Polar Effects on Di-π-methane Rearrangements. Regiospecificity in the Triplet-Sensitized Photoisomerizations of 2-Cyanobenzonorbornadienes Carrying Methoxy Aryl Substituents

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Abstract: A series of four 2-cyano aryl-methoxy substituted benzonorbornadienes was synthesized and the triplet state photoisomerization of these compounds was investigated. Full regiospecificity as a function of the (vinyl) cyano substituent was observed for the di-π-methane rearrangement, such that the individual 3-cyano-X-methoxytetracyclo[5.4.0.0^{2,4}.0^{3,6}]undeca-1(7),8,10-trienes were isolated in isomerically pure form in each instance. The overall reactivity pattern, which reveals that the cyano group totally controls the pivotal bond-forming step, is shown to conform to expectations based on molecular orbital theory and supported by photoelectron spectroscopy.

The attachment of a polar substituent to the aromatic ring of benzonorbornadiene, a molecule capable of competitive aryl-vinyl bridging to either terminus of its double bond, is recognized to impart profound regiochemical control during triplet-sensitized di-π-methane rearrangement.[1,2] The preceding paper describes the total neutralization of the powerful directional effects produced by an ortho or meta cyano group by simple substitution of a second cyano group at C_2 of the vinyl double bond.[3] Irrespective of the locus of the aryl-bonded cyano, regiospecific bridging to C_3 results, even when this is fully contrary to the reaction channel which operates in the absence of this vinyl substituent.

In an effort to probe further the nature of polar substituent control on such di-π-methane bonding processes, we have undertaken a companion study of the photoisomerization of the four possible 2-cyanobenzonorbornadienes substituted by methoxyl on the aromatic ring. Selection of this group of compounds was predicated on the fact that the aryl substituent is of a polar nature opposite to that present on the vinyl bridge, thereby presenting an opportunity to examine the possible consequences of "push-pull" interactions (AX-type photocycloadditions[4]) without concern for steric encumbrances.

Results

Synthetic Considerations. Preparation of meta isomers **4a** and **4b** was based in large part on earlier methodology developed by Tanida and his co-workers for obtaining the ketones **2a** and **2b**.[5] Through hydrochlorination of **1** and selective aqueous hydrolysis of the more reactive homo-para chloride, it proved possible ultimately to isolate isomerically pure ketone samples. As indicated in Scheme I, the subsequent steps were modeled after those found suitable for the dicyano derivatives.[3]

As expected on the basis of potentially available pπ aryl participation in **5**, its hydroboration–oxidation gave rise to a predominance of **6b** (Scheme II). Alternative treatment with mercuric acetate, followed by demercuration and oxidation, furnished a 2.3:1 mixture of **6a** and **6b**. Sequential conversion to vinyl iodides **7a** and **7b**, respectively, and reaction with cuprous cyanide in HMPA gave **8a** and **8b**.

The four cyanomethoxybenzonorbornadienes are easily distinguished by their ^{1}H NMR spectra. In the ortho methoxy series, the chemical shifts of the two bridgehead benzylic protons are particularly revealing of the substitution plan

Scheme I
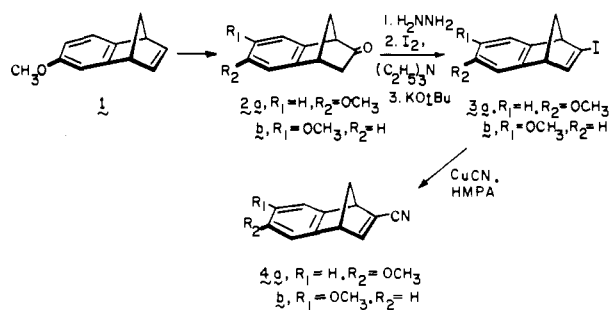
Scheme II
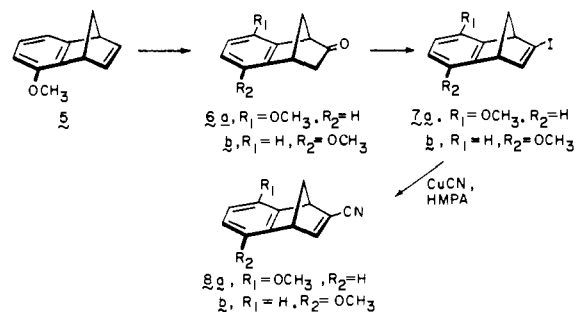
adopted by the methoxyl and cyano groups and serve as additional confirmation of structure. As seen in Figure 1, the more extensively coupled bridgehead proton in **8a**, which must be distal from the cyano substituent (i.e., H_4) for reasons of multiplicity, is located *upfield* (δ 4.06) of the narrower multiplet at δ 4.33 due to H_1. Importantly, the chemical shift of H_4 compares closely to those of the overlapping bridgehead protons in **4a** and **4b** (δ 4.0), indicating that it is not perturbed by a flanking ether substituent. The deshielding at H_1 arises because of its close proximity to methoxyl. In contrast, the more extensively coupled bridgehead proton in **8b**, which must again be more remote from cyano, appears at δ 4.29 *downfield* of H_1 (δ 4.02). This crossover is, of course, a direct consequence of the deshielding effect of ether oxygen on the nearby aliphatic proton, in this case H_4.

Photorearrangement of the Benzonorbornadienes. In all cases, the particular benzonorbornadiene was dissolved in benzene containing a small amount of acetophenone as sensitizer and these solutions were irradiated in Pyrex tubes by using a band of 3500-Å lamps in a Rayonet reactor. Under these conditions, neither the starting materials nor the photoproducts
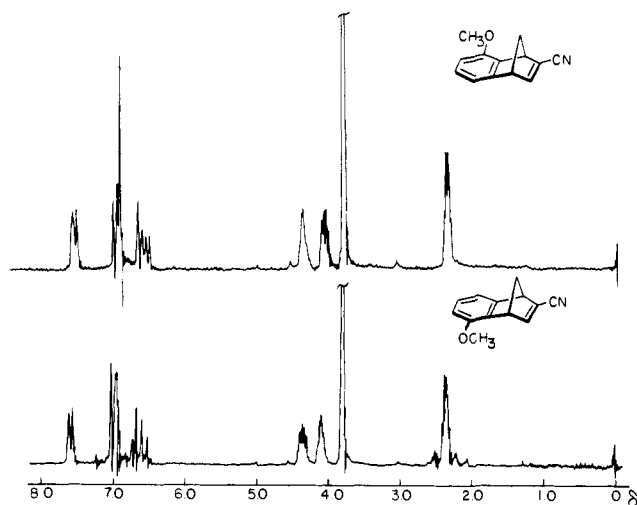
Figure 1. ^{1}H NMR spectra (60 MHz, $CDCl_3$ solution) of **8a** (top) and **8b** (bottom).

Figure 2. Correlation between π ionization potentials of the cyanomethoxybenzonorbornadienes and monosubstituted analogues.

absorbed significant amounts of incident light. When **4a** was photoisomerized under these conditions, rearrangement was judged to be complete in less than 20 min. The single photoproduct was directly purified by sublimation. Elemental and mass spectral analysis indicated that this colorless solid was isomeric with starting material. ^{1}H and ^{13}C NMR analysis generated data uniquely in accord with structure **9a**. As noted

9a, R_1=OCH$_3$,R_2=H   **10a**, R_1=OCH$_3$,R_2=H
b, R_1=H ,R_2=OCH$_3$ **b**, R_1=H,R_2= OCH$_3$
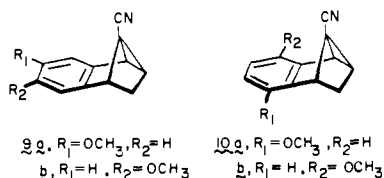
elsewhere,[1-3] the tetracyclo[5.4.0.0^{2,4}.0^{3,6}]undeca-1(7),-8,10-triene ring system comprises a rather unique framework for three-, four-, five-, and six-membered rings which are rigidly fused together. Well-defined dihedral angle relationships materialize among the aliphatic protons. Furthermore, each tetrahedrally bound proton exhibits a characteristic chemical shift. These factors greatly facilitate analysis of the site of substitution. As concerns **9a**, H$_3$ is clearly seen to be lacking, while all other observable coupling constants persist: $J_{5exo,6}$ = 7.3 Hz, $J_{4,6}$ = 2.6 Hz, $J_{5exo,5endo}$ = 9.4 Hz, $J_{2,4}$ = 5.6 Hz, and $J_{4,5exo}$ = 3.8 Hz. In line with the structural features of **4a** and the mechanistic features of the di-π-methane rearrangement, the aryl methoxyl should find itself at C$_{10}$ in photoproduct **9a**. The ^{1}H NMR spectrum likewise supports this substitution plan.

When **4b** was comparably irradiated, the isomeric meta photoproduct **9b** was formed exclusively within our present limits of detectability. The aliphatic region of the ^{1}H NMR spectrum of **9b** proved almost directly superimposable upon that of **9a**; the aryl region was appropriately distinctive, however. The ^{13}C NMR spectra confirmed that **9a** and **9b** were isomerically different only at C$_9$ and C$_{10}$ (see Experimental Section).

Turning attention to **8a** and **8b**, we noted again that the photoisomerizations were regiospecific. The spectral data revealed clearly that the cyano group was consistently bonded to C$_3$ and that **10a** and **10b** differ only in the locus of the aryl methoxyl group. In **10a** which arises from **8a**, bonding of –OCH$_3$ to C$_8$ is apparent on the basis of the anomalously low chemical shift of H$_6$ (δ 3.90) and the appearance of H$_2$ near its normal position (δ 3.21). For **10b**, the ordering is reversed, with H$_6$ now devoid of deshielding by the neighboring oxygen
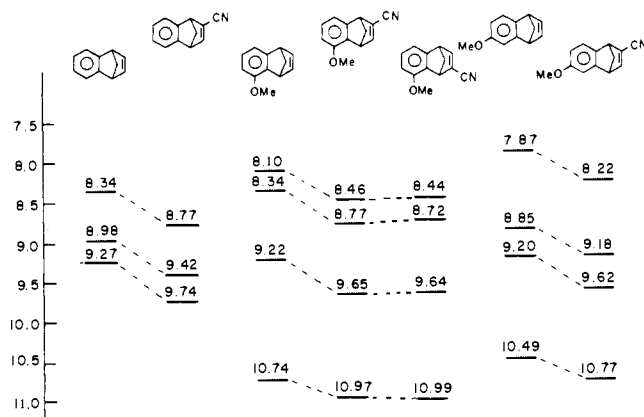
atom (δ 3.66) and H$_2$ now shifted downfield (δ 3.43) as a consequence of its proximity to methoxyl.
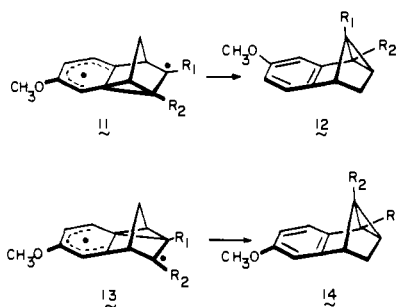
Thus, in all four examples, conversion to a tetracyclo[5.4.0.0^{2,4}.0^{3,6}]undecatriene carrying a cyano group at C$_3$ has been observed. As a consequence, the four possible 3-cyano derivatives monosubstituted with methoxy in the aromatic ring prove to be conveniently isolated and easily distinguished.

Photoelectron Spectroscopic Analysis. The photoelectron spectra of the cyanomethoxybenzonorbornadienes are not reproduced here, since they are remarkably similar in appearance to those of the simpler ortho and meta methoxy compounds which we reported earlier.[6] The four lowest ionization potentials of the three isomers studied are shown in Figure 2, along with those of model systems to be discussed below. The first three IP's are due to the well-known benzonorbornadiene π orbitals, while the fourth IP is due to an orbital heavily oxygen lone pair in character. As noted in previous publications,[3,7] substitution of a cyano group on the benzonorbornadiene skeleton raises all π IP's rather indiscriminately. For example, 2-cyanobenzonorbornadiene has IP's of 0.43–0.47 eV higher than those of the parent hydrocarbon.[6] Conversion of 5- or 6-cyanobenzonorbornadiene to dicyanobenzonorbornadienes by substitution of cyano at the 2- or 3-(vinyl) positions causes an 0.37 ± 0.07 eV increase in the three lowest IP's, and there is very little discrimination between orbitals.[6,7] This effect is also observed upon conversion of the 5- or 6-methoxy derivatives to the 2-cyano-X-methoxybenzonorbornadienes synthesized in the present study. Starting from the appropriate methoxy compound, the increase in π IP's upon 2- or 3-cyano substitution is 0.33–0.43 eV. Cyano does influence the third IP (0.42–0.48 eV) slightly more than the first and second (0.33–0.43 eV), while the oxygen lone pair ionizations are influenced least (0.23–0.28 eV). The third IP of 5- and 6-methoxybenzonorbornadiene arises from the orbital having the most olefinic π character.[6] In these molecules, the vinyl cyano group has a detectably different influence on the IP's originating from orbitals heavily concentrated on the vinyl carbons, but the effect is very small.

The methoxy group has a relatively large and specific effect on the IP's of benzonorbornadiene, and on the resultant shapes of the highest three π molecular orbitals. By contrast, a cyano substituent lowers all occupied orbital energies, but has a nonspecific influence on their shapes. Instead, a cyano group influences the π^* orbital shapes most.[6] The effects of methoxy and cyano groups are symptomatic of a much more general phenomenon: donors raise filled and vacant orbital energies, but have large and specific influences on the energies and shapes of filled orbitals only; acceptors lower all orbital energies, but have a specific influence only on vacant orbitals.

Discussion

The primary photoproducts of the sensitized irradiation of 6-methoxybenzonorbornadiene are **12** ($R_1 = R_2 = H$, 78%) and **14** ($R_1 = R_2 = H$, 22%).[1] Their dual formation is consis-

tent with di-π-methane rearrangement along both possible aryl-vinyl bridging modes (**11** and **13**, $R_1 = R_2 = H$), although with somewhat greater facility for the formation of **11**. When a cyano substituent is introduced at C_2 as in **4a**, the results show that the pathway through **11** ($R_1 = CN$, $R_2 = H$) now serves to dominate the energetics completely. In view of the established excited state behavior of 2-cyanobenzonorbornadiene,[3] the two substituents in **4a** are seen to be operating in additive fashion and contribute together to the observed regiospecificity.

In **4b**, this is not the situation, since the methoxyl group favors passage through **11** ($R_1 = H$, $R_2 = CN$) and the electronic features of the cyano substituent contribute to the preferred involvement of **13**. In fact, aryl-vinyl bridging via **13** is followed exclusively, in agreement with the dominant effects of vinyl cyano.

The pattern is similar in the ortho series. Since 5-methoxybenzonorbornadiene undergoes triplet-sensitized isomerization to give **16** and **18** ($R_1 = R_2 = H$) in a ratio of 89:11,[2]
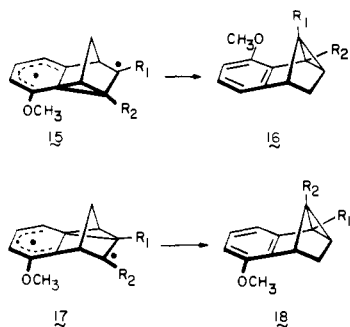
there exists a decided preference for bridging as in **15** ($R_1 = R_2 = H$). In **8b** which carries a cyano group at R_1, the excited state undergoes electronic reorganization solely via **15** ($R_1 = CN$, $R_2 = H$) in order to avail itself of both stabilizing influences. The triplet state of **8a** does not appear to experience bonding to give **15** ($R_1 = H$, $R_2 = CN$) where the cyano group is not transiently stabilizing an odd electron; rather, the reaction manifold is entirely dominated by **17** ($R_1 = H$, $R_2 = CN$).

Overall, we see a pattern of behavior which indicates that a vinyl cyano group totally controls the mode of bond formation in a doubly bridged triplet sensitized di-π-methane rearrangement. This regiospecificity is entirely comprehensible within the framework of molecular orbital theory. Thus, we described previously how donors on the aromatic ring have a large influence on the shapes of the occupied orbitals, but little effect on the vacant.[6] The orbitals for the methoxybenzonorbornadienes are very similar to those of the aminobenzonorbornadienes given earlier,[6] except that the methoxy effect is somewhat smaller than the amino effect. The regioselectivity of methoxybenzonorbornadiene bridging is not overwhelming

(see above), because of the opposite directing influence of occupied and vacant orbitals. The vinyl cyano group has a very large influence upon the LUMO shape and energy, so that the LUMO of 2-cyanobenzonorbornadiene is both highly polarized and quite low in energy. We adduce therefore that the lowest triplet state of each 2-cyano-X-methoxybenzonorbornadiene will be substantially aryl → vinyl charge transfer in character, with the result that LUMO polarization will dominate regioselectivity.

This localization of excitation energy in the olefinic moiety contrasts with that which operates in the absence of the cyano substituent. In these examples, the methoxyl substituted aromatic ring is the lower energy chromophore and excitation is concentrated in this portion of the molecules. There remains an important distinction, however, since the LUMO is the discriminating frontier molecular orbital for meta $-OCH_3$ whereas the HOMO controls in the ortho $-OCH_3$ example. Throughout, the first and product-determining part of the bond-making process would appear to be dictated by electron density considerations, with that carbon having the larger orbital coefficient engaging the nearby π electrons. When a vinyl cyano substituent is present, it is the β olefinic carbon which triggers reaction for reasons previously discussed.[3]

Although quantum yields have not been determined, all four cyanomethoxybenzonorbornadienes were found to react equally rapidly. In triplet excited state reactions, relative rate constants and relative quantum yields are known not to be correlatable. No single orientation of the two polar groups proved exceptional and no enhanced "push-pull" reactivity was apparent. We therefore agree with Zimmerman and Welter[8] that di-π-methane rearrangements of this general type show no obvious predilection for passage through zwitterionic transition states as suggested by Salem,[9] despite the fact that excited states are adequately energetic to have all gradations of possible charge separation. Our data suggest that we are not dealing with heavily polar species.

The present and preceding studies reveal a pattern of substituent effects which can be understood on a simple theoretical basis. Not only has this treatment of excited state reactivity proven useful and reliable, but it augurs in a promising way for enlarging the scope of the di-π-methane rearrangement in methodical, comprehensive fashion.

Experimental Section

Infrared spectra were recorded on a Perkin-Elmer Model 467 spectrophotometer. The ^1H NMR spectra were determined with Varian T-60, Varian A-60A, 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 AEl-MS9 spectrometer at an ionizing energy of 70 eV. The photoelectron spectra were recorded on a Perkin-Elmer PS-18 photoelectron spectrometer using xenon and argon as calibrants. The instrumental resolution was 25 meV. Preparative 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, Herlev, Denmark.

2-Iodo-6-methoxybenzonorbornadiene (3a). A solution of 6-methoxybenzonorbornen-2-one (**2a**)[5] (2.5 g, 13.3 mmol), hydrazine hydrate (9.0 g, 0.13 mol), and triethylamine (27.1 g, 0.268 mol) in ethanol (30 mL) was refluxed for 2 h. Hot water was added slowly until the solution became cloudy. The mixture was allowed to cool and was extracted with ether (3 × 40 mL). The combined organic phases were dried and evaporated to give 2.64 g (98%) of the hydrazone as a clear oil which was used without further purification.

The hydrazone (2.5 g, 12.4 mmol) in dry benzene (25 mL) containing triethylamine (12.1 g, 0.22 mmol) was treated slowly with iodine (6.29 g, 24.8 mmol) in benzene (20 mL) under a nitrogen atmosphere. Upon completion of the addition, the mixture was allowed to stand for 1 h at room temperature, poured into water, and extracted

into ether. The combined ethereal layers were shaken with 2 N hydrochloric acid, water, 10% sodium bisulfite solution, water, saturated sodium bicarbonate solution, and water before drying. The solvent was evaporated and the residue was taken up in anhydrous ether (25 mL) and treated in portions with solid potassium *tert*-butoxide (2.93 g, 26.1 mmol) with stirring at 0 °C. After 12 h, water was added, the ether layer was separated and dried, and the solvent was evaporated. The residual oil was distilled and the fraction boiling at 85–89 °C (0.4 mm) was chromatographed on silica gel (hexane elution) to give 1.07 g (29%) of **3a** as a clear oil: ^{1}H NMR (δ, CDCl$_3$) 7.13–6.6 (m, 3 H), 6.27 (dd, J = 8 and 2 Hz, 1 H), 3.80–3.7 (m, 2 H), 3.70 (s, 3 H), 2.6–2.4 (m, 1 H), and 2.3–2.1 (m, 1 H); *m/e* calcd 297.9856, obsd 297.9863.

2-Cyano-6-methoxybenzonorbornadiene (4a). A solution of **3a** (180 mg, 0.60 mmol) in HMPA (8 mL) containing cuprous cyanide (134 mg, 1.5 mmol) was heated at 90–95 °C for 3 h under nitrogen, cooled, and poured into aqueous ferric chloride solution to decompose the complex. The resulting brown oil which separated was purified by preparative thick-layer chromatography on silica gel (ether–pentane (3:2) elution) to give 116 mg (98%) of **4a** as a colorless crystalline solid, mp 54–55 °C (from ether–hexane): ^{1}H NMR (δ, CDCl$_3$) 7.39 (m, 1 H), 7.15 (d, J = 7.5 Hz, 1 H), 6.80 (d, J = 2 Hz, 1 H), 6.40 (dd, J = 7.5 and 2 Hz, 1 H), 4.0 (m, 2 H), 3.7 (s, 3 H), and 2.5–2.2 (m, 2 H); ^{13}C NMR (ppm, CDCl$_3$) 158.76, 158.12, 149.43, 140.02, 128.17, 122.88, 116.27, 111.37, 108.75, 69.47, 55.59, 52.77, and 51.95; *m/e* calcd 197.0841, obsd 197.0846.

Anal. Calcd for C$_{13}$H$_{11}$NO: C, 79.15; H, 5.63. Found: C, 79.38; H, 5.66.

2-Iodo-7-methoxybenzonorbornadiene (3b). A solution of somewhat impure **2b**[5] (contaminated with **2a**) was converted to its hydrazone and then to **3b** in the previously described fashion (overall yield 18%). Preparative thick-layer chromatography gave **3b** as a colorless solid, mp 80–81 °C: ^{1}H NMR (δ, CDCl$_3$) 7.03–6.80 (m, 3 H), 6.36 (dd, J = 8 and 4 Hz, 1 H), 3.78 (s, 3 H), 2.47 (m, 1 H), and 2.13 (m, 1 H); *m/e* calcd 297.9856, obsd 297.9865.

2-Cyano-7-methoxybenzonorbornadiene (4b). Treatment of **3b** (110 mg, 0.37 mmol) with cuprous cyanide in HMPA for 3 h at 95 °C in the predescribed manner, followed by thick-layer chromatography of the crude reaction mixture, gave **4b** (61 mg, 84%) as a light yellow oil: ^{1}H NMR (δ, CDCl$_3$) 7.48 (m, 1 H), 7.08 (d, J = 8 Hz, 1 H), 6.93 (d, J = 3 Hz, 1 H), 6.33 (dd, J = 8 and 3 Hz, 1 H), 4.0 (m, 2 H), 3.73 (s, 3 H), and 2.53–2.26 (m, 2 H); the more intense ^{13}C NMR peaks of **4b** are positioned at (ppm, CDCl$_3$) 159.82, 157.98, 150.40, 138.85, 111.03, 109.33, 108.75, 53.74, and 50.93; *m/e* calcd 197.0841, obsd 197.0846.

2-Iodo-8-methoxybenzonorbornadiene (7a). To a cold solution of mercuric acetate (6.09 g, 19.1 mmol) in water (20 mL) and tetrahydrofuran (20 mL) was added 330 mg (1.91 mmol) of **5**.[2] After the mixture was stirred at room temperature for 2 h, 10 mL of 3 M sodium hydroxide solution was introduced dropwise at 0 °C followed by 10 mL of 0.5 M sodium borohydride in 3 M NaOH. The elemental mercury was allowed to settle, solid sodium chloride was added to saturate the aqueous phase, and the upper tetrahydrofuran layer was separated and taken into ether. The ethereal solution was washed with water, dried, and evaporated. The resulting colorless oil was subjected to preparative thick-layer chromatography on silica gel (elution with 5% ether in hexane) to give 90 mg of the major component considered to be *exo*-2-hydroxy-8-methoxybenzonorbornadiene and 40 mg of the minor component assigned the 3-hydroxy-8-methoxy structure.

These alcohols were individually oxidized with Jones reagent to give **6a** and **6b**, respectively. For **6a**: ^{1}H NMR (δ, CDCl$_3$) 7.2–6.5 (m, 3 H), 3.93–3.70 (m, 1 H), 3.80 (s, 3 H), 3.67–3.50 (m, 1 H), and 2.50–1.98 (br m, 4 H). For **6b**: ^{1}H NMR (δ, CDCl$_3$) 7.1–6.3 (m, 3 H), 3.93–3.67 (m, 1 H), 3.80 (s, 3 H), 3.67–3.50 (m, 1 H), and 2.5–2.0 (br m, 4 H).

Ketone **6a** was converted to its hydrazone and then to **7a** as described earlier. The vinyl iodide was obtained in 34% yield as a clear faintly yellow oil: ^{1}H NMR (δ, CDCl$_3$), 7.02–6.47 (m, 4 H), 4.23–4.03 (m, 1 H), 3.80 (s, 3 H), 3.93–3.75 (m, 1 H), 2.58–2.40 (m, 1 H), and 2.27–2.06 (m, 1 H); *m/e* calcd 297.9856, obsd 297.9862.

2-Cyano-8-methoxybenzonorbornadiene (8a). Reaction of **7a** (95 mg, 0.32 mmol) with cuprous cyanide in HMPA according to the general procedure furnished **8a** (58 mg, 92%) as a colorless crystalline solid, mp 43–44 °C (from ether–hexane): ^{1}H NMR (δ, CDCl$_3$) 7.53 (d with additional fine coupling, J = 2.8 Hz, 1 H), 7.02–6.96 (m, 2 H), 6.67–6.53 (dd, J = 5 and 3 Hz, 1 H), 4.33 (m, 1 H), 4.06 (m, 1

H), 3.83 (s, 3 H), and 2.4 (m, 2 H); ^{13}C NMR (ppm, CDCl$_3$) 159.53, 154.58, 150.89, 133.75, 127.68, 127.00, 116.32, 115.89, 109.62, 69.76, 55.49, 53.80, and 47.77; *m/e* calcd 197.0841, obsd 197.0843.

Hydroboration–Oxidation of 5. An 11.0-g (63.9 mmol) sample of **5**[2] in ice-cold dry tetrahydrofuran (125 mL) was treated with excess diborane introduced in a nitrogen stream. Upon completion of the addition, the mixture was heated at reflux for 2 h, cooled, to 0 °C, and treated sequentially with ice chips, 1.5 equiv of 3 N sodium hydroxide solution, and 1.5 equiv of 30% hydrogen peroxide solution at 0 °C. The resultant solution was stirred at room temperature for 2 h, diluted with ether, washed with water, and dried. Solvent removal left a colorless oil which was directly subjected to Jones oxidation. There was isolated 7.7 g (64%) of a 1:1.5 mixture of **6a** and **6b** which was not separated.

2-Iodo-5-methoxybenzonorbornadiene (7b). By means of the general procedure, the preceding mixture of ketones was transformed into the corresponding vinyl iodides (27% yield) which were separated by thick-layer silica gel chromatography (elution with 5% ether in hexane). The major isomer was identified as **7b**: ^{1}H NMR (δ, CDCl$_3$) 7.0–6.37 (m, 4 H), 4.23–4.05 (m, 1 H), 3.93–3.75 (m, 1 H), 3.80 (s, 3 H), 2.49 (m, 1 H), and 2.13 (m, 1 H); *m/e* calcd 297.8956, obsd 297.9863.

The minor component was identical with **7a** obtained earlier.

2-Cyano-5-methoxybenzonorbornadiene (8b). Reaction of **7b** (100 mg, 0.33 mmol) with cuprous cyanide in HMPA according to the general procedure furnished **8b** (60 mg, 92%) as a colorless crystalline solid, mp 57–58 ° C: ^{1}H NMR (δ, CDCl$_3$) 7.47 (d, J = 2.8 Hz, 1 H), 6.97–6.83 (m, 2 H), 6.63–6.4 (dd, J = 5 and 3 Hz, 1 H), 4.28 (m, 1 H), 4.02 (m, 1 H), 3.73 (s, 3 H), and 2.30 (m, 2 H); ^{13}C NMR (ppm, CDCl$_3$) 159.53, 154.68, 150.02, 134.97, 127.73, 127.20, 127.05, 116.37, 115.89, 109.87, 69.91, 55.78, 52.14, and 49.66; *m/e* calcd 197.0841, obsd 197.0843.

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

3-Cyano-10-methoxytetracyclo[5.4.0.0^{2,4}.0^{3,6}]undeca-1(7),8,10-triene (9a). The photolysate from 20 mg of **4a** was directly sublimed and shown spectroscopically to consist only of **9a** (16 mg, 80%). The photoproduct was obtained as a colorless solid, mp 87–88 °C: ^{1}H NMR (δ, CDCl$_3$) 7.02 (d, J = 1.3 Hz, 1 H), 6.80 (d, J = 9 Hz, 1 H), 6.64 (dd, J = 9 and 1.3 Hz, 1 H), 3.81 (s, 3 H), 3.64 (dd, J = 7.3 and 2.6 Hz, 1 H), 3.18 (d, J = 5.6 Hz, 1 H), 3.10–2.87 (ddd, J = 9.4, 7.3, and 3.8 Hz, 1 H), 2.8–2.69 (ddd, J = 5.6, 3.8, and 2.6 Hz, 1 H), and 0.83 (d, J = 9.4 Hz, 1 H); ^{13}C NMR (ppm, CDCl$_3$) 159.43, 139.46, 138.58, 120.94, 117.83, 111.10, 55.61, 45.81, 38.33, 37.80, 29.37, and 29.13; *m/e* calcd 197.0840, obsd 197.0846.

Anal. Calcd for C$_{13}$H$_{11}$NO: C, 79.15; H, 5.63. Found: C, 78.80; H, 5.47.

3-Cyano-9-methoxytetracyclo[5.4.0.0^{2,4}.0^{3,6}]undeca-1(7),8,10-triene (9b). Irradiation of 18 mg of **4b** afforded a single photoisomer which was identified as **9b**: ^{1}H NMR (δ, CDCl$_3$) 7.37–6.51 (m, 3 H), 3.78 (s, 3 H), 3.64 (dd, J = 7.3 and 2.6 Hz, 1 H), 3.14 (d, J = 5.6 Hz, 1 H), 3.10–2.87 (ddd, J = 9.4, 7.3, and 3.8 Hz, 1 H), 2.82–2.69 (ddd, J = 5.6, 3.8, and 2.6 Hz, 1 H), and 0.83 (d, J = 9.4 Hz, 1 H); the nonquaternary carbons of **9b** appear at (ppm, CDCl$_3$) 124.24, 111.37, 111.08, 110.98, 107.63, 55.59, 46.41, 37.09, and 28.84; *m/e* calcd 197.0840, obsd 197.0846.

3-Cyano-8-methoxytetracyclo[5.4.0.0^{2,4}.0^{3,6}]undeca-1(7),8,10-triene (10a). The photolysate from photoisomerization of **8a** (20 mg) in the predescribed manner proved to be homogeneous by thin-layer chromatography and spectroscopic analysis: ^{1}H NMR (δ, CDCl$_3$) 7.27–6.60 (m, 3 H), 3.90 (dd, J = 7.3 and 2.6 Hz, 1 H), 3.78 (d, 3 H), 3.21 (d, J = 5.6 Hz, 1 H), 3.11–2.89 (ddd, J = 9.7, 7.3, and 3.5 Hz, 1 H), 2.81–2.68 (ddd, J = 5.6, 3.5, and 2.6 Hz, 1 H), and 0.82 (d, J = 9.7 Hz, 1 H); *m/e* calcd 197.0840, obsd 197.0846.

3-Cyano-11-methoxytetracyclo[5.4.0.0^{2,4}.0^{3,6}]undeca-1(7),8,10-triene (10b). The product from photoisomerization of **8b** (30 mg) was a homogeneous pale yellow oil (26 mg) identified as **10b**: ^{1}H NMR (δ, CDCl$_3$) 7.25–6.64 (m, 3 H), 3.89 (s, 3 H), 3.66 (dd, J = 7.5 and 2.6 Hz, 1 H), 3.43 (d, J = 5.6 Hz, 1 H), 3.10–2.88 (ddd, J = 9.4, 7.5, and 3.5 Hz), 2.86–2.73 (ddd, J = 5.6, 3.5, and 2.6 Hz, 1 H), and 0.82 (d, J = 9.4 Hz, 1 H); *m/e* calcd 197.0840, obsd 197.0846.

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Kinetics and Mechanism of the Hydrolysis of Aryloxyphosphonium Salts. Salt Effects

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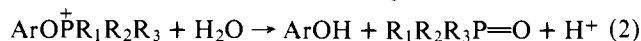
Abstract: The rates of hydrolysis of methyltris(2,6-dimethylphenoxy)phosphonium triflate, I, of methylphenyldiphenoxyphosphonium triflate, II, and of methyldiphenylphenoxyphosphonium triflate, III, are decreased 30-, 63-, and 83-fold, respectively, by the addition of 1.8 M lithium triflate in 34% aqueous acetonitrile. These enormous salt effects are ascribed to a decrease in the activity of water in the mixed solvent. Substitution of triflic acid for lithium triflate at a constant ionic strength of 1.8 M further decreases the rate of hydrolysis of I and II by factors of 2.6 and 3.2, respectively, but has no influence on that of III. These data can most simply be interpreted to mean that the rates of hydrolysis of I and II are inhibited by acids per se, and that the observed decreases in rate with increasing concentration of acid at constant ionic strength are not simply caused by a difference between the effects of hydrogen and lithium ions on the activity coefficient of water. The inhibition by acid provides evidence that the hydrolysis proceeds by way of a phosphorane as intermediate.

Introduction

The hydrolysis of aryloxyphosphonium salts[1,2] provides a model for an essential step in the acid hydrolysis of phosphates, phosphonates, and phosphonites; the detailed mechanisms of such hydrolyses[3-5] are of interest because of the ubiquitous occurrence of phosphates in intermediary metabolism. Presumably phosphates are protonated to yield hydroxyphosphonium salts that in turn react with water:

$$(RO)_3PO + H^+ \rightleftharpoons (RO)_3\overset{+}{P}OH$$

$$(RO)_3\overset{+}{P}OH + H_2O \rightarrow products \tag{1}$$
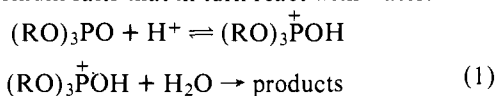
The reactions summarized by eq 2 model the second step in this mechanism; ArOH is a phenol, and R_1, R_2, and R_3 can represent alkyl, aryl, or aryloxy groups.

$$ArO\overset{+}{P}R_1R_2R_3 + H_2O \rightarrow ArOH + R_1R_2R_3P{=}O + H^+ \tag{2}$$

A major question arises as to whether the hydrolyses shown in eq 1 and 2 proceed by way of phosphoranes as intermediates, or by way of pentacoordinate transition states (or even, perhaps, through hexacoordinated intermediates).

The rates of hydrolysis of methyltriphenoxyphosphonium triflate, IV, and of methyltris(2,6-dimethylphenoxy)phosphonium triflate, I, as functions of the concentration of water and acid in aqueous acetonitrile have been measured previously by stopped-flow techniques.[1] The rates of hydrolysis in that solvent increase a millionfold between 0.2% and 34% water, but the rate at any given concentration of water is sharply diminished by added acid; 1.8 M triflic acid in 34% aqueous acetonitrile decreases the rate about 100-fold. The rates are also strongly inhibited by salts,[2] and, in particular, the rate of hydrolysis of I in 34% aqueous acetonitrile is decreased 30-fold by 1.8 M lithium triflate; the rate of hydrolysis is diminished
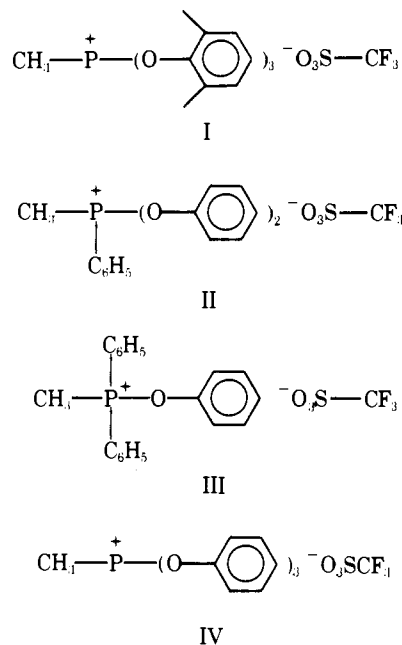
another factor of 2.6 by replacing the lithium triflate by 1.8 M triflic acid. The question naturally arises as to whether this further decrease in rate, caused by the substitution of hydrogen ions for lithium ions, is the result of an inhibitory effect of acid, per se, or whether it represents a difference between the salt effects of lithium and hydrogen ions on the activity coefficient of water or other reaction species. The mechanism of the hydrolysis of the phosphonium salts under study obviously depends on the answer to this question.