

FORMATIONS AND REACTIONS OF 1-ALLYLTOSYLHYDRAZIDES

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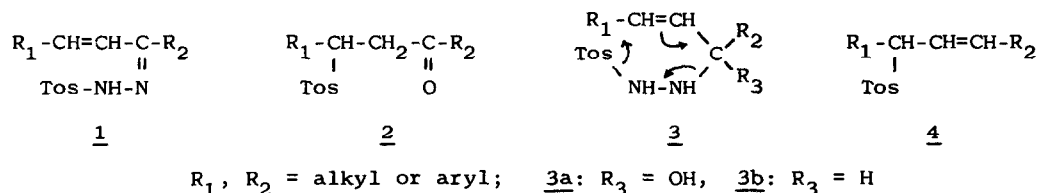
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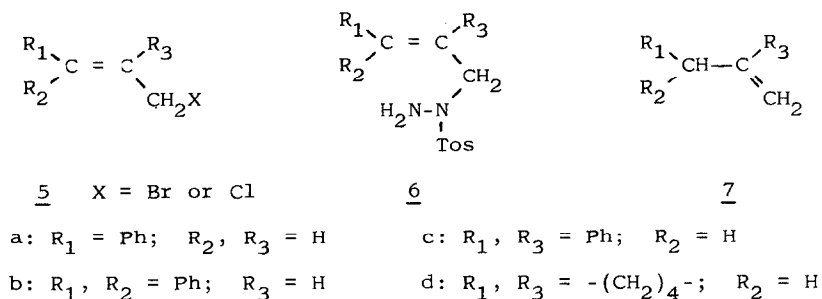
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We found that α,β -unsaturated ketone tosylhydrazones 1, when refluxed in aqueous acetic acid, afforded β -tosylketones 2 in good yield and proposed a concerted fragmentation of the hydrated intermediates 3a (1).

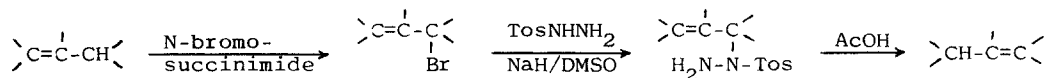
For a study of some aspect of the concerted mechanism in this reaction, we wished to prepare and decompose tosylhydrazone derivatives of the type 3b, expecting a similar concerted fragmentation leading to tosyl olefins 4. The reaction did actually occur (2), but during the course of the study we found a reaction which could conveniently be used for migrating double bond.



Whereas the reaction of allyl halides with tosylhydrazide in pyridine afforded 2-allyltosylhydrazides 3b, the reaction in NaH/DMSO afforded 1-allyl derivatives 6. Typically, the treatment of DMSO solution of tosylhydrazide with sodium hydride, followed by addition of cinnamyl chloride 5a, afforded 1-cinnamyl-tosylhydrazone 6a in 86% yield. The presence of a primary amino group in 6a was shown by deriving 6a to benzalamino derivative. When 6a was heated in acetic acid at 30-60°, allylbenzene 7a was obtained in 70% yield. Allylbenzene was also obtained when 6a was pyrolyzed at 110°, but the yield was much lower in this case. Notably, the reaction proceeded so as to isolate double bond from cinnamyl conjugation.

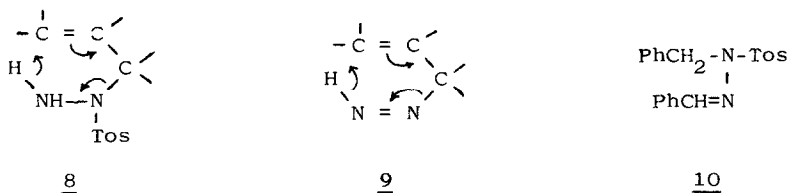


As an extension of this type of reaction, some allyl halides 5b-5d were reacted with tosylhydrazide by NaH/DMSO method. The resulted 1-allyltosylhydrazides 6b-6d, when warmed in acetic acid, afforded expected products 7b-7d in 55-70% yields. The structures of the products were determined from IR and NMR spectra. It should be noted that the reaction proceeded cleanly, no other double bond isomers being detected in each product by gas chromatography and NMR spectrum, and the reaction could generally be used for migrating double bond even for the thermodynamically unfavorable direction by the sequence shown below.



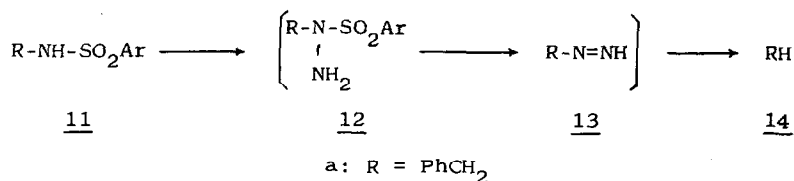
The similar type of double bond migration have been reported in cases of the reaction of allylamines with difluoramine (3) and the Wolff-Kishner reduction of α,β -unsaturated carbonyl compounds (4). However, both reactions have limitation for general applicability because, in the former case, special experimental technique is necessary for handling difluoramine and, in the latter case, the reaction frequently gives product as a mixture of double bond isomers, or proceeds in another direction.

An exclusive formation of only one isomer in the present reaction would show that the concerted fragmentation of 1-allyltosylhydrazide 8, or allyldiimide 9



formed in situ by elimination of p-toluenesulfonic acid from 8, could be a preferred pathway for this reaction.

Nickon and Hill (5) showed that treatment of N-substituted sulfonamides 11 with an excess of hydroxylamine-O-sulfonic acid in the presence of aqueous alkali yielded the corresponding hydrocarbons 14 and proposed a following scheme as the possible pathway (6). As an example they obtained toluene from N-benzylsulfon-



amide 11a (Ar = Ph) in good yield. When 1-cinnamyltosylhydrazide 6a was treated with sodium methoxide, two isomers, allylbenzene and 1-phenylpropene, were obtained in a ratio of 5 : 2. In separate experiments we treated allylbenzene under the same conditions as those for the sodium methoxide decomposition of 6a and found that allylbenzene was converted into 1-phenylpropene to an extent of 1/8. Presumably, concerted and non-concerted fragmentations of 6a occurred competitively in the alkaline decomposition.

When 1-benzyltosylhydrazide 12a (Ar = p-Tol) was treated with acetic acid, a benzalmino derivative 10 was obtained in 54% yield (calculated stoichiometrically). Obviously, lacking of olefinic group in 12a forced the reaction to proceed in another way. A reasonable scheme for the formation of this compound would involve steps: a) elimination of p-toluenesulfonic acid from 12a affording benzylidiimide 13a, b) tautomerization of the diimide into benzaldehyde hydrazone, and c) reaction of the hydrazone, or benzaldehyde formed therefrom, with the starting material 12a.

References

1. T. Sato and I. Homma, Abstracts of papers presented at the 21st meeting of the Chemical Society of Japan, Vol. III, p. 1814, Osaka, April, 1968.
2. The details of this reaction will be reported in a separate paper.
3. C. L. Bumgardner and J. P. Freeman, J. Am. Chem. Soc., 86, 2233 (1964).
4. R. Fischer, G. Lardelli and O. Jeger, Helv. Chim. Acta, 34, 1577 (1951), and preceding papers in series.
5. A. Nickon and A. S. Hill, J. Am. Chem. Soc., 86, 1152 (1964).
6. Some N-aminosulfonamides have been isolated and decomposed to hydrocarbons:
L. A. Carpino, J. Org. Chem., 30, 321 (1964).