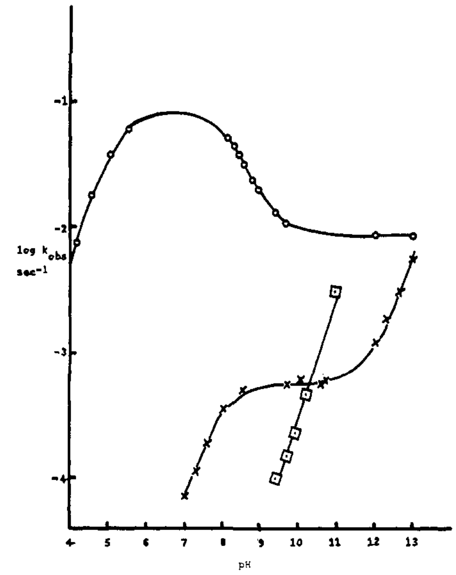
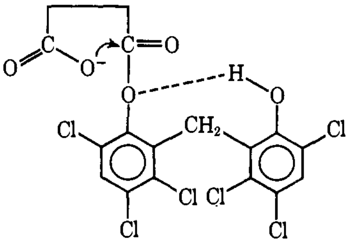


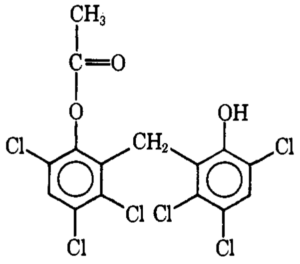
Figure 1. pH–rate profile for hexachlorophene monoacetate (×), diacetate (□), and monosuccinate (○).

that considerations based on the pK_a values of the reactant (monoanion of I, pK_a 8.14) and product (monoanion of hexachlorophene, pK_a 11.54) suggest that an intramolecular hydrogen bond such as that in structure II is formed during the reaction and leads to general acid catalysis.[6] The absence of strong intramolecular hydrogen bonding in the reactant is indicated by the similarity of its pK_a value to that of *O*-methylhexachlorophene (pK_a 8.22) in which the substituted phenolic oxygen would be considerably more basic. By comparison, the high value of the pK_a value of the product as well as its low basisity (pK_B 8.54) suggest that its acidic proton is strongly intramolecularly hydrogen bonded in a cyclic structure such as in II.

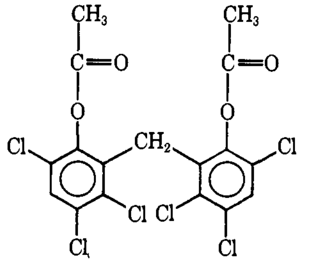


II

Further kinetic evidence for the formation of such an eight-membered ring is obtained when the pH–rate profiles of the monoacetate ester (III) and diacetate ester (IV) of hexachlorophene are examined[7] (Figure 1). On statistical grounds, the conversion of the diacetate to monoacetate would be expected to be twice as fast as that of the monoacetate to hexachlorophene, if the same mechanisms of hydrolysis occurred. However, it is evident from Figure 1 that below pH 8, the monoacetate undergoes hydrolysis at much greater rate, approximately 500 times faster. The facilitated hydrolysis of III can be explained by the two possible isokinetic mechanisms, V and VI, both of which involve the formation of an eight-membered ring in the transition state.

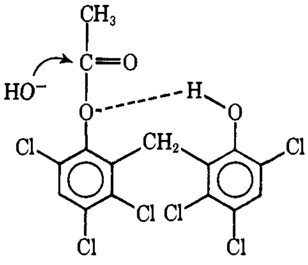


III

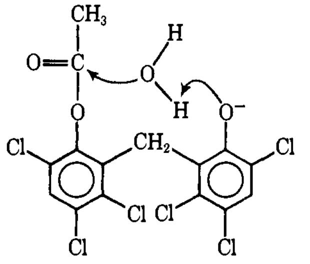


IV

Thus, the 500-fold enhancement of rate of hydrolysis, below pH 8, of the monoacetate over that of the diacetate represents an intramolecular general acid monofunctional facilitation, whereas the approximately 3 × 10^4-fold increase in rate of hydrolysis of the monosuccinate over that of the monoacetate, below pH 5, represents additional intramolecular nucleophilic monofunctional facilitation. The approximately 1.5 × 10^7-fold increase in hydrolysis rate of the monosuccinate over that of the diacetate, therefore, represents an intramolecular bifunctional facilitation in the monosuccinate.



V



VI

Acknowledgment. This work was supported in part by Vick Divisions Research and Development, Richardson-Merrell, Inc.

T. Higuchi, H. Takechi
I. H. Pitman, H. L. Fung
Department of Analytical Pharmaceutical Chemistry and Pharmaceutics
The University of Kansas, Lawrence, Kansas 66044
Received May 22, 1970

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[6] A referee suggested that the extent of intramolecular general acid catalysis in this reaction may be better appreciated if rates of hydrolysis of the succinate of *O*-methylhexachlorophene were known. Unfortunately repeated attempts to synthesize this compound were unsuccessful.

[7] T. Higuchi and H. Takechi, to be published.

Low-Temperature Photochemistry of *p*-Diazidobenzene and 4,4′-Diazidoazobenzene

Sir:

Recent esr studies by Trozzolo, *et al.*,[1] have shown that photolysis of *p*-diazidobenzene (I) in rigid matrices at 77°K produces a triplet ground-state species A with absorptions at 1578, 2500, 2852, 3566, and 3972 G which may be described by the spin Hamiltonian

$$H = g\beta HS + DS_z^2 + E(S_x^2 - S_y^2)$$

with $|D| = 0.067$ cm^{-1} and $E \approx 0$. On the basis of the close similarity of its esr spectrum and the

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[1] A. M. Trozzolo, R. W. Murray, G. Smolinsky, W. A. Yager, and E. Wasserman, *J. Amer. Chem. Soc.*, **85**, 2526 (1963).

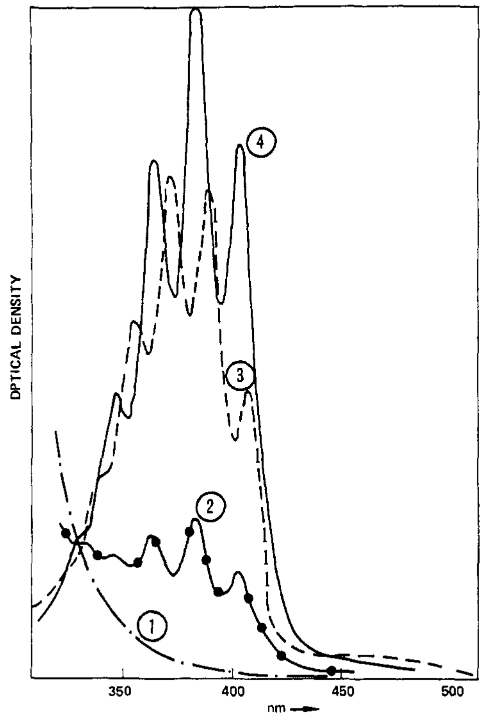
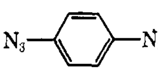
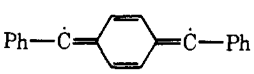


Figure 1. Low-temperature absorption spectra of (1) *p*-diazidobenzene (-·-·-) and (3) 4,4′-diazidoazobenzene (---) in methylcyclohexane. Curve 2 (-●-●-●) is the spectrum obtained by photolyzing solution (1) first with 313-nm light, then with 436-nm light. Curve 4 (—) is the spectrum obtained by photolyzing solution (3) with 313-nm light.

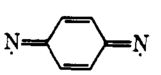
magnitude of its zero-field splitting parameters with those of the dicarbene II ($|D| = 0.0521$ cm^{-1} and $E < 0.002$ cm^{-1}) also reported by these authors they concluded that the species A possesses the quinonoid dinitrene structure III in which the two unpaired electrons are separated by a distance of approximately 5–6 Å.



I

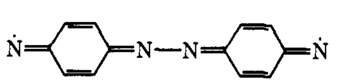


II

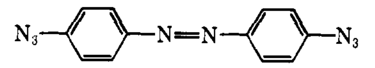


III

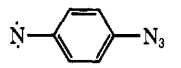
We have reexamined the photolysis of I and have verified the above observations! However, we wish to present evidence which shows that the species A should instead be represented by the 4,4′-dinitrenoazobenzene structure IV since the same species is also formed in the photolysis of 4,4′-diazidoazobenzene (V).



IV



V



VI

An additional set of lines due to another triplet ground-state species B was also reported in the footnotes.[1] These lines at 1227, 1473, 2062, and 4115 G were shown to fit the spin Hamiltonian with $|D| = 0.171$ cm^{-1} and $E \approx 0$. No structural assignment was made for this species. Our data also suggest that the species B giving rise to this spectrum best fits the *p*-dinitrenobenzene structure III, with the exception that the line observed at 1473 G[1] belongs to yet another ground-state triplet species.

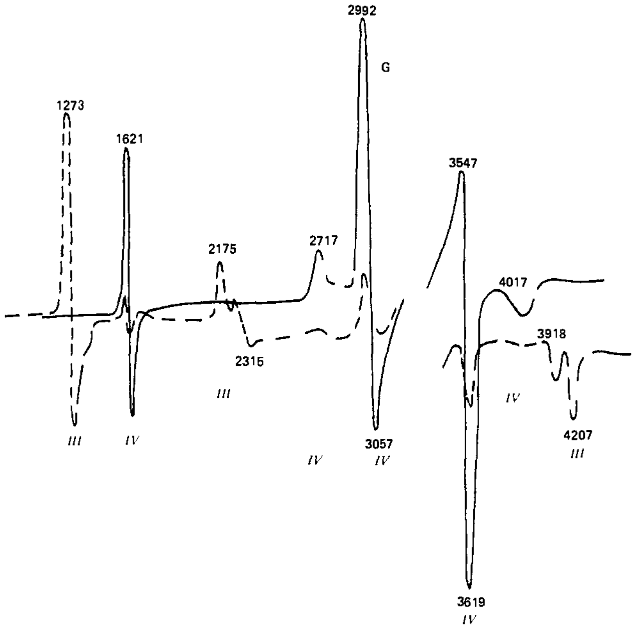


Figure 2. Electron spin resonance spectra of the photoproducts of *p*-diazidobenzene (---) and 4,4′-diazidoazobenzene (—) in halocarbon oil at 77°K. Similar spectra were obtained in 3-methylpentane and methylcyclohexane. The field positions for the lines assigned to 1,4-dinitrenobenzene (III) and 4,4′-dinitrenoazobenzene (IV) are indicated on the spectra.

Initial photolysis of *p*-diazidobenzene[2] (I) [$\lambda_{\max}^{\text{hexane}}$ 271 nm (ϵ 21,175), long-wavelength absorption spectrum shown in Figure 1 (curve 1)] at 77°K with 313- or 365-nm radiation results in the formation of 1-azido-4-nitrenobenzene (VI).[3] Continued irradiation of the mononitrene VI with 313-nm radiation results in the formation of new esr lines and an accompanying decrease in the intensity of the 6700-G line from VI (Figure 2, dashed curve; the line belonging to VI is not shown). The lines observed are those reported by Trozzolo, *et al.*[1] (species A and B), with the exception of the line at 1473 G which is extremely weak in the spectrum shown here.

Subsequent exposure to 436-nm light, which is relatively strongly absorbed by the mononitrene VI, results in the complete destruction of both the esr and optical spectra of VI. The other features of the esr spectrum remain unchanged (Figure 2, dashed line). The corresponding optical spectrum is shown in Figure 1 (curve 2).

The photolysis of 4,4′-diazidoazobenzene (V)[4] [$\lambda_{\max}^{\text{hexane}}$ 362 nm (ϵ, 37,874), 430 (5500)] at 77°K (Figure 1, curve 3) with 313-nm radiation results in the formation of the triplet ground-state species IV.

[2] D. L. Herring, *J. Org. Chem.*, **26**, 3998 (1961).

[3] This species is characterized by both its optical spectrum which is identical with that reported by Reiser, *et al.*,[4] and by its esr spectrum which consists of a single $\Delta m = 1$ line (within the limitations of our spectrometer) at ~6700 G. The corresponding nitrene from azidobenzene shows a single line at ~6900 G in agreement with the previous reported work.[5a,b]

[4] A. Reiser, H. M. Wagner, R. Marley, and G. Bowes, *Trans. Faraday Soc.*, **62**, 3162 (1967).

[5] (a) G. Smolinsky, E. Wasserman, and W. A. Yager, *J. Amer. Chem. Soc.*, **84**, 3320 (1962); (b) J. A. R. Coope, J. B. Farmer, C. L. Gardner, and C. A. McDowell, *J. Chem. Phys.*, **42**, 54 (1965).

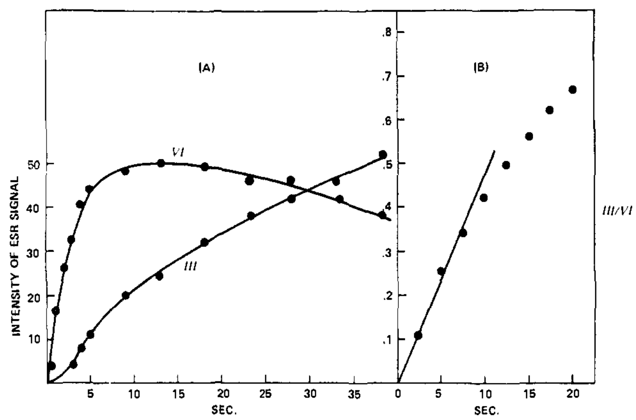


Figure 3. (a) The intensities of esr signals from 1,4-dinitrenobenzene (III) and 1-azido-4-nitrenobenzene (VI) in methylcyclohexane at 77 °K as a function of irradiation time (313 nm). (b) The ratio of concentration of 1,4-dinitrenobenzene to 1-azido-4-nitrenobenzene (III/VI) extrapolated to zero time.

The esr spectrum of the latter species is shown in Figure 2 (solid curve). The corresponding optical spectrum (Figure 1, curve 4) is in agreement with that reported for species IV.[4] It should be noted that the esr lines observed for this species are essentially those reported by Trozzolo, *et al.*,[1] for the species A obtained in the photolysis of *p*-diazidobenzene (*vide supra*). Furthermore, the ratio of the intensities of esr signals measured for solutions 2 and 4 (Figure 1) is nearly the same as the ratio of the observed optical densities.

The esr and optical spectral data presented above lead to the conclusion that a common dinitrene triplet ground-state species A is observed in the photolysis of the diazides I and V. For I, two species, A and B (other than the mononitrene), are observed characterized by $D^* = 0.059$ cm^{-1} and $D^* = 0.172$ cm^{-1}, respectively, while for V only one ground-state triplet species A with $D^* = 0.059$ cm^{-1} is observed.

It is unlikely that radiation of 313 nm would result in the cleavage of the relatively stable azo linkage in IV. This, and the absence of species B ($D^* = 0.172$ cm^{-1}) in the photolysis of 4,4′-diazidoazobenzene, lead us to assign the 4,4′-dinitrenoazobenzene structure IV to the species A ($D^* = 0.059$ cm^{-1}). The low value of the zero-field splitting parameter ($D^* = 0.059$ cm^{-1}) further suggests that the two unpaired electrons are considerably delocalized, as indeed would be expected from the presently assigned structure IV.[6] As a consequence of the above discussion we propose structure III to the species B ($D^* = 0.172$ cm^{-1}). A value of $D = 0.181$ cm^{-1} for the species III has been calculated[7] which is in excellent agreement with the value reported here.[8] Further support for this assignment is obtained from the measurement of the irradiation time dependence of the esr signals from 1-azido-4-nitrenobenzene (VI) and *p*-dinitrenobenzene (III). This is shown in Figure 3a and is reminiscent of the kinetics of consecutive reactions. If III is formed from VI by absorption of radiation of energy which is identical with that which produces VI from I, then a square dependence on irradiation time is expected. If this were the case, the ratio of the concentration of III/IV extrapolated to zero irradiation time should be linear, which is indeed observed (Figure 3b). Furthermore, this species is the major product of prolonged photolysis (~30–60 sec) in all the solvent systems in which this photolysis was examined.

An additional feature of considerable interest was observed when frozen solutions containing the ground-state triplet species VI were allowed to stand in stoppered (but nondegassed) tubes for several hours at 77°K. Under these conditions a new ground-state triplet species with $D^* = 0.110$ cm^{-1} was formed. This corresponds to the line at 1473 G reported by Trozzolo, *et al.*[1] The structure of this species and its optical and esr spectra will be the subject of a subsequent communication.[10]

Acknowledgment. We wish to acknowledge several stimulating discussions with Professor A. C. Albrecht.

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[6] The formation of the dinitrenoazobenzene IV in the photolysis of diazidobenzene I is not too surprising particularly since azo compounds are invariably formed in the photolysis of aromatic azides.

[7] J. Serre and F. Schneider, *J. Chem. Phys.*, **61**, 1655 (1964).

[8] The formation of the species A (IV) in the photolysis of I may occur by dimerization of the species B or by its reaction with the unreacted diazide I followed by photochemical decomposition of the resulting mononitrene to the species A. When solutions of the diazide are frozen there may be a tendency for the molecules of I to associate in pairs or groups. This may especially be true in more concentrated solutions ($>10^{-3}$ *M*) in MCH, 3MP, and HC where room temperature solubilities are poor to begin with. It should be noted that this species is not observed in MTHF which is a far better solvent. The heat of formation of an azide group is 205–208 kcal/mol and consequently considerable energy is liberated when such molecules decompose.[9] This could result in local melting of the matrix facilitating the dimerization process to form the azo linkage.

[9] P. A. S. Smith, "The Chemistry of Open-Chain Organic Nitrogen Compounds," Vol. II, W. A. Benjamin, New York, N. Y., 1966, p 214.

[10] J. S. Brinen and B. Singh, submitted for publication.

Balwant Singh,* Jacob S. Brinen
Central Research Division, American Cyanamid Company
Stamford, Connecticut 06904

Received October 2, 1970

Evidence Supporting a Common Transition State for Rotation and Inversion in *tert*-Butylbenzylmethylamine

Sir:

In recent communications, evidence from variable-temperature nmr spectroscopy has been presented for nitrogen *inversion* in dibenzylmethylamine[1] and C–N bond *rotation* in *tert*-butyldimethylamine.[2] In these two cases, the barriers ($\Delta G^{\neq}$) for two apparently different processes are very similar, *i.e.*, 6.2 ± 0.2 kcal/mol at −142° for inversion in dibenzylmethylamine and 6.0 ± 0.1 kcal/mol at −153° for *tert*-butyl–nitrogen bond rotation in *tert*-butyldimethylamine. The similarity in these barriers may be fortuitous or may indicate a common transition state for rotation–inversion in trialkylamines.[3] Indeed, there have been no reports to date concerning the observation of multiple nmr coalescence phenomena in acyclic amines indicating unequivocal evidence for both processes. Examination of the temperature dependence of the nmr spectrum of

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[1] C. H. Bushweller and J. W. O'Neil, *J. Amer. Chem. Soc.*, **92**, 2159 (1970); M. J. S. Dewar and W. B. Jennings, *Tetrahedron Lett.*, 339 (1970). See also: M. Saunders and F. Yamada, *J. Amer. Chem. Soc.*, **85**, 1882 (1963).

[2] C. H. Bushweller, J. W. O'Neil, and H. S. Bilofsky, *ibid.*, **92**, 6349 (1970).

[3] A. Rauk, L. C. Allen, and K. Mislow, *Angew. Chem., Int. Ed. Engl.*, **9**, 400 (1970).