from hexane–ethyl acetate yielded beige prisms: mp 88–90 °C; ^{1}H NMR ($CDCl_3$) δ 7.74, 7.25 (q, 4, J = 8 Hz), 3.90 (s, 4), 2.46 (s, 3), 2.0–1.5 (m, 8), 1.44 (s, 3).

Anal. Calcd for $C_{16}H_{22}O_4S$: C, 61.91; H, 7.14. Found: C, 61.79; H, 7.26.

3-Methyl-2-cyclohexen-1-one. A sample (0.5180 g, 1.67 mmol) of methylated ketal sulfone was dissolved in 11 mL of acidic aqueous 1,4-dioxane (3.5 mL of 50% $HClO_4$ in 7.5 mL of dioxane) and warmed (50 °C) for 12 h. The resulting auburn solution was made strongly alkaline with excess solid K_2CO_3, and after 30 min, extracted with three 50-mL portions of ether, dried over Na_2SO_4, and evaporated to a clear orange liquid. The residual dioxane was eliminated by preparative TLC (20 × 20 cm, 1000-μm silica gel GF in chloroform) to afford the crude ketone (0.156 g) which was isolated as the 2,4-DNP derivative. Recrystallization from ethyl acetate gave 0.242 g (50%) of dark red flakes, mp 176–178 °C corrected (lit.[9] mp 177–178 °C).

Registry No.—1, 28269-19-4; 2, 61476-93-5; 15, 61476-94-6; 16, 61476-95-7; 17, 61476-96-8; 18, 61476-97-9; methyl vinyl ketone, 78-94-4; sodium p-toluenesulfinate, 824-79-3; 2-ethyl-2-methyl-1,3-dioxolane, 126-39-6; benzyl chloride, 100-44-7; 5-phenyl-3-penten-2-one, 10521-97-8; 5-phenyl-4-penten-2-one, 877-94-1; 3-p-toluenesulfonylcyclohexanone, 14444-30-5; 2-cyclohexen-1-one, 930-68-7; 3-(p-toluenesulfonyl)-1,1-ethylenedioxycyclohexane, 61476-98-0; 3-(p-toluenesulfonyl)-3-methyl-1,1-ethylenedioxycyclohexane, 61476-99-1; 3-methyl-2-cyclohexen-1-one, 1193-18-6; methyl iodide, 74-88-4.

References and Notes

(1) Camille and Henry Dreyfus Foundation Awardee, 1972–1977.
(2) L. Dolby, S. Esfandiari, C. A. Elliger, and K. S. Marshall, *J. Org. Chem.*, **36**, 1277 (1971).
(3) G. Germain, P. Main, and M. M. Woolfson, *Acta Crystallogr., Sect. A*, **27**, 368 (1971).
(4) H. Gilman and L. F. Cason, *J. Am. Chem. Soc.*, **72**, 3469 (1950).
(5) K. Kondo and D. Tunemoto, *Tetrahedron Lett.*, 1007 (1975).
(6) R. P. Linstead and L. Williams, *J. Chem. Soc.*, 2735 (1926).
(7) D. R. Coulson, *Tetrahedron Lett.*, 3323 (1964).
(8) Infrared spectra were measured with either Beckman IR-5A or IR-7 infrared spectrophotometers. Proton magnetic resonance spectra were determined at 100 MHz with a Varian Model XL-100 spectrometer. The chemical shift values are expressed in δ values (ppm) relative to tetramethylsilane internal standard. In the presentation of the ^{1}H NMR spectra the following notations are used: b, broad; u, unsymmetrical; s, singlet; d, doublet; t, triplet; q, quartet; p, pentuplet; and m, multiplet. All reactions, except ketalization, were diluted with three volumes of water before extraction with ether.
(9) G. F. Woods, P. H. Griswold, Jr., B. H. Armbrecht, D. I. Blumenthal, and R. Plapinger, *J. Am. Chem. Soc.*, **71**, 2028 (1949).

Decomposition of Conjugated p-Tosylhydrazones in Base. Partition between Solvolysis and Cycloaddition Products

Romano Grandi, Walter Messerotti, Ugo M. Pagnoni,* and Roberto Trave

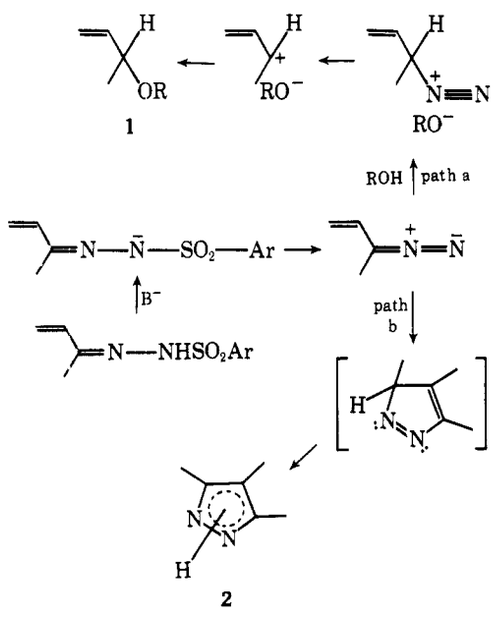
Istituto di Chimica Organica, Università di Modena, Via Campi 183, 41100 Modena, Italy

Received August 11, 1976

The p-tosylhydrazones of conjugated carbonyl compounds are not deoxygenated by $NaBH_4$ in methanol, but undergo an alkaline decomposition to diazoalkenes. The partition of the diazo compound between the solvolysis and intramolecular 1,3-dipolar cycloaddition processes depends on the degree and type of substitution at the β position. The use of base ($NaBH_4$, NaOR, or K_2CO_3) in alcoholic solvents provides a mild, convenient, and high-yield procedure for the preparation of a variety of (a) allylic ethers, in the case of cyclohexenones and β,β-dialkyl substituted carbonyl compounds; and (b) pyrazoles, in the case of acyclic α,β-unsaturated substrates having a β hydrogen.

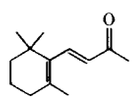
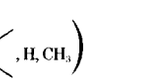
Recently, we have found[1] that p-tosylhydrazones of some conjugated carbonyl compounds on treatment with $NaBH_4$ in alcoholic solvents undergo an elimination–substitution reaction in preference to the expected deoxygenation.[2,3] Allylic ethers are obtained in high yields by this method. A similar behavior was observed when RONa or K_2CO_3 was used instead of $NaBH_4$. The sequence p-tosylhydrazone → diazoalkene (aryldiazomethane) → diazonium–alkoxide ion pair[4] → ether (1) was suggested as the most suitable mechanistic description (path a). Hart and Brewbaker have shown[5,6] that 3-diazoalkenes, generated from the corresponding alkyl allylnitrosocarbamates, rapidly undergo intramolecular cycloaddition[7] to form pyrazoles (path b).[8] Although for the cyclohexenone and aromatic substrates previously examined by us[1] this cycloaddition was clearly impossible, the formation of only products of solvolysis (e.g., methyl ethers) for the case of the acyclic substrate, neral, was surprising since some intramolecular cycloaddition product may reasonably have been expected.

Scheme I



In a continuation of our studies on the anomalous behavior of p-tosylhydrazones of conjugated carbonyls toward $NaBH_4$ we wished to investigate how structural factors may determine the course of decomposition of these compounds. We therefore chose substrates (entries 1, 2, 5–8, Table I) which would yield diazoalkenes structurally analogous to those studied by Hart and Brewbaker. In these cases it could be expected that intramolecular cycloaddition should compete favorably with the elimination–substitution reaction process. In fact, treatment of these substrates with each of the three basic reagents employed previously[1] ($NaBH_4$, MeONa, and K_2CO_3 in methanol) leads to pyrazoles (**2a,b,c–f**) in high yields. No methyl ethers could be detected in the reaction mixtures. In Table I are reported the data for the reagent that is more generally useful (K_2CO_3 in methanol). With $NaBH_4$ or

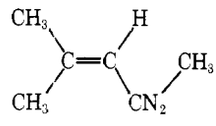
Table I. Decomposition of Conjugated *p*-Tosylhydrazones with K_2CO_3 in Methanol

Registry no.	Entry	*p*-Tosylhydrazone of	Time, h	Product 2 (R, R′, R″)	Physical Data of Pyrazoles: Yield,[a] %	Bp, °C (mmHg)	Mp, °C	UV,[b] nm ($\epsilon \times 10^3$)	NMR data, δ [c] (60 MHz, $CDCl_3$)
4170-30-3	1	$CH_3CH{=}CHCHO$	6	a (CH_3, H, H)	78	204[d]		212 (4.1)[e]	2.32 (3 H, s, CH_3C), 6.06 and 7.48 (1 H each, d (J = 1.7 Hz), H_4 and H_5)[25b]
13019-16-4	2	$C_5H_{11}CH{=}C(C_4H_9){-}CHO$[f]	30	b (C_5H_{11}, H, C_4H_9)	81	116–118 (10)		222 (5.0)	0.6–1.9 (16 H, CH_3C, CH_2C), 2.1–2.8 (4 H, m, $CH_2C{=}$), 7.31 (1 H, br s, H_5)
	3	$CH_3C(CH_3){=}CH(CH_2)_2C(CH_3){=}CHCHO$[g,h]	40	[methyl ether,[i,g] 69[l]]					
141-79-7	4	$CH_3C(CH_3){=}CHCCH_3$ (O)	30	[methyl ether, 64[l]]					
14371-10-9	5	PhCH=CHCHO (trans)	24	c (Ph, H, H)	93		75–76[m]	207 (11.0); 248 (14.3)[n]	6.60 (1 H, d (J = 2.2 Hz), H_4), 7.60 (1 H, d (J = 2.2 Hz), H_5), 7.2–8.0 (5 H, aromatic)[26]
6203-18-5	6	*p*-$N(CH_3)_2PhCH{=}CHCHO$	12	d (*p*-$N(CH_3)_2Ph$, H, H)	86		147–149	208 (10.1); 289 (18.3)	2.98 (6 H, s, $(CH_3)_2N$), 6.50 (1 H, br s, H_4), 7.61 (1 H, br s, H_5), 6.74 and 7.64 (2 H each, d, aromatic)
1466-88-2	7	*o*-$NO_2PhCH{=}CHCHO$	12	e (*o*-NO_2Ph, H, H)	94		74–76	209 (13.5); 234 (13.0)	6.48 (1 H, d (J = 2 Hz), H_4), 7.60 (1 H, d (J = 2 Hz), H_5), 7.40–7.85 (4 H, aromatic)
122-57-6	8	$PhCH{=}CHCCH_3$ (O)	24	f (Ph, H, CH_3)	96		125–126	207 (18.5); 252 (15.9)[p]	2.20 (3 H, s, CH_3C), 6.31 (1 H, s, H_4), 7.1–7.9 (5 H, aromatic)[25b]
1210-39-5	9	PhC(Ph)=CHCHO	12	g (Ph, Ph, H) [methyl ether, 25[l]]	59		153–154	209 (19.6); 227 (16.6); 251 (10.2)	7.37 (10 H, aromatic), 7.61 (1 H, s, H_5)
5910-85-0	10	$C_2H_5(CH{=}CH)_2CHO$	24	h ($C_2H_5CH{=}CH$, H, H)	87	120–122 (10)		240 (10.8)	1.08 (3 H, t, CH_3C), 2.25 (2 H, m, CH_2C), 6.35 (1 H, d (J = 2 Hz), H_4), 6.42 (2 H, m, CH=), 7.57 (1 H, d (J = 2 Hz), H_5)
79-77-6	11		70	i 	92	148–150 (0.01)		212 (7.5)	0.97 (6 H, s, $(CH_3)_2C$), 1.46 (3 H, s, $CH_3C{=}$); 2.3 (3 H, s, CH_3C), 5.84 (1 H, s, H_4)
	12	$CH_3C(CH_3){=}CHC(CH_3){=}CHCHO$[h]	12	[methyl ether,[i] 39[l]]					

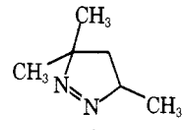
[a] Yields were determined by isolation. Pyrazoles gave satisfactory elemental analyses the results of which have been provided to the Editor. [b] Recorded in absolute EtOH. [c] Downfield from Me_4Si standard. [d] Lit. 204°C (ref 22). [e] Lit. 213°C (3.7) in 95% EtOH (ref 25a). [f] Oily *p*-tosylhydrazone, not purified. [g] See ref 1. [h] *p*-Tosylhydrazone not isolated. [i] Mixture of isomers. [l] Yields of allylic methyl ethers. [m] Lit. 78°C (ref 23); 72–73°C (ref 5). [n] Lit. 248°C (13.8) in 95% EtOH (ref 25a). [o] Lit. 124°C (ref 24). [p] Lit. 251°C (15.6) in MeOH (ref 24); 252.5°C (15.8) in 95% EtOH (ref 25a).

MeONa the same products are obtained in slightly lower yields.

The clear difference between the behavior of these substrates on the one hand and neral (entry 3) on the other agrees with the finding that alkyl disubstitution in the β position of 3-diazoalkenes drastically reduces the rate of cycloaddition, both for thermal[9] and photochemical[10] processes. In order to see whether the enhanced[5,8] reactivity of secondary diazoalkenes could lead, at least in part, to cycloaddition in a β,β-dialkyl substituted substrate, we used mesityl oxide as a probe (entry 4). In this case only the methyl ether was formed. It is useful to note that, in contrast to a previous report,[9] the cycloaddition of the diazoalkene **3**, generated from the *p*-tosylhydrazone of mesityl oxide, is possible. Although in methanol the diazoalkene **3** reacts rapidly to form the methyl ether, in an aprotic solvent (diglyme) it is slowly transformed into the pyrazolenine **4**.



3

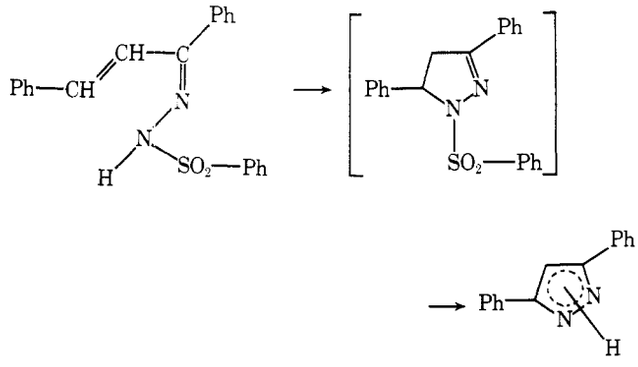


4

Thus, α,β-unsaturated carbonyl derivatives lacking hydrogens in the β position (entries 3, 4) undergo an elimination–substitution process to form ethers, as previously observed for cyclohexenone derivatives.

The rather different result obtained with β-phenylcinnamaldehyde (entry 9), a β,β-diaryl substituted substrate, deserves some comment. On treatment with base the corresponding *p*-tosylhydrazone produces a deep red color after only 30 min.[11] From the reaction mixtures both the allylic methyl ether and the pyrazole **2g**, in which a phenyl group has migrated,[12] could be obtained.[13] That under these conditions the diazoalkene was the intermediate common to both products was confirmed by another experiment, in which the diazo compound from the *p*-tosylhydrazone of β-phenylcinnamaldehyde was isolated and then allowed to react with boiling methanol. Both the pyrazole **2g** and the allylic methyl ether increased by 62 and 30%, respectively (determined by using an internal standard), compared to the amounts found to be present after isolation of the diazoalkene.

Thus, the pyrazole appears to be formed from the *p*-tosylhydrazone by a cycloaddition mechanism involving a 3-diazoalkene, rather than by an internal Michael addition followed by elimination of sulfinate.[14] This latter path was proposed,[15] for example, in the "unusual" formation of 3,5-diphenylpyrazole from the benzenesulfonylhydrazone of benzalacetophenone by EtONa in boiling acetonitrile.[16]



The observation that for entry 9 the cycloaddition process occurs to some extent is in contrast with the behavior of the neral and mesityl oxide derivatives (entries 3, 4). This difference may be due to one or both of the following factors: (a) the enhancement[5,17] of dipolarophilicity in the β,β-diphenyl derivative due to extensive conjugation, and/or (b) the greater migratory aptitude of the phenyl group compared to that of the methyl, thus favoring[18] the formation of a stable pyrazole.

Table II. Carbonyl Tosylhydrazones[a]

Tosylhydrazone	Mp, °C	Yield, %
Crotonaldehyde	124[b]	81
Mesityl oxide	110–114[c]	79
trans-Cinnamaldehyde	162–164	85
p-Dimethylaminocinnamaldehyde	180–181	77
o-Nitrocinnamaldehyde	165–167	69
Benzalacetone	201–203	86
β-Phenylcinnamaldehyde	174–175	81
2,4-Heptadienal	124–125	68
β-Ionone	170–171[d]	83

[a] All tosylhydrazones gave satisfactory elemental analyses the results of which have been provided to the Editor. [b] Lit. 125 °C (ref 9). [c] Lit. 105–110 °C (ref 9). [d] Lit. 169–171 °C (ref 3).

A γ–δ carbon–carbon double bond, extending the conjugation, does not confer sufficient activation to induce a β,β-dialkyl substituted substrate (entry 12) to undergo cycloaddition. Again the methyl ether derivative was the only transformation product obtained from the reaction mixtures.

On the other hand, similarly conjugated systems containing a β hydrogen (entries 10, 11) readily undergo intramolecular cycloaddition and the pyrazoles **2h,i** can be obtained in high yields, uncontaminated by the methyl ethers.

In conclusion, the results presented in this and our previous[1] paper on this topic provide methods for the synthesis of allylic ethers or pyrazoles. In fact, treatment of the *p*-tosylhydrazones of conjugated cyclohexenones or acyclic β,β-dialkyl substituted carbonyl compounds with base in alcoholic solvents is a mild, convenient, and efficient procedure for the preparation of a variety of allylic ethers (Scheme I, path a). For acyclic α,β-unsaturated *p*-tosylhydrazones containing a β hydrogen pyrazoles are, virtually, the sole conversion products (path b). Furthermore these results should be useful as a caution for those who might expect to obtain hydrocarbons in the reactions of conjugated *p*-tosylhydrazones with $NaBH_4$ in alcoholic solvents.

Experimental Section

$NaBH_4$ was obtained from Carlo Erba and used without purification. 2-*n*-Butyl-2-octen-1-al and 3,5-dimethyl-2,4-hexadien-1-al were prepared according to literature methods.[19,20] The other ketones and aldehydes used were commercial products. The physical characteristics were obtained as follows: melting points in a Mel-Temp apparatus (uncorrected); UV curves on a Beckman DB-GT; mass spectra on a Varian MAT 112 by GLC insertion; NMR spectra on a JEOL C-60 using Me_4Si as internal standard. Microanalyses were performed by the Istituto di Chimica Generale, University of Modena. The allylic ethers were compared (GC/MS, IR, and NMR) with samples prepared from the corresponding carbonyl compounds by hydride reduction and subsequent methylation (NaH/CH_3I).[21]

***p*-Tosylhydrazone Formation. General Procedure.** The *p*-tosylhydrazones were readily prepared in good yields by addition of *p*-tosylhydrazine (10% mole excess) to a solution of the carbonyl compound in methanol and heating under reflux for 0.5–5 h. Cooling afforded crystalline products in good to excellent yields (Table II).

General Decomposition Procedures. 1. With $NaBH_4$ in Methanol. To a stirred solution of 3 mmol of the *p*-tosylhydrazone in 40–50 mL of methanol, $NaBH_4$ (45 mmol) was added in small portions during 1.5 h. The solution was then refluxed for the appropriate length of time (Table I), the reaction being monitored by TLC and GLC. Water was then added and the mixture extracted with $CHCl_3$ (3 × 25 mL); the organic solution was then washed with water, dried (Na_2SO_4), and concentrated. The residue was analyzed by GLC on a 4 m 5% DEGS column and on a 2 m 5% SE-30 column, giving es-

sentially identical information; for methyl ethers the first column was more convenient and for pyrazoles the second column. The products were fractionated by using a silica gel column (*n*-hexane–ether gradient) and purified by distillation or crystallization. The physical data of the pyrazoles are reported in Table I.

2. With MeONa in Methanol. Reaction mixtures made 0.045 M in the *p*-tosylhydrazone and 0.05 M in MeONa in methanol were refluxed for the appropriate length of time (Table I). Water was then added and the above workup employed to obtain the reaction products.

3. With K_2CO_3 in Methanol. The procedure was identical, except that the solution was 0.06 M in anhydrous K_2CO_3.

As a representative preparative application, the reaction of β-phenylcinnamaldehyde is described (entry 9). Anhydrous K_2CO_3 (1.5 g, 11 mmol) was added to a solution of *p*-tosylhydrazone (1 g, 2.7 mmol) in methanol (50 mL), which was then heated to reflux for 12 h. After dilution with water (150 mL), extraction with light petroleum (3 × 30 ml) and evaporation of the solvent afforded a residue which was purified by chromatography and distillation to yield 0.15 g (0.67 mmol, 25% yield) of β-phenylcinnamyl methyl ether: bp 138–140 °C (0.01 mm); *m/e* (rel intensity) 224 (M^+, 17), 192 ($M^+ - 32$, 100); NMR ($CDCl_3$) δ 3.32 (3 H, s, CH_3O); 4.01 [2 H, d (J = 6.9 Hz), CH_2O], 6.22 (1 H, t (J = 6.9 Hz), CH=), and 7.1–7.7 (10 H, aromatic).

Anal. Calcd for $C_{16}H_{16}O$: C, 85.67; H, 7.19. Found: C, 85.51; H, 7.34.

The aqueous phase was further extracted (3 × 40 mL) with $CHCl_3$, and the organic solution dried and concentrated to a residue which was twice crystallized (diisopropyl ether) to obtain pure 3,4-diphenylpyrazole (see Table I), *m/e* 220 (M^+, 100).

In a parallel run, after 40 min, the diazo compound was extracted with *n*-pentane (4 × 10 mL). The organic solution was concentrated under vacuum (at 15 °C) to 20 mL and then methanol (10 mL) added. After addition of naphthalene as internal standard for GLC monitoring, the mixture was refluxed for 2 h; then, the increase (62 and 32%, respectively) in the amounts of pyrazole **2g** and methyl ether was determined.

2-Methyl-4-methoxy-2-pentene: *m/e* (rel intensity) 114 (M^+, 5), 99 ($M^+ - 15$, 100); NMR ($CDCl_3$) δ 1.2 (3 H, d, CH_3C), 1.72 (6 H, br s, CH_3C=), 3.26 (3 H, s, CH_3O), 4.0 (1 H, m, CHO), and 5.07 (1 H, d, CH=).

2-*n*-Butyl-2-octen-1-al. This was prepared according to ref 19: bp 74–76 °C (10 mm); *m/e* (rel intensity) 182 (M^+, 8); NMR ($CDCl_3$) δ 0.7–1.8 (16 H, aliphatic), 2.0–2.6 (4 H, m, CH_2C=), 6.48 [1 H, t (J = 7.5 Hz), CH=], and 9.34 (1 H, s, CHO).

Anal. Calcd for $C_{12}H_{22}O$: C, 79.06; H, 12.17. Found: C, 79.30; H, 11.94.

3,5-Dimethyl-2,4-hexadien-1-al. This was prepared according to ref 20: bp 108–110 °C (18 mm); *m/e* (rel intensity) 124 (M^+, 3), 109 ($M^+ - 15$, 100); NMR ($CDCl_3$) δ 1.88 (6 H, s, CH_3C=), 2.23 (3 H, s, CH_3C=), 5.76 (1 H, br s, CH=), 5.85 [1 H, d (J = 8 Hz), CH=], and 9.96 [1 H, d (J = 8 Hz), CHO].

Dimethylhexadienyl Methyl Ether (mixture of isomers): bp 75–79 °C (25 mm); NMR ($CDCl_3$) δ 1.77 (9 H, CH_3C=), 3.29, 3.33, 3.45 (three s, 3 H, CH_3O), 3.4–4.0 (2 H, CH_2O), and 5.2–5.7 (2 H, CH=). The mixture of isomers (three) proved to be identical (GC/MS) with that obtained from the aldehyde by the procedure described above in the introduction to the Experimental Section.

Reactions of 4-Diazo-2-methyl-2-pentene (3). The title compound was prepared according to Closs et al.,[9] by the action of NaH on the *p*-tosylhydrazone of mesityl oxide in triglyme. 3,3,5-Trimethylpyrazolenine 4 accompanied the diazo derivative. The following reactions were monitored by GLC using *tert*-butylbenzene as internal standard.

a. Reaction with Methanol. To a 0.5 M solution (10 mL) of the diazoalkene in diglyme, methanol (10 mL) was added. After 3 h at room temperature the red-violet color faded and the mixture was analyzed by GLC for 2-methyl-4-methoxy-2-pentene (47% yield), which was then isolated by the general procedure described above.

b. Conversion to 3,3,5-Trimethylpyrazolenine (3). A 0.5 M solution (10 mL) of the diazoalkene in diglyme was heated at 95 °C for 1 h. By this time the color faded and the pyrazolenine content was found to be clearly increased (+51%). **3:** *m/e* (rel intensity) 110 (M^+, 8), 109 ($M^+ - 1$, 11), 82 ($M^+ - 28$, 19), 67 ($M^+ - 43$, 100); the other physical data corresponded to those reported in ref 9.

Acknowledgment. We gratefully acknowledge support of this work by the Consiglio Nazionale delle Ricerche, Rome.

Registry No.—**2b,** 61490-97-9; **2d,** 61490-98-0; **2e,** 59844-05-2; **2g,** 24567-08-6; **2h,** 61490-99-1; **2i,** 61490-96-8; **3,** 61491-00-7; **4,** 2721-30-4; β-phenylcinnamyl methyl ether, 61491-01-8; 2-methyl-4-methoxy-2-pentene, 61491-02-9; 2-butyl-2-octen-1-al, 13019-16-4; 3,5-dimethyl-2,4-hexadien-1-al, 61491-03-0; dimethylhexadienyl methyl ether, 61528-78-9.

References and Notes

(1) R. Grandi, A. Marchesini, U. M. Pagnoni, and R. Trave, *J. Org. Chem.*, **41,** 1755 (1976).
(2) L. Caglioti and P. Grasselli, *Chem. Ind. (London)*, 153 (1964); L. Caglioti, *tetrahedron*, **22,** 487 (1966); M. Fischer, Z. Pelah, D. H. Williams, and C. Djerassi, *Chem. Ber.*, **98,** 3236 (1965).
(3) R. O. Hutchins, M. Kacher, and L. Rua, *J. Org. Chem.*, **40,** 923 (1975).
(4) Even if the possibility of competing thermal reactions cannot be excluded, the protic reaction medium and the mild conditions employed suggest that the diazo derivative reacts with a weakly acidic proton donor, such as the hydroxyl solvent, to form a diazonium ion followed by N_2 elimination to a carbonium ion.
(5) J. L. Brewbaker and H. Hart, *J. Am. Chem. Soc.*, **91,** 711 (1969).
(6) H. Hart and J. L. Brewbaker, *J. Am. Chem. Soc.*, **91,** 716 (1969).
(7) A. Padwa, *Angew. Chem., Int. Ed. Engl.*, **15,** 123 (1976).
(8) In these cases it was shown that methyl substituents in the β or γ position have little effect on the rate of cyclization of 3-diazopropenes, whereas a methyl in the α position (e.g., a secondary diazoalkene) or a phenyl substituent in the γ position have a marked accelerating effect, 13- and 6-fold respectively, compared to 3-diazopropene itself.
(9) G. L. Closs, L. E. Closs, and W. A. Boll, *J. Am. Chem. Soc.*, **85,** 3796 (1963).
(10) H. Durr, *Chem. Ber.*, **103,** 369 (1970).
(11) In the case of substrates having a β hydrogen, the red color of the diazo derivative is virtually lacking, probably owing to the greater cycloaddition rate.
(12) W. Kirmse and L. Horner, *Justus Liebigs Ann. Chem.*, **614,** 1 (1958).
(13) The mole ratio of pyrazole to methyl ether formed was found to depend on the method used to generate the basic medium and was 0.8, 1.2, and 2.5 for $NaBH_4$, MeONa, or K_2CO_3, respectively.
(14) G. Ege, *Tetrahedron Lett.*, 1665 (1963).
(15) A. N. Kost and I. I. Grandberg, *Adv. Heterocyl. Chem.*, **6,** 385 (1966).
(16) A. Dornow and W. Bartsch, *Justus Liebigs Ann. Chem.*, **602,** 23 (1957).
(17) R. Huisgen, *Angew. Chem., Int. Ed. Engl.*, **7,** 321 (1968).
(18) M. Franck-Neumann and C. Dietrich-Buchecker, *Tetrahedron Lett.*, 2069 (1976).
(19) A. T. Nielsen and W. J. Houlihan, *Org. React.*, **16,** 1 (1968).
(20) J. Attenburrow, A. F. B. Cameron, J. H. Chapman, R. M. Evans, B. A. Hems, A. B. A. Jansen, and T. Walker, *J. Chem. Soc.*, 1094 (1952).
(21) R. Grandi, U. M. Pagnoni, R. Trave, and L. Garanti, *Tetrahedron*, **30,** 4037 (1974).
(22) M. Cola and A. Perotti, *Gazz. Chim. Ital.*, **94,** 1268 (1964).
(23) K. B. Bowden and E. R. H. Jones, *J. Chem. Soc.*, 953 (1946).
(24) D. C. Dittmer and R. Glassman, *J. Org. Chem.*, **35,** 999 (1970).
(25) (a) J. Elguero, R. Jacquier, and H. C. N. Tien Duc, *Bull. Soc. Chim. Fr.*, 3744 (1966); (b) *ibid.*, 3727 (1966).
(26) L. G. Tensmeyer and C. Ainsworth, *J. Org. Chem.*, **31,** 1878 (1966).