(20) In order to ascertain possible complications arising from trace amounts of water in the Me_2SO, orientation was measured for reactions of **4** induced by *t*-BuOK in the commercial solvent as received and after the solvent had been dried over calcium hydride and distilled under vacuum. Since the results were the same, within experimental error, the Me_2SO was used as received.
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A Study of Substituent Effects on Nitrogen Elimination from Azo Compounds via Cationic Intermediates. Acetolysis of (5-Aryl-3,5-dimethyl-1-pyrazolin-3-yl)methyl Trifluoromethanesulfonates

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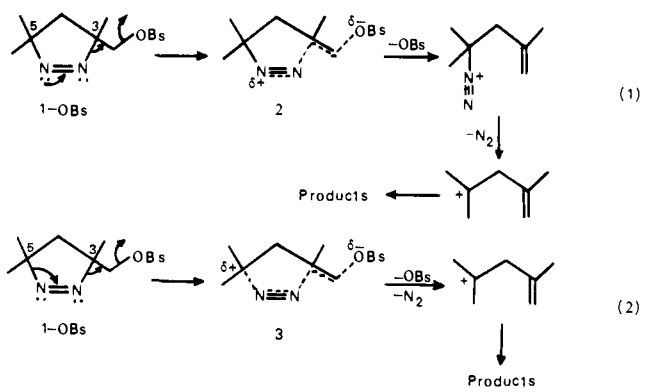
Abstract: Acetolyses of (3,5,5-trimethyl-1-pyrazolin-3-yl)methyl trifluoromethanesulfonate and a series of (5-aryl-3,5-dimethyl-1-pyrazolin-3-yl)methyl trifluoromethanesulfonates containing *p*-CH_3O, *p*-CH_3, *p*-H, and *p*-Cl substituents on the aryl ring were compared to see if the charge-stabilizing 5-aryl groups could induce a concerted one-step ionization–nitrogen elimination mechanism with C_5–N bond breaking in the rate-determining transition state. All acetolysis kinetics were strictly first order. The total reactivity spread for all of the pyrazoline trifluoromethanesulfonates was ca. 6. This compares to an expected total reactivity difference of 10^7 if appreciable C_5–N bond breaking occurs in the rate-determining step. A study with (3,5-dimethyl-5-phenyl-1-pyrazolin-3-yl)methyl and (3-methyl-5-methyl-d_3-5-phenyl-1-pyrazolin-3-yl)methyl trifluoromethanesulfonates showed a kinetic k_H/k_D value of 0.98 ± 0.01 for acetolysis. The products from acetolysis of (3,5-dimethyl-5-phenyl-1-pyrazolin-3-yl)methyl trifluoromethanesulfonate were three isomeric dienes of unrearranged carbon skeleton and a quantitative yield of nitrogen. For the 5-aryl-substituted pyrazoline trifluoromethanesulfonates, all of this is evidence that C_5–N bond breaking is not of importance in the rate-determining step. The results show that a stepwise mechanism involving C_3–N bond breaking in the rate-determining transition state to give a diazonium ion intermediate followed by formation of a 2-aryl-4-methyl-4-penten-2-yl cation is the strongly favored reaction route.

During the last 8 years investigations involving azo compound reactions have shown that the -N=N- group is one of the mechanistically most versatile functional groups in chemistry.[1-9] Examples of reactions by radical,[2,3] zwitterion,[4] carbene,[5] and cationic[6] mechanisms have been reported. Cases of concerted reaction pathways without formation of reactive intermediates[7,8] and retro-Diels–Alder processes[9] also are known.

A current research interest of ours is concerned with the mechanistic details associated with reactions of azo compounds which involve cationic intermediates.[6d] Recently we found that solvolysis of azo-*p*-bromobenzenesulfonate **1**-OBs occurs by way of a cationic mechanism which involves neighboring-group participation and extrusion of nitrogen.[6a,b] Two obvious possibilities for ionization–nitrogen elimination are shown by eq 1 and 2. A number of observations, including the nature of the products, a substantially enhanced reactivity, and a variety of different isotope effects, clearly indicate that **1**-OBs reacts via transition state **2** and eq 1.[6a] We have continued this investigation to learn more about the generality of process 1 and to see if the concerted one-step ionization–nitrogen elimination mechanism 2 can be made to occur. To evaluate these points, we have altered the structure of system **1** to include aryl groups so that the potential ability of C_5 to support positive charge can be varied in a known way. The compounds chosen for study consisted of trifluoromethanesulfonates **1**-OTf and **4**–**7**. In this paper we report the results of the investigation and discuss the mechanistic implications.



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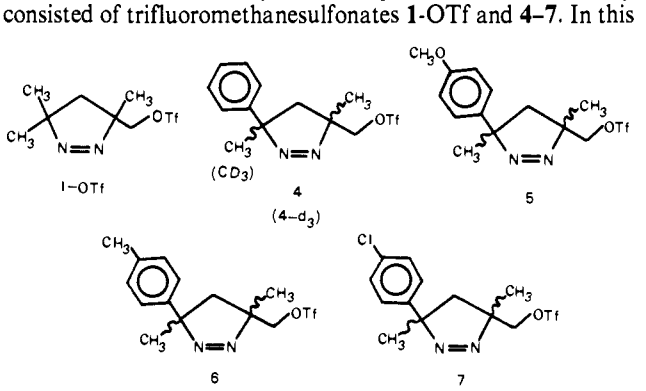

Results

Synthesis of the (5-Aryl-3,5-dimethyl-1-pyrazolin-3-yl)-methyl Systems. The required compounds **4**–**7** were prepared from the appropriate acetophenone and methyl 2-methylpro-

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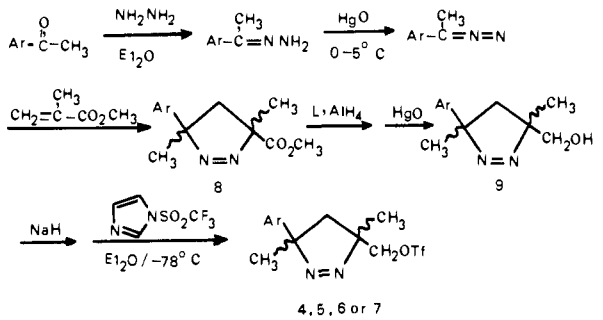
Table I. Acetolysis Rate Data and Secondary Kinetic Isotope Effect Results for **4**, **4**-d_3, and **1**-OBs-d_6

compd	temp, °C	10^4k, s^{-1}	k_H/k_D
4 (90% major isomer)[a,b]	75.09[d]	2.184 ± 0.005	
(90% minor isomer)[a,b]	75.09[d]	2.177 ± 0.004	
(2.3:1 isomer mixture)[a,c]	75.09[d]	2.166 ± 0.088[e]	
4-d_3 (1.5:1 isomer mixture)[a,c]	75.09[d]	2.207 ± 0.074[e]	0.98 ± 0.01[f]
1-OBs[g]	130.0	1.098 ± 0.010	
1-OBs-d_6[g]	130.0	1.117 ± 0.013	0.98 ± 0.03[h]

[a] Dry acetic acid with 0.017 M NaOAc and 0.007–0.01 M **4**. [b] Stereoisomer enrichment accomplished at the alcohol stage (9) by dry column chromatography.[11] [c] The mixture of stereoisomers obtained from ROTf recrystallization. [d] ±0.05 °C. [e] Average value from three separate kinetic measurements. Each measurement consisted of simultaneous acetolysis of **4** and **4**-d_3 under identical conditions. [f] For three deuterium atoms. [g] From ref 6a. [h] For six deuterium atoms.

Scheme I



penoate as key starting materials. The sequence of steps making use of the well-known addition of diazomethane derivatives to unsaturated C–C bonds[10] is presented in Scheme I. A slight modification of the scheme was used to prepare deuterium-labeled structure **4**-d_3 from hydrazine-d_4·D_2O and aceto-d_3-phenone. The deuterium-containing reactants were of >98% isotopic purity and NMR spectral analysis showed the deuterium content of **4**-d_3 to be >98% at the indicated position.

The structures assigned to the intermediates **8** and **9** and to **4–7** derive directly from the synthetic method and from the NMR spectra which all have the correct numbers of the expected $-CH_3$, $-CH_2-$, and aryl proton signals. Examination of the spectra showed that each reaction product consisted of two stereoisomers with ratios in the range of ca. 1.5:1. In the case of **4**, the two components were separated at the alcohol stage by dry column chromatography.[11] However, examination of the kinetic behavior showed that isomer separations or a knowledge of exact configuration is not of importance to the present mechanistic investigation (vide infra). For this reason no attempt was made to assign isomer configuration or to separate the isomer pairs comprising **5, 6,** and **7**.

Reference system **1**-OTf was prepared from known **1**-OH[6a] by the last steps shown in Scheme I.

Acetolysis Kinetics. Azo trifluoromethanesulfonates **1**-OTf and **4–7** were solvolyzed in dry acetic acid buffered with sodium acetate. The rate measurements were made by conventional means. For the general reactivity comparisons of **1**-OTf and **4–7**, titration of the developing trifluoromethanesulfonic acid was carried out with a pH meter–combination electrode system. A Metrohm potentiograph Model E-436 high-precision automatic titrator was used for the kinetic isotope measurements with **4** and **4**-d_3. All rate measurements covered the entire reaction range (ca. 10–90%). The rate constants were calculated from the standard first-order rate law using a least-squares computer program.

The reactivity of system **4** was scrutinized by comparing the rate constant of the synthetic mixture with those obtained from stereoisomer samples which contained about 90% major or 90% minor component. All rate constants were strictly first order, with the same numerical value. Table I summarizes the results.

Table II. Acetolysis Rate Data and Reactivity Comparisons for the (5-Aryl-3,5-dimethyl-1-pyrazolin-3-yl)methyl Trifluoromethanesulfonates[a]

compd	55.1 °C	10^5k, s^{-1} 65.1 °C	75.1 °C	rel rate at 65.1 °C
1-OTf	6.03 ± 0.08	19.7 ± 0.2		1.0
4[b]	1.80 ± 0.01	6.37 ± 0.07		0.32
5[c]		9.35 ± 0.05	30.8 ± 0.5	0.48
6[d]		7.17 ± 0.07	22.7 ± 0.1	0.35
7[e]		3.22 ± 0.05	10.5 ± 0.1	0.16
10[f]		0.0020[g,h]		0.0001

[a] Dry acetic acid with 0.017 M NaOAc and ca. 0.014 M ROTf. [b] A stereoisomer mixture of 2.3:1 after recrystallization. [c] A stereoisomer mixture of 1.2:1 after recrystallization. [d] A stereoisomer mixture of 1.5:1 after recrystallization. [e] A stereoisomer mixture of 1.2:1 after recrystallization. [f] Methyl (3,5-dimethy-5-phenyl-1-pyrazolin-3-yl)methyl ether. [g] Extrapolated from data at higher temperature. k values: 4.38×10^{-4} s^{-1} (152.0 °C); 2.02×10^{-3} s^{-1} (168.7 °C); 5.28×10^{-3} s^{-1} (183.4 °C); 1.72×10^{-2} s^{-1} (197.1 °C). [h] Liquid-phase kinetics measured in diphenyl ether solvent by monitoring nitrogen evolution.

The rate constants for **5, 6,** and **7** were also first order over the full range of reaction with standard deviations of ca. ±2–3% and correlation coefficients >0.999. Any significant difference in stereoisomer reactivity would be reflected by a deviation from first-order kinetic behavior. All of this is clear indication that reactant configuration exerts little, if any, influence on the rate-determining step of the reaction. The pertinent kinetic data and reactivity comparisons are shown in Table II. A reactivity comparison of **1**-OTf and **4–7** acetolyses with the thermolysis of methyl (3,5-dimethyl-5-phenyl-1-pyrazolin-3-yl)methyl ether (**10**) in diphenyl ether solvent also is included.

For the determination of the kinetic isotope effect, the acetolyses of **4** and **4**-d_3 were performed simultaneously under identical conditions. The rate constants and the isotope effect are included in Table I. Each number used for calculating k_H/k_D represents the average of three separate kinetic measurements.

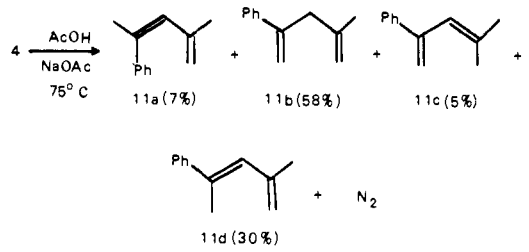
Acetolysis Products. The products from acetolysis of **4** were examined as a further check on mechanism and for comparison of the results with system **1**.[6a] Reaction of **4** in acetic acid–sodium acetate at 75 °C produced a quantitative yield of nitrogen and four GLC-detectable products. The latter were isolated by preparative GLC for identification. They all were shown to be dienes by mass spectra (*m/e* 158, M^+), NMR, and IR comparisons. Two of the products had NMR and IR spectra in good agreement with the data reported[12] for 2-phenyl-4-methyl-1,3-pentadiene and 2-methyl-4-phenyl-1,3-pentadiene. These are shown in eq 3 as **11a** (or **11d**) and **11c**, respectively.[13] Of the possible remaining diene isomers with the same carbon skeleton,[14] one was uniquely distinguishable since it has a single methyl group, a methylene

Table III. Reactivity Comparisons of **4–7** with the *tert*-Benzylic System **15a–d**

substituent	compd	rel rate at 65.1 °C	compd	rel rate at 25 °C[a]
p-CH_3O	**5**	1.5	**15a**	3360[b]
p-CH_3	**6**	1.1	**15b**	26[c]
p-H	**4**	1.0	**15c**	1.0[d]
p-Cl	**7**	0.5	**15d**	0.3[d]

[a] 90% aqueous acetone at 25 °C. [b] Data from ref 18a. [c] Data from ref 18b. [d] Data from ref 18c.

moiety, and four vinyl hydrogens. The NMR spectrum of **11b** was in complete accord with this. Thus, the remaining products have to be the geometric isomers **11a** and **11d**. We have not made a comprehensive configurational assignment in this regard. However, control experiments under acetolysis conditions showed that **11a** and **11b** are stable and that **11d** slowly converted to **11c**. The latter observation suggests that **11a** and **11d** have the *Z* and *E* configurations, respectively (vide infra). Since **11d** proved unstable under the reaction conditions, product composition measurements were made at ca. 11% acetolysis where **11d** → **11c** rearrangement was minimized. Quantitative analysis of the diene mixture from a sample of **4** which had about a 1:1 stereoisomer ratio was obtained by GLC using a flame ionization detector and a digital integrator. The results are summarized in eq 3.

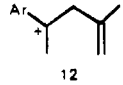


(3)

Discussion

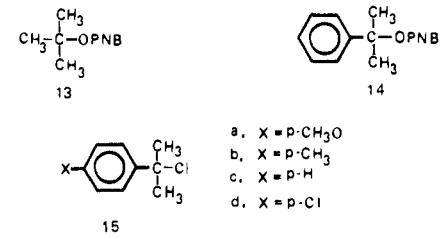
A Cationic Mechanism. Examination of the relative reactivities of **10** and **4–7** is instructive. The rate of thermal extrusion of nitrogen from **10** is in line with what is expected from 5-aryl-1-pyrazolines which undergo decomposition by a 1,3-diradical-like process.[15a] In contrast, the **4–7** acetolyses all proceed by rates $>10^3$ times faster than this. Such major rate enhancements are diagnostic of a different mechanistic pathway for solvolysis.

A comparison of the acetolysis of **1** and **4** provides additional insight. Earlier work has established that **1**-OBs solvolyzes via ionization–nitrogen elimination through a carbocation intermediate which affords dienes as major organic products.[6a] System **4** has a high reactivity like **1**-OTf, and it also gives a substantial yield of dienes.[15b] This correspondence and the similar reactivities of **4–7** are evidence for involvement of 2-aryl-4-methyl-4-penten-2-yl cations (**12**)[16] as key intermediates in the acetolyses of **4–7**.



Information concerning the nature of the ionization–nitrogen elimination step(s) is provided by comparing the reactivities of **1**-OTf and **4–7** with those found for solvolysis of *tert*-benzylic systems **13, 14,** and **15a–d**. The comparison of **4–7** with **15a–d** is summarized in Table III.

It has been observed that replacement of a methyl group in **13** by the phenyl group of **14** increases rate by a factor of 10^3.[17]



The most significant factor here is considered to be charge delocalization in the developing cationic center.[17] For **1**-OTf and **4** the result is opposite with the phenyl group decreasing the rate of **4** by a factor of 3 (Table II). This result is of the correct magnitude to be indicative of the rate-retarding inductive electron-withdrawing effect of the phenyl group when it is not bonded directly to the developing cationic center.[19]

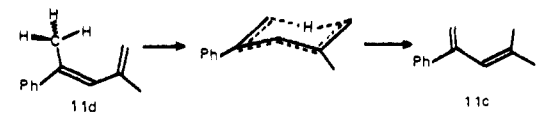
A total reactivity spread of $>10^4$ for **15a** → **15d** is typical of the substituent stabilization effect occurring when charge develops at tertiary carbons. Again, in sharp contrast, the relative rates for **4–7** differ by only a factor of 3. For the latter, the very small rate decrease from *p*-CH_3O to *p*-Cl is in line with inductive contributions from aryl groups not attached to developing cationic centers.[19]

The solvolysis rates for **4–7** also can be submitted to a Hammett treatment. The data treated by the appropriate log k-σ^+ relationship yields a ρ^+ value of only −0.41 with a correlation coefficient of 0.84. When compared to other well-studied systems,[20] this relatively positive ρ value and the poor linear fit of the data indicate that the electronic effects of the substituents have little influence on the solvolysis reactions.

The failure to find any rate enhancement by replacement of the methyl group with a phenyl group, the almost negligible rate effect by substituents on the aryl ring, and the lack of a Hammett substituent correlation are all evidence that little, if any, C_5–N bond breaking occurs in the rate-determining step of the solvolysis reactions of **4–7**.

The kinetic isotope effect observation for **4** and **4**-d_3 provides another kind of criterion for analyzing the question about the nature of the ionization–nitrogen loss mechanism for acetolysis of **4**. If C_5–N bond breaking and cationic charge development at C_5 are significant in the rate-determining transition state, the kinetic β-deuterium isotope effect will be large; if there is no C_5–N bond breaking in the rate-determining transition state, the effect will be near unity.[21,22] The observed k_H/k_D value of 0.98 ± 0.01 entirely rules out the kind of one-step concerted process depicted in eq 2. This kinetic isotope result parallels that found with **1**-OBs[6a] and it affords clear-cut evidence for reaction of **4** by a mechanism analogous to the stepwise pathway observed with **1**-OBs (eq 1).

Source of Product 11c. It is of interest to inquire about the origin of product **11c** since the observations indicate that little, if any, of the diene arises directly from acetolysis. In this connection, control experiments showed that **11a** and **11b** are stable and that **11d** converts to **11c** under reaction conditions. An examination of molecular models suggests a likely pathway for formation of **11c** as a secondary product. Diene **11d** is the one stereoisomer with a conformational arrangement appropriate for a thermally allowed [1,5] sigmatropic shift of a hydrogen atom to give **11c**.[23] This process is formulated in eq 4.[24]



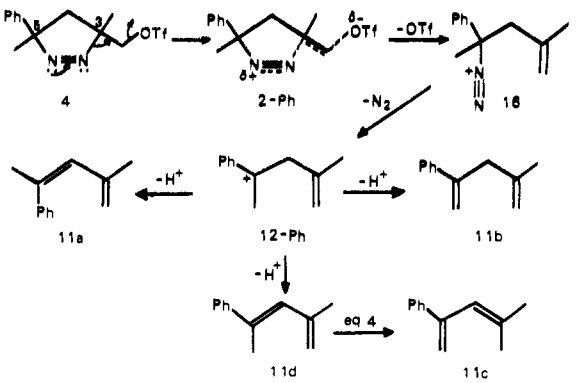
(4)

It is these considerations which have led us to tentatively assign the *E* configuration to **11d**.

Conclusions

A reaction mechanism formulation which accounts for the

Scheme II



currently known facts about the acetolysis of **4** is shown in Scheme II.[25] In view of the relative reactivity relationships, it is likely that **5-7** also solvolyze by the same kind of process.

The above evidence indicates that the stepwise mechanism involving C_3-N bond breaking in the rate-determining transition state to give first a diazonium ion intermediate and then a carbocation intermediate is a strongly favored reaction route.

Experimental Section

Melting points are uncorrected. Ultraviolet and infrared spectra were recorded with Cary 14 and Beckman IR-5A spectrophotometers, respectively. ^{1}H NMR spectra were obtained in $CDCl_3$ with either a Varian A-60 or EM-390 spectrometer using Me_4Si as an internal standard. Analytical GLC measurements were made at 120 °C with a Varian Hi-Fi III Model 1200 instrument equipped with a flame ionization detector, Hewlett-Packard 3370B integrator, and a 500 ft × 0.03 in. stainless steel open tubular column coated with Carbowax 20M. Preparative GLC separations were carried out with an Aerograph Autoprep Model A-700 chromatograph fitted with a 5 ft × 0.25 in. aluminum column packed with 10% Apiezon N on Anakron 70-80 ABS. Preparative dry column chromatography[11] was performed with silica gel (Woelm, dry column grade containing 0.05% inorganic fluorescent indicator) packed in a Nylon column using chloroform as eluent. Elemental analyses were obtained from M-H-W Laboratories, Phoenix, Ariz.

Deuterated Reactants. Aceto-d_3-phenone was prepared from an exchange reaction of acetophenone with 0.5 M NaOD-D_2O (NMR analysis showed 98.5% minimum isotope purity). Deuterium oxide had 99.8% isotopic purity (Stohler Isotope Chemicals). Methanol-d_1 was 99.5% minimum isotopic purity (Diaprep Inc.). Hydrazine hydrate-d_6 was of 98% isotopic purity (Merck Sharp & Dohme Ltd., Canada).

Trifluoromethanesulfonic Imidazolide. This reagent was prepared by a literature procedure[26] which consisted of reacting trifluoromethanesulfonic acid anhydride with imidazole in ethyl ether-dichloromethane at 20 °C.

3-Carbomethoxy-3,5-dimethyl-5-phenyl-1-pyrazoline. Acetophenone hydrazone was prepared by adding a solution of 40 g (0.33 mol) of acetophenone in 50 mL of ether to a stirred solution of 100 g (3.0 mol) of anhydrous hydrazine (97%) and 4.0 g of hydrazine dihydrochloride in 250 mL of ether. After 10 h of reaction time, the ether layer was separated, washed once with 10% aqueous Na_2CO_3 and twice with water, and dried over $MgSO_4$. Removal of the ether gave 40.3 g (91%, crude) of acetophenone hydrazone as a cream-colored liquid. The hydrazone was used immediately in the next reaction.

To a mixture of 70 g (0.32 mol) of red HgO, 10 mL of saturated methanolic KOH, and 250 mL of anhydrous ether cooled to 0 °C was added in portions 50 g (0.37 mol) of the hydrazone. Formation of the diazomethane derivative was monitored by observing the appearance of the intense diazo IR band at 2050 cm^{-1}. After ca. 1-2 days no further increase in the absorption was observed. The mercury sludge was allowed to settle and the deep red colored solution was transferred and collected under nitrogen. The diazo product solution was stirred at 5-10 °C and 50 g (0.05 mol) of methyl 2-methylpropenoate was added during a 15-min period. After the reaction mixture was stirred for 30 min the color was pale yellow. The solvent and excess methyl 2-methylpropenoate were removed by vacuum evaporation to give 32 g (37%) of the pyrazoline ester as a yellow liquid. (In some cases, it was necessary to filter the liquid to remove a small amount of diphenylazine formed during the reaction.) Inspection of the NMR spectrum showed that the product consisted of two stereoisomer components in a ratio of ca. 1.5:1: IR (film) 1740 (-CO_2CH_3) and 1565 cm^{-1} (-N=N-);[27] NMR (major isomer) δ 1.51 (3 H, s, -CH_3), 1.70 (3 H, s, -CH_3), 1.75 and 2.37 (2 H, AB q, $J \sim 13$ Hz, -CH_2-), 3.75 (3 H, s, -OCH_3), 7.28 (5 H, br s, ArH); (minor isomer) δ 1.71 (6 H, s, two -CH_3), 1.67 and 2.43 (2 H, AB q, $J \sim 13$ Hz, -CH_2-), 3.60 (3 H, s, -OCH_3), 7.28 (5 H, br s, ArH).

(3,5-Dimethyl-5-phenyl-1-pyrazolin-3-yl)methanol. A 33.2-g (0.14 mol) sample of the pyrazoline ester in 50 mL of anhydrous ether was added dropwise to a rapidly stirring slurry of 15 g (0.4 mol) of $LiAlH_4$ in 200 mL of ether. Following addition, the reaction mixture was heated at reflux for 24 h. IR examination showed that some ester remained. An additional 5 g (0.13 mol) of $LiAlH_4$ was added and the mixture was refluxed for another 18 h. The excess hydride was destroyed by cautious addition of water at 0 °C. After standing, the solution was decanted into a flask and stirred mechanically at high speed, and then 30 g (0.14 mol) of HgO was added. At the end of 3 h the mercury salts were removed by filtration through a Celite pad, and the filtrate was washed twice with water and dried ($MgSO_4$). Evaporation of the solvent afforded 27.7 g (94%) of the pyrazoline alcohol which consisted of two stereoisomers in a 1.5:1 mixture. Separation by dry column chromatography[11] (vide supra) afforded upper and lower bands. Extraction of each silica gel section with ether followed by evaporation of solvent gave two semisolid alcohol fractions. Repeating the chromatography yielded samples of the major and minor isomers each of >90% purity: IR (film) 3350 (-OH) and 1565 cm^{-1} (-N=N-); NMR (major isomer) δ 1.18 (3 H, s, -CH_3), 1.63 and 2.00 (2 H, AB q, $J \sim 13$ Hz, -CH_2-), 1.74 (3 H, s, -CH_3), 3.60 (1 H, br s, -OH), 3.53 and 4.18 (2 H, AB q, $J \sim 12$ Hz, -CH_2O-), 7.30 (5 H, m, ArH); (minor isomer) δ 1.39 and 2.10 (2 H, AB q, $J \sim 13$ Hz, -CH_2-), 1.40 (3 H, s, -CH_3), 1.65 (3 H, s, -CH_3), 3.20 (1 H, br s, -OH), 3.50 and 4.01 (2 H, AB q, $J \sim 12$ Hz, -CH_2O), 7.30 (5 H, m, ArH).

(3,5-Dimethyl-5-phenyl-1-pyrazolin-3-yl)methyl Trifluoromethanesulfonate (4). To a stirred slurry of 0.31 g (0.013 mol) of NaH in 100 mL of dry ether was added 2.15 g (0.01 mol) of the above pyrazoline alcohol in 15 mL of dry ether. The reaction mixture was refluxed for 30 min, then cooled to −78 °C, and a solution of 2.16 g (0.071 mol) of trifluoromethanesulfonic imidazolide in 15 mL of ether was added dropwise over a 30-min period. The mixture was stirred for an additional 30 min and was then stored overnight at 0 °C. After filtration and evaporation of the solvent, 3.45 g (97%) of trifluoromethanesulfonate **4** was isolated as a pale yellow oil. Purification of this sample by dry column chromatography followed by recrystallization from cold pentane provided crystalline **4**: mp 42-44 °C; UV (dioxane) 330 nm (ϵ 134); IR 1560 (-N=N-), 1415 (-SO_2O-), and 1200 cm^{-1} (-SO_2O-); NMR (90 MHz, CCl_4) (major isomer) δ 1.23 (3 H, s, -CH_3), 1.75 (3 H, s, -CH_3), 1.83 (2 H, s, -CH_2-), 4.56 and 4.88 (2 H, AB q, $J \sim 10$ Hz, -CH_2O-), 7.28 (5 H, br s, ArH); (minor isomer) δ 1.53 (3 H, s, -CH_3), 1.71 (3 H, s, -CH_3), 1.62 and 2.00 (2 H, AB q, $J \sim 13$ Hz, -CH_2-), 4.48 (2 H, s, -CH_2O-), 7.32 (5 H, br s, ArH).

(3,5-Dimethyl-5-phenyl-1-pyrazolin-3-yl)methyl 3,5-Dinitrobenzoate. For the purposes of elemental analyses, the above isomeric mixture of pyrazoline alcohol was converted to the 3,5-dinitrobenzoate derivative by reaction with 3,5-dinitrobenzoyl chloride in pyridine in the usual manner. Recrystallization of the crude product from ethanol provided an analytical sample: mp 152-154 °C; NMR (major isomer) δ 1.32 (3 H, s, -CH_3), 1.83 (3 H, s, -CH_3), 1.95 (2 H, s, -CH_2-), 4.57 and 5.02 (2 H, AB q, $J \sim 12$ Hz, -CH_2O-), 7.30 (5 H, br s, ArH), 9.20 (3 H, m, ArH); (minor isomer) δ 1.62 (3 H, s, -CH_3), 1.67 (3 H, s, -CH_3), 1.4-2.2 (2 H, m, -CH_2-), 4.75 (2 H, s, -CH_2O-), 7.30 (5 H, br s, ArH), 8.60 (2 H, d, ArH), 9.20 (1 H, m, ArH).

Anal. Calcd for $C_{19}H_{18}N_4O_6$: C, 57.28; H, 4.55. Found: C, 57.23; H, 4.34.

(3-Methyl-5-methyl-d_3-5-phenyl-1-pyrazolin-3-yl)methyl Trifluoromethanesulfonate (4-d_3). A mixture of 4.4 g (35.8 mmol) of aceto-d_3-phenone and 6.1 g (80.3 mmol) of hydrazine hydrate-d_6 in 15 mL of methanol-d_1 was heated at reflux for ca. 30 h. After this period, the reaction mixture was cooled, poured into 25 mL of 10% aqueous $NaHCO_3$, and extracted with three 25-mL portions of ether. The combined extracts were washed with two 25-mL portions of water

and dried over $MgSO_4$. Removal of the solvent under vacuum yielded 4.4 g (90%) of hydrazone-d_3 as a pale yellow oil: IR (film) 3400 cm^{-1} (-NH_2); NMR δ 1.98 (0.06 H, s, 98% -CD_3), 5.3 (br s, -NH_2), 7.26 (3 H, m, ArH), 7.60 (2 H, m, ArH). This crude product was used immediately in the next step of the sequence (Scheme I).

A 4.4-g (32 mmol) portion of hydrazone-d_3 was converted by the above-described sequence of steps to give 1.6 g (15% overall yield) of **4**-d_3 as a mixture of two stereoisomers: after recrystallization from pentane mp 40–42 °C; NMR (90 MHz, CCl_4) (major isomer) δ 1.23 (3 H, s, -CH_3), 1.83 (2 H, s, -CH_2-), 4.56 and 4.88 (2 H, AB q, $J \sim$ 10 Hz, -CH_2O-), 7.27 (5 H, br s, ArH); (minor isomer) δ 1.53 (3 H, s, -CH_3), 1.62 and 2.00 (2 H, AB q, $J \sim$ 13 Hz, -CH_2-), 4.48 (2 H, s, -CH_2O-), 7.32 (5 H, br s, ArH). The NMR signals for the C_5 methyl groups of each steroisomer (δ 1.75 and 1.71) were not detectable.

Methyl (3,5-Dimethyl-5-phenyl-1-pyrazolin-3-yl)methyl Ether (10). To a stirring slurry of 0.58 g (0.024 mol) of NaH in 50 mL of anhydrous ether was slowly added 1.84 g (0.009 mol) of the above pyrazoline alcohol in 25 mL of ether. The reaction mixture was stirred at 38 °C for 10 min, 10 mL of iodomethane was added, and the mixture was stirred for 18 h. After this the excess NaH was destroyed with water, the mixture was filtered, and the filtrate was washed twice with saturated aqueous NaCl. Drying the solution (Na_2SO_4) and removal of the solvent gave 1.81 g (86%) of **10** as a crude solid. Recrystallization from pentane–ether afforded a sample of **10**: mp 143–144 °C; NMR (major isomer) δ 1.20 (3 H, s, -CH_3), 1.72 (3 H, s, -CH_3) 1.1–1.6 and 1.95 (2 H, AB q, $J \sim$ 13 Hz, -CH_2-, exact position of one doublet hidden), 3.35 (3 H, s, -OCH_3), 3.45 and 3.88 (2 H, AB q, $J \sim$ 10 Hz, -CH_2O-), 7.28 (5 H, m, ArH); (minor isomer) δ 1.42 (3 H, s, -CH_3), 1.67 (3 H, s, -CH_3), 1.1–1.6 and 2.10 (2 H, AB q, $J \sim$ 13 Hz, -CH_2-, exact position of one doublet hidden), 3.22 (3 H, s, -OCH_3), 3.55 and 3.70 (2 H, AB q, $J \sim$ 10 Hz, -CH_2O-), 7.28 (5 H, m, ArH).

(3,5,5-Trimethyl-1-pyrazolin-3-yl)methyl Trifluoromethanesulfonate (1-OTf). A 1.5-g (0.010 mol) sample of (3,5,5-trimethyl-1-pyrazolin-3-yl)methanol[6a] was treated with 0.3 g (0.016 mol) of NaH in 200 mL of anhydrous ether and then reacted with 2.2 g (0.011 mol) of trifluoromethanesulfonic imidazolide as outlined above for the preparation of **4**. The workup afforded 2.9 g of crude product. Purification by dry column chromatography and recrystallization from pentane yielded **1**-OTf as a colorless, crystalline solid: mp 32–34 °C; UV (dioxane) 326 nm (ϵ 204); IR (film) 1565 (-N=N-), 1415 (-OSO_2-), and 1220 cm^{-1} (-OSO_2-); NMR δ 1.46 (11 H, apparent overlapping singlets), 4.50 and 4.92 (2 H, AB q, $J \sim$ 10 Hz, -CH_2O-).

3-Carbomethoxy-3,5-dimethyl-5-(*p*-chlorophenyl)-1-pyrazoline. *p*-Chloroacetophenone hydrazone was prepared, as described above, from 80 g (0.52 mol) of *p*-chloroacetophenone, 150 mL of anhydrous hydrazine (97%), and 3 g of hydrazine dihydrochloride. The hydrazone was a waxy solid: NMR δ 2.06 (3 H, s, -CH_3), 5.40 (2 H, br s, -NH_2), 7.28 and 7.58 (4 H, AB q, $J \sim$ 10 Hz, ArH). This material was used immediately without further purification.

A 50-g (0.3 mol) sample of the hydrazone, 50 g (0.23 mol) of red HgO, and 7 mL of saturated methanolic KOH in 600 mL of anhydrous ether were converted to the corresponding diazomethane derivative by the procedure outlined above. After 4 h reaction time, the deep purple liquid mixture was removed by decantation, 50 g (0.5 mol) of methyl 2-methylpropenoate was added, and the resulting solution was stirred overnight. The workup yielded 52 g (65%) of the pyrazoline ester as a yellow liquid. The NMR spectrum showed a mixture of two stereoisomers in a 1.5:1 ratio: NMR (major isomer) δ 1.55 (3 H, s, -CH_3), 1.68 (3 H, s, -CH_3), 1.3–2.5 (2 H, m, -CH_2-), 3.78 (3 H, s, -OCH_3), 7.32 (4 H, s, ArH); (minor isomer) δ 1.65 (3 H, s, -CH_3), 1.68 (3 H, s, -CH_3), 1.3–2.5 (2 H, m, -CH_2-), 3.65 (3 H, s, -OCH_3), 7.32 (4 H, s, ArH). The product was used directly without further purification.

[3,5-Dimethyl-5-(*p*-chlorophenyl)-1-pyrazolin-3-yl]methyl Trifluoromethanesulfonate (7). A 15-g (0.056 mol) sample of the chloro pyrazoline ester was reduced with 4 g (0.11 mol) of $LiAlH_4$ in 200 mL of anhydrous ether. The reaction slurry was worked up and then treated with 17 g (0.078 mol) of HgO as described above. The recovered concentrate consisting of two stereoisomers was cleaned up by chromatography (no separation attempted) yielding 10.1 g (76%) of chloro pyrazoline alcohol: NMR (major isomer) δ 1.42 (3 H, s, -CH_3), 1.65 (3 H, s, -CH_3), 1.1–2.1 (2 H, m, -CH_2-), 2.50 (1 H, br s, -OH), 3.53 and 4.23 (2 H, AB q, $J \sim$ 12 Hz, -CH_2O-), 7.33 (4 H, m, ArH); (minor isomer) δ 1.18 (3 H, s, -CH_3), 1.73 (3 H, s, -CH_3), 1.1–2.1 (2 H, m, -CH_2-), 2.50 (1 H, br s, -OH), 3.50 and 4.11 (2 H, AB q, $J \sim$ 12 Hz, -CH_2O-), 7.33 (4 H, m, ArH).

A 5-g (0.021 mol) sample of the alcohol was reacted with 0.57 g (0.024 mol) of NaH in dry ether and then with 4.5 g (0.023 mol) of trifluoromethanesulfonic imidazolide as described above. The reaction workup afforded 4.3 g (76%) of **7**: mp 52–54 °C; NMR (major isomer) δ 1.21 (3 H, s, -CH_3), 1.73 (3 H, s, -CH_3), 1.2–2.2 (2 H, m, -CH_2-), 4.54 and 5.02 (2 H, AB q, $J \sim$ 10 Hz, -CH_2O-), 7.33 (4 H, br s, ArH); (minor isomer) δ 1.52 (3 H, s, -CH_3), 1.70 (3 H, s, -CH_3), 1.2–2.2 (2 H, m, -CH_2-), 4.48 and 4.84 (2 H, AB q, $J \sim$ 10 Hz, -CH_2O-), 7.33 (4 H, br s, ArH).

The chloro pyrazoline alcohol was converted to the 3,5-dinitrobenzoate derivative for the purpose of elemental analyses. An analytical sample, mp 128–130 °C, was secured by recrystallization from ethanol: NMR (major isomer) δ 1.28 (3 H, s, -CH_3), 1.81 (3 H, s, -CH_3), 1.91 (2 H, s, -CH_2-), 4.56 and 5.0 (2 H, AB q, $J \sim$ 12 Hz, -CH_2O-), 7.30 (4 H, br s, ArH), 8.60 (1 H, d, ArH), 9.17 (2 H, m, ArH); (minor isomer) δ 1.57 (6 H, s, two -CH_3), 1.5–1.9 and 2.20 (2 H, AB q, $J \sim$ 12 Hz, -CH_2-, exact position of one doublet hidden), 4.74 (2 H, s, -CH_2O-), 7.00 and 7.21 (4 H, AB q, $J \sim$ 8 Hz, ArH), 8.60 (1 H, d, ArH), 9.17 (2 H, m, ArH).

Anal. Calcd for $C_{19}H_{17}N_4O_6Cl$: C, 52.73; H, 3.96. Found: C, 52.60; H, 3.79.

3-Carbomethoxy-3,5-dimethyl-5-(*p*-methoxyphenyl)-1-pyrazoline. The reaction of 80 g (0.53 mol) of *p*-methoxyacetophenone with 150 mL of anhydrous hydrazine (97%) and 3 g of hydrazine dihydrochloride in 200 mL of dry ether as described above yielded 76.5 g (88%) of the hydrazone as a colorless, crystalline solid: NMR δ 2.08 (3 H, s, -CH_3), 3.78 (3 H, s, -OCH_3), 5.25 (2 H, br s, -NH_2), 6.84 and 7.56 (4 H, AB q, $J \sim$ 9 Hz, ArH). The crude hydrazone was used immediately without purification.

A 45-g (0.27 mol) sample of the hydrazone, 50 g (0.23 mol) of red HgO, and 10 mL of saturated methanolic KOH in 300 mL of dry ether slowly converted to the red-colored diazomethane derivative. After 24 h the red ether mixture was separated and then reacted with 45 g (0.45 mol) of methyl 2-methylpropenoate. The workup gave 11.6 g (16%) of the pyrazoline ester as a semisolid product which the NMR spectrum showed to consist of a 1.5:1 mixture of two stereoisomers: NMR (major isomer) δ 1.52 (3 H, s, -CH_3), 1.67 (3 H, s, -CH_3), 1.4–2.5 (2 H, m, -CH_2-), 3.57 (3 H, s, -OCH_3), 3.72 (3 H, s, -OCH_3), 6.84 and 7.23 (4 H, AB q, $J \sim$ 8 Hz, ArH); (minor isomer) δ 1.64 (3 H, s, -CH_3), 1.67 (3 H, s, -CH_3), 1.4–2.5 (2 H, m, -CH_2-), 3.65 (3 H, s, -OCH_3), 3.76 (3 H, s, -OCH_3), 6.84 and 7.23 (4 H, AB q, $J \sim$ 8 Hz, ArH).

[3,5-Dimethyl-5-(*p*-methoxyphenyl)-1-pyrazolin-3-yl]methyl Trifluoromethanesulfonate (5). A 26-g (0.1 mol) sample of the methoxy pyrazoline ester was reduced with 15 g (0.4 mol) of $LiAlH_4$ in 200 mL of dry ether. The reaction mixture was allowed to reflux for 60 h and then worked up as described above. Treatment of the ether solution with 26 g (0.12 mol) of HgO and removal of the mercury salts and solvent yielded 8.5 g (37%) of pyrazoline alcohol as a mixture of two stereoisomers: NMR (major isomer) δ 1.18 (3 H, s, -CH_3), 1.74 (3 H, s, -CH_3), 1.63 and 1.95 (2 H, AB q, $J \sim$ 12 Hz, -CH_2-), 2.20 (1 H, br s, -OH), 3.55 and 4.22 (2 H, AB q, $J \sim$ 12 Hz, -CH_2O-), 3.80 (3 H, s, -OCH_3), 6.84 and 7.24 (4 H, AB q, $J \sim$ 8 Hz, ArH); (minor isomer) δ 1.40 (3 H, s, -CH_3), 1.64 (3 H, s, -CH_3), 1.3–1.8 and 2.10 (2 H, AB q, $J \sim$ 12 Hz, -CH_2-, exact position of one doublet hidden), 2.20 (1 H, br s, -OH), 3.51 and 4.08 (2 H, AB q, $J \sim$ 12 Hz, -CH_2O-), 3.80 (3 H, s, -OCH_3), 6.82 and 7.20 (4 H, AB q, $J \sim$ 8 Hz, ArH).

A 4-g (0.017 mol) sample of the alcohol was reacted with 0.47 g (0.019 mol) of NaH in anhydrous ether and then with 3.9 g (0.02 mol) of trifluoromethanesulfonic imidazolide as previously described. Workup, purification by chromatography (no isomer separation was attempted), and recrystallization from pentane produced 3.5 g (56%) of **5**: mp 44–46 °C; NMR (major isomer) δ 1.23 (3 H, s, -CH_3), 1.73 (3 H, s, -CH_3), 1.0–2.0 (2 H, m, -CH_2-), 3.80 (3 H, s, -OCH_3), 4.55 and 4.98 (2 H, AB q, $J \sim$ 10 Hz, -CH_2O-), 6.85 and 7.20 (4 H, AB q, $J \sim$ 8 Hz, ArH); (minor isomer) δ 1.50 (3 H, s, -CH_3), 1.68 (3 H, s, -CH_3), 1.0–2.0 (2 H, m, -CH_2-), 3.80 (3 H, s, -OCH_3), 4.45 and 4.78 (2 H, AB q, $J \sim$ 10 Hz, -CH_2O-), 6.85 and 7.20 (4 H, AB q, $J \sim$ 8 Hz, ArH).

The 3,5-dinitrobenzoate derivative of the methoxy pyrazoline alcohol was prepared for obtaining elemental analyses. An analytical sample, mp 149–151 °C, was obtained by recrystallization from

ethanol: NMR (major isomer) δ 1.22 (3 H, s, $-CH_3$), 1.72 (3 H, s, $-CH_3$), 1.82 (2 H, s, $-CH_2-$), 3.70 (3 H, s, $-OCH_3$), 4.46 and 4.87 (2 H, AB q, $J \sim 12$ Hz, $-CH_2O-$), 7.00 and 7.30 (4 H, AB q, $J \sim 10$ Hz, ArH), 9.17 (3 H, m, ArH); (minor isomer) δ 1.62 (6 H, s, two $-CH_3$), 1.50–2.0 (2 H, m, $-CH_2-$), 3.55 (3 H, s, $-OCH_3$), 4.75 (2 H, s, $-CH_2O-$), 7.32 (4 H, s, ArH), 8.63 (1 H, d, ArH), 9.17 (2 H, m, ArH).

Anal. Calcd for $C_{20}H_{20}N_4O_7$: C, 56.07; H, 4.60. Found: C, 56.21; H, 4.71.

3-Carbomethoxy-3,5-dimethyl-5-(*p*-methylphenyl)-1-pyrazoline. The reaction of 80 g (0.59 mol) of *p*-methylacetophenone with 125 mL of anhydrous hydrazine (97%) and 1 g of hydrazine dihydrochloride as previously described gave 84 g (97%) of crystalline hydrazone: NMR δ 2.08 (3 H, s, $-CH_3$), 2.30 (3 H, s, $-CH_3$), 5.40 (2 H, br s, $-NH_2$), 7.20 and 7.60 (4 H, AB q, $J \sim 8$ Hz, ArH). The crude product was used immediately in the following reaction.

As described above, 19.5 g (0.13 mol) of the hydrazone, 20 g (0.09 mol) of HgO, and 5 mL of saturated methanolic KOH in 200 mL of dry ether reacted slowly over 24 h to give a red mixture of the diazomethane derivative. The red solution was separated by decantation and 20 g (0.2 mol) of methyl 2-methylpropenoate was added to the solution. Workup of the reaction mixture afforded 9.1 g (28%) of yellow semisolid pyrazoline ester composed of a 1.5:1 mixture of two stereoisomers: NMR (major isomer) δ 1.52 (3 H, s, $-CH_3$), 1.69 (3 H, s, $-CH_3$), 1.3–1.9 (2 H, m, $-CH_2-$), 2.33 (3 H, s, $ArCH_3$), 3.76 (3 H, s, $-OCH_3$), 7.20 (4 H, br s, ArH); (minor isomer) δ 1.67 (3 H, s, $-CH_3$), 1.69 (3 H, s, $-CH_3$), 1.3–1.9 (2 H, m, $-CH_2-$), 2.33 (3 H, s, $ArCH_3$), 3.64 (3 H, s, $-OCH_3$), 7.20 (4 H, br s, ArH).

[3,5-Dimethyl-5-(*p*-methylphenyl)-1-pyrazolin-3-yl]methyl Trifluoromethanesulfonate (6). A 9.1-g (0.04 mol) sample of the methyl pyrazoline ester was reduced with 12 g (0.32 mol) of $LiAlH_4$ in 200 mL of anhydrous ether. The reaction mixture was allowed to reflux for 60 h and then was worked up as described previously. Treatment of the ether solution with 26 g (0.12 mol) of HgO followed by removal of the mercury salts and solvent afforded 6.1 g (76%) of a pyrazoline alcohol mixture of two stereoisomers: IR (film) 3500 (–OH) and 1585 cm^{-1} ($-N{=}N-$); NMR (major isomer) δ 1.14 (3 H, s, $-CH_3$), 1.73 (3 H, s, $-CH_3$), 1.2–1.8 (2 H, m, $-CH_2-$), 2.33 (3 H, s, $ArCH_3$), 3.10 (1 H, br s, –OH), 3.52 and 4.20 (2 H, AB q, $J \sim 10$ Hz, $-CH_2O-$), 7.15 (4 H, br s, ArH); (minor isomer) δ 1.40 (3 H, s, $-CH_3$), 1.66 (3 H, s, $-CH_3$), 1.2–1.8 (2 H, m, $-CH_2-$), 2.33 (3 H, s, $ArCH_3$), 3.10 (1 H, br s, –OH), 3.50 and 4.05 (2 H, AB q, $J \sim 10$ Hz, $-CH_2O-$), 7.15 (4 H, br s, ArH).

A 4-g (0.018 mol) sample of the pyrazoline alcohol was reacted with 0.5 g (0.021 mol) of NaH in 200 mL of dry ether and then as described above with 3.9 g (0.02 mol) of trifluoromethanesulfonic imidazolide. Workup, purification by chromatography (no isomer separation attempted), and recrystallization from pentane afforded 3.1 g (49%) of **6**: mp 55–57 °C; NMR (major isomer) δ 1.23 (3 H, s, $-CH_3$), 1.73 (3 H, s, $-CH_3$), 1.85 (2 H, s, $-CH_2-$), 2.33 (3 H, s, $ArCH_3$), 4.55 and 4.98 (2 H, AB q, $J \sim 10$ Hz, $-CH_2O-$), 7.15 (4 H, br s, ArH); (minor isomer) δ 1.52 (3 H, s, $-CH_3$), 1.70 (3 H, s, $-CH_3$), 1.4–1.8 (2 H, m, $-CH_2-$), 2.33 (3 H, s, $ArCH_3$), 4.46 and 4.75 (2 H, AB q, $J \sim 10$ Hz, $-CH_2O-$), 7.15 (4 H, br s, ArH).

The methyl pyrazoline alcohol was converted to the 3,5-dinitrobenzoate for the purpose of obtaining elemental analyses. Recrystallization of the crude product gave an analytical sample: mp 165–166 °C; NMR δ 1.32 (3 H, s, $-CH_3$), 1.83 (3 H, s, $-CH_3$), 1.93 (2 H, s, $-CH_2-$), 2.35 (3 H, s, $ArCH_3$), 4.58 and 5.00 (2 H, AB q, $J \sim 12$ Hz, $-CH_2O-$), 7.23 (4 H, br s, ArH), 9.17 (3 H, m, ArH).

Anal. Calcd for $C_{20}H_{20}N_4O_6$: C, 58.25; H, 4.89. Found: C, 57.99; H, 4.86.

Measurement of the Thermolysis Kinetics of 10. The rate measurements were made with a solution of 166 mg of **10** in 1.808 g of solvent consisting of 90% diphenyl ether and 10% isoquinoline (both freshly distilled). A 0.5-mL sample of the solution was injected into 15 mL of the diphenyl ether solvent contained in an apparatus at temperature equilibrium in a precisely controlled constant-temperature bath. This apparatus follows the rate of decomposition by monitoring nitrogen evolution with a sensitive pressure transducer.[28] The rate constant values are listed in footnote *g*, Table II.

Acetolysis Kinetic Measurements. The acetic acid and titrant solution were prepared as described previously.[6a] The reaction solvent was acetic acid containing 0.017 M sodium acetate. For the general measurements of **1**-OTf and **4**–**7**, the reactions were carried out at ca. 0.01 M ROTf in stoppered 50-mL volumetric flasks placed in a constant-temperature bath at the desired temperature. The progress of the reaction was followed by periodically removing a sample with a pipet, delivering a standardized aliquot (3.00 mL) into 10 mL of cold acetic acid, and then titrating this solution with 0.016 M perchloric acid in acetic acid. The end points were determined with a Beckman pH meter equipped with a 39142-B7 combination electrode. Rate constant values are listed in Tables I and II.

Isotope effect measurements were conducted with **4** and **4**-d_3 by the usual sealed ampule technique.[29] Sets of **4** and **4**-d_3 solutions were solvolyzed at the same time under identical conditions. The standardized aliquot samples (4.02 and 4.09 mL) were titrated using a Metrohm potentiograph Model E-436 high-precision automatic titrator. Each of the values reported for **4** and **4**-d_3 (Table I) was the average of three kinetic measurements.

All rate measurements covered the reaction range of ca. 10–90%. The stereoisomer ratios are listed in Tables I and II. Rate constants were calculated with a least-squares computer program setup based on the usual standard first-order rate law.

Acetolysis Product Studies with 4. For product isolation and identification, a 1.5-g (4.5 mmol) sample of **4** in 10 mL of acetic acid 0.54 M in sodium acetate was kept in a constant-temperature bath at 75 °C for 18 h. After this the reaction mixture was cooled and poured into a saturated aqueous $NaHCO_3$ solution and the mixture was extracted with three portions of ether. The combined extract was washed with dilute aqueous $NaHCO_3$ and water, and then was dried ($MgSO_4$). After the solvent was removed by distillation, preparative GLC of the concentrate afforded four diene products **11a**, **11b**, **11c**, and **11d** listed in order of retention time.

2-Methyl-4-phenyl-1,3-pentadiene (**11a**): IR ($CHCl_3$) 3085, 1625, 1600, 1490, 1440, 1375, 860 cm^{-1}; NMR δ 1.45 (3 H, s, $-CH_3$), 2.08 (3 H, s, $-CH_3$), 4.77 (2 H, br s), 6.10 (1 H, br s), 7.25 (5 H, br s, ArH); *m/e* 158.2 (M^+). **11a** was tentatively assigned the *Z* configuration (vide supra).

2-Phenyl-4-methyl-1,4-pentadiene (**11b**): IR ($CHCl_3$) 3070, 1650, 1625, 1495, 1450, 1380, 890 cm^{-1}; NMR δ 1.72 (3 H, s, $-CH_3$), 3.24 (2 H, s, $-CH_2-$), 4.80 (2 H, br s), 5.14 (1 H, m), 5.42 (1 H, d, $J \sim 1$ Hz), 7.35 (5 H, m, ArH); *m/e* 158.2 (M^+).

Anal. Calcd for $C_{12}H_{14}$: C, 91.08; H, 8.92. Found: C, 91.12; H, 8.99.

2-Phenyl-4-methyl-1,3-pentadiene (**11c**): IR ($CHCl_3$) 3080, 1640, 1605, 1485, 1445, 1370, 880, 840 cm^{-1}; NMR δ 1.68 (3 H, d, $J \sim 1.8$ Hz), 1.86 (3 H, d, $J \sim 1.8$ Hz), 5.07 (1 H, m), 5.50 (1 H, d, $J \sim 2$ Hz), 5.93 (1 H, m), 7.30 (5 H, m);[12] *m/e* 158.2 (M^+).

2-Methyl-4-phenyl-1,3-pentadiene (**11d**): IR ($CHCl_3$) 3085, 1640, 1605, 1495, 1445, 1380, 860 cm^{-1}; NMR δ 1.90 (3 H, m, $-CH_3$), 2.19 (3 H, d, $J \sim 1$ Hz, $-CH_3$), 4.96 (1 H, m), 5.11 (1 H, m), 6.20 (1 H, m), 7.32 (5 H, m, ArH);[12] *m/e* 158.2 (M^+). **11d** was tentatively assigned the *E* configuration (vide supra).

Hydrogenation (Pd/C in ethanol) of a sample of the concentrated reaction mixture yielded a single product (GLC analysis). This is confirmation that dienes **11a–d** are structurally related by having the same carbon skeleton.

For quantitative analysis of the dienes, a 60.6-mg sample of **4** (~1:1 stereoisomer ratio) in 4 mL of 0.017 M sodium acetate in acetic acid was heated at 75 °C for 10 min (11% acetolysis). The reaction was quenched by pouring the acetic acid solution into H_2O–$NaHCO_3$. This mixture was extracted twice with ether and once with pentane. The combined extract was dried ($MgSO_4$) and then concentrated by careful distillation. Unreacted **4** was removed by placing the concentrate on a 10 × ½ in. column of silica gel (Woelm) and eluting with pentane. The eluant solution was concentrated and analyzed by GLC. The results are listed as a part of eq 3.

For the measurement of nitrogen evolution, 254 mg of **4** in 10 mL of acetic acid containing 0.54 M sodium acetate was placed in the gas monitoring apparatus described previously.[6a] The solution was heated at 75 °C, and after 63 min (1.16 half-lives) a 12.4-mL volume of nitrogen had collected. This corresponds to a 56% yield (>96% of theory).

Product Stability Control Experiments. Product compositions for acetolysis of **4** at 75 °C for increasing lengths of time up to 6 h (~6.7 half-lives) were determined as described in the preceding section. The results showed that the **11a**:**11b** ratio remained constant and the **11d**:**11b** ratio decreased as the relative amount of **11c** increased with increasing reaction time.

Separate control experiments were carried out with **11b** and **11d**. In each case a 9-mg diene sample in 10 mL of acetic acid with 0.017

M sodium acetate containing undecane as an internal standard was heated at 75 °C for 18 h (22 half-lives). After the workup of the solution, GLC analysis showed that the amount of **11b** remained unchanged but **11d** underwent substantial isomerization (ca. 57%) to **11c**.[24]

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Infrared Laser Induced Organic Reactions. 2.[1] Laser vs. Thermal Inducement of Unimolecular and Hydrogen Bromide Catalyzed Bimolecular Dehydration of Alcohols

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Abstract: It has been demonstrated that a mixture of reactant molecules can be induced by pulsed infrared laser radiation to react via a route which is totally different from the pathway resulting from heating the mixture at 300 °C. The high-energy unimolecular elimination of H_2O from ethanol in the presence of 2-propanol and HBr can be selectively induced with a pulsed CO_2 laser in preference to either a lower energy bimolecular HBr-catalyzed dehydration or the more facile dehydration of 2-propanol. Heating the mixture resulted in the almost exclusive reaction of 2-propanol to produce propylene. It was demonstrated that the bimolecular ethanol + HBr reaction cannot be effectively induced by the infrared laser radiation as evidenced by the detrimental effect on the yield of ethylene as the HBr pressure was increased. The selective, nonthermal inducement of H_2O elimination from vibrationally excited ethanol in the presence of 2-propanol required relatively low reactant pressures. At higher pressures intermolecular V–V energy transfer allowed the thermally more facile dehydration from 2-propanol to become the predominant reaction channel.

There is currently much interest in the application of high-intensity, pulsed infrared lasers to induce or augment chemical reactions.[3] Excitation of a molecule with such a laser can result in the absorption of many infrared photons and promotion of the molecule to high vibrationally excited states. Most of the chemical systems investigated to date have involved

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