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MIGRATORY APTITUDE OF THE ETHYL AND THE METHYL GROUPS DURING STEVENS REARRANGEMENT OF N,N-DIALKYL-2-ARYLBENZOTHIAZOLINIUM SALTS

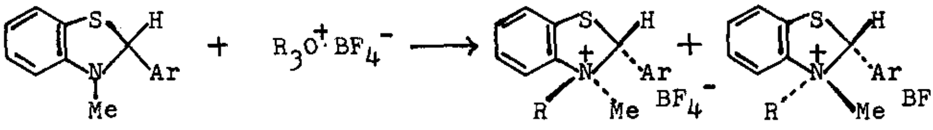
Kin-ya Akiba,* Yoshio Ohara, and Naoki Inamoto

Department of Chemistry, Faculty of Science,
The University of Tokyo, Hongo, Tokyo 113, Japan

Stereochemical relation between the migrating group on the ammonium nitrogen and the carbanion was investigated on Stevens rearrangement of N, N-dialkylbenzothiazolinium salts to show large migratory aptitude of the ethyl against the methyl group (Et: Me $\gtrsim$ 20:1), where cyclic ammonium ylide with planar π-type carbanion was proposed to be the intermediate.

Intramolecular nature and conservation of stereochemistry of the migratory group have been proved for Stevens rearrangement and some more detailed mechanisms were also discussed.[1] However, there have been almost no experimental investigations on the migratory aptitude of substituents, other than substituted benzyl groups, of the ammonium group and on the stereochemical relation between the migratory group and the carbanion of the ylide.

Recently, we reported the preparation of N,N-dialkylbenzothiazolinium salts according to equation (1),[2] where pure stereoisomer (**1**) was obtained in the case of **1-a** (R=Et and Ar=p-ClC_6H_4) and **1-b** (R=Et, Ar=Ph) whereas only 1:1 mixture of **1** and **2** was obtained in the case of **1-c** (R=Et and Ar=p-MeC_6H_4) and **1-d** (R=Et and Ar=p-$MeOC_6H_4$) after recrystallization from ethanol.

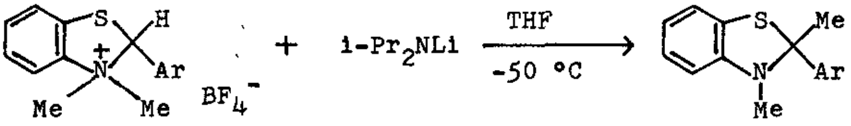


(1)

1 **2**

These salts should be very good models to study stereochemical relation between the migratory group (R or Me) and the carbanion, because the configuration of the intermediate ammonium ylide may well be the same as that of the starting salt. First, we tried the Stevens rearrangement of 2-aryl-3,3-dimethylbenzothiazolinium tetrafluoroborate (**3**) by deprotonation with lithium diisopropylamide in THF at -50 °C under nitrogen and obtained the expected benzothiazoline (**4**)[3] in the following yield; i.e., **4**: Ar, %; **a**: p-ClC_6H_4, 62; **b**: Ph, 41; **c**: p-MeC_6H_4, 47; **d**: p-$MeOC_6H_4$, 20.

When there is no aryl group at 2-C, i.e., hydrogen or methyl instead of Ar, the rearrangement did not take place at all under the same conditions.

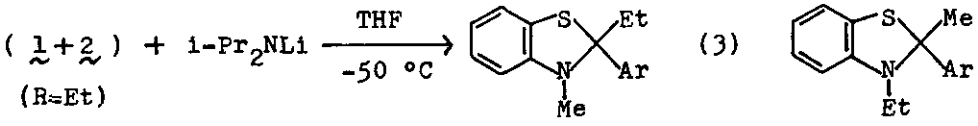


(2)

3 **4**

Then, the rearrangement of pure isomer of 1a and 1b was tried to afford the corresponding 5 in the yield of 33% (5a: Ar=p-ClC_6H_4) and 22% (5b: Ar=Ph). No 6 could be detected by NMR and glc,[4] indicating that only the ethyl group syn to the hydrogen migrated. This fact may be explained by S_N2 type nucleophilic attack with the carbanion whose original configuration was retained as sp^3.

However, when the 1:1 mixture of 1 and 2 was used as the starting material, only the corresponding 5 was again obtained in the yield of 30% (5c: Ar=p-MeC_6H_4) and 54% (5d: Ar=p-$MeOC_6H_4$) without any detectable amount of 6.



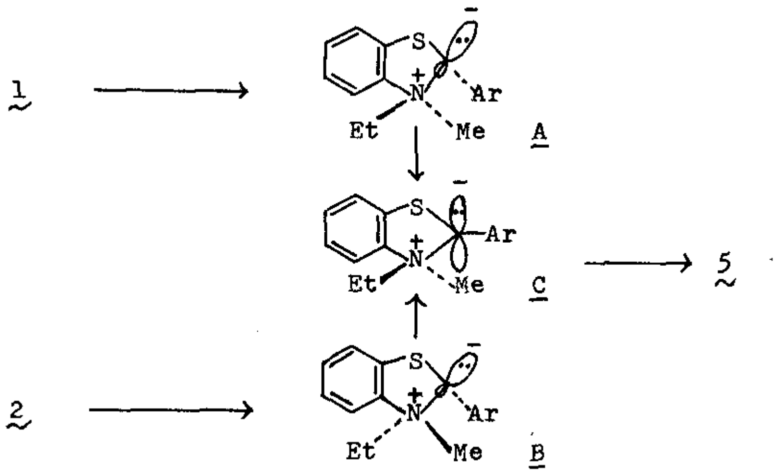
(3)

5

6

All these facts indicate that the ethyl group migrates exclusively irrespective of the stereochemistry of the original benzothiazolinium salts. To realize these phenomena, it is necessary to invoke the planar carbanion (C) conjugated with the aryl group as an intermediate, because very rapid interconversion between A and B can be ruled out.[5]

The great difference of migratory aptitude between the ethyl and the methyl (Et: Me $\gtrsim$20:1) in equation (3) is similar to the observation for Wittig rearrangement in which analogous radical pair mechanism as Stevens rearrangement is accepted.[6] Large migratory aptitude of ethyl compared with methyl has also been reported in the rearrangement of isoindene to indene, although the mechanism seems to be different.[7]



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4 Absence of **6** was checked by using authentic samples of **5** and **6** prepared by the method of ref. 3 (OV-1, 1 m, 220 °C).

5 Inversion of sp^3 type carbanion is known to be slow enough to retain its configuration (J. W. Henderson, *Chem. Soc. Rev.*, 1973, **2**, 397) and there is no reason to support that S_N2 type attack of carbanion to ethyl is faster than to methyl.

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