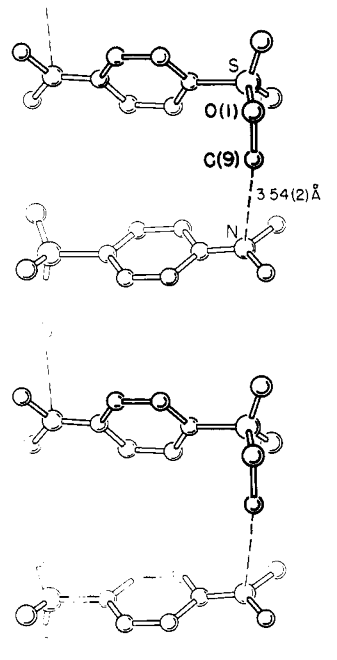

Figure 2. A view of the stacking along one chain of molecules in crystals of methyl *p*-dimethylaminobenzenesulfonate (I), as seen perpendicular to the [101] plane. Distance indicated is that between the carbon atom of the methyl group, which undergoes transfer in the solid state reaction, and the nitrogen atom to which it moves.

with the fact that the melting point of the material is in a temperature region where the reaction proceeds at a measurable rate, has allowed us to identify it as a rare example of a nonpolymerizing thermal reaction whose rate is actually accelerated by proper orientation in a crystal. It is now clear that such systems can exist; we look forward to the discovery of other solid state accelerated reactions in the future.[10]

Acknowledgments. We gratefully acknowledge financial support from the National Science Foundation (Grant MPS74-14711) the National Institutes of Health (Grant GM-16231), and the Chevron Research Corporation. J.A.P.B. wishes to acknowledge Conselho Nacional de Pesquisas of Brasil for its support. G. W. acknowledges a major equipment grant and generous support from the National Research Council of Canada.

Supplementary Material Available. A summary of the physical properties of I and II, an ORTEP drawing of a molecule of I, and interatomic distances and angles, fractional coordinates, and intensity data will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Business Office, Books and Journals Division, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.50 for photocopy or $2.50 for microfiche, referring to code number JACS-75-5290.

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(2) For leading references, see (a) I. C. Paul and D. Y. Curtin, *Acc. Chem. Res.*, **6**, 217 (1973); (b) M. D. Cohen and B. S. Green, *Chem. Brit.*, **9**, 490 (1973); (c) H. Morawetz, *Science*, **152**, 705 (1966).

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(7) Because the concept of a rate constant in the crystalline state is somewhat ill-defined, we have chosen to present our velocity data in simple concentration vs. time form. The initial rates are probably those which should be attributed to the reactivity of the crystalline compound. Examination of crystals of I using a polarizing microscope indicates that reaction is initiated at random isolated sites and then is presumably propagated along chains of molecules (vide infra) until a defect is reached. It is important to point out that as the reaction proceeds, the original crystal morphology is destroyed (as is evidenced both visually and crystallographically), and loss of long-range crystallinity concomitantly decreases the rate of conversion of I to II (Figure 1). In all of these reactions compounds I and II were the only detectable species; reactions were run by filtering an ether solution of I, evaporating it to dryness, and heating the residual solid under vacuum. These rates were identical with those done on material crystallized from methanol. Product analysis was carried out by NMR.

(8) Because II is extremely nonvolatile, it proved impossible to obtain conventional mass spectra of the material. Using FDMS, however, good spectra having appreciable parent peaks were obtained, and this allowed us to carry out the isotopic analysis conveniently. FDMS analysis of a standard synthetic mixture of II-d_0 and II-d_9 showed that significant, but not complete, label scrambling occurs during the FDMS experiment. To determine the extent of intermolecularity in the I → II reaction, therefore, the peak intensities measured on the product formed from the I-d_0/I-d_9 mixture were corrected for FDMS scrambling as measured using the synthetic mixture. The data indicate that the I → II solid state reaction is ≥75% intermolecular. To our knowledge, this constitutes the first evaluation of FDMS as a quantitative technique. Reproducibility was fairly good (relative error ca. 10% on 5–15 scans), suggesting that the technique may find application in biomedical quantitation studies.

(9) For some recent efforts to circumvent this problem by using a series of crystal structures of related compounds to construct a model for part of a reaction coordinate, see (a) H. B. Bürgi, J. D. Dunitz, J. M. Lehn, and G. Wipff, *Tetrahedron*, **30**, 1563 (1974); (b) H. B. Bürgi, J. D. Dunitz, and E. Shefter, *Acta Crystallogr., Sect. B*, **30**, 1517 (1974); (c) *J. Am. Chem. Soc.*, **95**, 5065 (1973); (d) H. B. Bürgi, *Inorg. Chem.*, **12**, 2321 (1973). None of the structures investigated in these studies appears to undergo actual chemical reaction.

(10) Perhaps possible candidates for such studies are reactions reported by (a) R. W. Addor, *J. Org., Chem.*, **29**, 738 (1964), and (b) L. A. Ae. Sluyterman and M. Kooistra, *Recl. Trav. Chim. Pays-Bas*, **71**, 277 (1952).

(11) Achievement Rewards for College Scientists Foundation Fellow, 1973–1975. National Science Foundation Trainee, 1972–1974.

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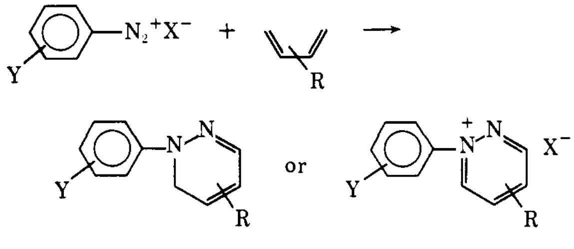
The Reaction of Diazonium Salts with Dienes. A Route to Pyridazines and Pyridazinium Salts

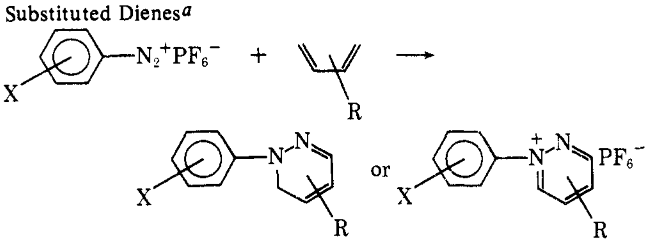
Sir:

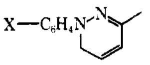
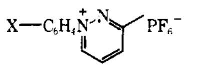
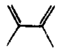
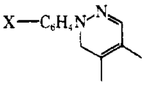
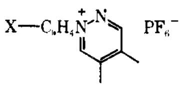
Aromatic diazonium salts undergo cycloaddition to dienes to produce N-substituted 1,6-dihydropyridazines or pyridazinium salts depending on the nature of the substituents on the aromatic ring (eq 1).



(1)

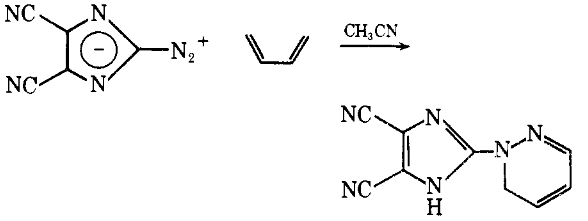
Table I. Reaction of Aromatic Diazonium Salts with Substituted Dienes[a]



Diene	Product	Yield of pyridazine,[b] % X = H	p-Cl	m-F	p-F	p-NO$_2$
		–	–	–	–	73[c]
		Trace	26	–	–	–
		–	–	–	–	79
		42	60	52	72	–

[a] All reactions were carried out in acetonitrile at room temperature unless otherwise specified. [b] Isolated yields. All products gave correct elemental and spectral analyses. [c] Reaction according to the procedure of K. H. Meyer[1] using the diazonium chloride in aqueous solution.

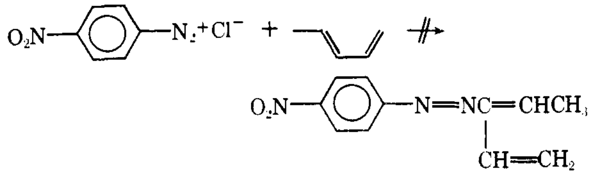
The addition of 2-diazo-4,5-dicyanoimidazole to butadiene to give the corresponding 1,6-dihydropyridazine[1] (eq 2)



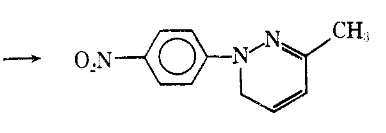
(2)

led us to investigate the potential for aromatic diazonium ions to undergo the same type of reaction. Although we found that butadiene did not react even with the p-nitrophenyldiazonium salt, more nucleophilic dienes underwent the reaction readily in both acetonitrile and protic solvents with a variety of aromatic diazonium ions. Thus, this reaction provides an interesting and useful route to substituted pyridazines (Table I).

Our results contradict reports by early workers in diazonium chemistry who proposed linear structures for the products of reaction between diazonium salts and dienes. In 1919, Meyer[2] first proposed linear structures for the adducts (eq 3). Subsequent workers also assigned linear structures to the products of diazonium salts and dienes.[3-5] In our hands Meyer's reaction gave a 73% yield of 1,6-dihydro-3-methyl-1-(4-nitrophenyl)pyridazine (**1**) (eq 4). Conclusive evidence for the cyclic structure is provided by NMR. The pyridazine, **1**, has a methyl singlet, δ 2.02 (3 H), a doublet of doublets δ 4.37 (CH_2), and a multiplet ca. δ 6.05 (vinyl, 2 H).



(3)

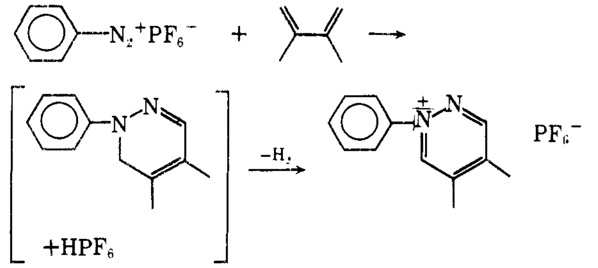


(4)

1

The cycloaddition reaction is favored by more electrophilic diazonium species and more nucleophilic dienes. Catalysis of the reaction by Lewis acids such as boron trifluoride etherate is ineffective.

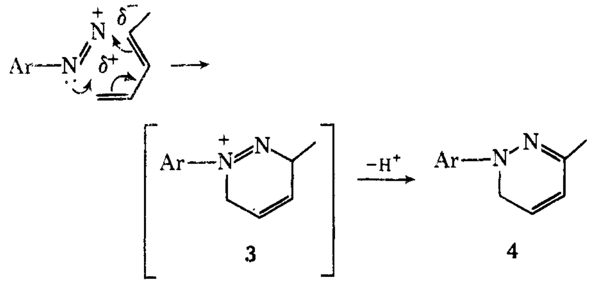
An unusual result is the in situ oxidation of the 1,6-dihydropyridazines to pyridazinium salts. In all cases except those with a para-nitro substituent on the aromatic ring the initially formed 1,6-dihydropyridazines are oxidized rapidly in situ, possibly by air, to the corresponding pyridazinium salts, and those are the only products isolated (eq 5). The remarkable ability of the para-nitro substituent to stabilize the 1,6-dihydropyridazines toward oxidation is apparently due to its ability to inhibit quaternization of the ring nitrogen by its strong electron-withdrawing influence. (The pK_a's[7] of the corresponding anilines are: aniline, pK_a 4.63; p-chloroaniline, pK_a 4.15; p-fluoroaniline, pK_a 4.65; p-nitroaniline, pK_a 1.0).



(5)

Azo compounds are reactive dienophiles in cycloaddition reactions. Their dienophilic reactivity parallels the electron-deficient nature of the azo linkage as in carbon analogs. Diazonium salts should also be reactive as dienophiles, but surprisingly, this behavior has never been reported. An analogous reaction has been observed between a dialkyldiazenium salt and isoprene to give a tetrahydropyridazine.[8]

A reasonable mechanism for the net cycloaddition is a concerted 2 + 4 process followed by loss of a proton (eq 6).

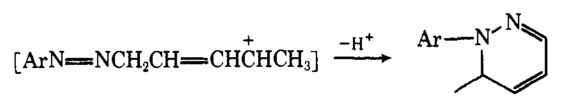


(6)

3

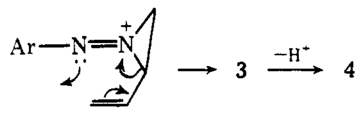
4

A nonconcerted ionic mechanism appears to be ruled out by the product orientation in the additions of *trans*-piperylene. Initial carbonium ion stabilization should lead to the opposite configuration from that observed (eq 7). However, note that a concerted process would not necessarily lead to the observed orientation.



(7)

A mechanistic alternative is reaction via an initially formed aziridinium ion intermediate, **5**.[9] Rearrangement of the aziridinium ion could occur by a concerted [2,3]-sigmatropic process to give the observed products in an analogous



5

manner to the rearrangements of allylic diazenes described by Baldwin.[10]

The reaction is highly sensitive to the stereochemistry of the diene. Thus, *trans*-piperylene reacts exothermically with the *p*-nitrophenyldiazonium salt to give the corresponding 1,6-dihydropyridazine in 73% yield after 1 hr, whereas the cis isomer did not react even after 6 hr. This observation is difficult to rationalize on the basis of the aziridinium ion mechanism but is expected in a concerted 2 + 4 process.

The reactions of diazonium salts with dienes are conveniently carried out using the stable hexafluorophosphate salts of the diazonium ions in acetonitrile. Aqueous solutions of other diazonium salts, however, also appear to work well as evidenced by the reaction of *p*-nitrophenyldiazonium chloride with *trans*-piperylene above (Table I). A typical procedure is as follows.

p-Nitrophenyldiazonium hexafluorophosphate,[11] 4.42 g, was dissolved in 35 ml of acetonitrile. 2,3-Dimethyl-1,3-butadiene, 2.46 g, was added in 10 ml of acetonitrile at room temperature and a mildly exothermic reaction ensued. After 30 min the mixture was cooled to 0° and the product was collected on a filter. This gave 2.7 g of yellow needles (79%). The product was recrystallized from acetonitrile at −30°: mp 178–180° dec; NMR (CD_2Cl_2) δ 1.80 (s, 6 H), 4.18 (bs, 2 H), 6.79 (s, 1 H), ca. 7.60 (AB q, 4 H).

The reactions in which the pyridazinium salts were isolated required a modified procedure. *p*-Fluorophenyldiazonium hexafluorophosphate, 5.36 g, was dissolved in 50 ml of acetonitrile and 2,3-dimethyl-1,3-butadiene, 1.64 g, was added. After 90 min the reaction mixture was stirred with saturated sodium acetate solution and filtered and the acetonitrile layer separated and dried. Evaporation left 5.0 g of residue which was triturated with ether (chloroform works well in some cases) giving 4.3 g of crude product. The product was recrystallized from acetonitrile-ether, mp 221–223° dec. Anal. Calcd: C, 41.39; H, 3.47, N, 8.05. Found: C, 41.88; H, 3.63; N, 8.03.

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(3) For a review see "Organic Reactions", Vol. 10, R. Adams, Ed., Wiley, New York, N.Y., 1959.
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(9) We thank Professor Barry M. Trost for suggesting this mechanism.
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(11) Many of the stable diazonium hexafluorophosphates are available from Cationics, Inc., or were prepared by the procedure of K. G. Rutherford and W. Redmon, "Organic Syntheses", Collect. Vol. 5, Wiley, New York, N.Y., 1973, p 133.

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A Very Simple Quantum Mechanical Model of the Directed Covalent Bond

Sir:

Chemists use a variety of models[1-9] to predict bond angles and geometries in molecules. In attempting to correlate these models with one another and with quantum theory, it might be useful to search out the simplest quantum mechanical model which can predict a bond angle, given some specific number of valence electrons, bonding and nonbonding, about a central atom in a molecule. A very simple model is here presented, and the results are compared with established trends.

The wave function for N electron pair is a complicated function of $6N$ variables, three for each electron, plus spins. If, however, electron–electron repulsions are neglected, this problem is exactly separable into one three-coordinate problem per electron, and one need only find the orbitals in three-dimensional space, doubly occupy those of lowest energy, and sum the resulting electron energies to get a total energy for the system. If, in addition, we confine our attention to the plane in which the bond lies, and to one typical radius in that plane, we can hold two of the usual three spherical polar coordinates constant and study a function of only one angular variable per electron. If the potential energy is not dependent on ϕ, for this problem (an electron on a circle) the Schroedinger equation has the familiar solutions:[10]

$$\begin{aligned} \psi_0 &= 1/\sqrt{2\pi}; & w_0{}^0 &= 0 \\ \psi_{c,k}(\phi) &= \cos\,(k\phi)/\sqrt{\pi} & & \\ \psi_{s,k}(\phi) &= \sin\,(k\phi)/\sqrt{\pi} & w_k{}^0 &= k^2 w_1{}^0;\; k = 1,2,3,\;\ldots \end{aligned} \tag{1}$$

If, however, the central atom is bonded to two or more neighbors, the bond directions correspond to regions of lowered potential energy, in which these oscillating functions will have enhanced second derivatives. A computationally tractable limit is that in which this sharp curvature is concentrated at the bond direction. This corresponds to a δ function in the potential energy, i.e., the limit of a very narrow potential well the product of whose depth and width is a constant λ. The resultant functions have a discontinuous first derivative at each bond, but elsewhere are made up of sinusoidal segments analogous to equations 1. For two bonds at angles $\phi = \alpha$ and $-\alpha$,

$$\begin{aligned} \psi_0(\phi) &= \begin{cases} N\cosh ak\phi & 0 < \phi < \alpha \\ N'\cosh ak(\pi-\phi) & \alpha < \phi < \pi \end{cases} \\ &= \psi_0(-\phi); \qquad w_0 = -a^2 w_1{}^0 \\ \psi_{s,k}(\phi) &= \begin{cases} N\sin ak\phi & 0 < \phi < \alpha \\ N'\sin ak(\pi-\phi) & \alpha < \phi < \pi \end{cases} \\ &= -\psi_{s,k}(-\phi); \qquad w_{s,k} = a^2k^2 w_1{}^0 \\ \psi_{c,k}(\phi) &= \begin{cases} N\cos ak\phi & 0 < \phi < \alpha \\ N'\cos ak(\pi-\phi) & \alpha < \phi < \pi \end{cases} \\ &= \psi_{c,k}(-\phi); \qquad w_{c,k} = a^2k^2 w_1{}^0 \end{aligned} \tag{2}$$

where a is in every case less than one. Two conditions at the bonds suffice to define a and N'/N in each case: the wave functions are continuous, and have cusps such that

$$[d\psi/d\phi]_+ - [d\psi/d\phi]_- = -\psi\cdot\lambda/w_1{}^0 \tag{3}$$

where the subscripts + and − denote derivatives approaching the bond angle from above and below, respectively.

Figure 1 shows the "molecular" energy obtained for $\lambda\cdot w_1{}^0 = 0.5$ for two-, three-, four-, and five-electron pair, by summing the orbital energies as a function of the bond