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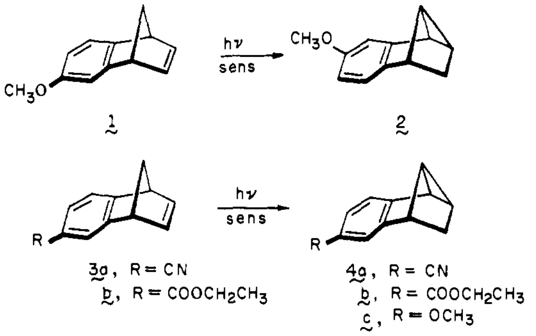
Substituent Control of Regiospecific Pathways in Di-π-methane Photorearrangements Which Utilize Benzo–Vinyl Bonding Schemes

Sir:

So vaguely understood are polar substituent influences on π-electron distribution in electronically excited molecules, that this question now commands consideration as a major unsettled issue in organic photochemistry. Intriguing subtleties are to be anticipated since photoexcited species possess electronic distributions quite unlike those of their ground state progenitors.[1] Currently, little basis exists for predicting which course a π → π* rearrangement will take when proximal electron-withdrawing or -donating substituents are introduced.[2] With regard to this question, we have uncovered striking crossovers in otherwise fully regiospecific product formation which result upon substituent alteration from cyano to methoxy in the di-π-methane photorearrangements of the benzonorbornadiene[3] and *anti*-7,8-benzotricyclo[4.2.2.0^{2,5}]deca-3,7,9-triene systems.[4]

Sensitized irradiation (3500 Å) through Pyrex of dilute benzene solutions of **1**,[5] **3a**,[6] and **3b** resulted in ready photoisomerization with formation of a *single* product in each instance. Sensitizers ranging in triplet energy from 65.5 (thioxanthone) to 73.6 kcal/mol (acetophenone) were utilized. Direct irradiation at various wavelengths proved ineffective. The ^{1}H NMR spectrum (CCl_4) of **2**, which consists of a highly structured aromatic pattern (δ 6.30–6.92, 3 H), a methoxyl singlet (3.70, 3 H), and higher field multiplets centered at 3.19 (2 H), 2.75 (1 H), 2.38 (1 H), 1.88 (1 H), and 0.74 (1 H), differs notably from that of **4c**, particularly in the downfield sector. The latter anisole was prepared from **4b** by sequential saponification, reaction with methyllithium, Baeyer–Villiger rearrangement, hydrolysis, and exposure to dimethyl sulfate in alkali. Treatment of **4a** with methylmagnesium iodide produced the identical acetyl derivative, thus completing the requisite interconversions. Absolute positional assignment to the substituents in **2** and **4** follows principally from direct ^{1}H NMR spectral comparisons with the homologous compounds of unequivocal structure described below. Simultaneous irradiation of benzonorbornadiene, **1** and **3a**, under controlled conditions revealed no substantial differences in the individual rates of starting material disappearance or product formation.[7]

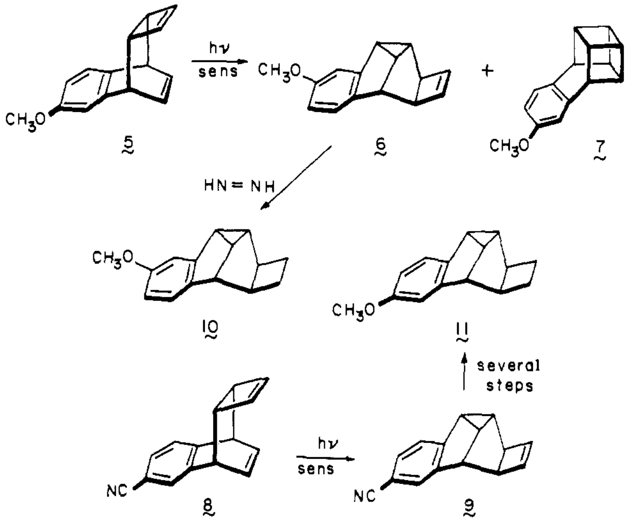


3a, R = CN
b, R = $COOCH_2CH_3$

4a, R = CN
b, R = $COOCH_2CH_3$
c, R = OCH_3

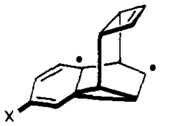
To further assess this dramatic change in bonding preference, the photochemistry of **5** and **8** was also examined. Initial detailed studies with the parent hydrocarbon of this series[4] revealed its triplet state (E_T = 69–74 kcal/mol) to enjoy the capacity for bifurcate reactivity. In this instance, bond reorganization along the di-π-methane pathway leading to cyclopropane product is slightly favored (1.2:1) over the ($_\pi 2 + {}_\pi 2$) bonding process which gives rise to benzobasketene. The photorearrangements of **5** and **8** were conducted analogously and likewise followed closely by gas chromatography. As with the hydrocarbon, ether **5** was unreactive to sensitization by benzophenone (E_T = 69 kcal/mol); however, this was not the case with nitrile **8**, a finding which signals the lower triplet energy of this diene. Direct irradiation failed to promote these isomerizations in both instances.

Whereas triplet excitation of **5** provided a 0.8:1 mixture of **6** (oil) and **7** (mp 53–54°), nitrile **8** gave only **9** (mp 62–63.5°). Complete structure elucidation of **9** was achieved by single-crystal X-ray analysis, its crystals belonging to a triclinic space group with a = 9.608 (1) Å, b = 7.995 (1) Å, c = 8.324 (1) Å, α = 112.79 (1)°, β = 112.07 (1), and γ = 84.03 (1)°. A calculated and measured density indicated two molecules of $C_{15}H_{11}N$ per unit cell or one molecule per asymmetric unit in space group $P\bar{1}$. A total of 1345 unique reflections with $\theta \leq 55°$ were measured (Cu Kα radiation); after Lorentz, polarization, and background corrections, 1334 reflections were judged observed ($F_o \geq 3\sigma(F_o)$). Full-matrix least-squares refinements of positional and anisotropic temperature factor parameters for all atoms converged to an unweighted residual of 0.035. All bond distances and angles agree with generally accepted values.



Diimide reduction of **9** and subsequent treatment of this dihydronitrile as above produced **11** (oil; $\delta_{TMS}^{CCl_4}$ 6.27–7.12 (m, 3), 3.66 (s, 3), 3.35 (d, J = 5 Hz, 1), and 1.50–3.10 (m, 9)). Comparable saturation of the cyclobutene double bond in **6** led to the oily ether **10** whose properties, most especially the aryl region of its pmr spectrum ($\delta_{TMS}^{CCl_4}$ 6.30–7.07 (m, 3), 3.69 (s, 3), 3.34 (d, J = 5 Hz, 1), and 1.48–3.14 (m, 9)), denote the methoxy group to be meta-oriented relative to the cyclopropane ring.

These results are quite revealing and carry a number of far-reaching implications. Firstly, as concerns the di-π-methane rearrangement of *anti*-7,8-benzotricyclo[4.2.2.0^{2,5}]deca-3,7,9-triene which requires benzo-vinyl bridging,[3,4] the meta (**12**, X = H) and para bonding schemes (**13**, X = H) are equivalent. The experimental data indicate a slight preference (1.2:1) for isomerization along this reaction channel instead of the closely competitive ($_\pi2 + _\pi2$) pathway which presumably involves transient intervention of biradical **14** (X = H). When X becomes methoxy, C–C bond formation in the di-π-methane manifold chooses to be exclusively meta to the substituent as in **12**, (X = OCH_3) and the 2 + 2 cycloaddition reaction is somewhat favored. For the cyano example, para bonding as in **13** (X = CN) is seen to operate exclusively and no intramolecular cycloaddition is evident. Dimethoxydiene **15**, which has the benefit of symmetrical placement of its two functional groups, has also been studied. In this instance, the observed ratio of **16**:**17** (sensitized or direct irradiation; intersystem crossing now operates) was 10:1.



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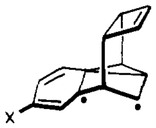

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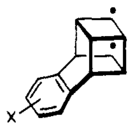

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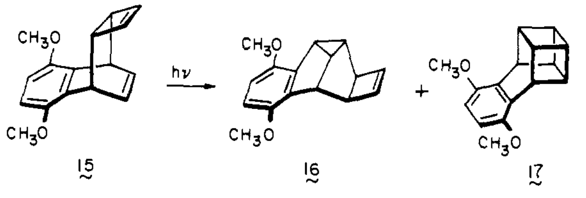

As concerns the anisole derivatives, therefore, the methoxy group is seen to dramatically alter initial bonding preferences so as to produce that biradical of lesser stability.[9] One simple working explanation is that electron transmission from this substituent in the triplet manifold is chiefly to the meta position[1] and that initial benzo-vinyl bonding is governed principally by interaction between those sites of higher π-electron density. Because cyano groups direct excited state bonding to the para position, the level of stabilization available to the di-π-methane intermediate now appears adequately large to dominate the product-forming situation. Progressive decline of triplet energy localization in the aromatic ring may, however, also contribute to the onset of that reaction confined to the two double bonds. Further elaboration upon these initial findings, currently in progress, is expected to enlarge the experimental base needed to realize fully comprehensive mechanistic understanding.[9]

Supplementary Material Available. A computer generated three-dimensional drawing of structure **9** (Figure 1), together with fractional coordinates and temperature factors (Table I), selected bond distances (Table II), and selected bond angles (Table III) will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.00 for photocopy or $2.50 for microfiche, referring to code number JACS-75-3275.

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