Acetolysis of (3,5,5-Trimethyl-1-pyrazolin-3-yl)methyl *p*-Bromobenzenesulfonate. Elimination of Nitrogen from an Azo Compound *via* Cationic Intermediates

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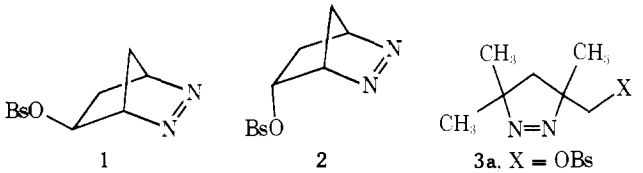
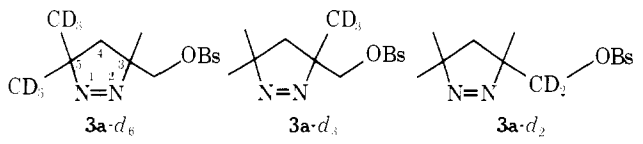
Abstract: Acetolysis of (3,5,5-trimethyl-1-pyrazolin-3-yl)methyl *p*-bromobenzenesulfonate (**3a**) gives a quantitative yield of nitrogen and produces a mixture (100% total yield) of 2,4-dimethyl-4-penten-2-yl acetate, 2,4-dimethyl-1,4-pentadiene, and 2,4-dimethyl-1,3-pentadiene as the only glpc detectable products. The acetolysis kinetics are strictly first order. Comparison of the product and kinetic results with those of model systems indicates that azo compound **3a** eliminates nitrogen with accompanying cation formation and that the -N=N- group anchimerically assists ionization. Studies with deuterium labeled reactants **3a**-d_6, **3a**-d_3, and **3a**-d_2 were made to further delineate the mechanistic details. A variety of isotope effect observations provide unequivocal evidence for a stepwise reaction pathway which is characterized by the intervention of a product-determining intermediate after the rate determining step. The results are interpreted in terms of C-N bond breaking to give a diazonium ion intermediate which loses nitrogen and forms the 3,4-dimethyl-4-penten-2-yl cation.

Until recently it was generally assumed that aliphatic azo compounds lose nitrogen only by free-radical processes.[1] However, new observations make it apparent that the -N=N- group is mechanistically a good deal more versatile than this. A number of examples of nitrogen elimination by concerted pathways without formation of reactive intermediates are now known.[2] In addition, instances of nitrogen loss by way of dipolar ion,[3] cationic,[4] and carbene[5] mechanisms have been reported. Some of these observations suggest new investigations which promise to provide significant information regarding a variety of different important chemical problems. One such research area involves nitrogen elimination which generates cationic intermediates. Accordingly, we have set out to elucidate the mechanistic details of these kinds of processes. Our preliminary work indicated that azo compounds **1, 2,** and **3a** lose nitrogen with accompanying cation formation and that the -N=N- group can anchimerically assist ionization.[4] System **3a** with an assortment of convenient sites for isotope labeling (**3a**-d_6, **3a**-d_3, and **3a**-d_2) is particularly suited for definitive elucidation of mechanism. This paper amplifies the earlier report regarding **3a**,[4b] presents some new results, and discusses the mechanistic implications.



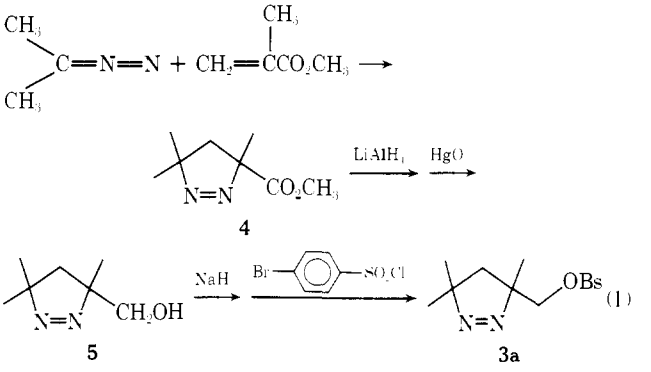
1 2 3a. X = OBs b. X = OAc



3a-d_6 3a-d_3 3a-d_2

Results

Synthesis of System 3. (3,5,5-Trimethyl-1-pyrazolin-3-yl)methyl *p*-bromobenzenesulfonate (**3a**) was prepared from the readily available starting materials 2-diazopropane[6] and methyl 2-methylpropenoate by way of the well-known addition of diazoalkanes to unsaturated C-C bonds.[7] The sequence of steps is presented in eq 1 and the details are given in the Experimental Section. Deuterium labeled structures **3a**-d_6 and **3a**-d_3 were prepared from 2-diazopropane-d_6 and methyl 2-methyl-d_3-propenoate, respectively. Compound **3a**-d_2 was readily available from reduction of **4** with lithium aluminum deuteride. All deuterium containing starting reagents were of >99% isotopic purity and analyses of **3a**-d_6, **3a**-d_3, and **3a**-d_2 by nmr spectroscopy showed the deuterium content to be >99% in the indicated positions.



(1)

4 5 3a

The structures assigned to **4, 5,** and **3a** derive directly from the synthetic method, the expected simple proton nmr spectra with the correct numbers and kinds of signals, and lastly the occurrence of the expected change in the nmr spectra as the deuterium labels were introduced to give **3a**-d_6, **3a**-d_3 and **3a**-d_2, respectively.

Acetolysis Kinetics. Azo *p*-bromobenzenesulfonate (**3a**) was solvolyzed in dry acetic acid buffered with sodium acetate. Rate measurements were made by the usual sealed ampoule technique. Titration of the developing *p*-bromobenzenesulfonic acid was performed with a Metrohm Potentiograph Model E-436 high-precision automatic titrator. The rate constants were calculated from the standard first-order rate law using a least-squares computer program. For determination of the kinetic isotope effects, the acetolyses of labeled and unlabeled *p*-bromobenzenesulfonate were performed simultaneously under identical conditions. The rate constants and the isotope effects are summarized in Table I. Each number used for calculating k_H/k_D represents the average of four kinetic measurements. All rate constants were strictly first order, with the infinity titers being within experimental error of the theoretical value.

A reactivity comparison between **3a** and **3b** was made by subjecting **3b** to the acetolysis conditions at 130°. The azo

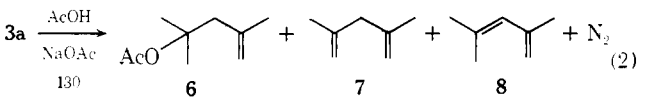
Table I. Acetolysis Rate Data and Secondary Kinetic Isotope Effect Results for 3a, 3a-d_6, 3a-d_3, and 3a-d_2

Compd	ROBs concn, M	Temp, °C	$10^4 k_1$, sec^{-1}	k_H/k_D
3a	0.016[a]	121.0	0.412 ± 0.004	
	0.016[a]	150.0	7.343 ± 0.006[d]	
	0.016[b]	150.0	7.546 ± 0.11	
3a	0.016[a]	130.0	1.098 ± 0.010[e]	
3a-d_6	0.016[a]	130.0	1.117 ± 0.013[e]	0.98 ± 0.03[f]
3a	0.008[c]	130.0	1.121 ± 0.014[e]	
3a-d_3	0.008[c]	130.0	1.103 ± 0.009[e]	1.02 ± 0.03[g,h]
3a	0.008[c]	130.0	1.134 ± 0.010[e]	
3a-d_2	0.008[c]	130.0	0.941 ± 0.006[e]	1.21 ± 0.03[i]

[a] Dry acetic acid with 0.017 M NaOAc. [b] Dry acetic acid without NaOAc. [c] Dry acetic acid with 0.0085 M NaOAc. [d] ΔH^* is 32.1 kcal/mol and ΔS^* is +2.2 eu. [e] Average value from four separate kinetic measurements. Each measurement consisted of simultaneous acetolysis of unlabeled and labeled compounds under identical conditions. [f] For six deuterium atoms. [g] For three deuterium atoms. [h] Two kinetic measurements were made at 0.016 M ROBs and they gave identical rate constants. [i] For two deuterium atoms.

acetate **3b** was stable for at least 25 acetolysis half-lives of **3a**.

Acetolysis Products. Acetolysis of **3a** produced a quantitative yield of nitrogen and a mixture of acetate **6** and dienes **7** and **8** as shown in eq 2; no **3b** acetate was detected.

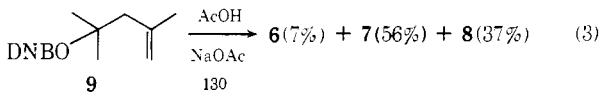


(2)

The organic products were isolated by preparative glpc and identified by nmr spectral comparisons with authentic samples of **6, 7,** and **8.** Control experiments indicated that prolonged heating of the acetolysis mixture resulted in formation of some diene dimer and caused **6** to decompose to **7** and **8.** For this reason product measurements were made at *ca.* 10% acetolysis where dimerization and decomposition were shown to be negligible factors. The product yields and compositions were obtained by glpc using a flame ionization detector. The values were determined from chromatogram peak areas using an internal standard technique and response correction factors obtained from standard mixtures made from the pure compounds. The results for **3a**, **3a-d_6**, **3a-d_3**, and **3a-d_2** are summarized in Table II.

Other Product Studies. Three additional acetolysis product investigations which bear directly on the question of the mechanism for nitrogen elimination from **3a** are relevant.

Reaction of 2,4-dimethyl-4-penten-2-yl 3,5-dinitrobenzoate (**9**) in acetic acid–sodium acetate at 130° for 7 min yielded **6, 7,** and **8** as the only glpc detectable products. Each product was isolated by glpc and its identity was verified by the nmr spectrum. Glpc analysis using the internal standard method showed that acetolysis of **9** had proceeded to the extent of 20–25% under these conditions. The product results are summarized in eq 3.



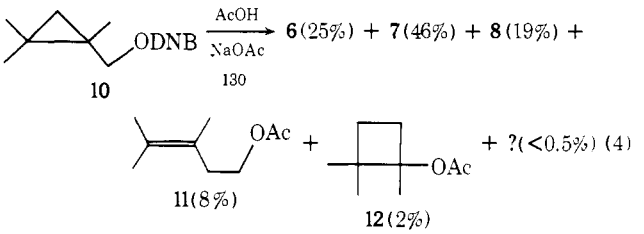
(3)

Acetolysis of (1,2,2-trimethylcyclopropyl)methyl 3,5-dinitrobenzoate (**10**) at 130° for 5 min yielded **6, 7, 8,** and three other products. Glpc analysis indicated 20–25% solvolysis under these conditions. Products **6, 7,** and **8** were isolated by glpc and their identities were confirmed by the nmr spectra. Two of the other products also were isolated. One of these was identified as **11** by nmr spectral comparison with authentic 3,4-dimethyl-3-penten-1-yl acetate. The nmr spectrum of the second compound suggested it to be either 1,2,2-trimethylcyclobutan-1-yl acetate (**12**) or 1,3,3-trimethylcyclobutan-1-yl acetate (**13**). Synthesis of authentic **13** (see Experimental Section) and a comparison of the nmr spectra eliminated this structure from consideration. The second substance thus is assigned structure **12.** The solvolysis results are summarized in eq 4.

Table II. The Effect of Deuterium Substitution on the Product Yield from the Acetolysis of 3a, 3a-d_6, 3a-d_3, and 3a-d_2[a]

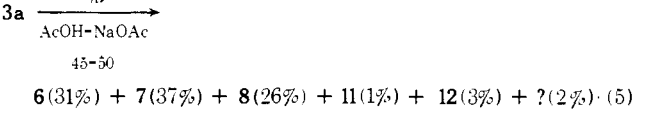
Compd	Temp, °C	% acetolysis[b]	Total % product yield[c,d]	% product composition 6	7	8
3a	121.0	10	100	18.8	37.2	44.0
3a	130.0	9	101	16.8[f]	38.3[f]	44.9[f]
3a-d_6[e]	130.0	9	100	20.6[g]	24.1[g]	55.3[g]
3a-d_3	130.0	9	97	17.9	38.6	43.4
3a-d_2	130.0	9	100	17.2	36.0	46.7

[a] In 0.016 M ROBs and 0.017 M NaOAc. [b] Determined from kinetic data and checked by titration. [c] Determined by glpc using internal standards of tridecane for **6** and *n*-octane for **7** and **8.** Reproducibility ±3%. [d] In a separate experiment, measurement with a gas buret showed a quantitative yield of N_2. [e] The product k_H/k_D value is 1.9. This is based on a calculation from the product ratios of **7** and **8** from **3a** and **3a-d_6** according to the procedure of M. C. Silver, *J. Amer. Chem. Soc.*, **83,** 3487 (1961). [f] Values are the average of four experiments. [g] Values are the average of three experiments.



(4)

As a check on the mechanism, it was of interest to see if **3a** could be induced to produce the products found in eq 4. When irradiated in acetic acid–sodium acetate at 45–50° for 8.5 hr with 3500-Å light, **3a** readily lost nitrogen (72%) and yielded the same six products. The results are listed in eq 5.



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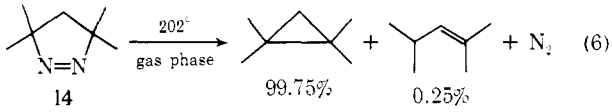
Discussion

Concerning a Diradical Mechanism. The best available evidence indicates that the most common mechanism(s) for the thermal loss of nitrogen from simple cyclic azo compounds with the 1-pyrazoline structure involves diradical-like intermediates.[8,9] Several observations make it clear that **3a** is atypical in this regard and that **3a** loses nitrogen in acetic acid–sodium acetate by a fundamentally different kind of reaction process. If a diradical mechanism was involved, similarities between the acetolysis of **3a** and the gas-phase thermolysis of structurally related 3,3,5,5-tetramethyl-1-pyrazoline (**14**) would be expected. A comparison of the reactivity of the two systems at 121° shows that **3a**

reacts faster than **14** by the substantial factor of 125.[10] The higher reactivity of **3a** is also shown by the fact that acetate **3b** is completely stable to the acetolysis conditions. As shown in eq 6, thermolysis of **14** gives 1,1,2,2-tetramethyl-



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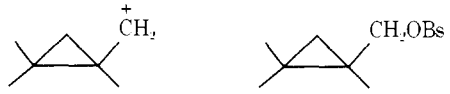
cyclopropane as the product from closure of the diradical intermediate.[9e] If a diradical mechanism was involved in the extrusion of nitrogen from **3a,** the products should include (1,2,2-trimethylcyclopropyl)methyl acetate and/or other compounds which derive from the cyclopropylmethyl cation **15**[11] by way of the diradical closure product (1,2,2-trimethylcyclopropyl)methyl *p*-bromobenzenesulfonate (**16**). These expectations are not realized in the simple ace-

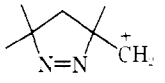


15 16

tolysis of **3a** (eq 2), but they are attainable when an acetic acid solution of **3a** is photolyzed (compare eq 4 and 5[12]). In the latter regard, photodecomposition of 1-pyrazolines is known to produce diradical intermediates which close to cyclopropane derivatives.[9a,13] The results are thus strong evidence that **16** is not an intermediate in reaction 2 and that a diradical mechanism is not involved.

A totally different kind of evidence concerning the formation of diradical intermediates in nitrogen loss from **3a** comes from the kinetic isotope effect studies. Replacement of hydrogen by deuterium on a carbon β to the -N=N- linkage can be expected to cause a secondary kinetic isotope effect of 1.02–1.06 per deuterium for formation of free radicals from azo compounds.[8b,14] Thus C_5—N bond cleavage with radical formation at C_5 would be expected to give an easily detectable isotope effect for **3a–3a**-d_6, with the k_H/k_D ratio being in the range of 1.1–1.3. Cleavage of the C_3—N bond with radical formation at C_3 would be expected to give k_H/k_D ratios between 1.06 and 1.2 for **3a–3a**-d_3 and 1.04 and 1.1 for **3a–3a**-d_2. As shown in Table I, there is no significant isotope effect with **3a–3a**-d_6 or **3a–3a**-d_3 whereas **3a–3a**-d_2 exhibits a very large k_H/k_D value of 1.21. These results collectively also make it evident that a diradical mechanism is not involved in reaction 2. The result with **3a–3a**-d_2 clearly indicates that the $-CH_2-$ unit is involved in the rate-determining step.

A Cationic Mechanism. The foregoing conclusions and a consideration of the nature of the products suggest that extrusion of nitrogen from **3a** during acetolysis occurs by an ionic reaction pathway. In this connection, the product observations offer some insight into the mechanistic details. Failure to observe acetate **3b** is evidence against mechanisms involving the intermediacy of the (3,5,5-trimethyl-1-pyrazolin-3-yl)methyl cation (**17**). The formation of **6, 7,**



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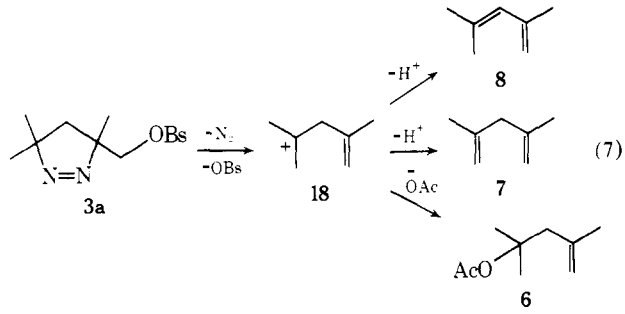
and **8** as the only products rules out mechanisms which involve carbonium ion rearrangements. The correspondence in the structures of the products obtained in the acetolyses of **9** and **3a** strongly implicates the 2,4-dimethyl-4-penten-2-yl cation (**18**) as a key intermediate in the reaction of **3a.** A mechanistic scheme which accounts for the results in terms of **18** is formulated in eq 7.



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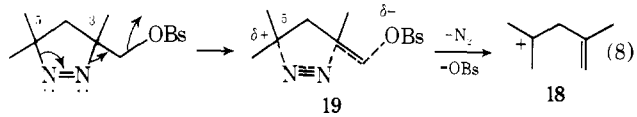
The question of the nature of the ionization–nitrogen elimination step(s) for eq 7 is of fundamental interest. Two attractive possibilities leading to **18** are illustrated by eq 8 and 9.



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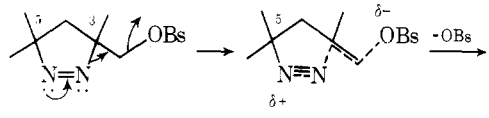

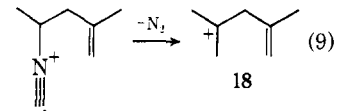

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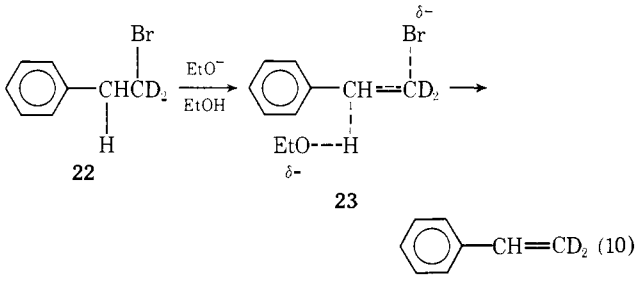
In both transition states **19** and **20,** neighboring group participation involving the -N=N- moiety is indicated. For azo *p*-bromobenzenesulfonates **1** and **2,** the large difference in reactivity of 155 is convincing evidence for anchimerically assisted ionization by the -N=N- group of **1.**[4a] In the case of **3a** a similar geometry favorable for participation is readily available. Since the structure surrounding the -OBs group of **3a** resembles a neopentyl structure, neopentyl *p*-bromobenzenesulfonate is a satisfactory reference compound for estimating the degree of assistance. Direct comparison shows that the reactivity of **3a** and neopentyl *p*-bromobenzenesulfonate is essentially the same, the relative rate being 0.7.[15] This value needs to be corrected for the inductive effects of nitrogen and the double bond. The relative reactivity of *endo*-2-norbornyl *p*-bromobenzenesulfonate and *endo*-**2** provides a reasonable approximation of these factors. Applying the observed relative rate of 160[16,17] to the **3a**-neopentyl *p*-bromobenzenesulfonate comparison leads to a corrected reactivity enhancement of *ca.* 100 for **3a.** It is clear that participation by the -N=N- function is substantial in the ionization step. This is also further confirmation that carbonium ion **17** is not a part of the acetolysis reaction.

The isotope effect results for **3a** and **3a**-d_6 provide criteria for distinguishing between pathways 8 and 9 and for describing the details of the mechanism. If C_5–N bond breaking and charge development at C_5 are important in the rate-determining transition state (**19,** eq 8), the kinetic β-deuterium isotope effect will be large; if there is little C_5–N bond breaking in the rate-determining transition state (**20,** eq 9), the effect will be near unity.[18,19] The observed k_H/k_D value of 0.98 ± 0.03 rules out the totally concerted pathway 8 and supports the stepwise pathway 9. While the rate-determining step remains essentially unchanged upon deuterium substitution at the C_5 methyl groups, the product proportions change markedly (Table II). This amounts to a product k_H/k_D value of 1.9.[20] Lack of a kinetic isotope ef-

fect but the presence of a product isotope effect is unequivocal evidence for the intervention of a product-determining intermediate after the rate-determining step. Candidates for the intermediate are diazonium ion **21** and carbonium ion **18.** Since alkyl diazonium ions lose nitrogen with very low energies of activation and since nitrogen departs from a tertiary carbon of **21,**[21] it is logical to conclude that **18** is responsible for the product isotope effect.

The substantial kinetic secondary α-deuterium k_H/k_D value of 1.21 associated with **3a–3a-d_2** is clear-cut evidence for a rehybridization process occurring at the $-CH_2-$ group during the rate-determining step.[22] The fact that primary carbonium ion **17** does not play an important role in the mechanism and, therefore, that appreciable charge does not develop at the $-CH_2-$ carbon leads to the conclusion that the isotope effect is a consequence of the change to $=CH_2$. This interpretation is in accord with expectations based on the α-deuterium effect in E2 elimination reactions where the α-carbon undergoes a change analogous to that in transition state **20.** An example of this where k_H/k_D is 1.17 is illustrated with the well-studied 2-phenylethyl system in eq 10.[23] This similarity in the magnitude of isotope effects is additional evidence for an ionization–nitrogen elimination process like eq 9. For **22,** the sum of the evidence indicates considerable C–Br bond weakening in transition state **23.**[23,24] On the basis of comparison, it is reasonable to suggest that there is a considerable amount of C–O bond breaking in **20.**



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$$\text{CH=CD}_2 \quad (10)$$

In another regard, the observed lack of significant change in product proportions in going from **3a** to **3a-d_2** (Table II) is in harmony with the mechanistic formulations in eq 7 and 9 since deuterium is located on a carbon of **18** which is not involved in the product-forming step.

The absence of a significant kinetic β-isotope effect with **3a–3a-d_3** indicates that there is little charge development at C_3. In this case, a lack of a product isotope effect is also consistent with eq 7 and 9 since the deuterium-containing carbon of **18** does not become involved in product formation.

In summary, all of the observations with **3a,** the nature of the products, a substantially enhanced reactivity, and the variety of isotope effect results, taken collectively, indicate that the azo compound extrudes nitrogen *via* a cationic mechanism which involves a diazonium ion intermediate. Clearly much work remains to determine the boundaries of this new facet of the chemistry of the azo group. One area of special interest is the possibility of obtaining valuable new mechanistic insight into the intriguing equations associated with deamination and diazonium ion reactions. Further exploration is presently in progress in this laboratory.

Experimental Section

Melting points are uncorrected. Infrared and ultraviolet spectra were obtained with Beckman IR-5A and Cary 14 spectrophotometers, respectively. Proton nmr spectra were recorded with either a Varian A-60 or A-56/60 spectrometer using tetramethylsilane as an internal standard. Analytical glpc measurements were made with a Varian Hi-Fi 111 Model 1200 chromatograph equipped with a flame ionization detector. Preparative separations were carried out with an Aerograph Autoprep Model A-700 instrument. Elemental analyses were obtained from M-H-W Laboratories, Garden City, Mich. Irradiations were performed with a Rayonet Photochemical Reactor Model RPR-100 fitted with either 16 General Electric G8T5 (2500 Å) or 16 F8T5/BLB (3500 Å) lamps.

Deuterated Reactants. Acetone-d_6 was of 99.5% minimum isotopic purity (Diaprep Inc.). Methyl-d_3 iodide had 99.5% minimum isotopic purity (Stohler Isotope Chemicals). Lithium aluminum deuteride was of 99% minimum isotopic purity (Stohler Isotope Chemicals).

3-Carbomethoxy-3,5,5-trimethyl-1-pyrazoline (4). Acetone hydrazone was obtained by a reported procedure[6,25] from acetoneazine and anhydrous hydrazine (96%), bp 115–120° (lit.[6,25] bp 115–120° and 122–126°). 2-Diazopropane was prepared from acetone hydrazone by a procedure based on a reported method.[6] After a cold (−10°) ether solution of 2-diazopropane had been filtered through a cotton plug onto potassium hydroxide pellets and refiltered, it was used directly for reaction. To a cooled solution of 2-diazopropane in 1700 ml of ether which had been prepared from 170 g (2.4 mol) of acetone hydrazone was added 65 g (0.65 mol) of methyl 2-methylpropenoate. At this point the orange-red color of 2-diazopropane had disappeared. After standing overnight, the reaction mixture was dried ($MgSO_4$) and filtered, and the solvent was removed by distillation. The concentrate was distilled under reduced pressure to yield 97 g of **4** (89% based on methyl 2-methylpropenoate): bp 67–73° (1.5 mm); ir (film) 5.76 ($-CO_2CH_3$) and 6.39 μ (-N=N-);[26] uv (hexane) 327 nm (ϵ 163); nmr ($CDCl_3$) δ 1.33 (1 H, doublet, J = 13 Hz), 1.40 (3 H, singlet), 1.45 (3 H, singlet), 1.62 (3 H, singlet), 2.02 (1 H, doublet, J = 13 Hz), 3.75 (3 H, singlet).

Anal. Calcd for $C_8H_{14}N_2O_2$: C, 56.45; H, 8.29; N, 16.46. Found: C, 56.31; H, 8.31; N, 16.35.

(3,5,5-Trimethyl-1-pyrazolin-3-yl)methanol (5). A 30-g (0.18 mol) sample of **4** was added to a stirring slurry of 10 g (0.26 mol) of lithium aluminum hydride in 250 ml of ether cooled to 0°. Following addition, the reaction mixture was heated at reflux for 30 min. The excess lithium aluminum hydride was destroyed by cautious addition of water. After standing overnight, 40 g (0.18 mol) of yellow mercuric oxide was added to the hydrolyzed mixture. Immediate reaction occurred as evidenced by the appearance of black mercury. The mercury and inorganic salts were removed by filtration through a Celite pad, and the filtrate was dried ($MgSO_4$) and filtered again. Removal of the ether and distillation of the concentrate under reduced pressure provided 18 g (72%) of **5,** bp 88–90° (1.2 mm). Upon standing the product crystallized: mp 53–54°; ir (Nujol) 3.03 (-OH) and 6.36 μ (-N=N-);[26] uv (cyclohexane) 328 nm (ϵ 216) (-N=N-);[26] nmr ($CDCl_3$) δ 1.07 (1 H, doublet, J = 12.5 Hz), 1.23 (3 H, singlet), 1.32 (3 H, singlet), 1.38 (3 H, singlet), 1.64 (1 H, doublet, J = 12.5 Hz), 3.30 (1 H, broadened doublet, J = 10 Hz), 3.97 (1 H, broadened doublet, J = 10 Hz).

Anal. Calcd for $C_7H_{14}N_2O$: C, 59.12; H, 9.92; N, 19.70. Found: C, 59.34; H, 9.80; N, 19.95.

(3,5,5-Trimethyl-1-pyrazolin-3-yl)methyl *p*-Bromobenzenesulfonate (3a). To a solution of 4.14 g (29.2 mmol) of **5** in 160 ml of anhydrous ether was added 0.74 g (30.8 mmol) of sodium hydride. The reacting mixture was stirred under reflux for 30 min. The reaction mixture was treated with 7.0 g (27.5 mmol) of *p*-bromobenzenesulfonyl chloride and then was allowed to stir overnight. After this, the reaction mixture was filtered through a Celite pad. Concentration of the filtrate caused white crystals of **3a** to separate (55% yield). Three recrystallizations from ether–pentane provided an analytical sample of **3a:** mp 109–111°, ir (Nujol) 6.39 μ (shoulder) (-N=N-);[26] uv (cyclohexane) 328 nm (ϵ 238) (-N=N-);[26] nmr ($CDCl_3$) δ 1.25 (1 H, doublet, J = 13 Hz), 1.32 (3 H, singlet), 1.37 (6 H, singlet), 1.58 (1 H, doublet, J = 13 Hz), 4.13 (1 H, doublet, J = 10 Hz), 4.36 (1 H, doublet, J = 10 Hz), 7.70 (4 H, singlet).

Anal. Calcd for $C_{13}H_{17}BrN_2O_3S$: C, 43.22; H, 4.75; N, 7.76. Found: C, 43.09; H, 4.79; N, 7.58.

3-Carbomethoxy-3-methyl-5,5-dimethyl-d_6-1-pyrazoline. A sample of 3-carbomethoxy-3-methyl-5,5-dimethyl-d_6-1-pyrazoline was prepared by the sequence given above for **4** using acetone-d_6 hydrazone obtained from acetone-d_6 as the starting material: bp 65–75° (1.6 mm); nmr ($CDCl_3$) δ 1.33 (1 H, doublet, J = 13 Hz), 1.61 (3 H, singlet), 2.02 (1 H, doublet, J = 13 Hz), 3.74 (3

H, singlet). No trace of an nmr signal was detectable at δ 1.40 or 1.45, the signal positions for the C_5 methyl groups of **4**.

(3-Methyl-5,5-dimethyl-d_6-1-pyrazolin-3-yl)methanol. Reduction of 3-carbomethoxy-3-methyl-5,5-dimethyl-d_6-1-pyrazoline with lithium aluminum hydride followed by oxidation with yellow mercuric oxide gave (3-methyl-5,5-dimethyl-d_6-1-pyrazolin-3-yl)methanol: bp 94–96° (1.5 mm); nmr ($CDCl_3$) δ 1.17 (1 H, doublet, J = 12.5 Hz), 1.28 (3 H, singlet), 1.65 (1 H, doublet, J = 12.5 Hz), 3.45 (1 H, doublet, J = 12 Hz), 4.06 (1 H, doublet, J = 12 Hz). No nmr signals attributable to the C_5 methyl groups were discernible.

(3-Methyl-5,5-dimethyl-d_6-1-pyrazolin-3-yl)methyl *p*-Bromobenzenesulfonate (3a-d_6). Reaction of (3-methyl-5,5-dimethyl-d_6-1-pyrazolin-3-yl)methanol with sodium hydride followed by treatment of the resulting salt with *p*-bromobenzenesulfonyl chloride gave a 60% yield of **3a**-d_6: mp 106–108°; nmr ($CDCl_3$) δ 1.24 (1 H, doublet, J = 13 Hz), 1.30 (3 H, singlet), 1.58 (1 H, doublet, J = 13 Hz), 4.13 (1 H, doublet, J = 10 Hz), 4.36 (1 H, doublet, J = 10 Hz), 7.69 (4 H, singlet). The nmr signals for the C_5 methyl groups were totally missing.

Methyl 2-Methyl-d_3-propenoate. The synthesis of methyl 2-methyl-d_3-propenoate was accomplished using a modification of a procedure described for the preparation of other deuterium labeled methyl 2-methylpropenoates.[27]

Dimethyl methyl-d_3-malonate was prepared from 46.6 g (0.35 mol) of dimethyl malonate and 50 g (0.34 mol) of methyl-d_3 iodide in 85% yield by the usual malonic ester alkylation procedure: bp 70–73° (18–19 mm) (lit.[28] unlabeled, bp 68–70° (10 mm)); nmr ($CDCl_3$) δ 3.44 (1 H, broadened singlet), 3.75 (6 H, singlet). The 3 H methyl doublet found at δ 1.41 for dimethyl methylmalonate was not discernible.

An equimolar mixture of dimethyl methyl-d_3-malonate (43 g, 0.29 mol) and potassium hydroxide (16.2 g, 0.29 mol) in absolute methanol (325 ml) was refluxed for 3 hr, neutralized (litmus) with hydrochloric acid, diluted with water, filtered, and then extracted with ether. The combined extracts were dried ($MgSO_4$) and concentrated (distillation). Fractional distillation gave a 54% yield of monomethyl methyl-d_3-malonate: bp 91–94° (0.75 mm) (lit.[29] unlabeled, bp 131° (16 mm)); nmr ($CDCl_3$) δ 3.50 (1 H, broadened singlet), 3.78 (3 H, singlet). The methyl doublet found at δ 1.44 for monomethyl methylmalonate was not observed.

Dropwise addition of 10 g (0.12 mol) of 37% formaldehyde in water to a cold (5°) stirring mixture of 17.5 g (0.13 mol) of monomethyl methyl-d_3-malonate and 8.1 g (0.11 mol) of diethylamine caused gas evolution. While stirring overnight at 5°, the reaction mixture separated into two layers. The upper layer was taken up in ether and the aqueous layer was extracted with ether. The combined ether solution was dried ($MgSO_4$), concentrated, and distilled giving 7.5 g (56%) of methyl 2-methyl-d_3-propenoate: bp 90–93° (650 mm) (lit.[30] unlabeled, bp 100°); nmr ($CDCl_3$) δ 3.76 (3 H, singlet), 5.54 (1 H, doublet, J = 2 Hz), 6.08 (1 H, doublet, J = 2 Hz). The C_2 methyl multiplet found at δ 1.94 for methyl 2-methylpropenoate was not detectable.

3-Carbomethoxy-3-methyl-d_3-5,5-dimethyl-1-pyrazoline. Reaction of methyl 2-methyl-d_3-propenoate with 2-diazopropane as described for **4** gave 3-carbomethoxy-3-methyl-d_3-5,5-dimethyl-1-pyrazoline: bp 67–70° (1.6 mm); nmr ($CDCl_3$) δ 1.33 (1 H, doublet, J = 13 Hz), 1.42 (3 H, singlet), 1.47 (3 H, singlet), 2.04 (1 H, doublet, J = 13 Hz), 3.80 (3 H, singlet). The C_3 methyl signal at δ 1.62 for **4** was not discernible.

(3-Methyl-d_3-5,5-dimethyl-1-pyrazolin-3-yl)methyl *p*-Bromobenzenesulfonate (3a-d_3). 3-Methyl-d_3-5,5-dimethyl-1-pyrazolin-3-yl)methanol, bp 84–89° (0.75 mm), was prepared in a manner analogous to that described for **5** from 3-carbomethoxy-3-methyl-d_3-5,5-dimethyl-1-pyrazoline. The procedure used to prepare **3a** was used to convert the azo-d_3 alcohol to **3a**-d_3: mp 101–104°; nmr ($CDCl_3$) δ 1.25 (1 H, doublet, J = 13 Hz), 1.40 (6 H, singlet), 1.57 (1 H, doublet, J = 13 Hz), 4.13 (1 H, doublet, J = 10 Hz), 4.48 (1 H, doublet, J = 10 Hz), 7.71 (4 H, singlet). The C_3 methyl signal at δ 1.37 for **3a** was completely missing.

(3-Methyl-5,5-dimethyl-1-pyrazolin-3-yl)methyl-d_2 *p*-Bromobenzenesulfonate (3a-d_2). Reduction of **4** with lithium aluminum deuteride in a manner analogous to the method for preparation of **5** gave (3,5,5-trimethyl-1-pyrazolin-3-yl)methan-d_2-ol: bp 79–81° (0.75 mm); nmr ($CDCl_3$) δ 1.18 (1 H, doublet, J = 12.5 Hz), 1.28 (3 H, singlet), 1.36 (3 H, singlet), 1.42 (3 H, singlet), 1.67 (1 H, doublet, J = 12.5 Hz). The 1 H doublets at δ 3.30 and 3.97 for **5** were not discernible.

The procedure used to prepare **3a** was used to convert the azo-d_2 alcohol to **3a**-d_2: mp 107–109°; nmr ($CDCl_3$) δ 1.24 (1 H, doublet, J = 13 Hz), 1.29 (3 H, singlet, 1.35 (6 H, singlet), 1.55 (1 H, doublet, J = 13 Hz), 7.61 (4 H, singlet). The 1 H doublets at δ 4.13 and 4.36 for **3a** were entirely missing.

2,4-Dimethyl-4-penten-2-yl Acetate (6). To a solution of 5.0 g (0.044 mol) of 2,4-dimethyl-4-penten-2-ol (Chemical Samples Co.) in 50 ml of dry ether was added 1.14 g (0.047 mol) of sodium hydride. This slurry was allowed to reflux overnight and then it was cooled to −20°. To this cold mixture was added 4.0 g (0.051 mol) of acetyl chloride dissolved in 10 ml of ether. The reaction mixture was allowed to stir overnight. Following this the salts were removed by filtration, and the ether was removed by distillation. Fractional distillation of the concentrate with a spinning band column gave 3.5 g (51%) of **6**: bp 150–155°; nmr ($CDCl_3$) δ 1.46 (6 H, singlet), 1.78 (3 H, multiplet), 1.95 (3 H, singlet), 2.49 (2 H, broadened singlet), 4.72 (1 H, multiplet), 4.85 (1 H, multiplet).

Anal. Calcd for $C_9H_{16}O_2$: C, 69.19; H, 10.33. Found: C, 69.32; H, 10.27.

2,4-Dimethyl-1,4-pentadiene (7). This diene was obtained from the Chemical Samples Co.: nmr ($CDCl_3$) δ 1.67 (6 H, multiplet), 2.72 (2 H, broadened singlet), 4.76 (4 H, multiplet).

2,4-Dimethyl-1,3-pentadiene (8) was prepared by a published procedure:[31] bp 85–86° (lit.[31a] 89–94° and 91.2–91.5° [31b]); nmr ($CDCl_3$) δ 1.79 (9 H, multiplet), 4.74 (1 H, broadened singlet), 4.89 (1 H, multiplet), 5.64 (1 H, multiplet).

2,4-Dimethyl-4-penten-2-yl 3,5-Dinitrobenzoate (9). To a solution of 4.0 g (0.035 mol) of 2,4-dimethyl-4-penten-2-ol in 60 ml of pyridine at 0° was added 8.25 g (0.036 mol) of 3,5-dinitrobenzoyl chloride. After standing overnight at 0°, the reaction mixture was poured into 100 ml of water and the dinitrobenzoate was recovered by extraction with ether. The combined extract was washed with 3% HCl followed by water, treated with activated charcoal, dried ($MgSO_4$), and filtered. Concentration of the filtrate gave 4 g (37%) of **9**. Two recrystallizations from ether–pentane gave an analytical sample: mp 67–71°; nmr ($CDCl_3$) δ 1.69 (6 H, singlet), 1.85 (3 H, multiplet), 2.72 (2 H, broadened singlet), 4.84 (1 H, multiplet), 4.96 (1 H, multiplet), 9.09 (3 H, multiplet).

Anal. Calcd for $C_{14}H_{16}N_2O_6$: C, 54.54; H, 5.23; N, 9.09. Found: C, 54.31; H, 5.19; N, 9.12.

1-Carbomethoxy-1,2,2-trimethylcyclopropane. A stirred solution of 10 g (0.06 mol) of **4** in 750 ml of pentane was irradiated through quartz for 27 hr with 2537-Å light. After this, the pentane was removed and the concentrate was distilled to give 6.8 g (82%) of 1-carbomethoxy-1,2,2-trimethylcyclopropane: bp 49–52° (20 mm); nmr ($CDCl_3$) δ 0.45 (1 H, doublet, J = 5 Hz), 1.11 (3 H, singlet), 1.16 (3 H, singlet), 1.31 (3 H, singlet), 1.33 (1 H, doublet, J = 5 Hz), 3.65 (3 H, singlet).

Anal. Calcd for $C_8H_{14}O_2$: C, 67.62; H, 9.92. Found: C, 67.70; H, 10.08.

(1,2,2-Trimethylcyclopropyl)methyl 3,5-Dinitrobenzoate (10). Reduction of 1-carbomethoxy-1,2,2-trimethylcyclopropane with lithium aluminum hydride by the usual procedure gave (1,2,2-trimethylcyclopropyl)methanol (80%): bp 56–62° (18 mm); nmr ($CDCl_3$) δ 0.18 (1 H, doublet, J = 4.5 Hz), 0.32 (1 H, doublet, J = 4.5 Hz), 1.12 (3 H, singlet), 1.17 (3 H, singlet), 1.20 (3 H, singlet), 3.49 (1 H, doublet, J = 11 Hz), 3.64 (1 H, doublet, J = 11 Hz).

Anal. Calcd for $C_7H_{10}O$: C, 73.76; H, 12.36. Found: C, 73.63; H, 12.18.

The procedure used to prepare **9** was used to convert (1,2,2-trimethylcyclopropyl)methanol to **10** (64%): mp 83–85°; nmr ($CDCl_3$) δ 0.38 (1 H, doublet, J = 6 Hz), 0.58 (1 H, doublet, J = 6 Hz), 1.25 (6 H, singlet), 1.31 (3 H, singlet), 4.33 (1 H, doublet, J = 11.5 Hz), 4.59 (1 H, doublet, J = 11.5 Hz), 9.13 (3 H, multiplet).

Anal. Calcd for $C_{14}H_{16}N_2O_6$: C, 54.54; H, 5.23; N, 9.09. Found: C, 54.25; H, 5.25; N, 9.06.

3,4-Dimethyl-3-penten-1-yl Acetate (11). An approximately 50:50 mixture of methyl 3,4-dimethyl-3-pentenoate and methyl 3,4-dimethyl-2-pentenoate (bp 64–70° (20 mm)) was prepared by the method[32] used for the corresponding ethyl esters. Reduction of the methyl ester mixture with lithium aluminum hydride in the usual way gave a mixture of 3,4-dimethyl-3-penten-1-ol and 3,4-di-

methyl-2-penten-1-ol (70%), bp 79–81° (22 mm).

To an 8-g (0.07 mol) sample of the alcohol mixture in 100 ml of anhydrous ether was added 2.2 g (0.09 mol) of sodium hydride. After this slurry was refluxed for 2 hr, 5.5 g of acetyl chloride in ether was added and the resulting mixture was refluxed for 1 hr. The salt was removed by filtration through a Celite pad, the filtrate was concentrated, and the residue was distilled to give 6.0 g (55%) of a mixture to two acetates, bp 70–80° (22 mm). The acetates were separated by preparative glpc (15 ft × 0.25 in. column, 15% FFAP on Chromosorb W 60–80 mesh). The characteristic nmr spectra of each component allowed for unequivocal structure assignment.

3,4-Dimethyl-2-penten-1-yl acetate: nmr ($CDCl_3$) δ 1.02 (6 H, doublet, J = 6.5 Hz), 1.65 (3 H, broadened singlet), 2.01 (3 H, singlet), 1.9–2.4 (1 H, septet), 4.55 (2 H, broadened doublet, J = 7 Hz), 5.26 (1 H, multiplet).

3,4-Dimethyl-3-penten-1-yl acetate (**11**): nmr ($CDCl_3$) δ 1.64 (9 H, singlet), 2.01 (3 H, singlet), 2.35 (2 H, triplet, J = 7.5 Hz), 4.05 (2 H, triplet, J = 7.5 Hz).

Anal. Calcd for $C_9H_{16}O_2$: C, 69.19; H, 10.33. Found: C, 69.38; H, 10.54.

1,3,3-Trimethylcyclobutan-1-ol was synthesized from the tosylhydrazone of 2,2-dimethyl-1-acetylcyclopropane by conversion to 1,3,3-trimethylcyclobutene and subsequent oxymercuration–demercuration. 2,2-Dimethyl-1-acetylcyclopropane was prepared by the method described in the literature,[33] bp 55–61° (50 mm) (lit.[33] bp 45–53° (20 mm)). Treatment of this ketone with *p*-toluenesulfonylhydrazine in ethanol containing acetic acid gave the tosylhydrazone (50%), mp 121–125°. Pyrolysis of the tosylhydrazone at 165° based on the procedure described in the literature[34] gave 1,3,3-trimethylcyclobutene (37%): nmr ($CDCl_3$) δ 1.13 (6 H, singlet), 1.64 (3 H, multiplet), 2.10 (2 H, multiplet), 5.68 (1 H, multiplet). Oxymercuration–demercuration of 1,3,3-trimethylcyclobutene by the well-known procedure[35] afforded 1,3,3-trimethylcyclobutan-1-ol (68%): bp 58–61° (38 mm); nmr ($CDCl_3$) δ 1.07 (3 H, singlet), 1.18 (3 H, singlet), 1.37 (3 H, singlet), 1.91 (4 H, singlet).

Anal. Calcd for $C_7H_{10}O$: C, 73.88; H, 12.20. Found: C, 73.63; H, 12.36.

1,3,3-Trimethylcyclobutan-1-yl Acetate (13). The procedure used to prepare **6** was used to convert 1,3,3-trimethylcyclobutan-1-ol to **13**. An analytical sample was isolated by preparative glpc (10 ft × 0.25 in. column, 20% diethylene glycol succinate on Chromosorb W 60–80 mesh); nmr ($CDCl_3$) δ 1.11 (3 H, singlet), 1.14 (3 H, singlet), 1.53 (3 H, singlet), 1.95 (3 H, singlet), 2.08 (4 H, multiplet).

Anal. Calcd for $C_9H_{16}O_2$: C, 69.19; H, 10.33. Found: C, 69.12; H, 10.51.

(3,5,5-Trimethyl-1-pyrazolin-3-yl)methyl Acetate (3b). An authentic sample of acetate **3b** was prepared for product identification purposes and for evaluation of the stability of the 3,5,5-trimethyl-1-pyrazolin-3-yl structure in acetic acid. An 8.0-g (0.078 mol) sample of acetic anhydride was added with stirring to 2.0 g (0.014 mol) of **5** in 20 ml of anhydrous pyridine. After 1 hr the reaction mixture was poured into ice water and then extracted with pentane. The combined extracts were washed with 5% HCl followed by water, dried ($MgSO_4$), concentrated, and then distilled to give **3b:** bp 74–75° (2.5 mm); ir (film) 6.40 (–N=N–)[26] and 5.73 μ (CH_3CO_2–); uv (CH_3OH) 323 nm (ϵ 160); nmr ($CDCl_3$) δ 1.29 (1 H, doublet, J = 13 Hz), 1.38 (3 H, singlet), 1.39 (3 H, singlet), 1.43 (3 H, singlet), 1.52 (1 H, doublet, J = 13 Hz), 2.01 (3 H, singlet), 4.15 (1 H, doublet, J = 11.5 Hz), 4.44 (1 H, doublet, J = 11.5 Hz).

Anal. Calcd for $C_9H_{16}N_2O_2$: C, 57.73; H, 10.23; N, 14.96. Found: C, 57.34; H, 10.14; N, 14.90.

(1,2,2-Trimethylcyclopropyl)methyl Acetate. An authentic sample of this acetate was prepared for product identification purposes from (1,2,2-trimethylcyclopropyl)methanol by the method used to synthesize **6.** An analytical sample of (1,2,2-trimethylcyclopropyl)methyl acetate was obtained *via* preparative glpc (10 ft × 0.25 in. column, 20% diethylene glycol succinate on Chromosorb W 60–80 mesh): nmr ($CDCl_3$) δ 0.23 (1 H, doublet, J = 4.5 Hz), 0.39 (1 H, doublet, J = 4.5 Hz), 1.13 (6 H, singlet), 1.16 (3 H, singlet), 2.06 (3 H, singlet), 3.88 (1 H, doublet, J = 11.5 Hz), 4.16 (1 H, doublet, J = 11.5 Hz).

Anal. Calcd for $C_9H_{16}O_2$: C, 69.19; H, 10.33. Found: C, 69.10; H, 10.38.

2,4-Dimethyl-1,3-pentadiene Dimer. A sample of 2,4-dimethyl-1,3-pentadiene dimer was prepared for comparison purposes. A 2.0-g sample of **8** in 5.0 ml of glacial acetic acid was heated in a sealed Carrius tube at 121° for 6 days. The tube was cooled and opened and the contents were poured in water. After continuous extraction of the aqueous mixture with pentane for 16 hr, the extract was washed with dilute $NaHCO_3$ followed by water, dried ($MgSO_4$), and concentrated by distillation. Preparative glpc isolation (10 ft × 0.25 in. column, 20% diethylene glycol succinate on Chromosorb W 60–80 mesh) of the largest glpc peak gave an analytical sample of dimer. This sample had three groups of signals with an integration ratio of 3:9:12. No attempt was made to assign structure.

Anal. Calcd for $C_{14}H_{24}$: C, 87.41; H, 12.58. Found: C, 87.40; H, 12.68.

Kinetic Measurements. Anhydrous acetic acid containing 0.01 *M* acetic anhydride was prepared in the usual way.[36] The reaction solvent which contained 0.0170 *M* sodium acetate was prepared from the acetic acid by adding a proper amount of primary standard sodium carbonate and enough acetic anhydride to keep the solvent anhydrous. This solvent was refluxed for 18 hr before use. An anhydrous acetic acid solution 0.0160 *M* in perchloric acid was prepared from 69% perchloric acid for use in titration.

All measurements were carried out with acetic acid 0.0170 or 0.0085 *M* in sodium acetate and were conducted by the usual sealed ampoule technique[36] in a precisely controlled constant temperature bath. The progress of the reaction was followed by periodically removing an ampoule from the bath, cooling it, mixing a standardized aliquot (5.025 ml) from the ampoule with an equivalent amount (5.025 ml) of 0.0160 *M* perchloric acid, and back-titrating the resulting solution with 0.0170 *M* sodium acetate. The titrations were performed with a Metrohm Potentiograph Model E-436 high-precision automatic titrator. Isotope effect measurements were made with labeled and unlabeled *p*-bromobenzenesulfonates at the same time under identical conditions. Each of these reported values (Table I) were the average of four kinetic measurements.

Acetolysis Product Studies with 3a, 3a-d_6, 3a-d_3, and 3a-d_2. A reaction flask containing 1.32 g (0.037 mol) of **3a** in 25 ml of 0.0185 *M* sodium acetate in acetic acid was connected by a reflux condenser followed by an Ascarite tube to a gas buret assembly similar to one described by Wiberg.[37] The solution was heated at 117°, and after 7 hr (one half-life for acetolysis) a 50% yield of nitrogen had collected. At this point, the reaction mixture was cooled and poured into water and the aqueous mixture was extracted three times with pentane and then three times with ether. The combined pentane extracts were washed with dilute sodium bicarbonate followed by water, dried ($MgSO_4$), filtered, and concentrated by distillation. Preparative glpc (20 ft × 0.25 in. column, 15% tetraethylene glycol on Chromosorb P 60–80 mesh) resulted in isolation of **7** and **8.** These products had nmr spectra identical with those of authentic diene samples. Additional preparative glpc (15 ft × 0.25 in. column, 15% FFAP on Chromosorb W 60–80 mesh) resulted in isolation of **6** and 2,4-dimethyl-1,3-pentadiene dimer. A separate experiment showed that the dimer product arose from diene **8.** The two products had nmr spectra identical with those of authentic samples. The combined ether extracts were washed with aqueous sodium bicarbonate, dried ($MgSO_4$), filtered, and concentrated. A crystalline white solid was isolated from the concentrate which had spectral properties identical with starting **3a.**

Product compositions and yields for **3a, 3a-d_6, 3a-d_3,** and **3a-d_2** were determined after 9–10% acetolysis. All experiments were carried out in the following manner. A sealed Pyrex tube containing accurately known amounts of the *p*-bromobenzenesulfonate and internal standards octane and tridecane in 0.017 *M* sodium acetate in acetic acid was heated in the constant temperature bath for the appropriate time. After this, the tube was quickly cooled to room temperature, a part of the reaction mixture was titrated for % acetolysis, and the remaining mixture was poured into an equal volume of water. The aqueous mixture was extracted with four portions of pentane, and the combined extracts were stirred with solid sodium bicarbonate and magnesium sulfate. The pentane solution was directly analyzed by glpc with the above columns. The yields are listed in Table II.

Acetolysis Product Study with 9. A sealed Pyrex tube containing 0.050 g of dinitrobenzoate (**9**) and accurately known amounts of octane and tridecane in 10 ml of 0.0170 *M* sodium acetate in acetic acid was placed in a constant temperature at 130° for 7 min. After this, the tube was quickly cooled to room temperature, and the contents were poured into 10 ml of water. The aqueous mixture was extracted with three portions of pentane, and the combined extracts were stirred with solid sodium bicarbonate and magnesium sulfate. Direct analysis of the pentane solution by glpc with the appropriate columns showed **6, 7,** and **8** as the only detectable products. The product composition is listed with eq 3. The total estimated product yield indicated that **9** had solvolyzed to the extent of *ca.* 20–25%.

Acetolysis Product Study with 10. A sealed Pyrex tube containing 1.0 g of dinitrobenzoate **10** in 60 ml of 0.056 *M* sodium acetate in acetic acid was heated at 130° for 70 min. After this, the tube was cooled, and the contents were poured into 60 ml of water. The aqueous mixture was extracted with pentane, and the combined extracts were washed successively with dilute sodium bicarbonate and water. After drying ($MgSO_4$) the pentane solution was concentrated by distillation. Preparative glpc (20 ft × 0.25 in. column, 15% tetraethylene glycol on Chromosorb P 60–80 mesh) resulted in isolation of **7** and **8.** These products showed nmr spectra identical with those of authentic diene samples. Further glpc (15 ft × 0.25 in. column, 15% FFAP on Chromosorb W 60–80 mesh) resulted in the isolation of **6** and two other acetates. Product **6** and one of the other acetates (**11**) had nmr spectra identical with those of authentic samples. The second acetate has an nmr spectrum ($CDCl_3$) characteristic of a cyclobutane derivative: δ 1.06 (3 H, singlet), 1.10 (3 H, singlet), 1.46 (3 H, singlet), 1.95 (3 H, singlet), 1.0–2.3 (4 H, visible but not clearly defined resonances). This spectrum was similar to, but not identical with that of authentic cyclobutane derivative **13.** On this basis, the product was assigned structure **12.**

In a separate experiment, a sealed tube containing 0.021 g of **10** and accurately known amounts of octane and tridecane in 10 ml of 0.017 *M* sodium acetate in acetic acid was placed in a constant temperature bath at 130° for 5 min. After this, the tube was quickly cooled to room temperature, and the contents were worked-up as described for the acetolysis of **9.** Direct glpc analysis of the pentane extract showed the presence of **6, 7, 8, 11, 12,** and a trace of an unknown product with a retention time in the acetate region. No (1,2,2-trimethylcyclopropyl)methyl acetate was detected by the glpc analysis. The product composition is shown with eq 4. The total estimated product yield indicated that **10** had solvolyzed to the extent of *ca.* 20–25%.

Product Study of the Simultaneous Photolysis and Acetolysis of 3a. Into a Pyrex tube connected by an Ascarite column to a gas buret[37] was placed 0.090 g of **3a** in 150 ml of 0.0170 *M* sodium acetate in acetic acid. The mixture was irradiated with 3500-Å light for 8.5 hr at 45–50°. During this period of time a 72% yield of nitrogen was collected. The reaction solution was worked-up in a manner similar to that described for acetolysis of **9.** Glpc analysis showed the presence of **6, 7, 8, 11, 12,** and the unknown product found in the acetolysis of **10.** The product composition is listed with eq 5.

Product Stability Control Experiments. A solution of 0.046 g of acetate **6** and accurately known amounts of octane and tridecane in 25 ml of 0.0170 *M* sodium acetate in acetic acid in a sealed tube was heated at 121° for 5.5 hr. The cooled acetic acid solution was poured into 25 ml of water and the aqueous mixture was extracted with three portions of pentane. After stirring the combined extract with solid sodium bicarbonate and magnesium sulfate, direct glpc analysis showed 41% **6,** 32% **7,** and 27% **8.** The disappearance of 59% **6** in 5.5 hr at 121° corresponds to $k_{dec} = 4.6 \times 10^{-5}$ sec^{-1}.

A solution of 0.062 g of diene **7,** 0.068 g of diene **8,** and an accurately known amount of octane in 50 ml of 0.0170 *M* sodium acetate in a sealed tube was heated at 121° for 5 hr. The acetic acid solution was worked-up and analyzed in a manner similar to that for **6.** Glpc analysis showed both dienes to be present to >90% of the initial amount. A trace of diene dimer was also detected.

A solution containing 0.0078 g of (1,2,2-trimethylcyclopropyl)methyl acetate and accurately known amounts of octane and tridecane was heated in a sealed tube at 130° for 20 min. The acetic acid solution was worked-up in a manner analogous to that used for **6.** Glpc analysis showed 68% of the initial acetate and *ca.* 5% yields of **6, 7,** and **8.**

Stability of 3b. A solution of 0.0316 g of **3b** in 10 ml of 0.0170 *M* sodium acetate in acetic acid was prepared. A 1.5-ml aliquot of this solution diluted to 5 ml with methanol showed an $\epsilon = 159$ at 323 nm. A 2-ml sample of the original solution was heated in a sealed tube at 130° for 45 hr. The value of ϵ for the heated solution was unchanged within experimental error.

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Cis–Trans Isomerism in the Pyridyl Analogs of Azobenzene. A Kinetic and Molecular Orbital Analysis

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Abstract: Rate data have been obtained for cis–trans isomerizations of phenylazopyridines and symmetrical azopyridines in *n*-heptane. Activation energies ranged from 21 to 22.6 kcal mol^{-1}, with the 2- and 4-substituted compounds showing lower activation energies. Although the 2-substituted dyes had low E_a terms, the ΔS^* terms were considerably more negative than those of other compounds in the series. The slower isomerization rates for these compounds are attributed to coulombic interactions between the pyridyl nonbonded electrons and the azo electrons in the activated complex. The 2- and 4-substituted compounds showed a high sensitivity to acid catalysis. An activation energy of 9 kcal mol^{-1} was associated with the acid-catalyzed isomerization of *cis*-4-phenylazopyridine. CNDO/2 calculations were performed on the cis and trans configurations of these dyes and for the transition states. Inversion of one of the azo nitrogens was calculated to be overwhelmingly favored over rotation. Analysis of the results of the MO calculations showed facile inversion to be aided by electron withdrawal by the ring attached to the rehybridizing nitrogen which is manifested by a high C–N_{azo} π density and by a lowered electron density at the p orbital bearing the nonbonded electrons.

Since Hartley first studied the cis–trans isomerization of aromatic azo dyes,[1] a number of additional studies have been conducted.[2] Although both a rotational and an inversional transition state have been suggested for the mode of isomerization, the in-plane inversion mechanism in which one of the azo nitrogens is sp-hybridized in the transition state has found greater favor. Recently, however, the possibility of a rotational activated complex has been suggested[3a] for the isomerization of dipolar compounds substituted with para donor and para′-acceptor groups.[3]

The most remarkable observation for cis–trans isomerizations of para-substituted azobenzenes is nonlinearity in the Hammett plots for these compounds.[2c,f] Talaty and Fargo reported that the rates of isomerization of all para-substituted azobenzenes were greater than those of the parent compound.[2c]

The present study was designed to determine (1) activation parameters for the isomerization of the phenylazopyridines and azopyridines, (2) calculated activation parameters for isomerization, (3) the nature of the activated complex for these reactions, and (4) the electronic requirements for facile isomerization.

Experimental Section

Phenylazopyridines. These were prepared by the method of Campbell, *et al.*,[4] or by the modification of Brown.[5] In a typical procedure, 50 ml of 50% NaOH and 30 ml of pyridine were heated with the aminopyridine (8.0 g, 94 mmol) to 80°. Freshly sublimed nitrosobenzene (12.0 g, 110 mmol) was then added over a 45-min period. After an additional 30-min period, the reaction mixture was cooled and extracted with several portions of benzene. The solutions were dried, reduced *in vacuo*, and chromatographed on alumina. Fractions homogenous to tlc were combined and recrystallized from hexane to constant melting points with the following results: 2-phenylazopyridine (2-PAPy), mp 33–34° (lit.[4] 32–34°); 3-phenylazopyridine (3-PAPy), mp 52° (lit.[4] 52–53°); 4-phenylazopyridine (4-PAPy), 99–99.5° (lit.[4,6] 98–99°).

Azopyridines were synthesized by oxidation of the aminopyridines with NaOCl.[4,7] A cold aqueous solution of the aminopyridine (10 g in 200 ml) was added to 600 ml of 10% NaOCl. The reaction was carried out at 5–10° with a 45-min addition period. Extraction with ether, followed by drying over molecular sieves, reduction of solvent volume, and chromatography gave the azopyridines. Recrystallization from hexane gave crystals melting at 86–87° (lit.[4] 87°) for 2,2′-azopyridine (2,2′-APy); 140–140.5° (lit.[4] 140°) for 3,3′-azopyridine (3,3′-APy); 106.5–107.5° (lit.[4] 107.5–108°) for 4,4′-azopyridine (4,4′-APy).

Photolyses. The cis isomers of the compounds under investigation were generated by irradiation of hydrocarbon solutions of the dyes[8] by a Hanovia high-pressure, mercury-vapor lamp (No. 679A) suspended in an immersion well. The radiation was filtered by means of a Pyrex sleeve. Irradiation times were of the order of 30 min for 5-g samples of the dye.

***cis*-2,2′-APy and *cis*-3,3′-APy** were isolated by the procedures described by Campbell, *et al.*;[4] *cis*-2,2′-APy, mp 85° (lit.[4] 87°); *cis*-3,3′-APy, mp 80° (lit.[4] 82°).

***cis*-3-PAPy** was isolated by alumina column chromatography of irradiated solutions of the trans isomer by varying the eluent from benzene to ether. Recrystallization from hexane gave crystals melting 54–55°.

***cis*-4-PAPy and *cis*-2-PAPy.** A solution of 10 g of *trans*-4-PAPy in 200 ml of cyclohexane was irradiated for 30 min, followed by extraction with 500 ml of a pH 12 buffer. The aqueous extract was