Dowex 50W-X2 cation-exchange resin. The $Cr(phen)_3^{3+}$ fraction separated cleanly from the unreacted $Co(phen)_3^{3+}$ and was found to account almost quantitatively for the optical activity of the product solution. When *d*-$Co(phen)_3^{3+}$ was the reactant, *l*-$Cr(phen)_3^{3+}$ was the major product, and when *l*-$Co(phen)_3^{3+}$ was the reactant, *d*-$Cr(phen)_3^{3+}$ was the major product. From the optical activity of the product and the known[3] molar rotations of $Cr(phen)_3^{3+}$ and $Co(phen)_3^{3+}$, we estimate that oxidation of $Cr(phen)_3^{2+}$ by *d*-$Co(phen)_3^{3+}$ under our experimental conditions results in the formation of about 92% *l*-$Cr(phen)_3^{3+}$ and about 8% *d*-$Cr(phen)_3^{3+}$.

Since at the time of mixing $Cr(phen)_3^{2+}$ must be a 1:1 mixture of the *d* and *l* isomers the preferential generation of one optical isomer of $Cr(phen)_3^{3+}$ must mean that the redox reaction is substantially slower than the inversion reaction of $Cr(phen)_3^{2+}$, so that the optical isomer of $Cr(phen)_3^{2+}$ which is oxidized more rapidly is constantly replenished. If the redox reaction involving the less reactive isomer were faster than the inversion reaction of $Cr(phen)_3^{2+}$, then the product would be racemic $Cr(phen)_3^{3+}$.

Assuming that at all stages in the reaction the reducing agent is racemic $Cr(phen)_3^{2+}$, we estimate from the product ratios that the activated complex [*l*-$Co(phen)_3$-*d*-$Cr(phen)_3$]$^{5+}$ is about 1.2 kcal/mole more stable than the activated complex [*l*-$Co(phen)_3$-*l*-$Cr(phen)_3$]$^{5+}$. Since the energy of the separated reactants does not depend on optical configuration, our observations establish unequivocally that the reactants do not behave as though they had spherical symmetry. There is a configurational restriction on collisions leading to electron transfer. Assuming that the isomers of $Co(phen)_3^{3+}$ and $Cr(phen)_3^{3+}$ have the same sign of rotation for the same chirality, the electron transfer occurs more readily if the configurations of oxidizing and reducing agents are mirror images. A further implication of our results is that the two reactants are in intimate contact in the activated complex.

A much smaller effect of optical activity on reaction rate has been observed by Bruning and Weissman[4] for the electron-transfer reaction between potassium 1-(α-naphthyl)-1-phenylethanide and 1-(α-naphthyl)-1-phenylethane. Asymmetric induction is in principle a much more sensitive technique for probing the effect of optical activity on reaction rates than is the direct measurement of reaction rates as used by Bruning and Weissman. The generation of an optically active product from an inactive reactant is definite evidence for an effect of optical activity on rate, whereas small differences in directly measured rate constants may be due to experimental errors.

Acknowledgment. This work has been supported by the Public Health Service under Grant GM 12783, and a PRF Graduate Fellowship awarded to Joan H. Sutter during 1968–1969. We are also grateful for the use of the JASCO-DURRUM ORD-CD spectrometer at Georgetown University.

[4] W. Bruning and S. I. Weissman, *J. Am. Chem. Soc.*, **88**, 373 (1966).

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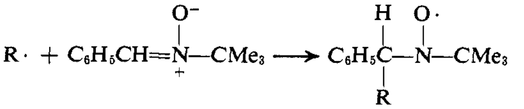
Received March 14, 1969

Substituent Effects on the Photochemistry and Nitroxide Radical Formation of Nitro Aromatic Compounds as Studied by Electron Spin Resonance Spin-Trapping Techniques[1]

Sir:

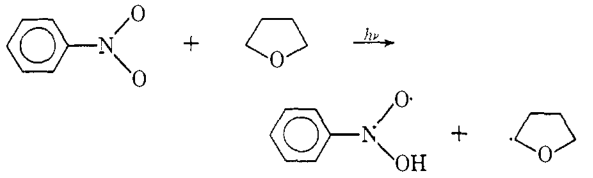
In connection with a general study of substituent effects on the electron spin resonance (esr) spectra of stable free radicals,[2] *meta*- and *para*-substituted nitrobenzenes have been photolyzed in tetrahydrofuran (THF) at room temperature and the esr spectra of the produced radicals obtained. In order to (1) establish the structure of the radicals produced and (2) provide an understanding of the photochemical process and subsequent reactions involved, recently developed spin-trapping techniques[3] have been applied to the study of this problem. This method involves addition of reactive free radicals to phenyl-*t*-butylnitrone (a "spin trap") to produce relatively stable *t*-butyl(α-substituted benzyl) nitroxides ("spinadducts "). The spin adducts



$$R\cdot + C_6H_5CH{=}\underset{+}{\overset{\overset{O^-}{|}}{N}}{-}CMe_3 \longrightarrow C_6H_5\underset{\underset{R}{|}}{\overset{\overset{H}{|}}{C}}{-}\overset{\overset{O\cdot}{|}}{N}{-}CMe_3$$

are detected by esr and the structure of R· is deduced from a comparison of the nitrogen and β-hydrogen coupling constants (N and β-H hfsc's) of the spin adduct with values obtained from spectra of authentic samples of the nitroxide.[3b,c] By this method methyl, trifluoromethyl, ethyl, *n*-butyl, benzyl, phenyl, acetoxy, benzoyloxy, and *t*-butoxy radicals have been detected.[3]

Ward[4] first published the esr spectrum of the radical produced from the photolysis of nitrobenzene in THF: $A_N = 15.00$, $A^H_{o,p} = 3.1$, $A^H_m = 1.08$, $A^H_{OH} = 0.38$ G. Ward "suspected" that the unique coupling was due to the hydrogen bonded to oxygen, and subsequent workers (including ourselves) have assumed this to be



(1)

correct.[5] However attempts to prepare the same radical by photolysis of nitrobenzenes in the presence of other good hydrogen atom donors either have been futile or have given other radicals.[6] The Ward spectrum can be obtained in THF containing lead dioxide[6b] or saturated with water. It is well known that the

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[1] Research supported by AFOSR(SRC)-OAR USAF Grant No. 1069-66.

[2] (a) E. G. Janzen, O. W. Maender, and J. L. Gerlock, Abstracts of Papers, 154th National Meeting of the American Chemical Society, Chicago, Ill., Sept 10–15, 1967, S-73; (b) E. G. Janzen, *Accounts Chem. Res.*, in press.

[3] (a) E. G. Janzen and B. J. Blackburn, Abstracts of Papers, 156th National Meeting of the American Chemical Society, Atlantic City, N. J. Sept 8–13, 1968, ORGN-86; (b) E. G. Janzen and B. J. Blackburn, *J. Am. Chem. Soc.*, 90, 5909 (1968); (c) *ibid.*, in press.

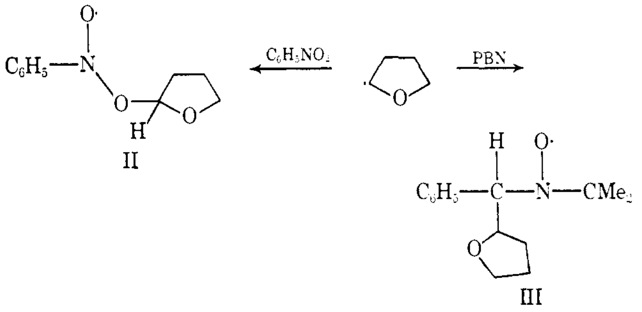
[4] R. L. Ward, *J. Chem. Phys.*, **38**, 2588 (1963).

[5] (a) A. Carrington, A. Hudson, and H. C. Longuet-Higgins, *Mol. Phys.*, **9**, 377 (1965); (b) W. Fox, J. M. Gross, and M. C. R. Symons, *J. Chem. Soc., A*, 448 (1966); (c) E. G. Janzen and J. L. Gerlock, *J. Am. Chem. Soc.*, **89**, 4902 (1967); J. L. Gerlock and E. G. Janzen, *ibid.*, **90**, 1652 (1968); (d) J. K. Brown and W. G. Williams, *Chem. Commun.*, 495 (1966); (e) R. Hurley and A. C. Testa, *J. Am. Chem. Soc.*, **88**, 4330 (1966).

[6] (a) Unpublished work of J. L. Gerlock; (b) unpublished work of O. W. Maender.

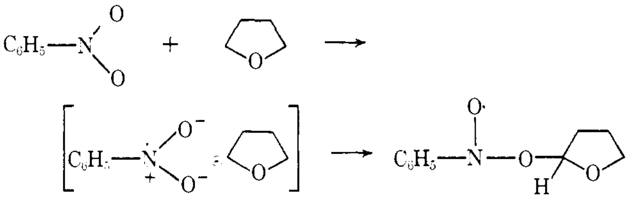
nitrobenzene radical anion can be obtained by photolysis of nitrobenzene in basic solutions.[7] Thus the radical *observed* does not appear to have an acidic or easily oxidized hydrogen atom.

More recent work on alkoxyarylnitroxides[8,9] suggests II as an alternate structural assignment for the Ward spectrum, a conclusion previously reached by Cowley and Sutcliffe[10] on the basis of the absence of a small doublet coupling in the spectrum obtained from the photolysis of nitrobenzene in diisopropyl ether. Results of spin-trapping experiments are in agreement with this new structural assignment. Thus the Ward spectrum is completely replaced by the characteristic triplet of doublets spectrum due to a phenyl-*t*-butylnitrone (PBN) spin adduct when nitrobenzene is photolyzed in 0.1 *M* PBN in THF.[11] Since the N and β-H hfsc's of the spin adduct are identical with those obtained in the photolysis of benzophenone in THF containing PBN, the structure of the spin adduct is assigned to III. This result establishes that the photolysis of nitrobenzene in THF *does* lead to the tetrahydrofuranyl radical and that the Ward spectrum is *not* produced when the tetrahydrofuranyl radical is efficiently removed from the system. Furthermore the production of II cannot be the result of a cage recombination reaction followed by hydrogen abstraction because both II and III should then be detected simultaneously since PBN would probably trap only those tetrahydrofuranyl radicals escaping the solvent cage.



Further experiments have shed some light on the photochemistry of nitrobenzene and the mechanism of formation of II. The photolysis of 26 *meta*- and *para*-substituted nitrobenzenes with electron-withdrawing groups (except chloro, bromo, and iodo) give the correspondingly substituted II in THF (also some *ortho*-substituted nitrobenzenes and polynitroaromatic compounds[6a]). Of the substituted nitrobenzenes with electron-donating groups (σ less than zero) *only* 4-phenyl-, 3- and 4-methyl-, 4-ethyl-, 4-isopropyl-, and 4-phenoxynitrobenzenes give the correspondingly substituted II. In the presence of 0.1 *M* PBN the photolysis of *p*-nitroanisole and *m*- or *p*-nitrophenol *does* and *m*- or *p*-N,N-dimethylnitroaniline[12] *does not* lead to III. None of these gives the correspondingly substituted II in the absence of PBN (note: photolysis of *m*-nitroanisole does give II). This substituent effect on the formation of II could be ascribed either to the absence of a "hydrogen-abstracting" excited state or to the inhibition of reactions leading to II for substituted nitrobenzenes having electron-donating groups.

The existence of a nitrobenzene $n \rightarrow \pi^*$ triplet state has been deduced from energy-transfer experiments[5d,13] and product studies.[5e] By analogy to the behavior of benzophenone derivatives,[14] the lack of hydrogen abstraction in the photolysis of N,N-dimethylnitroaniline is ascribed to the production of a relatively unreactive $\pi \rightarrow \pi^*$ triplet state. Nitrophenols and *p*-nitroanisole appear to undergo $n \rightarrow \pi^*$ excitation, although for benzophenone only the methoxy derivative is effective.[14] The lack of II-type radicals from these derivatives must be due to a substituent effect on the reactions leading to II. A simple addition of the tetrahydrofuranyl radical to nitrobenzene would be expected to have the substituent effect observed if charge-transfer occurs in the transition state or an intermediate contact ion pair[9,15] is formed.



No radicals are detected in the photolyses of chloro-, bromo-, and iodonitrobenzenes in THF. In the presence of PBN III is formed in THF and nitrophenyl spin adducts in benzene upon photolysis. Thus the halonitrobenzene excited state can either abstract hydrogens or undergo halogen–carbon bond scission in the absence of a hydrogen donor. No II or III radicals are detected in the photolysis of 1-nitronaphthalene[16] or 9-nitroanthracene[17] under appropriate conditions. 2-Nitrotriptycene gives both II and III.

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(10) D. J. Cowley and L. H. Sutcliffe, *Chem. Commun.*, 201 (1968).

(11) Filtered radiation from a Hanovia low-pressure mercury lamp was used since photolysis of PBN in THF itself leads to detectable amounts of spin adduct. The filter contained a solution of PBN in THF concentrated enough to completely eliminate this signal.

(12) A dark reaction between PBN and *m*- and *p*-nitroaniline, *m*- and *p*-N-methylnitroaniline, and *p*-nitroacetanilide which is not understood at this time leads to nitroxide radicals particularly in the presence of oxygen and makes results of experiments with these derivatives inconclusive.

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(17) T. D. Walsh, *ibid.*, **91**, 515 (1969); N. J. Turro, M. Tobin, L. Friedman, and J. B. Hamilton, *ibid.*, **91**, 516 (1969).

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Received March 20, 1969