1b and **1c** (total ~15%) were also detected in the reaction mixture, indicating that the hydrogenation of **8** must have provided a small amount of the trans isomer of **9**.[7] However, the fact that **1a** (all-cis) was one of the major products from this cyclization requires that the substituents on the pyrrolidine ring of the other major product must also have been cis.

Experimental details and additional work on this system will be reported at a later date.

References and Notes

(1) F. J. Ritter, I. E. M. Rotgans, E. Talman, P. E. J. Verwiel, and F. Stein, *Experientia*, **29**, 530 (1973).
(2) P. E. Sonnet, *J. Med. Chem.*, **15**, 97 (1972).
(3) Satisfactory elemental analyses and spectral data were obtained for all new compounds.
(4) B. Luning and C. Lundin, *Acta Chem. Scand.*, **21**, 2136 (1967).
(5) For examples of reductions of 2,6-disubstituted pyridines, see (a) R. K. Hill, T. H. Chan, and J. A. Joule, *Tetrahedron*, **21**, 147 (1965); (b) J. Pliml, E. Knobloch, and M. Protiva, *Chem. Listy*, **46**, 758 (1952).
(6) Although no systematic study of the stereochemistry of pyrrole reductions appears to have been published, cis hydrogenations have normally been assumed, and in some cases demonstrated: C. G. Overberger, L. C. Palmer, B. S. Marks, and N. R. Byrd, *J. Amer. Chem. Soc.*, **77**, 4100 (1955).
(7) Attempted analyses of **9** by gas chromatography on a variety of packed columns was unsuccessful, primarily because of excessive tailing.

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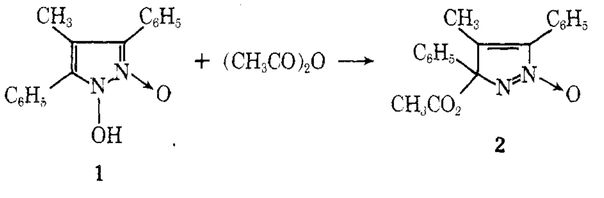
Molecular Rearrangements of *N*-Hydroxypyrazole Derivatives[1]

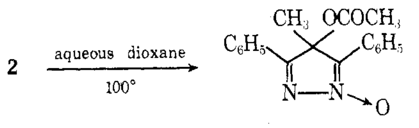
Summary: The tosylates of *N*-hydroxypyrazoles are hydrolyzed quantitatively to 5-pyrazolones, a reaction involving 1,2 migration in which anti-aromatic diazacyclopentadienyl cations are possible intermediates.

Sir: In an earlier investigation it was observed that acetylation of 1-hydroxy-3,5-diphenyl-4-methylpyrazole 2-oxide (**1**) yielded a *C*-acetoxy compound (**2**) rather than an *N*-acetoxy compound.[2] Recently others have reported analogous rearrangements in this heterocyclic series.[3] In many respects these reactions resemble some of those reported in the indole[4] and purine[5] series. In each instance the driving force appears to be the exchange of the weak N–O bond for a stronger C–O bond.



1 **2**

Some additional rearrangements have now been observed. Upon heating in aqueous dioxane, acetate **2** further rearranges to acetate **3**. The structure of **3** rests upon its elementary analysis and the similarity of its infrared and nmr spectra to that of the corresponding dioxide.[2,6] Similar sequential 1,2 rearrangements of *N*-methoxypyrazole oxides[3] and *N*-nitropyrazoles[8] have been observed.



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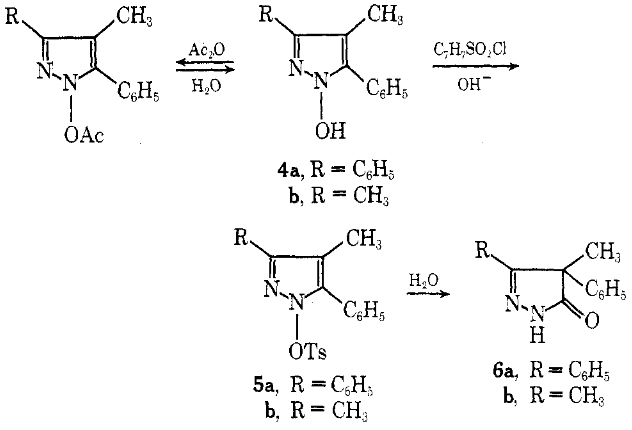
Acetylation of *N*-hydroxy-3,5-diphenyl-4-methylpyrazole (**4a**) produced the *N*-acetoxy derivative which did not rearrange after prolonged heating in boiling xylene. Hydrolysis regenerated the *N*-hydroxypyrazole. However, the corresponding *N*-tosyloxy compound (**5a**) was converted quantitatively, upon heating in aqueous dioxane, to 3,4-diphenyl-4-methyl-5-pyrazolone (**6a**). This transformation resembles the conversion of indoles into oxindoles by hypochlorite, a sequence which may begin by N-chlorination[4] yielding an intermediate analogous to the *N*-tosylate **5**.[9]



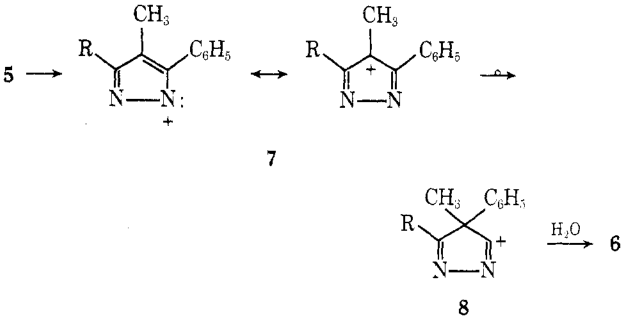
4a, $R = C_6H_5$
b, $R = CH_3$

5a, $R = C_6H_5$
b, $R = CH_3$

6a, $R = C_6H_5$
b, $R = CH_3$

When 3(5)-phenyl-4,5(3)-dimethyl-1-hydroxypyrazole was similarly tosylated and heated in water, the product was again that of phenyl migration, 3,4-dimethyl-4-phenyl-5-pyrazolone (**6b**).

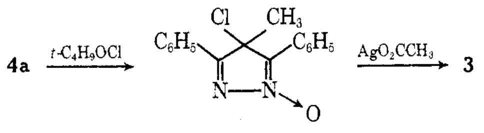
A possible mechanism analogous to those proposed for the indoles[4] involves ionization of **5** to ion **7**, a heterolog of the anti-aromatic cyclopentadiene cation.[10] Isomerization to ion **8** would lead to the product.[11,13] In an effort to determine the chemistry of possible precursors of ions like **7**, the electrophilic substitution reactions of the hydroxypyrazoles are being investigated as sources of such compounds. Treatment of **4a** with *tert*-butyl hypochlorite yields 4-chloro-4-methyl-3,5-diphenylpyrazolenine 1-oxide (**9**). While the *N*-oxide function may strongly influence the reactivity of **9** so that it is a poor model[14] for precursors of ion **7**, it was found that **9** reacts readily with silver acetate to yield acetate **3**. Thus, in this case at least, a reaction which most likely involves a carbonium ion intermediate proceeds



7

8

without rearrangement. Of some interest, however, is the comparative ease with which this antiaromatic heteroion is produced. Further studies of such ions are in progress.



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References and Notes

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(2) J. P. Freeman and J. J. Gannon, *J. Org. Chem.*, **34,** 194 (1969).

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(4) For leading references, see P. G. Gassman, G. A. Campbell, and G. Mehta, *Tetrahedron*, **28,** 2749 (1972).

(5) For leading references, see T-C. Lee, G. Salemnick, and G. B. Brown, *J. Org. Chem.*, **38,** 3102 (1973).

(6) 4,4-Dialkylpyrazole oxides analogous to **3** isomerize under the influence of light to dialkyl derivatives analogous to **2**.[7] It is not likely that the photochemical and thermal reactions are related mechanistically but the contrasting behavior is interesting.

(7) W. M. Williams and W. R. Dolbier, Jr., *J. Amer. Chem. Soc.*, **94,** 3955 (1972).

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(10) R. Breslow, *Accounts Chem. Res.*, **6,** 393 (1973).

(11) The uncertainty in the structure of **5b**[2,12] is unimportant if ion **7** is involved, but it is possible that the structure of the hydroxypyrazole and of the pyrazolone are more intimately related.

(12) F. T. Boyle and R. A. Y. Jones, *J. Chem. Soc., Perkin Trans. 1*, 170 (1973).

(13) Direct attack of water on the ring in an S$_N$2′-type substitution may also be involved, but good nucleophiles such as amines or alkoxide ion attack the sulfonyl group rather than the ring. Concerted mechanisms involving allowed suprafacial 1,5-sigmatropic shifts are among the many other possibilities.

(14) The recently reported silver ion catalyzed reactions of α-chloronitrones indicate extensive back-donation of electron density from oxygen to carbon: U. M. Kempe, T. K. Das Gupta, K. Blatt, P. Gygax, D. Felix, and A. Eschenmoser, *Helv. Chim. Acta*, **55,** 2187 (1972).

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