Tetrahedron Letters No. 5, pp 395 - 396, 1976. Pergamon Press. Printed in Great Britain.

RETENTION OF CONFIGURATION AT SP^2 CARBON IN BIMOLECULAR NUCLEOPHILIC DISPLACEMENT OF HALIDE ION FROM HYDRAZONYL HALIDES

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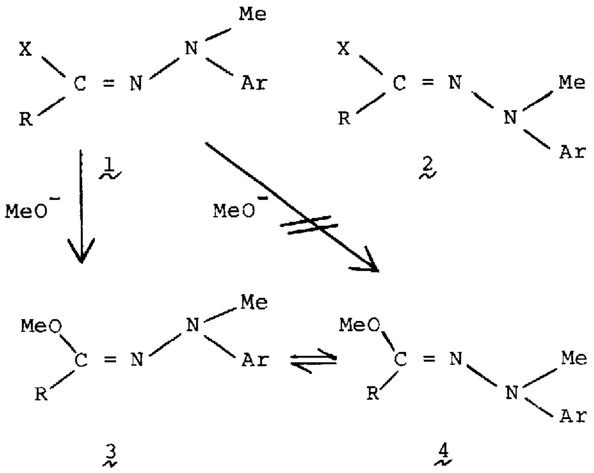
(Received in UK 5 December 1975; accepted for publication 22 December 1975)

Stereoselective nucleophilic substitution reactions at sp^2 hybridised carbon in vinyl systems proceed generally with retention of configuration.[1] One example of a stereospecific bimolecular nucleophilic displacement at an imino carbon has been reported by Johnson, Nally and Weidig;[2] using methoxide ion as nucleophile, (E)-O-methylbenzohydroximoyl chloride was converted to methyl-(Z)-O-methylbenzhydroximate with inversion of configuration. This result cannot be general, however, since we now report a bimolecular nucleophilic substitution at the carbon-nitrogen double bond which proceeds with retention of configuration.



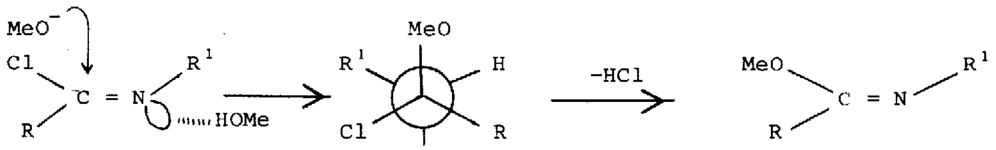
	R	Ar
a	t-Bu	2,4-$(NO_2)_2C_6H_3$
b	Ph	2,4-$(NO_2)_2C_6H_3$
c	Ph	p-$NO_2C_6H_4$
d	Ph	Ph

Hydrazonyl halides may exist in two geometrically isomeric forms **1** or **2** (X = Cl or Br), which do not rapidly interconvert at ambient temperatures.[3] We have found that the halide formed either on bromination of the corresponding hydrazone or treatment of the hydrazides with phosphorous pentachloride are exclusively (Z)-isomers (**1**). This is consistent with nmr evidence[4] and was unequivocally confirmed in one instance (**1a**, X = Br) by x-ray crystallographic analysis.

When treated with methoxide ion (under conditions where the reaction is bimolecular) the (Z) isomers **1** (X = Cl or Br) gave exclusively the (Z)-methyl hydrazonates **3** uncontaminated by the isomers **4**. The possibility arises that the observed formation of the (Z) isomers is not kinetically controlled but merely represents formation of the more stable product. However, this does not appear to be the case since at elevated temperature **3** undergoes thermal isomerisation to **4** and the ratios of **3** to **4** at equilibrium (Table) generally favour the E isomer 4. Methoxide ion catalysed isomerisation of the starting halide **1** or of the hydrazonate **3** was also investigated and shown to be insignificant under the reaction conditions.

TABLE: Z/E ISOMER RATIOS AT EQUILIBRIUM IN CHLOROBENZENE

Hydrazonates:	3a:4a	3b:4b	3c:4c	3d:4d
Isomer Ratios:	80:20	22:78	43:57	20:80



SCHEME

It is difficult to rationalise why bimolecular displacements in the related hydroxamoyl and hydrazonyl systems should take such a different stereochemical course. A possible factor might be the greater basicity of the imino nitrogen in **1**. This would promote hydrogen bonding (and thus proton transfer) to the nitrogen lone pair by the solvent at this site in the transition state (Scheme); the tetrahedral intermediate then formed could undergo anti-elimination of HCl without further C-N bond rotation or nitrogen inversion.

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