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SELECTIVE MIGRATION OF THE o-ALKYLTHIOPHENYL GROUP IN STEVENS REARRANGEMENT

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Abstract — 2-Aryl-3,3-dimethylbenzothiazolinium tetrafluoroborate (1) suffers nucleophilic attack at the ring sulfur atom by butyllithium to afford the ring-opened ammonium ylide (A), which collapses to the radical pair (B) to give unusual Stevens rearrangement product (2) as a major product, where the *o*-alkylthiophenyl group migrated selectively in preference to the methyl group.

Recently we reported the result on Stevens rearrangement[1)] of N,N-dialkylbenzothiazolinium salts (1)[2)] effected by deprotonation with lithium diisopropylamide (LDA), where the reaction was designed to show whether there could be any possibility for S_Ni type mechanism to take place during the migration of the alkyl group. This mechanism is not allowed by the Woodward-Hoffmann rule but was calculated to have a rather low activation energy (17 kcal/mol) in gas phase by MINDO/3[3)].

Now we report the reaction of the same salts with butyllithium which, to our surprise, followed totally different course.

Butyllithium (3.46 mmol) in hexane was added to a suspension of 3,3-dimethyl-2-phenylbenzothiazolinium tetrafluoroborate (1a, 950 mg, 2.89 mmol) in ether (15 ml)-benzene(8 ml) at −50 °C under nitrogen with stirring. The cooling bath was removed after 30 min and the stirring was continued for 4 h at room temperature. After usual work-up, the residue was separated into four fractions by dry column chromatography [SiO_2, CCl_4-CH_2Cl_2 (2:1)]. The following three compounds, *i.e.*, 2a, 3, and 4, were obtained in the order of increasing R_f values with some minor products in the yields of 38, 6, and 14 %, respectively.

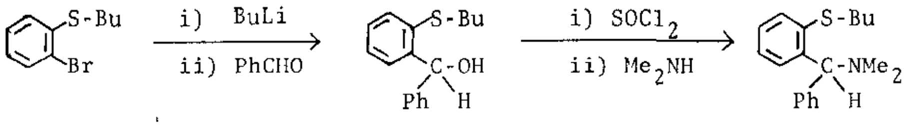
Spectroscopic data of 2a and 3 are shown below:

2a: mp 42-43 °C; NMR(δ from TMS in $CDCl_3$): 0.91 (3H, br t), 1.2-1.9 (4H, m), 2.22 (6H, s), 2.86 (2H, br t, J=7 Hz), 4.87 (1H, s), 7.0-8.0 (9H, m); MS: 299 (M^+, 74 %), 284 (M^+- Me, 100 %).

3: yellow oil; NMR($CDCl_3$): 0.91 (3H, br t), 1.2-1.9 (4H, m), 2.7-3.1 (2H, br t, J=7 Hz), 2.76 (6H, s), 6.8-7.4 (4H, m); MS: 209 (M^+, 62 %), 153 (M^+- Bu + H, 100 %).

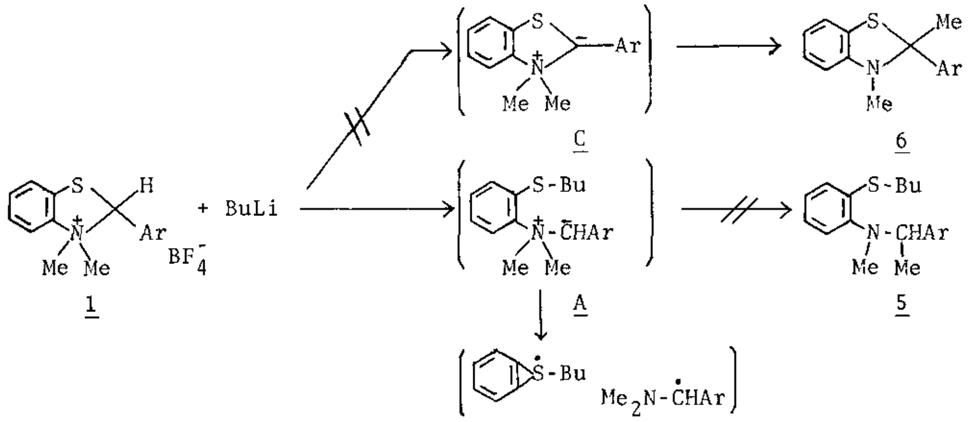
The structure of 2a is shown not to be 5, the normal Stevens rearrangement product of A, but to be that shown here by the presence of NMR absorption of a dimethylamino group at δ 2.22 which is in higher field than that attached to a benzene ring (cf. 3, δ 2.76).

The structure of 2a was determined unambiguously by the following synthesis. Reasonable spectroscopic data were obtained also for 2b and 2c.



2a (1)

Reaction scheme and yields of major products are shown below.



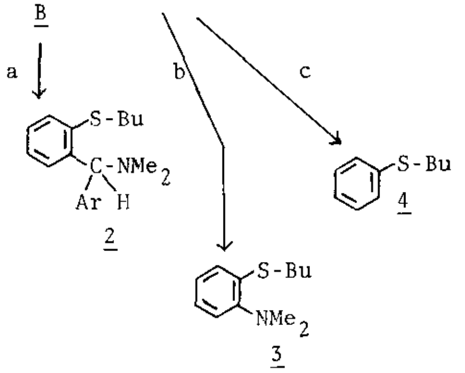
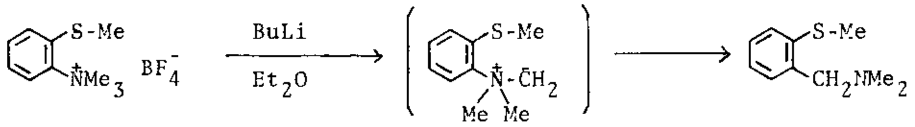


Table. Yields of Major Products

	2 (%)	3 (%)	4 (%)
a: Ar=C_6H_5	38	6	14
b: Ar=p-$MeOC_6H_4$	33	8	12
c: Ar=p-MeC_6H_4	27	8	16

Here, the Stevens rearrangement product (6) of cyclic ammonium ylide (C) was not obtained at all in contrast to the reaction of 1 with LDA.[1] Production of three major products can be rationalized by the formation of the ring-opened ammonium ylide (A) which then collapses to the radical pair (B). This intermediate (B) recombines to give 2 and also can afford 3 and 4 by usual way.

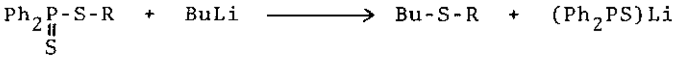
The most interesting point is that 2 is the isomer of the expected Stevens rearrangement product (5), because it is known that migratory aptitude of alkyl groups is usually higher than that of aryl groups in this kind of rearrangement.[4] The reason for this unusual aryl group migration can be ascribed to participation of the adjacent sulfur atom in stabilizing the aryl radical as shown in B. This was supported by the following reference reaction where the product due to aryl migration was obtained as a major product (22 %) under the same condition.



(2)

Similar attack at the divalent sulfur atom by butyllithium was already reported on the following reactions where there are rather stabilized anions as leaving groups.

(3)[5]



$$\mathrm{Ph_2}\underset{\overset{\|}{\mathrm{S}}}{\mathrm{P}}\mathrm{-S-R} + \mathrm{BuLi} \longrightarrow \mathrm{Bu-S-R} + (\mathrm{Ph_2PS})\mathrm{Li}$$

(4)[6]

Thus it was shown that the benzothiazolinium salt (1) suffers direct attack at the sulfur atom to give the ring-opened ammonium ylide (A) which yields the radical pair (B) by participation of the o-thioalkyl group.

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7) Compounds (**2a**, **b**, and **c**) gave correct elemental analyses.

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