Conversion of Conjugated p-Tosylhydrazones to the Corresponding Ethers by Sodium Borohydride, Sodium Alkoxide, or Potassium Carbonate in Alcohol Solvents

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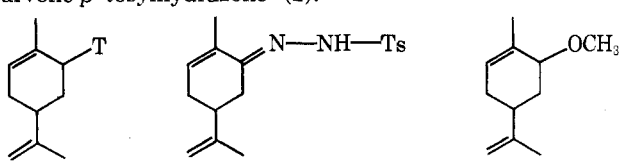
p-Tosylhydrazones of conjugated (olefinic or aromatic) carbonyl compounds undergo with $NaBH_4$ in methanol an elimination process in preference to reduction, thereby providing methyl ethers instead of hydrocarbons. The combination of base ($NaBH_4$, NaOR, or K_2CO_3) and alcohol provides an effective and convenient system for the transformation of these conjugatively deactivated derivatives into the corresponding ethers, mostly without allylic rearrangement. The sequence tosylhydrazone → diazoalkene (aryldiazomethane) → diazonium–alkoxide ion pair → ether is suggested as the most suitable mechanistic description.

The reduction of p-tosylhydrazones with $NaBH_4$ in methanol or in aprotic solvents (such as THF or dioxane) gives saturated hydrocarbons in high yields under mild conditions.[1-3] The mechanism of this reaction apparently involves[2,4,5] initial chelation of the tosylhydrazone by a Lewis acid followed by reduction to an intermediate tosylhydrazine (or its organometallic equivalent), and subsequent thermal decomposition.

A need for [6-^{3}H]limonene (**1**) for biogenetic studies prompted application of this reaction to the reduction of carvone p-tosylhydrazone[6] (**2**).



1 **2** **3**

Treatment of **2** with $NaBH_4$ in MeOH[1] gave, instead of the expected limonene (**1**), a high yield of carveyl methyl ether (**3**) as a mixture of stereoisomers. The corresponding reaction in dioxane was extremely slow, giving only traces of **1** after 48 h. This unexpected result led us to examine the behavior of other α,β-unsaturated and also aromatic carbonyl derivatives in this reaction.

As seen in Table I, the reaction in MeOH[10] afforded the corresponding methyl ethers in satisfactory yields for all the p-tosylhydrazones studied. However, in dioxane the yields of hydrocarbons were much lower for conjugated derivatives than for saturated examples,[1,2] under identical experimental conditions.

The results outlined in Table I demonstrate that, as with α,β-unsaturated carbonyls in the presence of nucleophilic reagents, the reactivity of the carbon–nitrogen double bond toward hydride is drastically reduced.[8a,b] The virtually quantitative recovery of the tosylhydrazones and absence of alkyltosylhydrazines in the reactions performed in dioxane indicate that the step which is blocked is the addition of hydride and not the subsequent decompositon of alkyltosylhydrazine.

From this it follows that, in methanol, the lower reactivity of the carbon–nitrogen double bond coupled with the protic and nucleophilic nature of the solvent and the alkalinity of the medium favor alkaline cleavage[11,12] analogous to the Bamford–Stevens reaction.[13] This view is strongly supported by the successful conversions of the conjugated p-tosylhydrazones with MeONa[14] or K_2CO_3 and methanol (Table I). The reactions effected by base in methanol may involve (Scheme I) the decomposition of the tosylhydrazone anion to an intermediate diazo derivative (as generally accepted for the Bamford–Stevens reaction). This is supported by the appearance, in the tests carried out on aromatic substrates, of a transient light-orange color. The formation of these diazo derivatives is more evident when working with MeONa in methanol; in fact, under these conditions the diazo derivatives can be isolated.[13,15,16] Although in the case of olefinic tosylhydrazones the presence of diazo derivatives in appreciable quantities could not be demonstrated,[17] we believe that they are formed during the first stage of the reaction, but, being less stable than aryldiazomethanes, evolve to final products at a much faster rate.

The reaction of 1-oxoalkanephosphonate p-tosylhydrazones with $NaBH_4$[18] is apparently intermediate between p-tosylhydrazones of saturated carbonyls and those in the present study. When working in THF, the former derivatives afford the corresponding products of normal reduction in high yield (65–72%), while in methanol the corresponding diazo derivatives are isolated (85–90%), resulting from a thermal decomposition of the tosylhydrazone anion.

Even if the possibility of competing thermal[19] reactions (path b) cannot be excluded, the protic reaction medium and the mild conditions employed in this study suggest that the diazo derivative reacts[20,21] with a weakly acidic proton donor, such as the hydroxyl solvent, to form a diazonium ion[22] followed by N_2 elimination to a carbonium ion (path a). In fact, vinyldiazoalkanes, which are less stable than their aromatic counterparts and thus more easily protonated,[20] cannot be detected in the reaction medium. Further, the reaction of phenyldiazomethane with methanol was much faster in the absence of MeONa, resulting in virtually immediate disap-

Scheme I

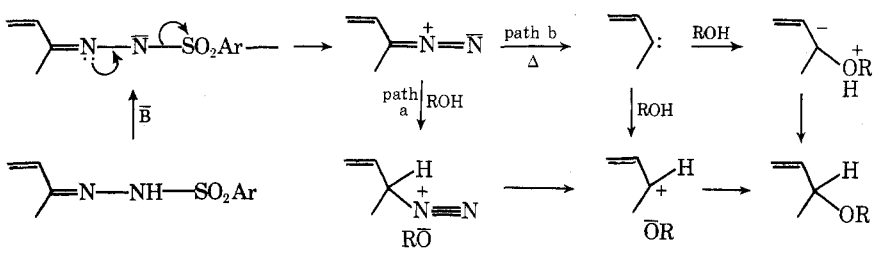
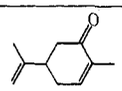
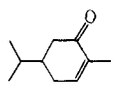
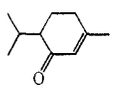
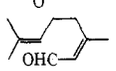
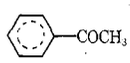
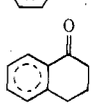
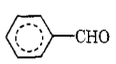


Table I. Conversion[a] of Conjugated *p*-Tosylhydrazones to Allylic (or Benzylic) Methyl Ethers

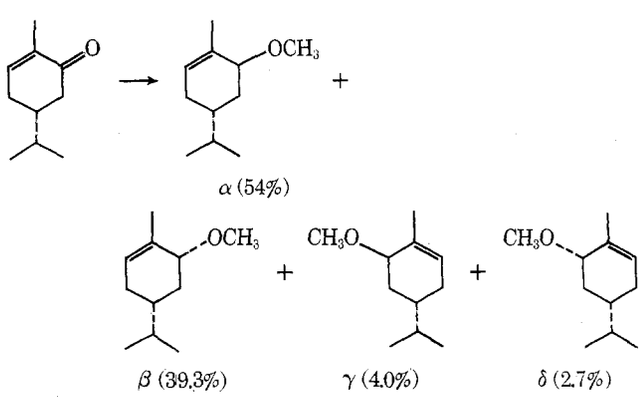
Registry no.	*p*-Tosylhydrazone[n] of	Mp, °C	$NaBH_4$ MeOH	(h)	$NaBH_4$ Dioxane	(h)	MeONa MeOH	(h)	K_2CO_3 MeOH	(h)
21195-60-8		156–157	77 [0.5][b]	(48)	[8.5][b]	(48)	69[c]	(48)	67	(48)
58548-70-2		137–138	86 [0.9][b]	(30)	[19][b]	(72)	80	(48)	70	(48)
21195-62-0		144–145[d]	80 [0.7][b]	(48)	st. m.	(72)	73	(48)	61	(48)
58580-63-5		125–127	67 [1.4][b]	(48)	[5.2][b]	(48)	56	(48)	54	(48)
58548-71-3			73[e,f] [0.7][b]	(40)			60[e,f]	(40)	69[e,f]	(40)
21301-41-7	Cholest-4-en-3-one	105–106	26	(48)	st. m.	(48)	19	(48)	16	(48)
4545-21-5		146–147[g]	69[h] [1][b]	(48)	st. m.	(48)	58	(48)	54	(48)
17336-59-3		177–179	74 [5][b,i,l]	(24)	[15][b,i]	(24)	70	(24)	76	(24)
1666-17-7		128–129[m]	64 [3][b]	(24)	[16][b]	(24)	60[c]	(24)	69	(24)

[a] Overall yields were determined by isolation and do not take into account recovered starting material. [b] Yields of allylic (benzylic) hydrocarbons. [c] Use of EtONa in ethanol and of *i*-PrONa in 2-propanol afforded the corresponding ethers (see Experimental Section). [d] Lit.[8b] 143.5–145 °C. [e] Tosylhydrazone not isolated. [f] Product consisted of a mixture (~7:3) of neryl and linalyl methyl ether. [g] Lit.[16] 147.5–150 °C. [h] Use of ethanol afforded the corresponding ethyl ether in 47% yield (see Experimental Section). [i] Mixture of hydronaphthalenes. [l] The amount of tetralin slowly increases with excess $NaBH_4$. The yields of 30% reported by Caglioti[2] is possibly due to a misleading computation of the gas chromatographic peak (L. Caglioti, private communication). [m] Lit.[8b] 128.5–130 °C. [n] All isolated *p*-tosylhydrazones gave satisfactory elemental analyses (±0.3% for C, H, N) the results of which have been provided to the Editor.

pearance of the diazo compound and excellent yields of ether; this strongly indicates an acid-catalyzed reaction of the diazo compound. A short-lived diazonium ion will then lead to the formation of a stable allylic or benzylic carbonium ion.

The nucleophile employed showed differing behavior with the aromatic systems than with the olefinic cases; this is probably due to the different stability of the carbocation. Thus, the *p*-tosylhydrazone of benzaldehyde exhibited a progressive reduction of reactivity (7:5:1, relative final yields) in parallel tests carried out with 0.05 M solutions of MeONa in methanol, EtONa in ethanol, and *i*-PrONa in 2-propanol, while the carvone derivative (**2**) exhibited almost identical reactivities with the three systems.

The analysis of the mixture of isomeric carvotanacetyl methyl ethers[23] obtained both with $NaBH_4$ and MeONa in methanol is of interest and is presented below.



The simplest explanation for the very small quantities of isomers resulting from allylic rearrangement (γ and δ) is that a diazonium–methoxide ion pair is formed which loses nitrogen unimolecularly without dissociation; the predominance of trans over cis isomers can best be explained by steric hindrance.

The mild reaction conditions and the satisfactory yields obtained in the reaction of conjugated *p*-tosylhydrazones with alcohols in basic medium suggest the latter as an attractive alternative to that in which the corresponding allylic and benzylic ethers are obtained from unsaturated ketones by means of initial reduction followed by ether formation.

The scope and applications of the reactions are currently in progress.

Experimental Section

Ir spectra were determined with a Perkin-Elmer 257 instrument. NMR spectra were measured on a JEOL C-60 instrument, with Me_4Si as internal standard; chemical shifts have been recorded in δ values. Mass spectra were determined with a Varian MAT 112 spectrometer. Optical rotations were measured on a Perkin-Elmer 141 instrument. Microanalyses were performed by Istituto di Chimica Generale, University of Modena.

All the conjugated ethers were compared (GLC, ir, and NMR) with authentic samples obtained commercially or prepared by standard procedures, usually[23] from the corresponding carbonyl compound by hydride reduction and subsequent methylation (NaH/CH_3I). The allylic hydrocarbons were identified on GC–MS by comparison with samples obtained commercially or prepared from the alcohol by mesylation followed by hydride reduction.

***p*-Tosylhydrazone Formation. General Procedure.** The *p*-tosylhydrazones were readily prepared in good yield by addition of *p*-tosylhydrazine (10% molar excess) to a solution of the carbonyl

compound in methanol followed by refluxing for 0.5–5 h. In all cases the products were identified through elemental analyses (which were made available to the Editor and which were well within the limits of acceptable error) and infrared and NMR spectra, which are available on request. The materials were pure enough for use in the reactions.

General Decomposition Procedures. A. With $NaBH_4$ in Methanol. To a stirred solution of 3 mmol of the tosylhydrazone in 35–50 ml of methanol was added $NaBH_4$ (45 mmol) 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 was extracted with ether (or methylene chloride in the case of the steroid) (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% WEAS column and on a 2-m 5% SE-30 column and the products were fractionated by using a silica gel column (*n*-hexane–ether gradient) and purified by distillation.

B. With MeONa in Methanol. Reaction mixtures made 0.045 M in the 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.

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

Reduction with $NaBH_4$ in Dioxane. The general procedure was that described by Caglioti.[1] The products were recovered in ether which was distilled at 1 atm pressure to give a residue which was analyzed by GC–MS in comparison with authentic samples.

Carveyl Methyl Ethers. The isomer mixture was analyzed on GC–MS in comparison with samples prepared[23] from the *cis*- and *trans*-carveol by NaH/CH_3I in THF: $[\alpha]^{20}D$ −69.5° (*c* 2.1, MeOH) from $NaBH_4$/MeOH, −66.7° (*c* 2.0, MeOH) from MeONa/MeOH and −68.1° (*c* 2.1, MeOH) from K_2CO_3/MeOH; NMR ($CDCl_3$) δ, 1.7 (6 H, br s, CH_3C=), 3.32 and 3.37 (3 H, two s, CH_3O), 3.45 (1 H, m, CHO), 4.72 (2 H, s, CH_2=C), and 5.57 (1 H, m, CH=C).

Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.91. Found: C, 79.63; H, 10.75.

Carveyl Ethyl Ethers. They were obtained as an isomer mixture (GC–MS), in 65% yield by 0.05 M EtONa in ethanol, following the general procedure (at 68 °C for 48 h): NMR (CCl_4) δ 1.2 (3 H, t, CH_3C), 1.77 (6 H, br s, CH_3C=); 3.52 (2 H, q, CH_2O), 3.76 (1 H, m, CHO), 4.78 (2 H, br s, CH_2=C), and 5.53 (1 H, br t, CH=C).

Anal. Calcd for $C_{12}H_{20}O$: C, 79.94; H, 11.18. Found: C, 79.95; H, 11.03.

Carveyl Isopropyl Ethers. They were obtained as an isomer mixture (GC–MS), in 62% yield by 0.05M *i*-PrONa in 2-propanol following the general procedure (at 68 °C for 48 h): NMR (CCl_4) δ 1.13 (6 H, d, CH_3C), 1.70, 1.72, and 1.74 (6 H, three s, CH_3C=), 3.5–4.0 (2 H, m, CHO), 4.73 (2 H, br s, CH_2=C), and 5.5 (1 H, m, CH=C).

Anal. Calcd for $C_{13}H_{22}O$: C, 80.35; H, 11.41. Found: C, 80.47; H, 11.58.

Carvotanacetyl Methyl Ethers. The cis and trans (1:1.4, GLC) isomers were separated by repeated column chromatography over silica gel using a *n*-hexane–benzene gradient and purified by distillation.

Cis isomer: $[\alpha]^{20}D$ −76.9° (*c* 2.05, MeOH).

Anal. Calcd for $C_{11}H_{20}O$: C, 78.51; H, 11.98. Found: C, 78.54; H, 12.07.

Trans isomer: $[\alpha]^{20}D$ −71.4° (*c* 2.1, MeOH).

Anal. Calcd for $C_{11}H_{20}O$: C, 78.51; H, 11.98. Found: C, 78.39; H, 11.93.

The ir and NMR spectra were identical with those previously obtained.[23]

Isophoryl Methyl Ether. The product was purified by distillation (82–83 °C (14 mm): NMR ($CDCl_3$) δ 0.88 and 0.98 (3 H each, s, CH_3C), 1.71 (3 H, br s, CH_3C=), 3.37 (3 H, s, CH_3O); 3.8 (1 H, m, CHO), and 5.52 (1 H, br s, CH=C). Its GLC retention time, ir, and NMR spectra were superimposable with those of a sample prepared according to the literature.[24]

Anal: Calcd for $C_{10}H_{18}O$: C, 77.87; H, 11.76. Found: C, 78.13; H, 11.90.

Piperityl Methyl Ether. The reaction mixtures consisted of two methyl ethers (~1:1, GLC), which showed (GC–MS) the same molecular ion (M^+ *m/e* 168) and identical fragmentation pattern. They were separated by preparative GLC (10% QF1, 100 °C) and purified by distillation, bp 90–93 °C (15 mm). NMR ($CDCl_3$) of the isomer with lower retention time showed signals at δ 0.93 [6 H, d (*J* = 6 Hz), CH_3C], 1.72 (3 H, br s, CH_3C=), 3.33 (3 H, s, CH_3O), 3.62 (1 H, m, CHO), and 5.70 (1 H, m, CH=C).

Anal. Calcd for $C_{11}H_{20}O$: C, 78.51; H, 11.98. Found: C, 78.56; H, 12.24.

NMR ($CDCl_3$) of the other isomer had signals at δ 0.85 and 0.95 [3 H each, d (*J* = 6 Hz), CH_3C], 1.68 (3 H, br s, CH_3C=), 3.30 (3 H, s, CH_3O), 3.62 (1 H, m, CHO), and 5.48 (1 H, br s, CH=C).

Anal. Calcd for $C_{11}H_{20}O$: C, 78.51; H, 11.98. Found: C, 78.80; H, 11.75.

The NMR spectra and ir absorptions were identical with those of the two epimeric methyl ethers (1:3, GLC) obtained from piperitone by the procedure above indicated.

Neryl and 1,5-Dimethyl-1-vinyl-4-hexenyl Methyl Ethers. The two methyl ethers (~7:3, GLC) were separated by chromatography over silica gel, eluting with a *n*-hexane–benzene gradient, and purified by distillation. **Neryl methyl ether:** NMR (CCl_4) δ 1.62 (3 H, s, CH_3C=), 1.68 (6 H, s, CH_3C=), 3.31 (3 H, s, CH_3O), 3.98 [2 H, d (*J* = 6.5 Hz), CH_2O], 5.1 (1 H, m, CH=C), and 5.4 (1 H, br t, CH=C).

Anal. Calcd for $C_{11}H_{20}O$: C, 78.51; H, 11.98. Found: C, 78.83; H, 11.81.

1,5-Dimethyl-1-vinyl-4-hexenyl methyl ether: NMR (CCl_4) δ 1.2 (3 H, s, CH_3C), 1.62 and 1.69 (3 H each, br s, CH_3C=), 3.11 (3 H, s, CH_3O), 4.9–5.3 (3 H, m, CH_2=C), and 5.5–6.1 (1 H, m, CH=C).

Anal. Calcd for $C_{11}H_{20}O$: C, 78.51; H, 11.98. Found: C, 78.68; H, 11.74.

Cholesteryl Methyl Ether. The mixture (GLC) of 3β and 3α derivative was not separated, but purified by distillation: bp 181–185 °C (0.01 mm); NMR ($CDCl_3$) δ 3.35 and 3.38 (3 H, two s, CH_3O), 3.4–3.9 (1 H, m, CHO), and 5.4 (1 H, m, CH=C).

Anal. Calcd for $C_{28}H_{48}O$: C, 83.93; H, 12.08. Found: C, 83.68; H, 12.30.

(α-Phenyl)ethyl Methyl Ether: NMR ($CDCl_3$) δ 1.37 [3 H, d (*J* = 6 Hz), CH_3C], 3.12 (3 H, s, CH_3O), 4.21 (1 H, q, CHO), and 7.17 (5 H, br s, phenyl).

Anal. Calcd for $C_9H_{12}O$: C, 79.37; H, 8.88. Found: C, 79.50; H, 8.72.

(α-Phenyl)ethyl Ethyl Ether. When the $NaBH_4$ decomposition was carried out in ethanol according to the general procedure the ethyl ether was obtained in 47% yield; no allylic hydrocarbon was detected in the product mixture. NMR ($CDCl_3$) δ 1.2 (3 H, t, CH_3C), 1.46 [3 H, d (*J* = 6 Hz), CH_3C], 3.37 (2 H, q, CH_2C), 4.41 (1 H, q, CHO), and 7.23 (5 H, br s, phenyl).

Anal. Calcd for $C_{10}H_{14}O$: C, 79.95; H, 9.39. Found: C, 80.06; H, 9.40.

α-Tetrahydronaphthalenyl Methyl Ether. The methyl ether was separated from the hydrocarbons by column chromatography on silica gel eluting with a *n*-hexane–ether gradient: NMR ($CDCl_3$) δ 1.7–2.2 (4 H, m, CH_2C), 2.8 (2 H, m, CH_2Ar); 3.42 (3 H, s, CH_3O), 4.32 (1 H, t, CHO), and 7.0–7.5 (4 H, m, aromatic).

Anal. Calcd for $C_{11}H_{14}O$: C, 81.44; H, 8.70. Found: C, 81.60; H, 8.73.

1,2-Dihydronaphthalene: NMR ($CDCl_3$) δ 2.4 (2 H, m, CH_2C=), 2.8 (2 H, m, CH_2Ar), 6.08 (1 H, m, CH=C), 6.5 [1 H, d (*J* = 9 Hz), CH=C], and 7.08 (4 H, br s, aromatic).

Tetralin: NMR ($CDCl_3$) δ 1.79 (4 H, m, CH_2C), 2.78 (4 H, m, CH_2Ar) and 7.08 (4 H, s, aromatic).

Benzyl Methyl Ether: NMR (CCl_4) δ 3.3 (3 H, s, CH_3O), 4.38 (2 H, s, CH_2O), and 7.27 (5 H, s, phenyl).

Anal. Calcd for $C_8H_{10}O$: C, 78.65; H, 8.25. Found: C, 78.82; H, 8.30.

Benzyl Ethyl Ether. It was obtained by 0.05 M EtONa in ethanol, following the general procedure (at 68 °C for 24 h), in 43% yield: NMR (CCl_4) δ 1.18 (3 H, t, CH_3C), 3.46 (2 H, q, CH_2O), 4.40 (2 H, s, CH_2O), and 7.27 (5 H, s, phenyl).

Anal. Calcd for $C_9H_{12}O$: C, 79.37; H, 8.88. Found: C, 79.42; H, 9.02.

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Registry No.—*cis*-Carveyl ethyl ether, 58580-64-6; *trans*-carveyl ethyl ether, 58580-65-7; *cis*-carveyl isopropyl ether, 58548-72-4; *trans*-carveyl isopropyl ether, 58548-73-5; *cis*-carvotanacetyl methyl ether, 55449-15-5; *trans*-carvotanacetyl methyl ether, 55378-54-6; isophoryl methyl ether, 50987-46-7; *cis*-piperityl methyl ether, 58548-74-6; *trans*-piperityl methyl ether, 58548-75-7; neryl methyl ether, 2565-83-5; 3β-cholesteryl methyl ether, 1981-91-5; 3α-cholesteryl methyl ether, 17320-23-9; (α-phenyl)ethyl methyl ether, 4013-34-7; (α-phenyl)ethyl ethyl ether, 3299-05-6; α-tetrahydronaphthaleneyl methyl ether, 1008-18-0; 1,2-dihydronaphthalene, 447-53-0; tetralin, 119-64-2; benzyl methyl ether, 538-86-3; benzyl ethyl ether, 539-30-0; 1,5-dimethyl-1-vinyl-4-hexenyl methyl ether, 2565-82-4.

References and Notes

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(5) S. Cacchi, L. Caglioti, and P. Paolucci, *Bull. Chem. Soc. Jpn.*, **47**, 2323 (1974).
(6) The action of $LiAlH_4$ on the tosylhydrazones of α,β-unsaturated ketones has already been investigated;[7] however, it proceeds by means of a vinylogous attack (Michael fashion) of the hydride with migration of the double bond, as sometimes happens in the reduction of α,β-unsaturated carbonyls. (It is well known that in the latter case the vinylogous attack is strongly depressed with the use of $NaBH_4$.) $NaBH_3CN$[8c] and catecholborane[9] are nonbasic reagents, and this apparently leads to quite different initial attacks in the reduction of conjugated *p*-tosylhydrazones.
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On the Mechanism of the Thermal *N*-Nitropyrazole Rearrangement. Evidence for a [1,5] Sigmatropic Nitro Migration[1]

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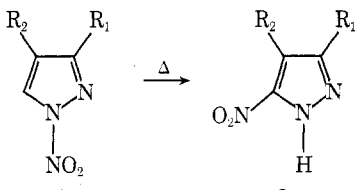
The title reaction, which smoothly proceeds at ca. 150 °C, displays first-order kinetics and is affected neither by acids or bases, nor scavengers for free radicals or for NO_2^+. Our kinetic studies further showed that replacement of 3(5)H by D has no effect on the rate of this intramolecular process. Solvent effects are surprisingly small. Substituents at the 3, 4, or 5 position exert only modest influence on rates and activation parameters; $\Delta H^{\ddagger}$ values are in the range 30–36 kcal mol^{-1}, $\Delta S^{\ddagger}$ being 2 ± 5 eu. The reaction, which can also be performed in the vapor phase, apparently does not proceed heterolytically; the type of solvent effect points to a transition state which is somewhat less polar than the starting compound. Isomerizations in benzene lead to trace amounts only of the corresponding (1−) phenylpyrazoles. The N–NO_2 bond strength is estimated to be 45–50 kcal mol^{-1}. Hence, a homolytic mechanism involving free (1−) pyrazolyl radicals is highly unlikely. All experimental data are compatible with a rate-determining [1,5] shift of NO_2 to give a 3*H*-pyrazole as an intermediate, which subsequently isomerizes into the 3(5)-nitropyrazole. The first step is discussed in some detail. As the reverse reaction could not be observed, the overall process is markedly exothermal. With 4-substituted 1-nitropyrazoles some denitration (apparently caused by steric hindrance) is competing with rearrangement.

Thermal rearrangement of *N*-nitropyrazoles unsubstituted at the 5 position (1) has been proven to be a convenient method for the preparation of 3(5)-nitropyrazoles (**2**)[2,3] (Scheme I). The isomerizations can be performed at moderate temperatures (120–190 °C) in various solvents. Normally, the 3(5)-nitropyrazoles are formed quantitatively; in some instances side reactions, particularly denitration, are observed.

Thermal N → C migration of NO_2 is not restricted to pyrazoles; analogous migrations were found in *N*-nitroindazoles,[4] triazoles,[5] and imidazoles.[6]

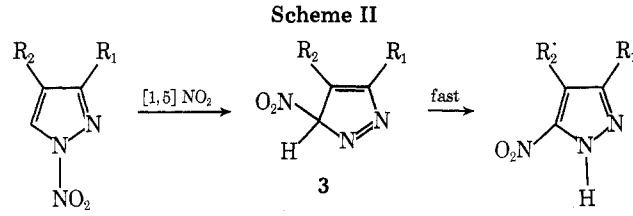
Scheme I



1 **2**

a, $R_1 = R_2 = H$
b, $R_1 = CH_3$; $R_2 = H$
c, $R_1 = C(CH_3)_3$; $R_2 = H$
d, $R_1 = C_6H_5$; $R_2 = H$
e, $R_1 = p\text{-}NO_2C_6H_5$; $R_2 = H$
f, $R_1 = NO_2$; $R_2 = H$
g, $R_1 = H$; $R_2 = CH_3$
h, $R_1 = H$; $R_2 = C_2H_5$

Scheme II



1 **3** **2**

For the mechanism of the rearrangement of *N*-nitro(pyr)-azoles, a two-step process has been proposed,[3,5] involving an unprecedented [1,5] sigmatropic shift of the nitro group and fast rearomatization of the intermediately formed 3*H*-pyrazole (**3**) (Scheme II). For thermal N → C migrations of alkenyl groups in pyrroles and, recently, imidazoles, similar mechanisms have been suggested.[7,8] Our proposition was based on the apparent intramolecularity of the *N*-nitropyrazole rearrangement. The isomerization obeys first-order kinetics perfectly and no divergent reaction paths were observed when the thermolyses were performed in the presence of reagents (e.g., phenol, quinoline, and toluene) which may act as catalyst or scavenger of intermediates (see ref 2). Moreover, a sigmatropic process adequately accounts for NO_2 migration to the 5(3) position. Migration to the 4 position has only been ob-