Effects of a Nitro Substituent on Di-π-methane Rearrangements of Benzonorbornadiene and Its [3.2.1] Homologue

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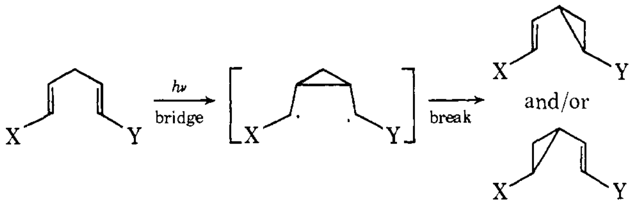
Abstract: β-Nitrobenzonorbornadiene (**1f**) undergoes a di-π-methane (DPM) rearrangement on direct irradiation; the only observed DPM product was derived from aryl-vinyl bridging para to the nitro group. The reduced quantum yield for this reaction (0.025) compared with the triplet DPM rearrangement of parent benzonorbornadiene (0.5) was attributed to inefficient singlet → triplet intersystem crossing and nitro-accelerated triplet decay. A mixture of β- and β'-nitrobenzo[6,7]bicyclo[3.2.1]octa-2,6-diene (β- and β'-NO_2-**4**; homologues of **1f**) was separated by highly selective DPM rearrangement of the β' isomer (aryl-vinyl bridging possible only para to the nitro group). Introduction of the β'-nitro group into the benzo[3.2.1] framework was less effective in lowering the DPM quantum yield than in the [2.2.1] system. This result was credited to the greater ability of the [3.2.1] hydrocarbon triplet to decay by twisting within the vinyl moiety, and to greater excitation localization in the nitroarene chromophore of β'-NO_2-**4**. A very low quantum yield (<0.0002) was observed for DPM rearrangement of β-NO_2-**4** (aryl-vinyl bridging possible only meta to the nitro group); the large ratio $\Phi_{\beta'\text{-}NO_2\text{-}4}/\Phi_{\beta\text{-}NO_2\text{-}4}$ (>35) is consistent with the assumption of electrophilic behavior by the vinyl group in aryl-vinyl DPM reactions, and with theoretical calculations of electron density distribution in acceptor-substituted arenes.

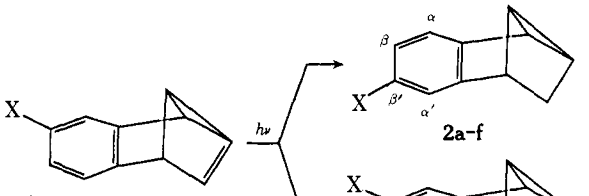
Over the past decade, the di-π-methane (DPM) rearrangement has been shown to be one of the most general of photochemical transformations.[2] Much understanding of this reaction has been acquired through studies of substituent effects; substituents can influence reaction rates[3a] and can impose striking regiospecificity where two otherwise degenerate modes of reaction would exist.[3b-h] However, despite sustained strong interest in the effects of polar substituents on DPM systems, remarkably little has been reported of the effects of one of the most polar substituents, the nitro group. We now present data showing that the nitro group can be as effective as any other known substituent in promoting intramolecular regiospecificity, and can exert a remarkable position-dependent effect on relative quantum yields of isomeric DPM substrates.

The context of some of the present observations requires delimitation. Conceptually, at least, there are two important stages in a DPM rearrangement; these will be termed the "bridge" step and the "break" step. In a singly connected DPM system (i.e., two distinct π moieties connected by only a single sp^3 carbon), only one bridge step is possible and the question of regiospecificity does not exist for this step. The break step, then, must be product determining, unless of course, the entire reaction is concerted.[2] The nature of substituent effects has been clearly elucidated for the numerous members of this class of DPM system; they consistently undergo the more exothermic break step.[2] For these (singlet) systems, the rate- and product-determining steps are distinct, the latter occurring later along the reaction coordinate.[3g]



In a doubly connected DPM system (two π moieties connected at two points by sp^3 carbons) such as benzonorbornadiene,[4] regiospecificity may be influenced at either step (Scheme I). In the many reported instances in which one of the π moieties was an arene,[2] the regiospecificity in the break step has been totally dominated by the exothermicity of rearomatization. In the present study, initial focus was on regiospecificity in the bridge step.

For earlier reported triplet rearrangements of doubly connected DPM systems, bridging regiospecificity was linked uniformly with the stabilities of the bridged species,[3b-f] and substituent effects thereon. More recently, as the present study neared completion, some rearrangements of DPM systems bearing polar substituents were reported in which regiospecificity was attributed to excited state π-electron distribution.[3h] Thus β-methoxybenzonorbornadiene (**1b**) gives predominantly[5] meta-bridged product **3b**, while the corresponding cyano and carbethoxy derivatives afford only para-bridged products **2c** and **2d**. These results contrast with the lack of regiospecificity observed earlier for the DPM rearrangement of methyl derivative **1e**.[4b]



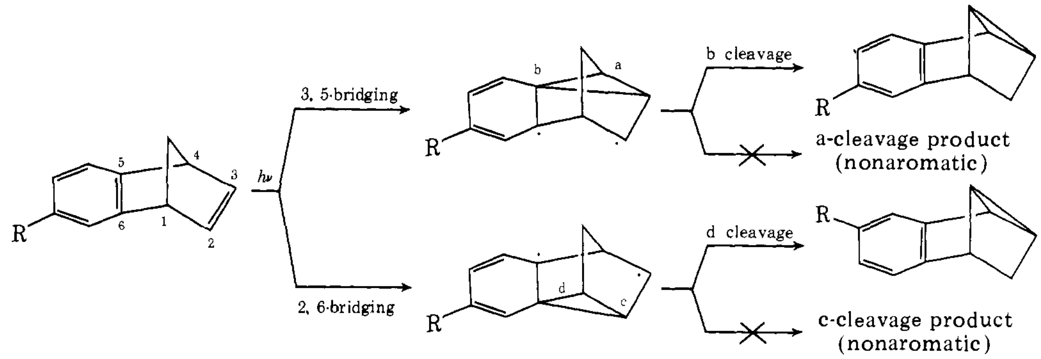
1a, X = H
b, X = OCH_3
c, X = CN
d, X = $CO_2C_2H_5$
e, X = CH_3
f, X = NO_2

2a-f

3a-f
(**2a** ≡ **3a**)

Our interest in the photochemistry of nitroarene DPM systems (e.g., **1f**)[6] was kindled by theoretical[7,8b] and experimental[7,8] studies of the spectroscopic and photochemical behavior of arenes bearing strongly electron-accepting and electron-donating substituents. These studies indicated that (in contrast to ground state behavior) excited state charge transfer to an electron-attracting substituent (e.g., NO_2) is more facile from the ortho and meta positions than from the para position. The photochemical behavior of **1f** was expected to show whether a homoconjugated double bond would interact more strongly with a relatively electron-rich arene carbon (para to NO_2) or an electron-poor one (meta to NO_2). The cited[3h] reactions of **1c** and **1d** answered this question, demonstrating that the para carbon is the preferred site of aryl-vinyl interaction in an acceptor-substituted benzonorbornadiene, and

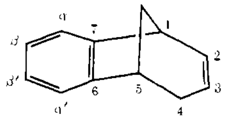
Scheme I



giving an empirical indication that **2f** would be the major (if not exclusive) DPM rearrangement product from **1f.**

However, in addition to merely broadening the range of electron acceptors capable of imposing DPM regiospecificity on **1**, **1f** posed questions unique among the reported members of its family of compounds. Substrates **1a–e** do not undergo DPM rearrangement on direct irradiation (i.e., reaction is initiated only from the triplet excited state).^{3h,4} In contrast, **1f**, by virtue of the known^{9} ability of the nitro group to facilitate intersystem crossing (isc), might show an unusual ability to react on direct irradition (albeit via the triplet state). On the other hand, this isc ability could *reduce* DPM efficiency in **1f** (relative to **1a–e**) by facilitating triplet decay.^{9} "No substantial differences" were reported in the reaction rates of **1a**, **1b**, and **1c** on sensitized irradiation.^{3h}

Previous work^{10} showed that benzo[6,7]bicyclo[3.2.1]-octa-2,6-diene (**4**), a homologue of **1a**, undergoes DPM rearrangement on direct *or* sensitized irradiation. The benzo[3.2.1] framework is a singly connected DPM system; one end of the alkene moiety is prevented by geometry from interacting with the arene portion of the molecule. Therefore, there is no possibility of bridging regiospecificity in the DPM rearrangement of **4** or its derivatives. However, the requirement that DPM rearrangement of **4** and its derivatives proceed only through 2,7-bonding gives this system the potential of furnishing *inter*molecular reactivity comparisons, which could parallel the *intra*molecular reactivity comparisons implicit in DPM rearrangements of **1b–f.** Again, our interest was focused on nitro derivatives (β-NO$_2$-**4** and β′-NO$_2$-**4**); these can rearrange only via bridging meta and para to the nitro group, respectively. This intermolecular comparison could provide, inter alia, some quantitation of relative positional reactivities in comparably substituted arenes in which one position is overwhelmingly more reactive than the other. Measurement of relative positional reactivities in **1c** and **1d** (and **1f**, as it turns out) has proved thus far to lie beyond experimental capabilities of separation and/or detection; one can presently describe the DPM reaction of each of these benzo[2.2.1] compounds only as "fully" regiospecific.^{3h} Because separation or detection of a very minor component of a mixture of positional isomers was not expected to be part of the problem in comparisons of separate benzo[3.2.1] DPM rearrangements, this system was considered inherently more suitable for quantitative determinations.



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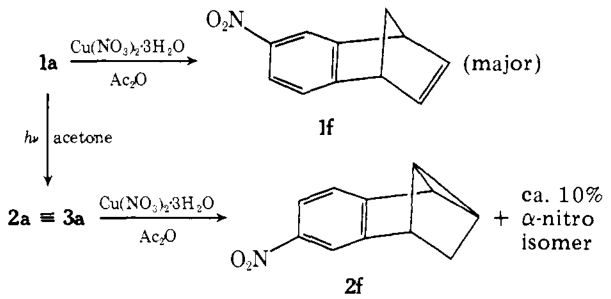
Synthesis of Reactants and Potential Photoproducts

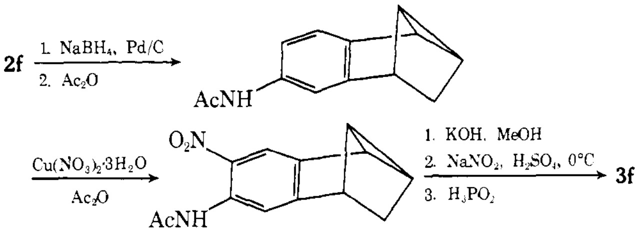
Scheme II outlines the preparation of **1f**^{6} and **2f**; these were major products of the respective nitrations and were readily purified by chromatography. The assigned structure of **2f** is consistent with the well-known para-directing effect of a suitably oriented cyclopropyl group.^{11}

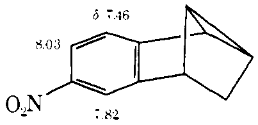
Scheme II



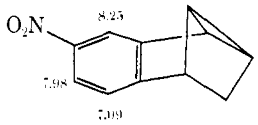
The isomeric β-nitro compound **3f** was synthesized via a classical sequence of conversions (Scheme III). Spectroscopic comparisons of **2f** and **3f** afforded unequivocal structure assignments. The UV spectra of **2f** (λ$_{max}^{EtOH}$ 307 nm) and **3f** (λ$_{max}^{EtOH}$ 285 nm) are characteristic of a *p*-nitro- and a *m*-nitrocyclopropylbenzene chromophore, respectively;^{11} the aromatic regions of the ^{1}H NMR spectra are uniquely consistent with anticipated^{12} anisotropic deshielding of the α proton by the proximate cyclopropane ring (below).

Scheme III





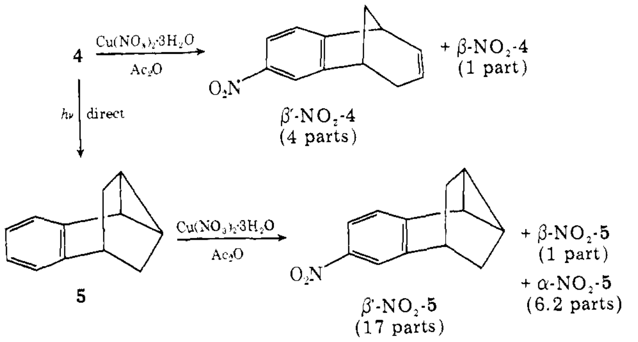
2f



3f

One synthesis of β- and β′-NO$_2$-**4** and their corresponding DPM photorearrangement products β- and β′-NO$_2$-**5** is outlined in Scheme IV. This approach afforded pure samples of β′-NO$_2$-**4** and β′-NO$_2$-**5**, but was unsatisfactory for obtaining pure β-NO$_2$-**4** and β-NO$_2$-**5** because these were minor products of the corresponding nitrations and were only poorly separable from the β′-nitro isomers by available methods, although NMR spectral differences allowed quantitative mixture analyses. The preferred β′ nitrations, attributable to homoconjugative stabilization by the remote double bond in **4** and conjugative stabilization by the perfectly aligned cyclopropyl group in **5**, proved useful in assigning isomer structures. These isomer assignments were further supported by UV and NMR

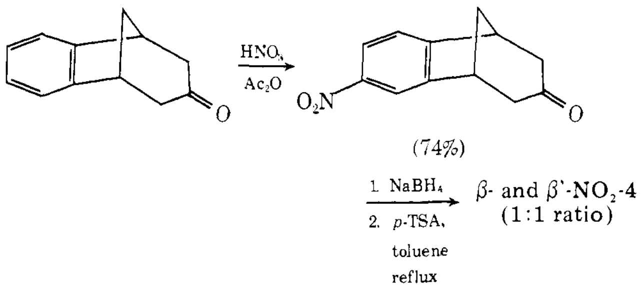
Scheme IV



spectral comparisons (as described above for **2f** and **3f**; see Experimental Section for data) and by photochemical correlation (see below).

A more fruitful method for preparation of β-NO_2-**4** is outlined in Scheme V; isolation of the pure isomer and its photoproduct (β-NO_2-**5**) are detailed under Results of Irradiations.

Scheme V



Results of Irradiations

Direct or sensitized irradiation of β-nitrobenzonorbornadiene (**1f**) led to isolation of a single isomeric photoproduct, readily identified as β'-nitro DPM product **2f.**[13] For the direct irradiation (solvent cyclohexane), this and recovered starting material afforded a mass balance greater than 93%. Sensitization (benzophenone) was less clean, but yields were satisfactory up to 60% conversion. Although **2f** and **3f** were inseparable on several VPC columns, analysis of crude reaction mixtures by ^{1}H NMR (with the spectrum of pure **3f** in hand) showed no trace of **3f.** It was estimated that 3% of **3f** would have been detectable; the observed regiospecificity of the DPM rearrangement thus is at least 32:1.

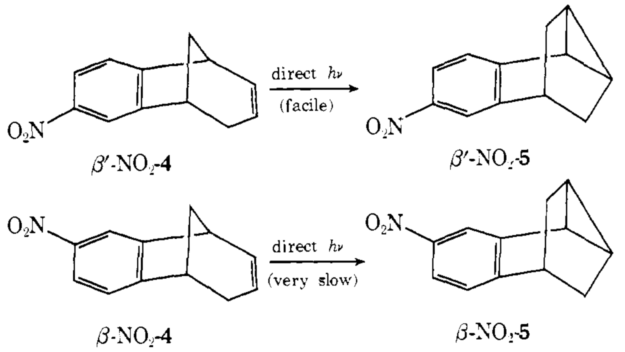
Direct irradiation of essentially pure β'-NO_2-**4** gave facile conversion to predicted DPM product β'-NO_2-**5.** At this point, in view of the previously described difficulty in obtaining pure β-NO_2-**4,** an optimistic extrapolation from the photochemical behavior of **1f** was made: Quantum yields for β- and β'-NO_2-**4** were assumed to be widely disparate, because the former is capable only of *homo-meta* and the latter only of *homo-para* interaction with the isolated double bond. A 1:1 mixture of the nitro isomers (via Scheme V) was irradiated for 3 h; VPC analysis indicated a product–starting material ratio of 50:50. After 3 h more the ratio was 51.5:48.5. Isolation (preparative VPC) yielded nearly pure β'-NO_2-**5** and quite pure unreacted β-NO_2-**4.**

Direct irradiation of pure β-NO_2-**4,** obtained by this unusual photochemical isomer separation, gave very slow conversion (ca. 70% after 29 h) to the expected β-NO_2-**5,** thus providing a pure sample of this substance. This experiment established that the disparity in reaction rates on irradiation of the nitroalkene mixture was not the result of selective light absorption by β'-NO_2-**4**; it also ruled out the possibility of photochemical transformation of β'-NO_2-**4** to its β-nitro isomer by an allylic 1,3-hydrogen shift.

Table I. Quantum Yields for DPM Rearrangements

Compd	Irradiation mode	Φ_{DPM}
1a	Sensitized	0.5[a]
4	Sensitized	0.05[b] (0.025)[c]
1f	Direct	0.025[d]
β'-NO_2-**4**	Direct	0.007[d]
β-NO_2-**4**	Direct	<0.0002[d]

[a] Ferrioxalate actinometry, 254 nm; taken as standard for determination of other Φ's. [b] Solvent acetone; 254 nm. [c] 20% acetone/hexane; >300 nm. [d] Cyclohexane; >300 nm.



To facilitate photochemical comparisons among **1f** and the nitro derivatives of **4,** quantum yields (Φ) were determined for the DPM rearrangements of these three compounds and the parent hydrocarbons. These are assembled in Table I. For benzonorbornadiene (**1a**), Φ for the sensitized reaction (0.5) was identical, within experimental error, with that reported;[4] **1a** was used as actinometer in subsequent determinations. The quantum yield for rearrangement of homologue **4** in 20% acetone–hexane (0.025) is in reasonable agreement with the reported[8b] value of 0.014. However, irradiation in solvent acetone afforded an increase in Φ to 0.05; this result is taken to indicate that the energy level of triplet excited state **4** is quite high, and that energy transfer (ET) from the sensitizer proceeds with less than unit efficiency. Nonetheless, on the assumption that ET in solvent acetone is not far from unit efficiency, we conclude that the triplet DPM rearrangement in the parent [3.2.1] system is intrinsically less efficient than in the [2.2.1] system, even when the statistical advantage of two available bridging sites is factored out of the latter; a fivefold decrease emerges from our data. The same qualitative difference was noted previously[8b] and attributed to the greater flexibility of the [3.2.1] system. A well-documented study of increasing triplet radiationless decay rates of 1-phenylcycloalkenes with increasing ring flexibility was reported recently;[14] rates were correlated with ability of the triplets to twist and thus decrease the T_1–S_0 energy gap. Relative Φ's for **1a** and **4** can be accounted for in similar fashion.[15]

Interpretative Discussion

Nitroarene Photochemistry. We consider first the identity of the excited state(s) initiating DPM rearrangement in the nitroaromatics. DPM reaction of **1f** on direct irradiation (in contrast to **1a–e**),[3h,4] as well as substantial precedent in nitroarene photochemistry,[9,16,17] strongly implicates a triplet state as the initiating species for this compound. Although there is reason to believe that a large portion of the DPM rearrangement of hydrocarbon **4** on direct irradiation proceeds through a singlet excited state,[10a] the data reported here and previous evidence concerning intersystem crossing (isc) rates and efficiencies of nitroaromatics[9] lead us to conclude that β- and β'-NO_2-**4** also rearrange via triplet states.

No clear choice appears possible between n,π^* and π,π^* triplets, which are believed to be close in energy in nitroaromatics.[17] The n,π^* triplet may be lower for nitrobenzene and some simple derivatives,[17a,b] but electron-donating substituents (such as the effective dialkyl substitution in the present systems) may favor a π,π^* triplet as the reactive species.[17c]

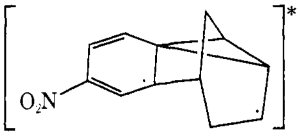
Two additional features of nitroarene photochemistry are useful in the interpretation of results. First, based on the 0–0 band of its phosphorescence emission, the triplet energy (E_T) of nitrobenzene has been placed at ca. 60 kcal/mol.[18] This may be considered an upper limit for triplets of nitroarene moieties involved in this study. It is to be contrasted with the E_T value of 70 kcal/mol reported for **1a**[4] and the E_T value of >75 kcal/mol established in the present work for **4** (sensitization by acetophenone, E_T = 73.7 kcal/mol, is ineffective; efficiency of sensitization by acetone, E_T = 79 kcal/mol, increases with acetone concentration). The triplet energy of ethylene appears to lie in the range 57–82 kcal/mol;[19] the extremes correspond to 90° twisted and planar ethylene, respectively. Assuming that triplet excitation energy localization in **1a, 4,** and their nitro derivatives depends on the relative energy levels of the aryl and vinyl chromophores, one can readily conclude from the above data that triplet energy in **1f** or β'-NO$_2$-**4** should be much more heavily localized in the aryl chromophore than in the vinyl one, and that arene triplet localization should be greater in the nitro derivatives than in the parent hydrocarbons. Consequently, [3.2.1] nitroarenes have less opportunity for use of skeletal flexibility than does parent **4,** as a means of triplet deactivation.[10b,14] Consistent with this hypothesis is the smaller drop in quantum efficiency on ring homologation in the nitro derivatives, compared with the parent hydrocarbons ($\Phi_{1a}/\Phi_4 = 10$; $\Phi_{1f}/\Phi_{\beta'\text{-NO}_2\text{-}4} \approx 3.5$).

A second characteristic of nitroaromatic triplets is their inherently high rate of radiationless decay (for nitrobenzene, $k_d \simeq 10^9\ \text{s}^{-1}$).[9] This is manifested in the low quantum yield previously reported for (e.g.) photoreduction of nitrobenzene in 2-propanol (Φ = 0.0114),[9] and in the lower DPM efficiencies presently observed for nitro derivatives, relative to the parent hydrocarbons. Quantum yields for **1f** and β'-NO$_2$-**4,** however, are not necessarily direct measurements of the efficiency of DPM reaction from the respective triplets. Triplet reactions initiated by direct irradiation must lose some overall efficiency because of inefficient singlet → triplet isc. Assuming that the isc values reported[9] for nitroarenes such as nitrobenzene (0.67) and 1-nitronaphthalene (0.63) are extrapolatable to the present nitroarenes, one can reasonably conclude that Φ's for rearrangement of **1f** and β'-NO$_2$-**4** from the *triplet* excited states still are no greater than 0.05 and 0.015, respectively. These values are markedly smaller than the Φ's for parents **1a** (0.5) and **4** (0.05), and consistent with facilitation of radiationless decay by a nitro group. The smaller ratio of Φ's (nitro derivative/parent) for the [3.2.1] system again can be accounted for by the energy localization concept described above.

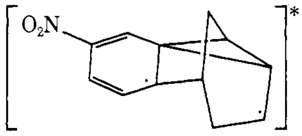
We note that the above data support no assumptions concerning the relative reaction *rates* of DPM rearrangements of nitro derivatives vs. parent systems.[20] It is clear only that DPM rearrangement of **1f** is faster via para than via meta bridging. However, in comparing the photochemistry of β- and β'-NO$_2$-**4,** a reasonable case can be made for using the DPM quantum yields of the two isomers to conclude that triplet excited β'-NO$_2$-**4** rearranges at a much faster rate than does the isomeric β-nitro triplet. For each isomer, the following essential steps (and corresponding rate constants or quantum yields) can be postulated: excited singlet → triplet intersystem crossing (Φ_{isc}), bridging (k_b), and breaking to go on to product (Φ_r; as in Scheme I).

Supporting one part of these basic assumptions is the recent elegant work by Zimmerman and co-workers[22] demonstrating (at least in the DPM systems they studied) that *ground* state bridged (cyclopropyldicarbinyl) diradicals revert only to starting dienes, and thereby necessitating the existence of a second (triplet excited state) bridged diradical. The two triplets (unbridged and bridged) each can undergo competitive radiationless decay with a characteristic rate constant. If k_{dt} is the rate of decay of the unbridged triplet and Φ_r is the quantum yield of product formation *from the bridged triplet*, the overall quantum yield can be expressed as $\Phi_{\text{DPM}} = \Phi_{\text{isc}}\Phi_r k_b/k_{dt}$.

Prior to bridging, as pointed out, excitation should be localized predominantly in the nitroarene chromophore.[18,19] It is reasonable, then, to assume that Φ_{isc}'s and unbridged triplet decay rates are quite similar for the two isomers. Although arguments for slight differences might be advanced, a 35:1 factor is difficult to rationalize. This leaves formation of the bridged triplet and its two modes of reaction (decay to ground state bridged diradical or "break" to lead to product) to account primarily for the difference in Φ_{dpm}'s. It appears unlikely that bridged triplet decay is faster for the β- than for the β'-nitro triplet (β- and β'-NO$_2$-**4d***), because the nitro group (which might facilitate the requisite spin inversion) can interact more strongly in β'-NO$_2$-**4d***, thus favoring the reverse inequality. The other mode of reaction available to the bridged triplet, the "break" step to product (k_r), should be extremely rapid for both isomers, since it involves rearomatization. If there is any effect of reactant stability on this step, the more stable β'-NO$_2$-**4d*** (by ground state analogy) should react more slowly, contrary to observation.



β'-NO$_2$-**4d***

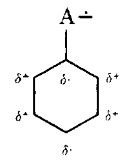


β-NO$_2$-**4d***

We thus conclude that a bridging rate (k_b) difference is the major source of the difference in Φ_{dpm}'s for β- and β'-NO$_2$-**4.** Consistently parallel reasoning implicates the bridging step as the source of regiospecificity in the DPM rearrangement of **1f** (and other substituted benzonorbornadienes),[3h] although the comparisons here are intramolecular.

Finally, we make some observations concerning the relation of the present results to some other nitroarene photochemistry, and to theoretical work in this area. The regiospecificity of the photorearrangement of **1f** and the large difference in Φ's for β- and β'-NO$_2$-**4** provide a contrast with nucleophilic photosubstitution reactions of nitroarenes.[8b] The latter undergo selective nucleophilic attack at position(s) meta to the nitro group, while in the DPM reactions under discussion, the ethylenic moiety clearly interacts (bridges) more readily at the arene site para to the nitro group. Thus, these two photoreactions of nitroarenes exhibit opposite regiospecific responses to the effects of a nitro group on excited state electron distribution.

Recognizing that the ethylenic function behaves as an electrophile in the DPM systems, preferentially bridging at the site of higher electron density, one can readily correlate both reaction types with the theoretical studies cited earlier.[7,8b] For acceptor-substituted arenes, these studies reported calculations of excited state electron distribution which may be represented as shown below. This representation affords clear correlation



of the two cited reaction types, but is limited in that it allows no insight into the orbital nature of aryl–vinyl interactions in the presently discussed DPM substrates, and cannot predict regiospecificity (i.e., ortho or meta bridging?) in the corresponding α-substituted systems.[23]

The presently demonstrated ability of the benzo[6,7]bicyclo[3.2.1]octadiene system to "detect" a very inefficient DPM rearrangement by precluding intramolecular competition should find further application in exploring other substituent and positional effects (e.g., α and α' positions); results of such studies will be reported in due course.

Experimental Section

Nuclear magnetic resonance spectra were obtained on Bruker HX-60E, or Varian A-60, T-60A, CFT-20, or XL-100 spectrometers, in either $CDCl_3$ or CCl_4. Vapor phase chromatographic analytical and preparative separations were done on a Varian Aerograph Model A-700 instrument, equipped with thermal conductivty detection. Peak areas were determined by cutting and weighing and are uncorrected for response factors. Ultraviolet spectra were obtained on a Cary Model 118 and infrared spectra on a Perkin-Elmer Model 137 sodium chloride spectrophotometer. Mass spectra were run on a Hitachi Perkin-Elmer Model RMU-6E single focusing spectrometer. High pressure liquid chromatography was carried out on a Waters Associates ALC-100 instrument.

β-Nitrobenzonorbornadiene (1f) was prepared by direct nitration of benzonorbornadiene with cupric nitrate in acetic anhydride at −5 to −10 °C. Silica gel chromatography (40:60 benzene–ligroin elution) and crystallization from pentane gave 34% of pale yellow crystals: mp 37.5–38 °C (lit.[6] 38–38.5 °C); λ_{max}^{EtOH} 290 nm (ϵ 7900); ^1H NMR spectrum as reported.[6]

β'-Nitrobenzo[2,3]tricyclo[2.2.1.0^{6,7}]heptene (2f). Direct Irradiations of 1f. Irradiations were carried out with dilute solutions in benzene, 2-methylpropanol, or cyclohexane. The following is typical: In a quartz immersion-well apparatus (Hanovia 450-W medium-pressure Hg arc lamp) equipped with Pyrex filter, a solution of 472 mg of **1f** in 155 mL of cyclohexane was purged with nitrogen 1 h previous to and throughout irradiation. Progress of irradiation was monitored by VPC analysis of aliquots (10% SF-96 on Chromosorb W, 6 ft × 0.25 in. column, 180 °C); apparent conversion was 54% after 62 min and 86% after 150 min. After 180 min, the reaction was terminated and solvent removed at reduced pressure to yield a light brown oil, which crystallized on cooling. The crude product was chromatographed on a column of silica gel (1.5 × 14 cm) impregnated with 20% silver nitrate. Elution with petroleum ether (250 ml) followed by benzene–petroleum ether mixtures yielded 399 mg (85%) of **2f** as a yellow oil which readily crystallized (mp 42–45 °C). Continued elution with pure benzene yielded 38 mg of unreacted starting material (total mass balance 93%). Recrystallization of **2f** from pentane gave pale yellow crystals: mp 44–45 °C; NMR ($CDCl_3$) aliphatic region similar to that of **2a**,[4] aromatic region δ 8.03 (dd, J = 8.2, 2.4 Hz, 1 H, H_β), 7.82 (d, J = 2.4 Hz, 1 H, $H_{\alpha'}$), 7.46 (d, J = 8.2 Hz, 1 H, H_α); λ_{max}^{EtOH} 307 (ϵ 8790), 228 nm (7650); IR (KBr) 1602, 1585, 1505, 1325, 786, 763, and 738 cm^{-1}; MS m/e (rel %) 187 (M^+, 100), P + 1 (13.0), P + 2 (1.16), $C_{11}H_9NO_2$ requires 12.49 and 1.16%.

Nitration (cupric nitrate–acetic anhydride) of hydrocarbon **2a** (obtained by irradiation of **1a**)[4] gave **2f** as the major product, identical in all respects with material from irradiation of **1f.**

β-Nitro Isomer 3f. Reduction of nitro compound **2f** with sodium borohydride in aqueous methanol in the presence of palladium on charcoal gave a 97% yield of crude amine. Recrystallization of a small sample from hexane gave white crystals: mp 69.5–70.5 °C; NMR ($CDCl_3$) δ 7.18 (d, J = 8.5 Hz, H_α), 6.33–6.57 (m, $H_{\alpha'}$, H_β), 3.38 (s, NH_2), and remainder of the spectrum was very similar to that of the parent hydrocarbon;[4] IR (KBr) 3400, 3310, 3200, 1630, and 1590 cm^{-1}.

One-pot acetylation (acetic anhydride) of the amine and nitration (cupric nitrate), followed by silica gel chromatography (5-10% ether–petroleum ether) afforded the desired nitroacetanilide (37%). Recrystallization from ether–pentane (1:1) afforded yellow crystals: mp 107–108.5 °C; NMR ($CDCl_3$) δ 8.20 (s, 1 H, $H_{\alpha'}$), 8.41 (s, 1 H, H_α), 2.28 (s, 3 H, acetoxy methyl); IR (KBr) 3300, 1696, 1630, and 1585 cm^{-1}.

The nitroacetanilide was hydrolyzed by potassium hydroxide in methanol–water (5:30 v/v) to afford a solid orange nitroamine (94%), which was diazotized without purification (sodium nitrite, aqueous sulfuric acid, 5°C). Reaction of the diazonium salt with 50% aqueous hypophosphorous acid (15-fold excess) gave **3f**, isolated by silica gel chromatography. Recrystallization from hexane gave a 15% yield of nearly colorless crystals: mp 83–84.5 °C; NMR ($CDCl_3$) δ 8.25 (d, J = 2.0 Hz, 1 H, H_α), 7.98 (dd, J = 8.0, 2.0, Hz, 1H, $H_{\beta'}$), 7.09 (d, J = 8.0 Hz, 1 H, $H_{\alpha'}$); λ_{max}^{EtOH} 285 (ϵ 7150), 233 (12 100), 219 nm (12 700); IR (KBr) 1590, 1510, 1335, 1075, 1028, 971, 909, 832, 822, 801, 785, 782, 762, 741, and 697 cm^{-1}; MS m/e (rel %) 187 (M^+, 100), P + 1 (13.25), P + 2 (1.8).

Nitration of Benzo[6,7]bicyclo[3.2.1]octa-2,6-diene (4). A solution of 2.037 g (12.9 mmol) of **4**[10] in 40 mL of acetic anhydride was stirred in an ice-salt bath while 3.11 g (12.9 mmol) of cupric nitrate trihydrate was added over 90 min. Workup as described earlier yielded 2.84 g of brown oil. Analysis by VPC (SF-96 column at 180 °C) showed a major peak assigned as the β- and β'-nitro derivatives, and several minor peaks; two of these were assigned as the α- and α'-nitro isomers, based on their VPC retention times and column chromatographic behavior (vide infra). The $\beta + \beta':\alpha + \alpha'$ ratio was ca. 10:1. From NMR, the $\beta':\beta$ ratio was found to be 4:1.

Chromatography of the crude product mixture on silica gel (elution with benzene–petroleum ether mixtures up to 60:40) yielded first mixtures of the α- and α'-nitro isomers, then β- and β'-nitro mixtures, followed by a small amount of essentially pure β'-NO_2-**4.** The total yield of nitroaromatics was 1.115 g (44%).

Data for β'-NO_2-**4** include: pale yellow liquid; NMR ($CDCl_3$) δ 7.19 (d, J = 8 Hz, H_α), 7.86–8.16 (m, H_β, $H_{\alpha'}$), and aliphatic region similar to that of parent **4**; λ_{max}^{EtOH} 292 (ϵ 6950), 224 nm (8110); IR (NaCl) 1512, 1340, 1060, 900, 892, 865, 841, 817, 759, 738, 699, and 671 cm^{-1}; MS m/e (rel %) 201 (100), 202 (13.7), 203 (1.8).

Nitration of Benzo[3,4]tricyclo[3.2.1.0^{2,7}]octene (5),[10] using cupric nitrate in acetic anhydride at −5 to −10 °C, gave a crude product separable by VPC (SF-96, 186 °C) into two major peaks (75:25). Silica gel chromatography (petroleum ether elution) gave, in order of elution, essentially pure β-NO_2-**5**, an $\alpha + \beta + \beta'$-nitro overlap fraction, and crystalline β'-NO_2-**5** (68% total yield of nitro isomers). Subjection of the overlap fraction to preparative VPC (SF-96 column) afforded a peak shown by NMR to be a 55:45 mixture of β- and β'-nitro isomers. The overall β'-:β-nitro ratio was estimated to be 17:1. In careful scrutiny of the β-nitro fractions (NMR), no evidence was found for the α'-nitro isomer. Cooling crystallized α-NO_2-**5**; it was recrystallized from hexane: mp 56–57 °C; NMR ($CDCl_3$) δ 7.84 (q, J = 6.5, 2.8 Hz, H_β), 7.10–7.36 (m, $H_{\beta'}$, $H_{\alpha'}$), 2.96–3.31 (m, H(2), H(5)), 1.66–2.10 (m, H(1), H(7), $H(6)_x$, $H(8)_x$), 0.98 (d, J = 12.0 Hz, $H(6)_n$, $H(8)_n$); λ_{max}^{EtOH} 221 (ϵ 12 480), 272 (4610), 319 nm (2730); IR (KBr) 1520, 1342, 1071, 1004, 888, 848, 828, 823, 776, 773, and 736 cm^{-1}; MS m/e (rel %) 201 (M^+ and base peak, 100), P + 1 (13.8), P + 2 (1.30), $C_{12}H_{11}NO_2$ requires 13.64 and 1.46%.

Recrystallization from hexane gave β'-NO_2-**5** as nearly colorless needles: mp 61.5–62.5 °C; NMR ($CDCl_3$) δ 7.38 (d, J = 8.2 Hz, H_α), 7.86–8.17 (m, $H_{\alpha'}$, H_β), aliphatic region essentially identical with that of parent **5**;[10] λ_{max}^{EtOH} 225 (ϵ 7020), 307 nm (10 890); IR (KBr) 1508, 1326, 1080, 1018, 1007, 985, 894, 876, 853, 826, 789, 772, 758, 751, and 738 cm^{-1}; MS m/e (rel %) 201 (M^+ and base peak, 100), P + 1 (14.0), P + 2 (1.58).

A Second Preparation of β- and β'-Nitro Derivatives of 4. Nitration of benzo[6,7]bicyclo[3.2.1]oct-6-en-2-one[24] (nitric acid in acetic anhydride, 5–10 °C) and recrystallization of the crude product (95% ethanol) gave the β-nitro ketone (74% yield) as light yellow crystals: mp 139–140.5 °C; NMR ($CDCl_3$) δ 7.95–8.19 (m, H_α, $H_{\beta'}$), 7.37 (d, J = 9 Hz, $H_{\alpha'}$), 3.43–3.75 (m, 2 benzyl H's), 2.0–3.06 (m, 6 other H's); λ_{max}^{EtOH} 205.5 (ϵ 13 600), 222 (9540), 275 nm (8770); IR (KBr) 1699 (C=O), 1510, 1345, 1165, 1076, 1050, 903, 886, 853, 831, 789, and 735 cm^{-1}; MS m/e (rel %) 217 (M^+ and base peak, 100), P + 1 (14.3), P + 2 (1.51), $C_{12}H_{11}NO_3$ requires 13.64 and 1.46%.

The nitro ketone (in 95% ethanol) was converted by reaction with sodium borohydride to the nitro alcohol (oil; IR (NaCl) 3300 cm^{-1}), which was dehydrated by refluxing in toluene with p-toluenesulfonic acid (Dean–Stark trap). The NMR spectrum of the product indicated a 50:50 mixture of β- and β'-NO_2-**4.** Chromatography on silica gel (petroleum ether and petroleum ether–benzene elution) failed to effectively separate these two isomers.

Irradiation of a 50:50 β–β'-NO_2-4 Mixture. A solution of 201 mg of mixed isomers ($\beta + \beta'$-NO_2-**4,** 50:50 by NMR analysis) in 155 mL of benzene was purged for 45 min with nitrogen and irradiated in the immersion-well apparatus through a Pyrex filter. After 180 min, VPC analysis of an aliquot showed one product peak and one starting material peak in a 50.1:49.9 ratio. After an additional 180 min, this ratio was 51.4:48.5. Evaporation of solvent yielded a brown oil, which was subjected to preparative VPC (SF-96 column at 185 °C) to yield 62 mg of β'-NO$_2$-**5** (>90% pure; identified by comparison with the major product from nitration of **5**), and 73 mg of unreacted β-NO$_2$-**4** (pure by NMR): pale yellow oil; NMR aromatic region (CDCl$_3$) δ 7.38 (d, $J = 8$ Hz, $H_{\alpha'}$), 7.86–8.14 (m, H_α, H_β), aliphatic region similar to that of the parent **4**;[10] $\lambda_{max}{}^{EtOH}$ 219 (ϵ 12 360), 225 (sh), 282 nm (7930); IR (NaCl) 1515, 1340, 1060, 926, 888, 840, 817, 768, and 704 cm^{-1}; MS *m/e* (rel %) 201 (M$^+$ and base peak, 100), P + 1 (13.7), P + 2 (1.48).

Irradiation of Pure β'-NO$_2$-4. A solution of 84 mg of nearly pure β'-NO$_2$-**4** in 155 mL of benzene was irradiated as above for 100 min. VPC analysis showed ca. 80% conversion to product. Solvent removal and preparative VPC (SF-96 column) yielded 54 mg (64%) of pure β'-NO$_2$-**5**, identical with material from nitration of **5**.

Irradiation of Pure β-NO$_2$-4. A solution of 60 mg of pure β-NO$_2$-**4** in 155 mL of benzene was irradiated as above (Pyrex filter) for 1730 min. Solvent removal yielded a brown oil, which was taken up in pentane–ether and filtered to remove insoluble material. Analysis by VPC showed product and starting material peaks in a 70:30 ratio. Preparative VPC yielded a crystalline photoproduct (22 mg, 37%), and unreacted starting material (ca. 8 mg, pure by IR). The photoproduct was readily characterized as β-NO$_2$-**5**: pale yellow needles from hexane, mp 67.5–68 °C; NMR aromatic region (CDCl$_3$) δ 7.13 (d, $J = 8.2$ Hz, $H_{\alpha'}$), 7.96 (dd, $J = 8.2$, 2.4 Hz, $H_{\beta'}$), 8.14 (d, $J = 2.4$ Hz, H_α); $\lambda_{max}{}^{EtOH}$ 218.5 (ϵ 12 500), 232 (sh, 9150), 282 nm (6460); IR (KBr) 1508, 1326, 1080, 1018, 1007, 985, 894, 876, 853, 826, 789, 772, 758, 751, and 738 cm^{-1}; MS *m/e* (rel %) 201 (M$^+$ and base peak), P + 1 (13.5), P + 2 (1.25).

Quantitative Irradiations. These were conducted in a Rayonet RPR-100 reactor, equipped with a "merry-go-round" apparatus (Model MGR-100). A variable number (2–16) of RUL-2537 (emitting ca. 90% at 253.7 nm) or RUL-3000 (emitting primarily in the region 270–350 nm) lamps were employed, with quartz or Pyrex reaction vessels, respectively. Samples were contained in quartz or Pyrex test tubes which were sealed with rubber serum caps. Prior to irradiation, nitrogen was bubbled through the solutions for at least 20 min using one long (inlet) and one short (outlet) needle.

For DPM rearrangement of benzonorbornadiene (**1a**), acetophenone sensitization and ferrioxalate actinometry[25] were used. Product formation (less than 15% conversion) was assessed by VPC analysis. When the quantum yield for this reaction proved to be identical with that reported (0.5),[4] it was used as an actinometer (9×10^{-3} M **1a** and 10^{-1} M acetophenone in cyclohexane) for the direct irradiation rearrangements of the nitroaromatics (ca. 5×10^{-3} M in cyclohexane). Both solutions were optically dense ($A \geq 2$) over the region 280–350 nm, which covers nearly all of the emission of the RUL-3000 lamps.

For triplet rearrangement of **4**, acetophenone sensitization proved ineffective; acetone was employed. One series of runs was made with pure acetone (RUL-2537 lamps, quartz tubes) and one series with acetone-hexane (20:80 v/v) (RUL-3000 lamps and Pyrex tubes). Acetone-sensitized rearrangement of **1a** (identical tubes, concentration, and solvent) was used as actinometer, on the assumption that the quantum yield would be the same as for acetophenone sensitization.

Results are summarized in Table I.

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