

DECOMPOSITION OF TOSYLHYDRAZONES OF BENZOIN, BENZOIN ACETATE
AND BENZOIN BENZOATE WITH ALKALI

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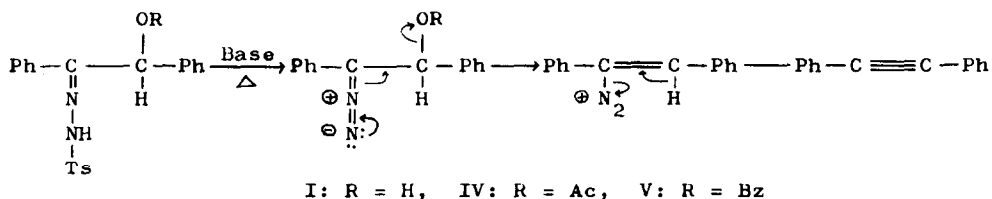
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While a number of papers on reactions of tosylhydrazones with alkali have been published in recent years, only a few examples have been reported of the reaction of tosylhydrazones containing leaving group on the adjacent carbon. Banford and Stevens (1) reported that tosylhydrazone (I) of benzoïn gave desoxybenzoïn (II) in 65% yield by the decomposition in a protic solvent. However, the reaction should involve the formation of diphenylacetylene (III) as well as II according to the following reaction sequence. In this paper we present evidence that the reaction indeed proceeds in this manner.



Benzoïn, benzoïn acetate and benzoïn benzoate were converted into the respective tosylhydrazones (I, IV, m.p. 127-129° and V, m.p. 153-154.5°) by the usual method and treated with alkali under protic and aprotic conditions. The product mixtures were separated by preparative TLC (2) and analysed by VPC, and the results are tabulated below.

Table

Tosylhydrazone	Reaction condition	Yield (%) of	
		II	III
I	Na/(CH ₂ OH) ₂	55.9	10.1
IV	"	42.7	52.6
V	"	41.5	42.1
I	CH ₃ ONa/(EtOCH ₂ CH ₂) ₂ O	71.8	13.3
IV	"	3.3	94.4
V	"	0	98.4

This result is summarized as follows. (i) The anticipated triple bond formation takes place in both under the protic and aprotic conditions. (ii) The increase in leaving aptitude of the adjacent group (acylation of the hydroxyl group) results in facile formation of III. (iii) The elimination of acetoxyl and benzoyloxyl groups in the decomposition of IV and V under the aprotic conditions remarkably predominates over the formation of carbene intermediate {3} leading to II.

Acknowledgement

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References

- (1) W. R. Banford and T. S. Stevens, *J. Chem. Soc.* 4735 (1952).
- (2) The identity of II and III was carried out by direct comparison with the authentic samples prepared by the known methods.
- (3) L. Freedman and H. Shechter, *J. Am. Chem. Soc.* 81, 5512 (1959).