spectrum, calcd $m/e$ 186.1045, found 186.1048.

For **28b**: $^1$H NMR ($CDCl_3$) $\delta$ 7.2–6.5 (m, 3 H), 3.7 (s, 3 H), 3.2–2.4 (series of overlapping m, 3 H), 2.0–1.77 (m, 1 H), 1.53 (s, 3 H), 0.73 (dd, $J$ = 9.0, 2.8 Hz, 1 H); mass spectrum, calcd $m/e$ 186.1045, found 186.1048.

**3-Methyl-10-cyano- and 2-Methyl-9-cyanotetracyclo-[5.4.0.0$^{2,4}$.0$^{3,6}$]undeca-1(7),8,10-triene (29a and 30a).** The photoisomerization of **18b** afforded a mixture of **29a** (12%) and **30a** (88%) which were separated by preparative VPC.

For **29a**: $^1$H NMR ($CDCl_3$) $\delta$ 7.65–7.0 (m, 3 H), 3.13 (dd, $J$ = 7.8, 2.8 Hz, 1 H), 2.8 (ddd, $J$ = 9.3, 7.8, 3.2 Hz, 1 H), 2.30 (d, $J$ = 5.7 Hz, 1 H), 2.05 (ddd, $J$ = 5.7, 3.2, 2.8 Hz, 1 H), 1.42 (s, 3 H), 0.60 (d, $J$ = 9.3 Hz, 1 H); mass spectrum, calcd $m/e$ 181.0891, found 181.0896.

For **30a**: $^1$H NMR ($CDCl_3$) $\delta$ 7.65–7.0 (m, 3 H), 3.4–3.0 (m, 2 H), 1.93–1.77 (m, 1 H), 1.50 (s, 3 H), 0.77 (dd, $J$ = 9.3, 2.1 Hz, 1 H); mass spectrum, calcd $m/e$ 181.0891, found 181.0896.

**3-Methyl-9-methoxy- and 2-Methyl-10-methoxytetracyclo[5.4.0.0$^{2,4}$.0$^{3,6}$]undeca-1(7),8,10-triene (29b and 30b).** Due to severely limited quantities of **15b**, its irradiation was conducted only on a single 30-mg scale. The resultant colorless oil was quantitatively analyzed by $^1$H NMR spectroscopy through appropriate integration of the methoxyl and methyl peaks of the two isomers: $\delta$ 3.83 and 1.47 for **29b**; $\delta$ 3.87 and 1.53 for **30b**. The ratio of the products was 60:40.

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# Mechanism of the Oxidation of Alkyl Aryl Sulfides by Phenyliodoso Diacetate

Chockalingam Srinivasan,* Arunachalam Chellamani, and Packiam Kuthalingam

*School of Chemistry, Madurai Kamaraj University, Madurai 625 021, India*

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The rates of oxidation of 16 alkyl aryl sulfides by phenyliodoso diacetate have been studied in acetonitrile–water mixtures. Those sulfides containing electron-donating groups in the benzene ring accelerate the rate while those with electron-withdrawing groups retard the rate. A plot of $\Delta H^{\ddagger}$ vs. $\Delta S^{\ddagger}$ for the aryl methyl sulfides is linear and suggests that the oxidation processes for all the sulfides are the same. A Hammett $\rho$ value of $-0.796 \pm 0.13$ obtained at 35 °C indicates an electron-deficient transition state. The kinetic results have been analyzed by the Yukawa–Tsuno equation. The separation of inductive and resonance effects shows that the reaction is controlled more by the delocalized factor (62.5%) rather than by the localized factor (37.5%). Rate studies with different alkyl phenyl sulfides $C_6H_5SR$ (R = Me, Et, *n*-Pr, *i*-Pr, *t*-Bu) results in a good correlation with Taft's steric substituent constant, $E_s$. A mechanism involving the rate-limiting step of formation of an iodine(III)–sulfonium ion intermediate complex decomposing by the attack of water in a fast step has been proposed.

Several studies have been reported on the kinetics of oxidation of organic sulfur compounds.[1-9] Both the mechanism and rate of oxidation of these compounds are largely affected by the nature of the oxidant. For example, the oxidation of alkyl aryl sulfides to sulfoxides by halogen[2] is generally assumed to proceed via the halogenosulfonium cation as in eq 1. However, our recent studies[7] have

$$R_2S + X_2 \rightleftharpoons R_2{}^+SX + X^- \xrightarrow{H_2O} R_2SO + 2H^+ + 2X^- \quad (1)$$

revealed that such a preequilibrium is not present in the oxidation of alkyl aryl sulfides by peroxodisulfate ion, a fact which has been confirmed by the fact that the addition of sulfate ions does not influence the rate, and the mechanism suggested is represented by Scheme I.

Scheme I

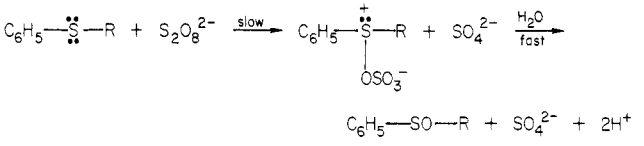


Table I. Pseudo-First-Order and Second-Order Rate Constants for the Reaction of MPS with PIA in 95% $CH_3CN$–5% $H_2O$ (v/v) at 35 °C

| $10^2 \times$ [MPS]$_0$, M | $10^3 \times$ [PIA]$_0$, M | $10^5 k_1$,[a] $s^{-1}$ | $10^3 k_2$,[a] $M^{-1}\ s^{-1}$ |
|---|---|---|---|
| 0.75 | 0.75 | 5.74 ± 0.32 | 7.65 ± 0.43 |
| 1.00 | 0.75 | 8.32 ± 0.46 | 8.32 ± 0.46 |
| 1.25 | 0.75 | 10.0 ± 0.20 | 8.00 ± 0.16 |
| 1.50 | 0.75 | 12.1 ± 0.83 | 8.08 ± 0.55 |
| 2.00 | 0.75 | 15.5 ± 1.66 | 7.73 ± 0.83 |
| 1.50 | 0.52 | 24.1 ± 1.53 | 16.1 ± 1.02 |
| 1.50 | 1.00 | 10.7 ± 0.51 | 7.15 ± 0.34 |
| 1.50 | 1.26 | 6.39 ± 0.20 | 4.26 ± 0.14 |
| 1.50 | 1.50 | 4.96 ± 0.21 | 3.31 ± 0.14 |

[a] The error quoted in $k$ is the 95% confidence limit of the Student's $t$ test.[8]

Though Szmant and Lapinski[10] prepared diphenyl sulfoxide by the oxidation of diphenyl sulfide by employing phenyliodoso diacetate (PIA), the kinetics of the oxidation of organic sulfur compounds by PIA have not been carried out so far. The mechanism of the oxidation of several

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