ca. 2.5% of 1-iodo-*F*-octane, and 1-iodo-*F*-decane] and benzoyl peroxide (1.0155 g, 4.198 mmol) were charged in a reactor tube[29] with a sintered disk gas inlet at the bottom and a sampling port on the side, attached to a dry ice cooled trap, and immersed in an oil bath at 100 °C. Propene (Matheson, C. P., from a cylinder) was bubbled through the oil at a rate of 10–20 bubbles/s; the rate of addition was adjusted to maintain a small excess of propene. After 40 and 86 min, respectively, GC (SE 30) showed that 50.3% and 73.7% conversion to **9** had occurred. After 2 h, 1-iodo-*F*-hexane (2.12%, retention time 3.5 min) and **9** (89.4%, 10.5 min) were present. After 1.5 h of additional time, the trap contained about 5 mL of propene; the reaction mixture was cooled and filtered from white, solid 4-(*F*-hexyl)benzoic acid, 0.23 g, mp 191°, and recrystallized from benzene, 0.25% conversion. NMR (acetone-d_6, 60 MHz) δ 7.87 and 8.30 (AA′BB′ pattern of p-substituted benzene), 5.10 (1 H, broad, exchangeable COOH). Anal. Calcd for $C_{13}H_5F_{13}O_2$: C, 35.5; H, 1.15; F, 56.1. Found: C, 35.0; H, 1.1; F, 57.6. The liquid filtrate (107.0 g) (GC indicated 2.63% of $C_6F_{13}H$, 0.78% of 1-iodo-*F*-hexane, 1.75% of 1-(*F*-butyl)-2-iodopropane, 91.8% of **9**, and 2.38% of iodobenzene; retention time 12.5 min) was fractionated using a 16-in. spinning band column operated at high reflux ratio. Fractions I and II, bp 70–74 °C (19 mm), 14.0 g, contained 75% and 89% of **9** and several side products listed above; fractions III–VI, bp 74–76 °C (19.5 mm), n^{25}_{D} 1.3670, 83.5%, contained 99.4% **9** and 0.6% iodobenzene. ^{13}C NMR (200 MHz) 94.277 ppm (the same spectrum as iodobenzene). A residue of soft, gummy solid (3.25 g) and trap liquid (5.34 g) were also recovered. The total conversion to **9** (GC) was 98.2 g or 96.3% of theory; 92.1% of **9** was recovered by distillation. NMR (100 MHz and 200 MHz, $CDCl_3$)[27] δ 2.04 (3 H, d, J = 7 and 1.25 Hz, long range coupling, CH_3), 2.47–3.21 (2 H, broad coupling, multiplet, CH_2), 4.45 (complex multiplet, 1 H, CHI). ^{13}C NMR (200 MHz) CH_3, 10.705 (q), CH, 29.269 and 29.218 (d, long range coupling to F), CH_2, 43.316 (t, splitting by CF_2). Anal. Calcd for $C_9H_6F_{13}I$: C, 22.1; H, 1.24; F, 50.6; I, 26.0. Found: C, 21.8; H, 1.3; F, 50.4; I, 25.8.

Acknowledgment. Acknowledgement is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research, to Research Corporation for research stipends for Lawrence Marshall, and to the Alexander von Humboldt-Stiftung for the Humboldt Prize, given to the senior author in 1972, that enabled part of this work to be done. Special thanks are due to Prof. Dr. R. Schmutzler at the Technische Universität Braunschweig for the hospitality he extended to the senior author during 1972. We thank Dr. Narl Hung for helpful discussions.

Registry No. **1**, 2043-57-4; **2**, 25291-17-2; **3**, 89889-20-3; **4**, 80806-68-4; **5**, 89889-21-4; **6**, 80793-18-6; **7**, 80793-20-0; **8**, 80793-19-7; **9**, 38550-34-4; **10**, 25291-12-7; **11**, 24961-66-8; **12**, 89889-22-5; **13**, 89889-23-6; **14**, 83310-90-1; **15**, 83311-03-9; **16**, 755-48-6; **17**, 57325-40-3; **18**, 57325-39-0; **19**, 89889-24-7; $CF_3(CF_2)_2(CH_2)_2I$, 1513-88-8; $CF_3(CF_2)_3(CH_2)_2I$, 2043-55-2; $CF_3(CF_2)_6(CH_2)_2I$, 2043-52-9; $CF_3(CF_2)_6(CH_2)_4I$, 1748-97-6; $CF_3(CF_2)_6(CH_2)_8I$, 2377-68-6; $CF_3(CF_2)_3CH_2CHI(CH_2)_3CH_3$, 40735-32-8; $CF_3(CF_2)_3CH_2CHI(CH_2)_4CH_3$, 40735-33-9; $CF_3(CF_2)_6CH_2CHI(CH_2)_5CH_3$, 918-32-1; 2-(*F*-hexyl)-1-ethanol, 647-42-7; 1-iodooctane, 629-27-6; 2-iodooctane, 557-36-8; 1-iodo-*F*-hexane, 355-43-1; propene, 115-07-1; 4-(*F*-hexyl)benzoic acid, 74701-31-8; 1-(*F*-butyl)-2-iodopropane, 89889-25-8.

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[29] Kharasch, M. S.; Friedlander, H. N. *J. Org. Chem.* **1969**, *14*, 239–247.

Photochemical Transformations. 37. Electron-Transfer Requirements for Photosolvolysis and Photo-Wagner–Meerwein Reactions of Some Dichlorodibenzobicyclo[2.2.2]octadienes in Singlet and Triplet Excited States[1]

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Received December 5, 1983

Substituted *trans*-7,8-dichloro-10-X-2,3:5,6-dibenzobicyclo[2.2.2]octa-2,5-dienes (X = $COCH_3$, CN, and NO_2) and corresponding dinitro-substituted compounds (10,15-dinitro and 10,14-dinitro) were solvolyzed with silver acetate in acetic acid and were irradiated in glacial acetic acid or acetonitrile with 254- and 300-nm light. The structures of the monoring-substituted diastereoisomeric dichlorides were demonstrated by proof of structures of the daughter solvolysis products. Unlike compounds previously studied, these compounds were either photochemically inert or photoinactive with respect to Wagner–Meerwein rearrangement or to solvolysis. These results have been rationalized in terms of the inability of the excited states of the light-absorbing chromophores in these compounds to transfer electrons to the carbon–chlorine bonds remote from these chromophores. While triplet states of a variety of *cis*- and *trans*-7,8-dichloro-2,3:5,6-dibenzobicyclo[2.2.2]octa-2,5-dienes are reported to be similarly inert, the 10,11-dimethoxy derivatives all were photoactive with acetone sensitization. The migration stereochemistries of the sensitized reactions were quite different from those of direct irradiations or of ground-state reactions. Estimations of the free energies of electron transfer were consistent with these and previously reported results.

Reports concerning the photosolvolyses of organic compounds have been numerous.[2] With only a few exceptions, these reports deal with compounds possessing at least two chromophores, one being the carbon–nucleofuge bond and the other often an aromatic ring or a carbonyl group. In general, the second chromophore absorbs the light, which is usually in a region of the spectrum where the carbon–nucleofuge bond does not absorb or has a relatively low extinction coefficient. After the initial excitation process, some or all of the excitation is transferred to the carbon–nucleofuge bond, which ultimately cleaves to form a carbocation and an anion (when the substrate is an uncharged species). The mechanism of this excitation transfer from

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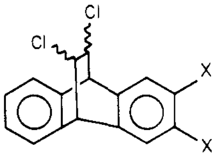
[1] Paper 36. Cristol, S. J.; Ali, M. Z. *Tetrahedron Lett.*, in press.

[2] For a review, see: Cristol, S. J.; Bindel, T. H. In "Organic Photochemistry"; Padwa, A., Ed.; Marcel Dekker: New York, 1983; Vol. 6, pp 327–415.

the light-absorbing chromophore to the carbon–nucleofuge bond is not, as of yet, completely understood, and there is no unanimity as to how this phenomenon occurs. Results from irradiations of compounds 1, in which the carbon–chlorine bonds are fixed relative to the light-absorbing chromophore (substituted benzo ring), have addressed the problem of how excitation is transferred intramolecularly and may also teach something about the more general problem of intermolecular excitation transfer.



1

Earlier work in our laboratory[3a,c] has shown that direct irradiations of 1 (X = H, Cl, or OCH_3) or of similar compounds[3b] give Wagner–Meerwein rearranged compounds with some degree of stereoselectivity. A large fraction of the photoproducts was shown to result from loss of the chlorine anti to the light-absorbing chromophore and migration of the aromatic ring syn to the carbon–chlorine bond that breaks. It was therefore postulated that electron transfer occurs from the light-absorbing chromophore most readily to the anti chlorine, thereby transferring excitation. Thus electron transfer was proposed as the key step[4] in the overall process, with subsequent steps determining the product(s), but the requirement for electron transfer determines whether reaction occurs or not. The preference for anti chlorine activation over the corresponding syn activation was rationalized[3] by noting that the lobe of the σ^* orbital of the carbon–chlorine bond anterior to the carbon atom in the anti system is much closer to the π (or π^*) orbital of the light-absorbing chromophore than is the lobe exterior to the chlorine atom in the syn system. Further, it was noted that electron density in an occupied carbon–chlorine σ^* orbital is greater in the lobe anterior to the carbon atom. If these factors are reflected in extra work (or in extra activation energy) required for electron transfer for syn groups over anti groups, the anti preference could be understood.

Morrison and his co-workers have similarly been interested in excitation transfer between photoexcited benzene rings and carbon–nucleofuge bonds.[5] As an alternative to the electron-transfer process, they proposed a "natural correlation" approach in which computations are made of the degree of stabilization of the avoided crossing in an analysis of a $\pi\pi^*/\sigma\sigma^*$ interaction. We discuss this below.

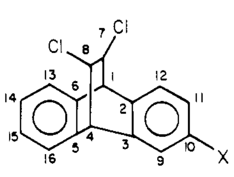
A method for the computation of the free energy change involved in the formation of ion pairs by electron-transfer processes in excited-state encounter complexes has been developed by Weller and his co-workers.[6] Equation 1 is

$$\Delta G = E_{ox}(D/D^+) - E_{red}(A/A^-) - {}^1E_{0-0}(D) - Ne^2/\epsilon r \quad (1)$$

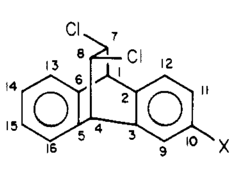
the appropriate one for such a process when the electron-donor molecule is the excited-state species. In this equation, ΔG is the free energy change associated with the process, $E_{ox}(D/D^+)$, the oxidation potential of the donor, $E_{red}(A/A^-)$, the reduction potential of the acceptor, ${}^1E_{0-0}(D)$, the singlet energy of the donor, N, Avogadro's number, e, the charge on the electron, ϵ, the effective dielectric constant of the medium separating the ions, and r, the distance between the ions.

Cristol, Seapy, and Aeling[3c] considered the difficulties associated with the use of this equation for biradical zwitterions related to 1, noting that thermodynamic reduction potentials for alkyl chlorides are not possible to obtain (as electron transfers are irreversible) and that the Coulombic term ($E_c = -Ne^2/\epsilon r$) may not be readily evaluated, as values for both the effective dielectric constant of "the medium" and the distance between the charges are uncertain. Nonetheless, with the known[7] value for half-wave potentials for secondary alkyl chlorides of −2.65 V (vs. SCE, but unfortunately not in the same solvent as the oxidation potential of the aromatic ring donor—DMF vs. acetonitrile), they computed values of $\Delta G - E_c$. It was of considerable interest, and they suggested it was not completely coincidental that there was a relationship between $\Delta G - E_c$ and the ability for activation of a syn chlorine. Thus, for the derivative of 1 where X = Cl, which, among the compounds studied, had the most unfavorable value (+23 kcal/mol), no activation of syn chlorine atoms was observed. Anti activation also seemed required in other systems, *without substituents on the aromatic ring.* On the other hand, with the naphtho analogue of 1 ($\Delta G - E_c$ = +10 kcal/mol), about 15% of syn activation was observed and, with the veratro analogue ($\Delta G - E_c$ = +3 kcal/mol), 26% of syn activation was observed.

It was of obvious interest to consider a continuation of this study with the analogues of 1, in which, on the one hand, electron transfer might occur more readily than in the excited state of 1-H or, on the other hand, might be less favorable (or more unfavorable) than that in 1-H. This paper describes work on some compounds of the latter type, and we will later describe work now in progress on compounds of the former type. The compounds utilized were similar to 1, with trans chlorine atoms substituted on the bridge and with one of the electron-withdrawing groups, aceto, cyano, or nitro, substituted in a β-position on one of the aromatic rings. Inspection of the formulas below shows that these compounds exist as two diastereoisomeric sets, one of which we have termed "7-syn" and one "7-anti". These designations are based upon the numbering system shown in the formulas below and upon the disposition of the chlorine at C-7 relative to the substituted ring.



7-*syn*-2



7-*anti*-3

Syntheses

Compounds 7-*syn*-2 (X = CN and $COCH_3$) and 7-*anti*-3 (X = CN and $COCH_3$) were synthesized by Diels–Alder reactions between the appropriate β-substituted anthracenes and *trans*-1,2-dichloroethene, reactions which yield mixtures of the two trans isomeric [2.2.2] products. The nitro analogues were synthesized by electrophilic aromatic ring nitration of 1 (X = H). Nitration took place entirely,

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(3) (a) Cristol, S. J.; Opitz, R. J.; Bindel, T. H.; Dickenson, W. A. *J. Am. Chem. Soc.* **1980**, *102*, 7977. (b) Cristol, S. J.; Dickenson, W. A.; Stanko, M. K. *Ibid.* **1983**, *105*, 1218. (c) Cristol, S. J.; Seapy, D. G.; Aeling, E. O. *Ibid.* **1983**, *105*, 7337.

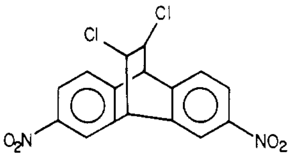
(4) Cristol, S. J.; Graf, G. A. *J. Org. Chem.* **1982**, *47*, 5186.

(5) (a) Morrison, H.; Miller, A. *J. Am. Chem. Soc.* **1980**, *102*, 372. (b) Morrison, H.; Miller, A.; Pandey, B.; Pandey, G.; Severance, D.; Strommer, R.; Bigot, B. *Pure Appl. Chem.* **1982**, *54*, 1723. (c) Morrison, H.; Miller, A.; Bigot, B. *J. Am. Chem. Soc.* **1983**, *105*, 2398.

(6) Rehm, D.; Weller, A. *Isr. J. Chem.* **1970**, *8*, 259.

(7) Lambert, F. L.; Ingall, G. B. *Tetrahedron Lett.* **1974**, 3231.

within our detection limits, at the 10-position (β-position) of **1** (X = H) to yield the two isomeric mononitro products **2**-NO_2 and **3**-NO_2. Two dinitration side products were also obtained from the nitration reaction (**4** and **5**). All compounds were separated and purified by fractional crystallization or column chromatography.



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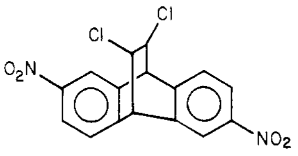


5

The structures (in terms of which is 7-anti and which is 7-syn) of the separated isomers were determined by subjecting the dichlorides to silver ion assisted acetolysis, which involves anti migration[8] of the unsubstituted ring,[9] followed by conversion of these acetates to the [3.2.1] ketones (see Scheme I). ^1H NMR analysis of these ketones identified the position of X from the multiplicity and chemical shift of the aromatic proton ortho to the carbonyl group.[8] The structure of the starting [2.2.2] compound is directly evident from the structure of [3.2.1] ketone.

Direct Irradiations

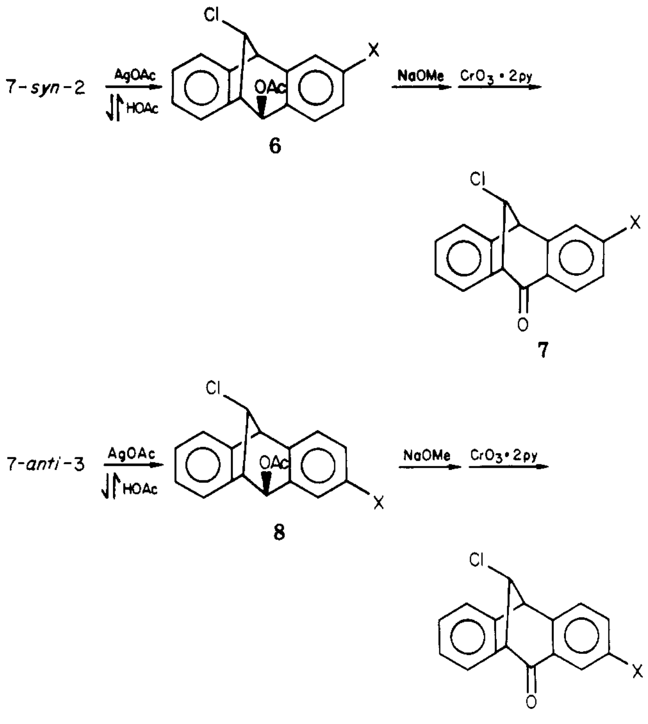
The ketone 7-*syn*-**2** (X = $COCH_3$) was irradiated in acetic acid at 300 and 254 nm and in acetonitrile at 300 nm for periods of time in which compounds **1** (X = H or OCH_3) would have reacted almost completely to give photo-Wagner–Meerwein rearranged products and photosolvolysis products. ^1H NMR analyses indicated that no reaction had occurred. Similar lack of photoreactivity was observed with the 7-*anti*-**3** (X = $COCH_3$) ketone when irradiated in acetic acid at 254 nm and 300 and with the nitrile 7-*syn*-**2** (X = CN) when irradiated in acetic acid at 300 nm. Irradiation of the latter compound in acetic acid at 254 nm led to loss of starting material, but no identifiable products were seen. The two mononitro compounds 7-*syn*-**2** (X = NO_2) and 7-*anti*-**3** (X = NO_2) were photoinert in acetic acid, when irradiated at 254 or 300 nm, as were the dinitro compounds **4** and **5**.

Discussion

Electron-Transfer Requirement. It is clear from the results given above that cyano, aceto, or nitro substitution completely inhibits the photorearrangements and photosolvolyses seen with compounds of type **1** when such substituents are not present. As it seems likely[1-4] that the key step in these reactions involves an electron transfer from the excited aromatic ring chromophore to the carbon–chlorine bond, we conclude that this step does not occur with such substituents present.

These results are reminiscent of those of Herz,[10] who studied the photochemical ionization in ethanol of a number of triarylmethyl leucocyanides. In these compounds, two of the three aryl groups were *p*-dimethylanilino ones and there were different substituents in the third aryl ring. Of the compounds studied, neither the *p*-acetophenyl nor the *p*-nitrophenyl derivatives showed the photocoloration (photoionization). Herz suggested that the failure to undergo photoionization when these groups were present was due to rapid intersystem crossing of the aromatic ketone or the aromatic nitro compound to the triplet state. The latter state presumably had too low an energy to continue on the reaction path. A similar interpretation may be given to our results with X = $COCH_3$ and NO_2, particularly as Opitz[11] has reported that 1-H species cannot be sensitized by acetone or by *o*-xylene. Thus, our original hope to test the question of electron transfer may be compromised with these compounds (see below).

Scheme I



On the other hand, the cyano compound does not suffer from this difficulty. Benzonitrile is reported[12] to have a singlet lifetime in solution at 25 °C of 9.6 ns and undergoes a variety of singlet intermolecular photocycloaddition reactions.[12] Thus, unlike the aceto and nitro compounds, whose singlet lifetimes may be anticipated to be much shorter,[11,13] the cyano compound would appear to offer a good test of the electron-transfer mechanism with its failure to undergo photoproduction of cations.

As described above, members of our group[3c] have recently proposed consideration of the Weller equation (eq 1) in a plausible rationalization of geometric preferences in electron transfer. We now propose extension to the compounds discussed in this paper. While the Weller equation was initially used[6] for electron transfer in singlets, there is no obvious reason for such a restriction.[14] Thus, in eq 1, the singlet energy $^1E_{0\text{-}0}$ may be replaced by the triplet energy $^3E_{0\text{-}0}$ of the excited donor species. We have computed values of $(\Delta G - E_c)_S$ for intramolecular electron transfer within the singlet and of $(\Delta G - E_c)_T$ for that of each of the triplets for the compounds studied by Cristol, Seapy, and Aeling and for the compounds studied by us. These are displayed in Table I. For those molecules whose

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[8] Cristol, S. J.; Kochansky, M. C. *J. Org. Chem.* **1975**, *40*, 2171 and references therein.

[9] It has been demonstrated earlier[8] that electron-withdrawing groups produce a profound decrease in participation and consequent migration in such reactions.

[10] Herz, M. L. *J. Am. Chem. Soc.* **1975**, *97*, 6777.

[11] Opitz, R. J. Ph.D. Dissertation, University of Colorado, Boulder, CO, 1980.

[12] Cantrell, T. S. *J. Org. Chem.* **1977**, *42*, 4239.

[13] Hurley, R.; Testa, A. C. *J. Am. Chem. Soc.* **1968**, *90*, 1949.

[14] (a) Arnold, D. R.; Maroulis, A. J. *J. Am. Chem. Soc.* **1976**, *98*, 5931. (b) Weller, A. In "Exciplex"; Gordon, M. S., Ware, W. R., Eds.; Academic Press: New York, 1975; Chapter 2.

Table I. Data for the Computation of Free Energies of Electron Transfer from Excited States of 7,8-Dichlorodibenzobicyclo[2.2.2]octadiene Derivatives

	$E(D/D^+)$[a]					
ring substituent	V	kcal/mol	$^1E_{0-0}$,[a] kcal/mol	$^3E_{0-0}$,[d] kcal/mol	$(\Delta G - E_c)_S$,[f] kcal/mol	$(\Delta G - E_c)_T$,[f] kcal/mol
H	2.30	53.0	100.3	84	+14	+30
10,11-dimethoxy	1.45	33.4	90.8	(80)[e]	+3	(+14)[e]
10,11-benzo	1.54	35.5	86.7	61	+10	+35
10,11-dichloro	>2.40	>55.3	94	82	+22	+34
10-aceto	2.63[b]	60.6	78	74	+44	+48
10-cyano	(2.9)[c]	(67)	97	77	(+31)[e]	(+51)[e]
10-nitro	(3.1)[c]	(71)	<77	<77	(+55)[e]	(+55)[e]

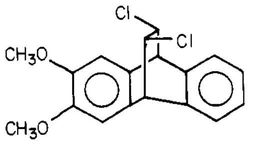
[a] References for first four values given in ref 3c. [b] Value given in ref 14a and corrected for reference electrode change. [c] Value from linear correlation between ionization potentials[16] and oxidation potentials. [d] Values for appropriately substituted benzenes.[17] [e] Values in parentheses are from correlative, rather than direct, data. [f] These values assume a value of −2.65 V. for the reduction potential of a carbon–chlorine bond.[3c]

oxidation potentials are not available, we have estimated their values by a linear correlation between ionization potentials and oxidation potentials. Such a correlation would appear to be a reasonable, if not highly accurate, one.[15]

Inspection of Table I reveals some interesting correlations. As noted earlier,[3c] those compounds that have low values (3–10 kcal/mol) for $(\Delta G - E_c)_S$ allow electron transfer from the aromatic chromophore to both syn and anti chlorine atoms and those with somewhat higher values (22 kcal/mol) require (or have a great preference for) electron transfer into carbon–chlorine bonds in which the chlorine is anti. We now note that those compounds which have still higher values of $(\Delta G - E_c)_S$, in the range of 31–55 kcal/mol, do not allow electron transfer at all, during the lifetime of the excited singlet, independent of the geometric disposition of the donor and acceptor species.

It is obvious that, as lowest excited triplet states of such systems always have lower energies than the singlet excited states, electron transfers from these triplet states will go less readily, if our assumptions are correct, than those from singlet states.[18] The values of $(\Delta G - E_c)_T$ are all considerably higher than those of $(\Delta G - E_c)_S$. It has been noted that the triplet state of 1-H is photoinert.[11] Inspection of Table I suggests that only the veratrole derivative may be anticipated to be photoactive in the triplet state.

Accordingly, we subjected the three dichloroveratro analogues of 1, that is, compounds **10**, **11**, and **12**, to irradiation at 300 nm in wet acetone, under conditions where substantially all of the incident light was absorbed by acetone, and thus where triplet sensitization would obtain. As anticipated from the data in Table I, we found that the isomers **10** and **11** were photoactive (anti activation), giving rearranged [3.2.1] alcohols and, in addition, compound **12** was active (syn activation), a result we were not in a position to predict. The latter compound, however, suffered photoreaction in substantially lower quantum yield than those when anti chlorines were available. That these reactions were, in fact, acetone triplet sensitized was demonstrated by complete quenching by 0.1 M piperylene.



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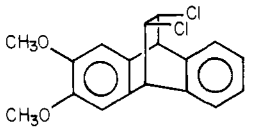

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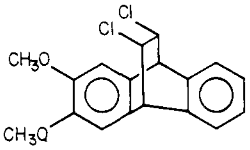

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In summary, the failure to see photosolvolysis or photo-Wagner–Meerwein rearrangements in compounds 7-*syn*-**2** and 7-*anti*-**3** (X = CN, $COCH_3$, or NO_2) is consistent with the idea that electron transfer from an excited aromatic chromophore to a remote carbon–halogen σ^* orbital is required for such reactions. Similarly, the observation that, when intramolecular electron transfer is favored, reaction occurs independent of the multiplicity of the excited state is also consistent with electron transfer as the key step in these processes. Work to test these ideas with other nucleofungal groups is in progress.

If the "natural correlation" concept[19] is used[5] to predict reactivities in these systems, it correctly predicts[5] anti activation to be favored over syn activation, even without consideration of electrostatic forces such as we have emphasized. If we understand the calculations correctly, it does not take into account explicitly either the electron-donating ability of the excited chromophore or the reduction potential of the carbon–nucleofuge bond, but only the location and stabilization by overlap of, and thus the energy difference between, the natural and the avoided crossing between the excited reactant surface and the intermediate product (presumed to be a radical pair) surface. Thus structure and reactivity should correlate, we perceive, with E_{0-0} alone (with a given nucleofuge) and not with the Weller equation. That this is not the case may be readily seen by inspection of the data in Table I. The "natural correlation" concept may, of course, be used for electron transfers,[19] as well as for other excitation[5] or atom transfers. It would be of obvious interest to make such computations, as these could be used to predict rate constants for electron transfers from different chromophores, rather than simply syn vs. anti electron-transfer ratios.

Migration Stereochemistry. In the work reported previously,[3c] in which direct irradiation of **10**, **11**, and **12** in acetic acid at 300 nm was conducted, photoreaction gave (in general) mixtures of various Wagner–Meerwein [3.2.1]

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(15) Wong, C. L.; Kochi, J. K. *J. Am. Chem. Soc.* **1979**, *101*, 5593.

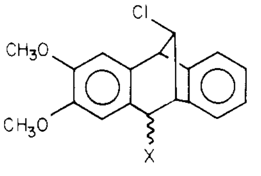
(16) Franklin, J. L.; Hang, P. In "CRC Handbook of Chemistry and Physics", 51st ed.; Weast, R. C., Ed.; CRC Press: Cleveland, OH, 1971; p E62 ff.

(17) Murov, S. L. "Handbook of Photochemistry"; Marcel Dekker: New York, 1973; Section I.

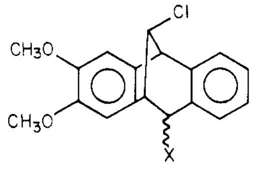
(18) A possible modification of this generalization may be necessary if the lifetime of the triplet state is much greater than that of the singlet, as the quantum yield of solvolysis is obviously the ratio of its rate constant to the sum of the rate constants of all decay modes of the excited state.

(19) Bigot, B.; Devaquet, A.; Turro, N. J. *J. Am. Chem. Soc.* **1981**, *103*, 6 and references therein.

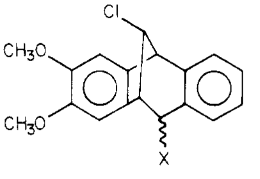
chlorides and acetates. Under these conditions, the major products were those resulting from anti electron transfer (when possible), rather than syn, and from syn migration, rather than anti. Thus the trans dichloride **10** gave 66% of **13** (anti activation, syn migration), 26% of **14** (syn activation, syn migration), and 6% of **15** (anti activation, anti migration). No measurable amount of the syn activation, anti migration product **16** was produced. The anti-cis dichloride **11** gave 76% of **16** (anti activation, syn migration) and 24% of **14** (anti activation, anti migration),[20] while the syn–cis compound **12** gave only the syn migration product **15**. These unusual results were discussed in the earlier paper[3c] and clearly demonstrated (a) that a common intermediate was *not* produced as the sole intermediate from **11** and by loss of syn chloride from **10** or from **12** and by loss of anti chloride from **10** and (b) that the principal migration stereochemistry is syn, whether or not the migrating group is the chromophoric veratrole or the benzene ring.



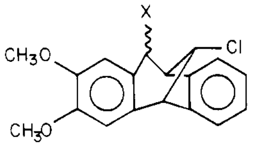
13



14



15

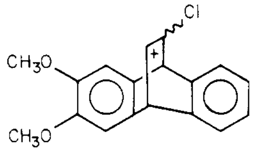


16

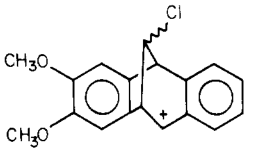
The triplet-sensitized reactions (in water–acetone) were quite different from the direct irradiations in their product outcomes. Thus, both the trans dichloride **10** and the syn-cis dichloride **12** gave as sole product the alcohol **15** (X = OH), and the anti-cis dichloride **11** gave solely the alcohol **14** (X = OH). Here, then, rather than the predominant migration of the ring syn to the nucleofuge observed in the direct irradiations, the triplets all led to migration of the veratro ring rather than the benzo ring, independent of structure of the dichloride.

The trans isomer **10** was irradiated in acetic acid–acetone (8.5:1). Calculations show that 95–97% of the light was absorbed by the acetone. The photoproducts of this irradiation were **15**-OAc (95–97%) and **13** (3–5%). Compound **10** was also triplet sensitized with *o*-xylene (acetic acid–*o*-xylene, 1:6), irradiating with 254-nm light. Computation indicated that more than 99% of the light was absorbed by the xylene. This resulted in the formation solely of **15**-OAc.

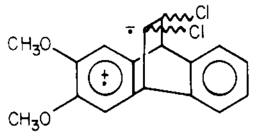
The results seem best rationalized by the intervention of the classical secondary cations **17** as the migration product determining intermediates. These would certainly lead, by migration of the veratro ring,[3c,8] to the cation **18**, in preference to the isomeric rearranged cation that would be formed by benzo migration. Our results unfortunately give no insight into the details of the transformation of the triplet zwitterionic biradical **19**, presumably formed by the electron-transfer process described above, into the ground-state secondary cation **17**, but it would not be unreasonable to assume that loss of chloride ion would lead to the triplet biradical cation **20**, which is, of course, an excited state of **17**.



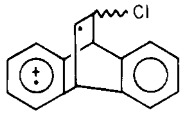
17



18



19

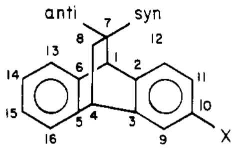


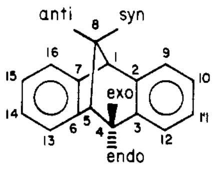
20

In the paper[3c] describing previous work in this area, the authors suggested that the principal syn migration noted in the direct irradiation was a concerted process, in which, for example, loss of chloride ion from the zwitterionic biradical **19** was synchronous with migration of the aryl ring, while the anti migration, seen as a minor process, was suggested to be due to intervention of a species such as **20**. Closer inspection of their data reveals that all of the "mixing", that is, all of the anti migration, involves migration of the veratro ring and would be consistent with involvement of species such as **17**. Whether all of these reactions occur on the excited singlet hypersurface, or whether this is a result of intersystem crossing following electron transfer, is unknown at this time.

Experimental Section

The locant systems used in this paper for indicating the structures and names of compounds are as follows (in order to avoid confusion, the locants are based on the hydrocarbon numbering system):





General Data. Proton nuclear magnetic resonance (^1H NMR) spectra were taken on a Varian Associates EM-390 (90-MHz) spectrometer. Chemical shifts (δ) are reported in parts per million downfield from tetramethylsilane and coupling constants (J) are reported in hertz (Hz). Ultraviolet (UV) spectra were taken on a Cary 17 instrument. Maxima are reported as max. All melting points were measured by using a Thomas-Hoover apparatus. Mass spectra were taken on a Varian MAT CH-5 spectrometer. Samples were irradiated in a Srinivasan-Griffen photochemical reactor equipped with either 300- or 254-nm lamps. All samples, before irradiation, were deaerated with a stream of nitrogen gas. Volatile organic solvents were removed in vacuo with the aid of a Büchi Rotovapor-R. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

Synthesis of *trans*-7-*syn*,8-*anti*-Dichloro-10-aceto-2,3:5,6-dibenzobicyclo[2.2.2]octa-2,5-diene (7-*syn*-2 (X = COCH$_3$)) and *trans*-7-*anti*,8-*syn*-Dichloro-10-aceto-2,3:5,6-dibenzobicyclo[2.2.2]octa-2,5-diene (7-*anti*-3 (X = COCH$_3$)). 2-Acetoanthracene[21] (7.5 g) and 90 mL of *trans*-1,2-dichloroethene, sealed in a thick-walled glass tube, were heated at 191–194 °C for 3 days. The tube was cooled and opened. The solvent was removed in vacuo, and the residue was eluted from a silica gel column with 20% ethyl acetate in *n*-pentane. The eluate (after removal of solvent in vacuo) was dissolved in hot 95% ethanol.

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[20] When the direct irradiation was conducted in the presence of 0.1 M piperylene, the formation of **14** from **11** was completely quenched. We now presume (see below) that this is a triplet, rather than a singlet, product, and our comments[3c] regarding this compound should be modified slightly.

[21] Laguerre, J.-P.; Marechal, E. *Ann. Chim. (Paris)* 1974, 163.

After being decolorized with charcoal, the solution was cooled in a freezer for 30 min and then rewarmed for 2 h at room temperature. The resulting heterogeneous solution (an orange residue on the bottom) was decanted to give a homogeneous solution from which 7-*syn*-**2** (X = $COCH_3$) crystallized. This material was collected by filtration (2.2 g). From the filtrate, the 7-*anti*-**3** (X = $COCH_3$) compound (1.5 g) was crystallized. 7-*syn*-**2** (X = $COCH_3$) was further purified by recrystallization from ether/*n*-pentane and then from ethanol to give leaflets: mp 165–166 °C; ^{1}H NMR ($CDCl_3$) δ 2.56 (3 H, s, CH_3) 4.20 (2 H, m, H-7 and H-8), 4.48 (2 H, br s, H-1 and H-4), 7.42 (5 H, m, ArH), 7.53 (1 H, d, $J_{12,11}$ = 8 Hz, H-12), 7.96 (1 H, dd, $J_{11,9}$ = 3 Hz, $J_{11,12}$ = 8 Hz, H-11), 8.03 (1 H, d, $J_{9,11}$ = 3 Hz, H-9); MS, *m/e* 320, 318, 316, 221, 220 (base), 205, 203, 202, 178, 177, 176; UV (CH_3CN) 350 nm (log ϵ 1.47), 300 (2.3), 292 (3.0, max), 254 (4.08, max). Anal. Calcd for $C_{18}H_{14}Cl_2O$: C, 68.16; H, 4.45. Found: C, 67.99; H, 4.54.

The 7-*anti*-**3** (X = $COCH_3$) compound was recrystallized from ethanol to give needles: mp 167–168 °C; ^{1}H NMR ($CDCl_3$) δ 2.59 (3 H, s, CH_3), 4.20 (2 H, m, H-7 and H-8), 4.48 (2 H, br s, H-1 and H-4), 7.40 (5 H, m, ArH), 7.50 (d, $J_{12,11}$ = 8 Hz, H-12), 7.95 (1 H, dd, $J_{11,9}$ = 2 Hz, $J_{11,12}$ = 8 Hz, H-11), 8.05 (1 H, d, $J_{9,11}$ = 2 Hz, H-9); MS, *m/e* 320, 318, 316, 221, 220 (base peak), 205, 203, 202, 178, 176; UV (CH_3CN) 350 nm (log ϵ 1.47), 320 (1.95), 300 (2.48), 292 (3.04, max), 254 (4.08, max). Anal. Calcd for $C_{18}H_{14}Cl_2O$: C, 68.16; H, 4.45. Found: C, 68.28; H, 4.51.

Synthesis of *trans*-7-*syn*,8-*anti*-Dichloro-10-cyano-2,3:5,6-dibenzobicyclo[2.2.2]octa-2,5-diene (7-*syn*-2 (X = CN)). 2-Anthronitrile[22] (2.0 g, 10 mmol) and *trans*-1,2-dichloroethene (30 mL), sealed in a thick-walled glass tube, was heated at 192 °C for 3 days.[23] The solvent was removed in vacuo, and the residue was eluted from a silica gel column with 10% ethyl acetate in *n*-pentane. Removal of solvent left a residue that was dissolved in hot 95% ethanol and decolorized with charcoal. Upon standing, yellow crystals formed in the ethanol solution. Filtration and recrystallization from 95% ethanol gave white crystals of 7-*syn*-**2** (X = CN): mp 182–184 °C; ^{1}H NMR ($CDCl_3$) δ 4.17 (2 H, m, H-7 and H-8), 4.48 (2 H, br s, H-1 and H-4), 7.55 (7 H, m, ArH), in the δ 7.55 multiplet there is what appears to be a singlet at δ 7.70 and another one at δ 7.60 (separation is 9 Hz); MS, *m/e* (relative intensity) 329 (5), 301 (4), 203 (100); UV (CH_3CN) 290 nm (log ϵ 1.88), 284 (2.85, max), 271 (2.92, max), 254 (3.52, max), 242 (3.81, max). Anal. Calcd for $C_{17}H_{11}Cl_2N$: C, 68.02; H, 3.69. Found: C, 67.83; H, 3.91.

The mother liquors gave a ^{1}H NMR ($CDCl_3$) spectrum that had signals at δ 4.17, 4.48, 7.55, and 7.65 (d, *J* = 2 Hz). The δ 7.65 signal suggests that 7-*anti*-**3** (X = CN) was probably present in the mother liquor.

Synthesis of *trans*-7-*syn*,8-*anti*-Dichloro-10-nitro-2,3:5,6-dibenzobicyclo[2.2.2]octa-2,5-diene (7-*syn*-2 (X = NO_2)) and *trans*-7-*anti*,8-*syn*-Dichloro-10-nitro-2,3:5,6-dibenzobicyclo[2.2.2]octadiene (7-*anti*-3 (X = NO_2)). *trans*-**1** (X = H) (10.4 g, 38.0 mmol) was dissolved in 55.9 mL of acetic anhydride (0.593 mol). To this solution was added slowly 3.0 mL of fuming nitric acid (57 mmol). The mixture was then heated at 75–85 °C for 62 h. The cooled mixture was taken up in dichloromethane and washed with water, with saturated sodium bicarbonate (until neutralization was complete), and then twice with brine. After the solution was dried ($MgSO_4$), the dichloromethane was removed in vacuo. The residue was purified by flash chromatography (15% ethyl acetate–hexanes). Order of elution: **1** (X = H) first, 7-*syn*-**2** (X = NO_2) second, 7-*anti*-**3** (X = NO_2) third, **5** fourth, and **4** last. Each compound was further purified easily by recrystallization from 15% ethyl acetate–hexanes. 7-*syn*-**2** (X = NO_2): mp 149–151 °C; ^{1}H NMR ($CDCl_3$) δ 4.20 (2 H, m, H-7 and H-8), 4.56 (2 H, m, H-1 and H-4), 7.44 (4 H, m, ArH), 7.63 (d, $J_{12,11}$ = 8 Hz, H-12), 8.23 (1 H, dd, $J_{11,12}$ = 8 Hz, $J_{11,9}$ = 2 Hz, H-11), 8.27 (1 H, d, $J_{9,11}$ = 2 Hz, H-9); UV (CH_3CN) 360 nm (log ϵ 2.00), 350 (2.00), 300 (3.58), 275 (3.88, max), 254 (3.75). Anal. Calcd for $C_{16}H_{11}Cl_2NO_2$: C, 60.02; H, 3.44; N, 4.38. Found: C, 59.95; H, 3.64; N, 4.11. 7-*anti*-**3** (X = NO_2): mp 144–145 °C; ^{1}H NMR ($CDCl_3$) δ 4.13 (2 H, m, H-7 and H-8), 4.46 (2 H, m, H-1 and H-4), 7.38 (4 H, m), 7.57 (d, $J_{12,11}$ = 8 Hz, H-12), 8.23 (1 H, dd, $J_{11,12}$ = 8 Hz, $J_{11,9}$ = 2 Hz, H-11), 8.33 (1 H, $J_{9,11}$ = 2 Hz, H-9). *trans*-7-*syn*,8-*anti*-Dichloro-10,14-dinitro-2,3:5,6-dibenzobicyclo[2.2.2]octa-2,5-diene (**5**): mp 229.5–230.0 °C; ^{1}H NMR ($CDCl_3$) δ 4.23 (2 H, m, H-7 and H-8), 4.74 (2 H, br s, H-1 and H-4), 7.70 (2 H, d, $J_{12,11}$ = $J_{16,15}$ = 8 Hz, H-12 and H-16), 8.30 (2 H, dd, $J_{15,16}$ = $J_{11,12}$ = 8 Hz, $J_{11,9}$ = $J_{15,13}$ = 2 Hz, H-11 and H-15), 8.34 (2 H, d, $J_{9,11}$ = $J_{13,15}$ = 2 Hz, H-9 and H-13); UV (CH_3CN) 360 nm (log ϵ 2.18), 350 (2.18), 300 (3.83), 272.5 (4.26, max), 254 (4.05). Anal. Calcd for $C_{16}H_{10}Cl_2N_2O_4$: C, 52.62; H, 2.74; N, 7.67. Found: C, 52.45; H, 2.92; N, 7.49. *trans*-7-*syn*,8-*anti*-Dichloro-10,15-dinitro-2,3:5,6-dibenzobicyclo[2.2.2]octa-2,5-diene (**4**): mp 206–207 °C; ^{1}H NMR ($CDCl_3$) δ 4.23 (2 H, m, H-7 and H-8), 4.72 (2 H, m, H-1 and H-4), 7.64 (1 H, d, $J_{13,14}$ = 8 Hz, H-13), 7.68 (1 H, d, $J_{12,11}$ = 8 Hz, H-12), 8.37 (4 H, m, ArH); UV (CH_3CN) 360 nm (log ϵ 2.30), 350 (2.30), 300 (3.88), 275 (4.25, max), 254 (4.25).

Structure Proofs

General Data. Each [2.2.2] compound and silver acetate were dissolved in 10 mL of glacial acetic acid. This mixture was heated at reflux for a few days. The cooled mixture was dissolved in dichloromethane and extracted once with water, twice with saturated sodium bicarbonate, and once with brine. After the solution was dried ($MgSO_4$), the solvent was removed in vacuo. The product is a [3.2.1] acetate. The acetate was dissolved in 10 mL of saturated sodium methoxide in methanol and heated at reflux for 10 min. The methanol was removed in vacuo. The residue was taken up in dichloromethane, and the solution was washed twice with water and once with brine. After the solution was dried ($MgSO_4$), the solvent was removed in vacuo. The product is a [3.2.1] alcohol. Chromium(VI) oxidation of the alcohol followed a procedure by Radcliffe and Rodehorst.[24] Dry pyridine (285 mg) and dichloromethane (4.5 mL) were mixed together. To this was added 180 mg of dry chromic anhydride. The product of the oxidation was a [3.2.1] ketone.

7-*anti*-3 (X = $COCH_3$). A 100-mg (0.315-mmol) sample of 7-*anti*-**3** (X = $COCH_3$) and 70 mg (0.42 mmol) of silver acetate in 10 mL of acetic acid were heated at reflux for 90 h. About 75% of the starting material had reacted to give *anti*-8-chloro-11-aceto-2,3:6,7-dibenzobicyclo[3.2.1]octa-2,6-dien-*exo*-4-ol acetate (**8**) (X = Ac, Y = OAc): ^{1}H NMR ($CDCl_3$) δ 2.15 (3 H, s, CH_3CO_2), 2.47 (3 H, s, CH_3CO), 3.77 (1 H, br s, H-5), 4.24 (1 H, br s, H-1), 4.97 (1 H, br s, H-8), 6.05 (1 H, d, $J_{4,5}$ = 3 Hz, H-4), 7.30 (4 H, m, ArH), 7.57 (1 H, m), 7.87 (2 H, m). This acetate was methanolyzed to *anti*-8-chloro-11-aceto-2,3:6,7-dibenzobicyclo[3.2.1]-octa-2,6-dien-*exo*-4-ol (**8**) (X = Ac, Y = OH): ^{1}H NMR ($CDCl_3$) δ 2.48 (3 H, s, CH_3CO), 3.20 (1 H, br s, OH), 3.73 (1 H, d, $J_{5,4}$ = 3 Hz, H-5), 4.18 (1 H, br s, H-1), 4.90 (1 H, d, $J_{4,5}$ = 3 Hz, H-4), 5.02 (1 H, br s, H-8), 7.37 (5 H, m), 7.88 (2 H, m). This alcohol was oxidized to *anti*-8-chloro-11-aceto-2,3:6,7-dibenzobicyclo-[3.2.1]octa-2,6-dien-4-one (**9**-Ac): ^{1}H NMR ($CDCl_3$) δ 2.53 (3 H, s, CH_3CO), 4.29 (1 H, br s, H-1), 4.48 (1 H, br s, H-5), 4.99 (1 H, br s, H-8), 7.42 (5 H, m, ArH), 7.52 (d, $J_{9,10}$ = 7 Hz, H-9), 8.18 (1 H, dd, $J_{10,9}$ = 8 Hz, $J_{10,12}$ = 2 Hz, H-10), 8.50 (1 H, dd, $J_{12,9}$ = 0.5 Hz, $J_{12,10}$ = 2 Hz, H-12).

7-*syn*-2 (X = $COCH_3$) (80 mg) was acetolyzed for 7 days to give *anti*-8-chloro-10-aceto-2,3:6,7-dibenzobicyclo[3.2.1]octa-2,6-dien-*exo*-4-ol acetate (**6**) (X = Ac, Y = OAc): ^{1}H NMR ($CDCl_3$) δ 2.17 (3 H, s, CH_3CO_2), 2.55 (3 H, s, $COCH_3$), 3.75 (1 H, br s, H-5), 4.28 (1 H, br s, H-1), 4.99 (1 H, br s, H-8), 6.07 (1 H, d, $J_{4,5}$ = 2 Hz, H-4), 7.31 (4 H, m), 7.55 (1 H, m), 7.88 (2 H, m). This acetate was methanolyzed to *anti*-8-chloro-10-aceto-2,3:6,7-dibenzobicyclo[3.2.1]octa-2,6-dien-*exo*-4-ol (**6**) (X = Ac, Y = OH): ^{1}H NMR ($CDCl_3$) δ 2.53 (3 H, s, $COCH_3$), 2.95 (1 H, br s, OH), 3.72 (1 H, br s, H-5), 4.20 (1 H, br s, H-1), 4.89 (1 H, br s, H-4), 5.00 (1 H, br s, H-8), 7.35 (5 H, m), 7.83 (2 H, m). This alcohol was oxidized to *anti*-8-chloro-10-aceto-2,3:6,7-dibenzobicyclo-[3.2.1]octa-2,6-dien-4-one (**7**-Ac): ^{1}H NMR ($CDCl_3$) δ 2.58 (3 H, s, $COCH_3$), 4.29 (1 H, br s, H-1), 4.49 (1 H, br s, H-5), 4.98 (1 H, br s, H-8), 7.40 (4 H, m), 7.99 (3 H, m).

7-*syn*-2 (X = CN) (75 mg, 0.25 mmol) and silver acetate (60 mg, 0.36 mmol) were reacted for 3.5 days to give *anti*-8-chloro-10-cyano-2,3:6,7-dibenzobicyclo[3.2.1]octa-2,6-dien-*exo*-4-ol acetate (**6**) (X = CN, Y = OAc): ^{1}H NMR ($CDCl_3$) δ 2.13 (3 H, s, CH_3CO_2),

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[22] Gore, P. *J. Chem. Soc. B* **1964**, 426.

[23] Figeys, H. F.; Dralants, A. *Tetrahedron* **1972**, *28*, 3031.

[24] Ratcliffe, R.; Rodehorst, R. *J. Org. Chem.* **1970**, *35*, 4000.

3.70 (1 H, br s, H-5), 4.16 (1 H, br s, H-1), 4.88 (1 H, br s, H-8), 5.95 (1 H, d, $J_{4,5}$ = 2 Hz, H-4), 7.32 (7 H, m, ArH). The acetate was methanolyzed to *anti*-8-chloro-10-cyano-2,3:6,7-dibenzobicyclo[3.2.1]octa-2,6-dien-*exo*-4-ol (**6**) (X = CN, Y = OH): ^{1}H NMR (CDCl$_3$) δ 3.67 (1 H, s, H-5), 4.18 (1 H, br s, H-1), 4.81 (1 H, d, $J_{4,5}$ = 2 Hz, H-4), 4.92 (1 H, br s, H-8), 7.33 (7 H, m, ArH). This alcohol was oxidized to *anti*-8-chloro-10-cyano-2,3:6,7-dibenzobicyclo[3.2.1]octa-2,6-dien-4-one (**7**-CN): ^{1}H NMR (CDCl$_3$) δ 4.26 (1 H, br s, H-1), 4.40 (1 H, br s, H-5), 4.92 (1 H, br s, H-8), 7.33 (6 H, m, ArH), 7.98 (1 H, d, $J_{12,11}$ = 8 Hz, H-12).

7-*syn*-2 (X = NO$_2$) (105 mg, 0.328 mmol) and silver acetate (89.1 mg, 0.535 mmol) were reacted to give *anti*-8-chloro-10-nitro-2,3:6,7-dibenzobicyclo[3.2.1]octa-2,6-dien-*exo*-4-ol acetate (**6**) (X = NO$_2$, Y = OAc): ^{1}H NMR (CDCl$_3$) δ 3.78 (1 H, d, $J_{5,4}$ = 2 Hz, H-5), 4.29 (1 H, s, H-1), 4.93 (1 H, br s, H-8), 6.05 (1 H, d, $J_{4,5}$ = 3 Hz, H-4), 7.2–7.7 (m), 8.0–8.2 (m). This acetate was methanolyzed to *anti*-8-chloro-10-nitro-2,3:6,7-dibenzobicyclo[3.2.1]octa-2,6-dien-*exo*-4-ol (**6**) (X = NO$_2$, Y = OH): ^{1}H NMR (CDCl$_3$) δ 3.77 (1 H, br s, H-5), 4.27 (1 H, br s, H-1), 4.93 (1 H, d, $J_{4,5}$ = 3 Hz, H-4), 5.04 (1 H, br s, H-8), 7.2–7.7 (m), 8.0–8.2 (m). This alcohol was oxidized to *anti*-8-chloro-10-nitro-2,3:6,7-dibenzobicyclo[3.2.1]octa-2,6-dien-4-one (**7**) (X = NO$_2$): ^{1}H NMR (CDCl$_3$) δ 4.27 (1 H, s, H-1), 4.49 (1 H, s, H-5), 4.96 (1 H, s, H-8), 7.2–7.8 (m), 8.2–8.35 (m). The absence of absorption below δ 8.4 is a clear indication that the nitro group is para to the carbonyl group rather than meta to it.[25]

Irradiations

7-*syn*-2 (X = COCH$_3$). A solution of 112 mg of 7-*syn*-**2** (X = COCH$_3$) in 100 mL of acetic acid was irradiated in Pyrex for 2.8 days with 300-nm light. The sample was worked up by adding dichloromethane and extracting twice with water, with saturated sodium bicarbonate until neutralization was complete, and then once with brine. After the solution was dried (MgSO$_4$), the solvent was removed in vacuo. ^{1}H NMR (CDCl$_3$) analysis of the residue gave no absorptions between δ 4.7 and 7.0. Besides the absorptions from the starting material, there were absorptions at δ 4.0, 2.3, and 1.25. This material was redissolved in 100 mL of glacial acetic and irradiated in quartz for 2.4 days with 254-nm light. The sample (dark yellow in color) was worked up and analyzed as above. The results of the analysis were the same as the 300-nm irradiation, except that the ratio of the starting material absorptions to the other absorptions was smaller than for the 300-nm light irradiation.

A solution of 50 mg of 7-*syn*-**2** (X = COCH$_3$) in 100 mL of spectral grade acetonitrile was irradiated in Pyrex for 4 days with 300-nm light. The acetonitrile was removed in vacuo. ^{1}H NMR (CDCl$_3$) analysis indicated that only starting material was present.

7-*anti*-3 (X = COCH$_3$) (100 mg) in 100 mL of acetic acid was irradiated through Pyrex for 2.8 days with 300-nm light. The acetic acid was removed in vacuo. ^{1}H NMR analysis indicated that only starting material and residual acetic acid were present. This material was redissolved in 100 mL of glacial acetic acid and irradiated in quartz for 2.9 days with 254-nm light. As before, ^{1}H NMR analysis of the residue (obtained from distillation in vacuo) indicated that only starting material and residual acetic acid were present.

7-*syn*-2 (X = CN) (50 mg) in 100 mL of acetic acid was irradiated in Pyrex for 3.9 days with 300-nm light. The acetic acid was removed in vacuo. ^{1}H NMR analysis of the residue indicated the presence of only starting material. This residue was redissolved in 200 mL of glacial acetic acid and irradiated for 2 days in quartz with 254-nm light. The residue, after removal of the acetic acid in vacuo, was only slightly soluble in chloroform. ^{1}H NMR (CDCl$_3$) analysis indicated no starting material and no rearranged dichlorides or acetates. The residue that did not dissolve in the chloroform was very soluble in acetic acid, and ^{1}H NMR (CD$_3$CO$_2$D) analysis gave no absorptions.

7-*syn*-2 (X = NO$_2$) (100 mg) in 100 mL of acetic acid was irradiated through Pyrex for 3 days with 300-nm light. The acetic acid was removed in vacuo. ^{1}H NMR (CDCl$_3$) analysis indicated that only starting material was present. This compound (51 mg) was dissolved in 50 mL of glacial acetic acid and irradiated through quartz for 5 days with 254-nm light. As before, analysis indicated the presence of only starting material.

7-*anti*-3 (X = NO$_2$) (38.5 mg) in 50 mL of acetic acid was irradiated through quartz for 5.3 days with 254-nm light. After removal of the acetic acid, ^{1}H NMR (CDCl$_3$) analysis of the residue indicated the presence of only starting material.

Compound 5 (100 mg) in 200 mL of acetic acid was irradiated through Pyrex for 7 days with 300-nm light. Analysis (^{1}H NMR) of the residue indicated the presence of only starting material. Compound **5** (48.1 mg) in 70 mL of glacial acetic acid was irradiated through quartz for 3.1 days with 254-nm light. Only starting material was present in the sample after irradiation.

Compound 4 (100 mg) in 100 mL of acetic acid was irradiated through Pyrex for 5 days with 300-nm light. After removal of the acetic acid in vacuo, analysis of the residue indicated only the presence of starting material. Irradiation of compound **4** (45.0 mg) in 50 mL of glacial acetic acid through quartz for 5 days with 254-nm light also gave no reaction.

Irradiation of 10 at 300 nm in Acetone. Compound **10** (25 mg, 0.075 mmol) was dissolved in 380 mL of spectrograde acetone; 10 mL of distilled water was added. The extinction coefficient of acetone at 300 nm is ~7 (5–8[17]) and that of **10** is 1560. Thus the fraction of light absorbed by **10** is about 0.3%. The sample was deoxygenated (all deoxygenations were conducted by nitrogen bubbling) for 20 min and then irradiated at 300 nm for 24 h. After removal of the solvent by distillation in vacuo, examination by ^{1}H NMR spectroscopy indicated that the photoreaction gave one product, **15**-OH, in a chemical yield of above 90%. No starting material was present.

Irradiation of 10 in Acetone–Acetic Acid at 300 nm. Compound **10** (30.2 mg, 0.09 mmol) was dissolved in a mixture of 40 mL of spectrograde acetone and 240 mL of acetic acid. Calculations indicate that 3–5% of the light was absorbed by **10**. The sample was deoxygenated for 20 min and irradiated for 24 h at 300 nm. The solvent was removed by distillation in vacuo, and the products were determined by examination of the proton NMR. No starting material was present. The major product, 95–97%, was **15**-OAc, and there was a small amount, 3–5%, of product with a chlorine at C-8 syn, largely **13**-OAc. Both products were identified by ^{1}H NMR spectral comparison with authentic samples.

Quenching of the Triplet Reaction of 10 with *cis*-Piperylene. Compound **10** (31.1 mg, 0.091 mmol) and 2.66 g (0.04 mol) of *cis*-piperylene were dissolved in 340 mL of spectrograde acetone and 10 mL of distilled water. The solution was deoxygenated for 20 min and irradiated at 300 nm for 24 h. The solvent was removed by distillation in vacuo and the residue examined by proton NMR. Only **10** was present.

Triplet Sensitization of 10 with *o*-Xylene. Compound **10** (33.1 mg, 0.10 mmol), 4 mL of *o*-xylene, and 24 mL of glacial acetic acid were placed in a quartz tube. The solution was deoxygenated for 20 min and irradiated at 254 nm for 1 h. The solvent was removed by distillation in vacuo and the residue examined by ^{1}H NMR spectroscopy. The spectrum showed the residue to contain 80–90% of **10** and 10–20% of **15**-OAc.

Acetone-Sensitized Irradiation of 11. A solution of 11.7 mg (0.04 mmol) of **11** in 50 mL of spectrograde acetone and 2.5 mL of distilled water was placed in a Pyrex tube. The solution was deoxygenated for 20 min and then irradiated at 300 nm for 45 min. Calculations indicate about 99% of the light was absorbed by the acetone. The solvent was removed by distillation in vacuo. ^{1}H NMR spectroscopy indicated that the residue was ca. 25% of **11** and 75% of **14**-OH.

Triplet Quenching of 11 in Acetone. A solution of 12.2 mg (0.036 mmol) of **11** and 400 mg (6 mmol) of *cis*-piperylene in 50 mL of spectrograde acetone and 2 mL of distilled water was deoxygenated for 20 min and irradiated for 2 h. The solvent was removed by distillation in vacuo, and the residue was examined by ^{1}H NMR spectroscopy. Only starting material was present.

Triplet Quenching of 11 in Acetic Acid. Compound **11** (27.2 mg, 0.081 mmol) and 180 mg (2.7 mmol) of piperylene were

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(25) Protons ortho to both nitro and carbonyl groups would be anticipated to have absorbances below 8.5 ppm. For example, *m*-nitroacetophenone has a triplet (J = 2 Hz) at δ 8.7, while *p*-nitroacetophenone has no absorbance at fields lower than δ 8.35.[26]

(26) "Aldrich Library of NMR Spectra"; 1974, Vol. 6, 41C, 41D (^{1}H NMR).

dissolved in 27 mL of glacial acetic acid. The solution was deoxygenated for 20 min and irradiated for 1 h. The solvent was removed by distillation in vacuo, and the residue was examined by ^{1}H NMR spectroscopy. In addition to some starting material, the only product observed was **16**. No **14** was apparent.

Triplet-Sensitized Irradiation of 12. Compound **12** (27.1 mg, 0.081 mmol) was dissolved in 100 mL of spectrograde acetone and 4 mL of distilled water. The solution was deoxygenated for 20 min and irradiated for 2 h. The solvent was removed by distillation in vacuo and the residue examined by ^{1}H NMR spectroscopy. The residue was a mixture of starting material **12** and **15-OH** in a ratio of 3:5.

Triplet Quenching of the Acetone-Sensitized Irradiation of 12. A solution of 25.8 mg (0.077 mmol) of **12** and 800 mg (12 mmol) of *cis*-piperylene in 100 mL of spectrograde acetone and 5 mL of water was deoxygenated for 20 min and irradiated at 300 nm for 2 h. The solvent was removed by distillation in vacuo and the residue examined by ^{1}H NMR spectroscopy. The proton NMR revealed only starting material.

Relative Photoreactivities for the Triplet Reactions of 10, 11, and 12. Solutions of **10**, **11**, and **12**, each containing 25–26 mg of substrate in 100 mL of acetone and 4 mL of water, were deoxygenated for 15 min, placed in a merry-go-round apparatus, and irradiated at 300 nm for 30 min. The solvent was removed by distillation in vacuo and the residue was examined by ^{1}H NMR spectroscopy. Fifty-five percent of **10** and 19% of **12** were converted to **15-OH**, while 71% of **11** was converted to **14-OH**.

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Registry No. *trans*-**1** (X = H), 6476-15-9; 7-*syn*-**2** (X = $COCH_3$), 89909-65-9; 7-*syn*-**2** (X = CN), 89955-36-2; 7-*syn*-**2** (X = NO_2), 89909-66-0; 7-*anti*-**3** (X = $COCH_3$), 89955-35-1; 7-*anti*-**3** (X = NO_2), 89955-37-3; 7-*anti*-**3** (X = CN), 89955-38-4; **4**, 89909-67-1; **5**, 89909-68-2; **6** (X = Ac, Y = OAc), 89909-72-8; **6** (X = Ac, Y = OH), 89909-73-9; **6** (X = CN, Y = OAc), 89909-75-1; **6** (X = CN, Y = OH), 89909-76-2; **6** (X = NO_2, Y = OAc), 89909-78-4; **6** (X = NO_2, Y = OH), 89909-79-5; **7**-Ac, 89909-74-0; **7**-CN, 89909-77-3; **7** (X = NO_2), 89909-80-8; **8** (X = Ac, Y = OAc), 89909-69-3; **8** (X = Ac, Y = OH), 89909-70-6; **9**-Ac, 89909-71-7; **10**, 75920-61-5; **11**, 87637-75-0; **12**, 87637-76-1; **14-OH**, 87637-68-1; **15-OH**, 87637-68-1; **15-OAc**, 87637-67-0; 2-acetoanthracene, 10210-32-9; *trans*-1,2-dichloroethene, 156-60-5; 2-anthronitrile, 1921-72-8; *cis*-piperylene, 1574-41-0; *o*-xylene, 95-47-6.

Cyano and Nitro Group Effect on the Rate of Methoxy Denitration Reaction in the Pyrrole and Benzene Ring

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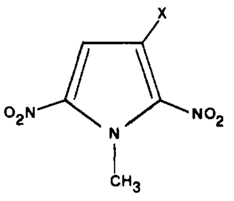
In both the pyrrole and benzene ring the methoxy denitration reaction is accelerated by a nitro or a cyano group flanking the reaction center. However, because of the different geometry of the rings, in the pyrrole ring a nitro group is more effective than a cyano group, at variance with what is observed in the benzene ring.

Nucleophilic aromatic substitution reactions can be carried out on activated pyrrole derivatives provided that a suitable leaving group is present and that the nitrogen atom is bound to a group other than hydrogen, in order to avoid the formation of the scarcely reactive conjugate base of the substrate.[1] In these substitution reactions the reactivity of the pyrrole ring has already been compared with that of the benzene ring by measuring the rates of the denitration reactions of 1-methyl-2,5-dinitropyrrole and 1,4-dinitrobenzene.[2]

Further information has now been obtained about the factors affecting the reactivity of the pyrrole ring by comparing the effects of electron-withdrawing substituents in the nucleophilic substitution in pyrrole and benzene rings. The rate of the methoxy denitration reaction in MeOH has been measured for the structurally related 3-X-1-methyl-2,5-dinitropyrroles (**1a–c**) and 2-X-1,4-dinitrobenzenes (**2a–c**) (X = H, CN, NO_2). Compounds of series **1** and **2** share a comparable pattern of activating groups and a nitro group as a leaving group.



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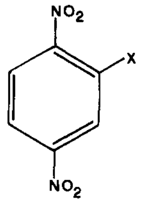

2

	X
a	H
b	NO_2
c	CN

Experimental Section

Melting points are uncorrected. UV spectra were recorded on a Cary 219 instrument. Electron-impact mass spectra were obtained on an AEI MS12 spectrometer. ^{1}H NMR spectra were

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(1) Doddi, G.; Mencarelli, P.; Stegel, F. *J. Chem. Soc., Chem. Commun.* **1975**, 273.

(2) (a) Doddi, G.; Illuminati, G.; Mencarelli, P.; Stegel, F. *J. Org. Chem.* **1976**, *41*, 2824. (b) Mencarelli, P.; Stegel, F. *Ibid.* **1977**, *42*, 3550.

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