Table I. Migratory Aptitudes in Rearrangements of
1-(p-X-phenyl)-1-phenylindenes

Energy Input	Substituent (-X)	Solvent	% reaction	Ratio[b] 3:2
Ultraviolet (direct)	-CN	Hexane	59	>98:2
	-CN	tert-Butyl[a] alcohol	75	>98:2
	-Br	Hexane	88	86:14
	-OCH₃	Hexane	89	95:5
Acetophenone sensitization	-CN	tert-Butyl[a] alcohol	62	>98:2
	-Br	Hexane	78	72:28
Heat (258°)	-CN	Diphenyl ether	100	82:18
	-Br		100	52:48
	-OCH₃		100	50:50

[a] The same result was obtained with 95% ethanol as solvent.
[b] Estimated *maximum* analytical error was ±5%.

(favoring migration of all three p-X-phenyl groups in preference to phenyl) than the ground-state process. As far as we are aware, there is no model, based on theory or experiment, which could have been used to predict this result.

A complete discussion is beyond the space limitations of this paper; however, we can make the following points. First, the excited-state process does parallel, at least qualitatively, the results of Hixson[5] on a related reaction in acyclic compounds. Hixson interpreted his results in terms of odd-electron character in the transition state for migration and pointed out that they were consistent with predictions of Hückel calculations.[16] However, an alternative interpretation based on charge-transfer interactions is also reasonable. It is well known that charge transfer is important in excited-state interactions,[17] and recent experimental work has demonstrated this for bimolecular processes.[18] The latter has shown that, in quenching of an excited state, the rate is high if one partner is a good electron donor and the other a good acceptor, and quantitative correlations with reduction, oxidation, and ionization potentials have been made. Similar factors could operate in the interaction between the nonconjugated chromophores in the excited state of 1 to make the substituted group the better migrator (vs. phenyl).[19-21]

For ground-state processes, theory predicts charge-transfer interaction to be much less important.[17] The

(16) H. E. Zimmerman and A. Zweig, J. Amer. Chem. Soc., 83, 1196 (1961).
(17) The theoretical basis for this statement was developed by Mulliken; R. S. Mulliken and W. B. Person, "Molecular Complexes," Wiley-Interscience, New York, N. Y., 1969.
(18) (a) D. Rehm and A. Weller, Isr. J. Chem., 8, 259 (1970), and references cited; (b) J. B. Guttenplan and S. G. Cohen, Tetrahedron Lett., 2163 (1972); J. Amer. Chem. Soc., 94, 4040 (1972); (c) S. Ander, H. Blume, G. Heinrich, and D. Schulte-Frohlinde, Chem. Commun., 745 (1968); (d) D. Schulte-Frohlinde and R. Pfefferkorn, Ber. Bunsenges. Phys. Chem., 72, 350 (1968); (e) H. S. Samant and A. J. Yarwood, Can. J. Chem., 49, 2053 (1971).
(19) Electron transfer between the styrene system and substituted aryl group is more favorable energetically in 1b and 1c, than it would be for an unsubstituted phenyl group. For example, E_{ox} (styrene)[20] + E_{red} (benzonitrile)[18a] = 94.4 kcal; E_{red} for benzene has not been measured directly on account of its high value, and therefore E_{ox} (stryrene) + E_{red} (benzene) > 94.4 kcal. Similarly, charge transfer from the p-methoxyphenyl group of 1c to the styrene chromophore should certainly be favored over the corresponding phenyl-styrene interaction.
(20) N. L. Weinberg and H. R. Weinberg, Chem. Rev., 68, 449 (1968).
(21) Hixson observed solvent incorporation on irradiation in methanol of 1,3-diphenylpropene derivatives (J. Amer. Chem. Soc., 94, 2505 (1972)). These products are consistent with highly polar intermediates, such as zwitterions, which could be formed by intramolecular electron transfer in the polar solvent.

relatively low selectivity in the thermal migrations could reflect a radical-like transition state. Ruckardt[2] showed that a p-cyanophenyl group had a much higher migratory amplitude than other aryl groups, to a free radical center.[22] Our results for the thermal reaction could therefore be consistent with a radical-like process.[23] A full discussion, including the orbital symmetry aspects, will be given in a full paper.

Acknowledgments. We are pleased to acknowledge discussions and exchange of information with Dr. L. L. Miller, who also measured the rate of rearrangement of 1b. We thank the National Research Council of Canada for financial support through an operating grant.

(22) (a) Ruckardt found that p-anisyl migrated more readily than phenyl in one case[22b] and less readily in another.[2] However, the differences between these two aryl groups was small, and p-cyanophenyl was by far the best migrator.[2] (b) C. Ruckardt and H. Trautwein, Ber., 96, 160 (1963).
(23) The p-cyanophenyl group does not exert its effect by retarding phenyl migration. The rate constants are (280°, diphenyl ether): 1,1-diphenylindene, 2.0 × 10⁻⁴ sec⁻¹; 1a, 0.7 × 10⁻⁴ sec⁻¹; 1b, 18 × 10⁻⁴ sec⁻¹.[24]
(24) Personal communication from Dr. L. L. Miller.

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Evidence for Electron Transfer in the Photoreduction of Aromatic Nitro Compounds

Sir:

Recently, we reported the efficient photoreduction of 4-nitropyridine to 4-hydroxylaminopyridine in 50% isopropyl alcohol–water containing HCl.[1] The enhanced photoreduction of nitrobenzene in the same solvent system has also been demonstrated.[2] The results indicated that protonation effects were important, but whether the primary process involved electron transfer or proton transfer to the $^3n,\pi^*$ state could not be distinguished. In the enhanced photoreduction of nitrobenzene in HCl solutions,[2] we suggested that protonation in the excited $^3n,\pi^*$ state may be operative, since the chloride ion alone does not lead to enhanced photoreduction; however, Wubbels, et al.,[3] have recently demonstrated that the enhanced photoreduction occurs in HCl but not in H_2SO_4. The results were interpreted in terms of an electron transfer from the chloride ion to nitrobenzene in its $^3n,\pi^*$ state, which is followed by protonation. It is noteworthy that Wubbels, et al.,[3] proposed the formation of a charge-transfer complex of the type [PhNO₂⁻, Cl·], but they were unable to demonstrate the intermediacy of the complex or of the nitrobenzene anion. It is appealing that such a mechanism can be tested by a flash photolysis experiment in which the absorption spectrum of the corresponding anion may be observed. Accordingly, we present the flash photolysis results obtained for nitrobenzene and 4-nitropyridine in aqueous isopropyl alcohol (IPA) solutions containing HCl. The nitrobenzene anion has been reported by Kemula and Sioda[4]

(1) A. Cu and A. C. Testa, J. Phys. Chem., 77, 1487 (1973).
(2) R. Hurley and A. C. Testa, J. Amer. Chem. Soc., 89, 6917 (1967).
(3) G. G. Wubbels, J. W. Jordan, and N. S. Mills, J. Amer. Chem. Soc., 95, 1281 (1973).
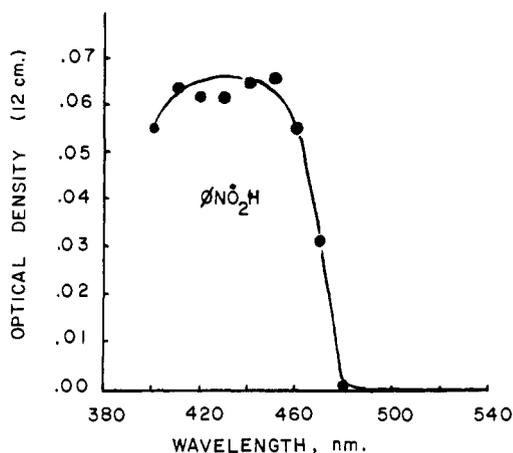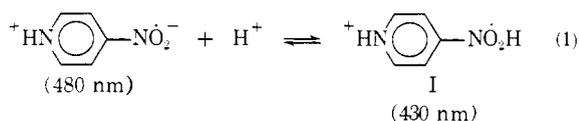(4) W. Kemula and R. Sioda, Nature (London), 197, 588 (1963).

Figure 1. The absorption transient observed in the flash photolysis of degassed 4×10^{-4} M nitrobenzene in 50% isopropyl alcohol–water, 6 M in HCl, 25°. Transient lifetime = 2.7 ± 0.5 msec (first-order process).
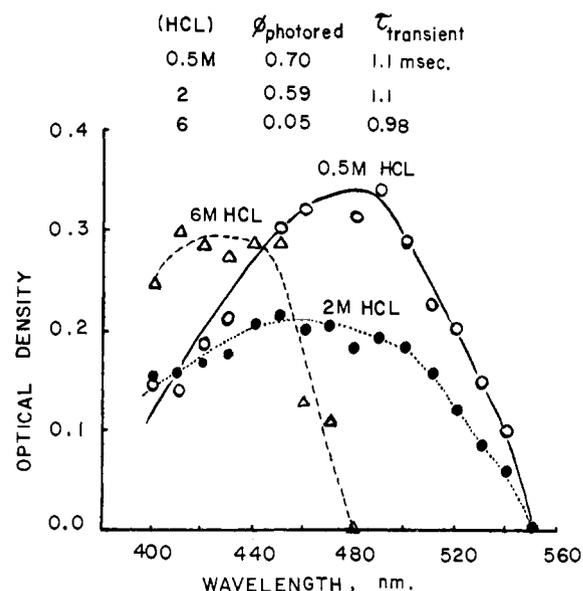

Figure 2. The absorption transient observed in the flash photolysis of degassed 4×10^{-4} M 4-nitropyridine in 50% isopropyl alcohol–water containing HCl, 25°.

to exhibit peaks at 435 and 465 nm, while Rao, et al.,[5] report 440 nm for the absorption maximum. The radical anion of 4-nitropyridine exhibits a peak at 440 nm when prepared from the potassium reduction in dimethoxyethane.[6]

Upon flashing (80 J, 40 μsec pulse) a degassed 4×10^{-4} M solution of nitrobenzene in 50% IPA–water, 6 M in HCl, a first-order transient with a lifetime of 2.7 ± 0.5 msec is observed, which exhibits a maximum at ~440 nm; see Figure 1. The spectrum is in satisfactory agreement with that of the protonated nitrobenzene anion, $PhN\dot{O}_2H$, which arises from a rapid protonation of the anion, and thus supports an electron transfer mechanism from the chloride ion to the $^3n,\pi^*$ state as a primary process. It is noteworthy that the absorption spectrum of $PhN\dot{O}_2^-$ and $PhN\dot{O}_2H$ are indistinguishable in the 400–460 nm range.[7] We were unable to find any experimental evidence for an encounter complex preceding electron transfer; however, it is difficult to exclude its participation. It is known that photoexcitation of nitrobenzene in 2 M lithium chloride does not lead to photoreduction; consequently, protons are also essential for the photoreduction.

Flashing a degassed 4×10^{-4} M solution of 4-nitropyridine in 50% IPA–water, 6 M in HCl, gives rise to a first-order transient with a lifetime of 1.0 msec and an absorption maximum at ~430 nm, which agrees satisfactorily with the one reported for the 4-nitropyridine anion, see Figure 2. When flash photolysis was performed on solutions 2.0 and 0.5 M in HCl, the first-order transients had their peaks shifted to 460 and 480 nm, respectively. This shift with acid concentration is most likely due to the equilibrium

The first-order decaying absorption in 0.5 and 2.0 M HCl was observed only in degassed solutions and reflects the fact that radical anions are generally air sensitive. The results for 4-nitropyridine are summarized in Figure 2.

In Figure 2 we have also summarized the photoreduction quantum yields for the conversion of 4-nitropyridine to 4-hydroxylaminopyridine in aqueous alcoholic solutions containing HCl, which we have reported elsewhere.[1] Although the lifetime of the absorbing transient does not show any significant variation in the range 0.5–6.0 M HCl, it is apparent that a significant inefficiency prevails for the photoreduction in 6 M HCl. This behavior contrasts with that observed for nitrobenzene, where the quantum yield for photoreduction increases continuously with increasing HCl concentration. The fact that the absorbing transient for 4-nitropyridine exhibits only wavelength shifts with increasing HCl concentration suggests that a deactivation mode involving protons occurs after an initial electron and proton transfer. The fact that the reactive species in 4-nitropyridine is charged, I, whereas in the case of nitrobenzene the reactive species is neutral, $PhN\dot{O}_2H$, may be a significant factor.

On the basis of the above results we believe that the electron transfer premise of Wubbels, et al.,[3] is corroborated and precedes proton transfer. The primary photochemical process in the photoreduction of 4-nitropyridine in the presence of HCl can thus be represented as

$$^+HN\langle\bigcirc\rangle\!-\!NO_2 \xrightarrow{\ *3\ } + Cl^- \longrightarrow {}^+HN\langle\bigcirc\rangle\!-\!N\dot{O}_2^- + Cl\cdot \quad (2)$$
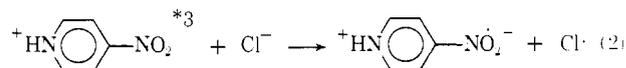
It appears that the radical species I is formed with greater efficiency when it arises from electron transfer in HCl solutions rather than from H-atom abstraction from isopropyl alcohol. In view of the presence of electron transfer to form the anion, it is now inviting to attribute the lack of phosphorescence at 77°K[1] and the short lifetime of the triplet of 4-nitropyridinium ion to electron transfer to the $^3n,\pi^*$ state. The results pre-

$$^+HN\langle\bigcirc\rangle\!-\!N\dot{O}_2^- + H^+ \rightleftharpoons {}^+HN\langle\bigcirc\rangle\!-\!N\dot{O}_2H \quad (1)$$

(480 nm)   I
(430 nm)

(5) V. Kalyaraman, C. N. R. Rao, and M. V. George, Tetrahedron Lett., 55, 4889 (1969).

(6) M. Itoh, T. Okamoto, and S. Nagakura, Bull. Chem. Soc. Jap., 36, 1665 (1963).

(7) K. D. Asmus, A. Wigger, and A. Henglein, Ber. Bunsenges. Phys. Chem., 70, 862 (1966). Since pK_a = 3.2 for the equilibrium $PhN\dot{O}_2H \rightleftharpoons PhN\dot{O}_2^- + H^+$, the observed transient is the protonated anion.

sented in this study provide the first direct evidence for the intermediacy of the nitroaromatic anion in the photoreduction of aromatic nitro compounds in 50% IPA–water containing HCl.

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Dipositive Ion of Hexachlorobenzene.
A Ground-State Triplet

Sir:

We have prepared the dipositive ion of hexachlorobenzene (I) by a two-step oxidation of the parent HCB. This ion is the first example of a benzene system having four π-electrons (A).[1] As predicted by simple Hückel theory, I is a ground-state triplet. The two unpaired electrons occupy degenerate orbitals and the molecule retains the sixfold symmetry of the parent. In contrast to I a Jahn–Teller distortion to lower symmetry can occur in the monopositive[2] and mononegative[3] ions as well as the excited states[4] of benzene. The π-electron configuration of I parallels that of the cyclopentadienyl cations[5] (II) which also have triplet ground states (B).

I (A)   IIa, R = H (B)
b, R = Cl
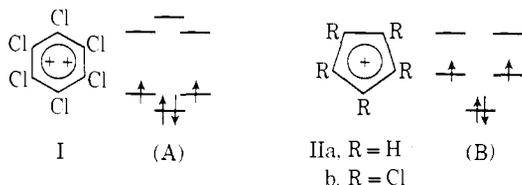
Solid HCB was mixed at room temperature with a viscous solution of SbF_5 saturated with Cl_2.[6] A deep purple coloration appeared and the resulting solution gave a strong esr signal at $g = 2.0156$. The most likely origin of this resonance is $C_6Cl_6^+$. Assuming the stoichiometry

$$2C_6Cl_6 + Cl_2 + 2SbF_5 \longrightarrow 2C_6Cl_6^+ + 2[ClSbF_5]^-$$

the signal intensity indicates that, within a factor of ~ 1.5, 40% of the C_6Cl_6 has reacted by this path. Upon cooling to 5 or 77°K and irradiation with light of $\lambda > 3100$ Å, an esr signal (Figure 1) characteristic of a

(1) A stable dication, $(CCH_3)_6^{2+}$, has been observed by H. Hogeveen and P. W. Kwant, *Tetrahedron Lett.*, 1665 (1973). This singlet species consists of a CH_3C^+ fragment interacting with a pentamethylcyclopentadienyl cation to form a pentagonal pyramid. The nmr observations preclude the possibility of a triplet electronic system so that this pyramidal structure is distinct from I.

(2) M. K. Carter and G. Vincow, *J. Chem. Phys.*, **47**, 292 (1967). Apparent sixfold symmetry is seen in the monocation and anion[3] presumably due to averaging over the distorted configurations.

(3) M. R. Das, S. B. Wagner, and J. H. Freed, *J. Chem. Phys.*, **52**, 5404 (1970), and references cited therein. R. G. Lawler, J. R. Bolton, G. K. Fraenkel, and T. H. Brown, *J. Amer. Chem. Soc.*, **86**, 520 (1964).

(4) L. Salem, "The Molecular Orbital Theory of Conjugated Systems," W. A. Benjamin, New York, 1966, pp 473–495.

(5) R. Breslow, H. W. Chang, R. Hill, and E. Wasserman, *J. Amer. Chem. Soc.*, **89**, 1112 (1967); M. Saunders, R. Berger, A. Jaffee, J. M. McBride, J. O'Neill, R. Breslow, J. M. Hoffman, Jr., C. Perchonock, E. Wasserman, R. S. Hutton, and V. J. Kuck, *ibid.*, **95**, 3017 (1973).

(6) The combination of Cl_2 and SbF_5 appears to be an unusually strong oxidizing agent. We observed no coloration upon the addition of BF_3 or $AlCl_3$ to suspensions of C_6Cl_6 in liquid Cl_2 ($-40°$). However, the addition of $SbCl_5$ to C_6Cl_6 and SbF_5 was able to generate the same purple color and I. The reaction of these two antimony pentahalides is exothermic and may be complex.
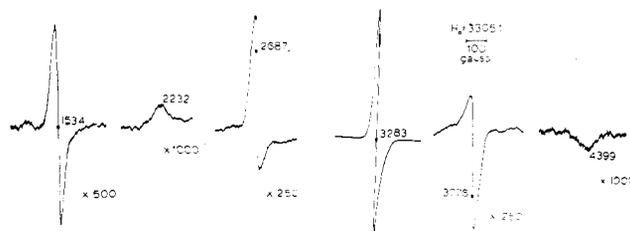

Figure 1. Esr spectrum of $C_6Cl_6^{2+}$ obtained by irradiation of a solution of HCB in SbF_5–Cl_2.

triplet state[7] (I) appeared within a few minutes. The species responsible for the triplet spectrum was stable indefinitely below 77°K but disappeared after a few minutes at 196°K. The signal intensity was proportional to $1/T$, indicating a ground state triplet or a species within a few calories/mole of the ground state. From the spectrum we determined the zero-field parameters[7] which measure the magnetic dipole interaction of the two unpaired electrons: $D_I = 0.1012 \pm 0.0001$ cm^{-1} and $E_I < 0.0003$ cm^{-1}; $g_{xy} = 2.0192, g = 1.9961$. We suggest that these data are best accommodated by the dipositive ion I. For comparison $D_{IIb} = 0.1445$ cm^{-1}, $E_{IIb} < 0.0003$ cm^{-1}, $g_{xy} = 2.0112$, and $g_z = 1.9986$.[5,8] A second ground-state triplet with parameters similar to those of IIb was observed on prolonged irradiation, particularly with $\lambda < 3100$ Å. Presumably a CCl fragment is lost producing IIb from I or a precursor of I.[9]

E indicates the deviation of the triplet from threefold or higher symmetry. The apparent zero value of E_I is compatible with the sixfold symmetry that might be expected from a benzene dipositive ion.

$$D \propto (3z^2 - r^2)/r^5$$

where r is the distance between the unpaired electrons and z the component of that distance along the axis perpendicular to the molecular plane. We use D_{IIb} to estimate D_I. We assume that the geometrical factors in the interaction between the unpaired spin densities on C–Cl fragments which are "ortho" or "meta" are the same in I and IIb. A justification for this approach is that most of the spin density is on carbon and the interactions will not be greatly affected by the changes in the CCCl angle between I and IIb. Then the difference in zero-field parameters for I and IIb is due chiefly to the increased spin density on the atoms of IIb because of the smaller ring size. The spin density on a C–Cl fragment of I is five-sixths as large as that on IIb and, as D is proportional to the product of spin densities, $D_{I(calcd)} = (\frac{5}{6})^2 D_{IIb}$. The "para" interaction which is found only in I will yield an increase of $\sim 4\%$. We then find that $D_{I(calcd)} = 0.104$ cm^{-1} in good agreement with that observed. The calculated value of D_I should be an upper limit as the dipositive charge in I will place more net charge and spin on chlorine than the monopositive charge in IIb.

Additional support for the assignment of the triplet spectrum to I arises from a comparison of the g factors for I and IIb, particularly g_{xy}. The substantial devi-

(7) E. Wasserman, L. C. Snyder, and W. A. Yager, *J. Chem. Phys.*, **41**, 1763 (1964).

(8) R. S. Hutton, unpublished results.

(9) An analogous $C_6 \rightarrow C_5$ transformation has yielded neutral $C_5H_5 \cdot$.[2] Also G. Porter and B. Ward, *Proc. Roy. Soc., Ser. A*, **303**, 139 (1968).