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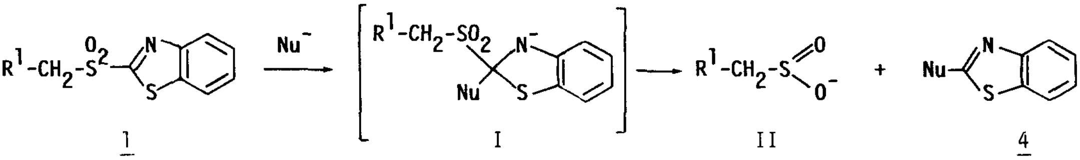
# A DIRECT SYNTHESIS OF OLEFINS BY REACTION OF CARBONYL COMPOUNDS WITH LITHIO DERIVATIVES OF 2-[ALKYL- OR (2'-ALKENYL)- OR BENZYL-SULFONYL]-BENZOTHIAZOLES.

Jean Bernard Baudin, Georges Hareau, Sylvestre A. Julia*, Odile Ruel.

Laboratoire de Chimie, Ecole Normale Supérieure,
24 rue Lhomond, 75231 Paris Cedex 05, France.

Summary: During the title reaction, the lithium alkoxides formed as intermediates undergo an intramolecular addition to the neighboring C=N group followed an S to O benzothiazole transfer and simultaneous extrusion of sulfur dioxide and ejection of 2(3H)-benzothiazolone anion.

During our earlier studies on the preparation of the unstable homoconjugated sulfinic acids for their regioselective loss of sulfur dioxide into various unsaturated systems [1], we became interested in the possibility of procuring aliphatic unsaturated sulfinic anions from [2-alkenylsulfonyl]-benzothiazoles by the known reaction of appropriate nucleophiles [2]:

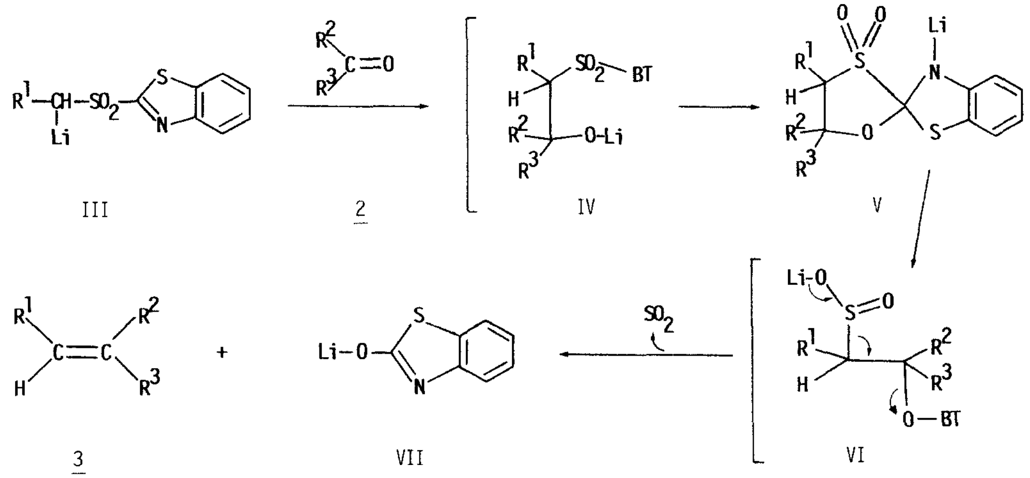


**SCHEME 1.**

Whereas the reaction with alkoxide anions RO$^-$ has been described in more or less harsh conditions [2a-d,f], it seemed very likely that an intramolecular version of this reaction should be much more facile. Similar alkoxide trappings have been recorded during the reaction of carbonyl compounds with lithiated 2-(alkylthio)-2-oxazolines [3] and during the treatment of 2-($\beta$-hydroxyalkylthio)-benzothiazoles with sodium hydride [4]. Although the sulfonyl group is increasingly attracting attention as a useful functionality in organic synthesis, there is however relatively little information concerning the chemistry of benzothiazolyl-sulfones (hereafter denoted as BT-sulfones). We have therefore taken up the questions of the preparation of the novel $\alpha$-lithio derivatives of the title BT-sulfones and their reactivity with carbonyl compounds.

The representative and stable BT-sulfones 1(a-d) [5] were easily prepared by oxidation of the corresponding sulfides with potassium permanganate (1a,c) or hydrogen peroxide (1b,d)[6].

When treated with a 1.1 equivalent of lithium diisopropylamide (LDA) in THF (0.5 M) at -78°C for 1 h, the allylic or benzylic BT-sulfones (1b,c,d) gave the corresponding α-lithio derivatives which after reaction with ketones 2 at -78°C for 3 h then at room temperature for 1 h and quenching with water (Procedure A) furnished straightforwardly the olefins (3f-i)(**TABLE** 1 entries 6,8,10,11) with acceptable yields.



**SCHEME 2.**

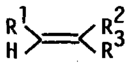
Application of the above procedure A to the methyl-BT-sulfone 1a and benzophenone gave a low yield (11%) of the olefin 3e along with starting materials and the compound 4 (Nu= BT-$SO_2CH_2$) as the major product. This result is probably due to the rapid reaction of α-lithiomethylsulfone with itself or with the starting methyl sulfone 1a to give an intermediate I ($R^1$=H or Li, Nu= BT-$SO_2CH_2$) which finally undergoes an elimination to provide the compound 4 (Nu= BT-$SO_2CH_2$).

As some successful lithiations of various aryl sulfones bearing a neighboring carbonyl group [7a-d] or of a vinyl sulfone in the presence of cyclohexanone [7e] ("Barbier" conditions) have been reported, a second procedure B was tried: to a cooled (-78°C) solution of stochiometric quantities of methyl BT-sulfones 1a and carbonyl compound in THF (0.5M), a solution of LDA (1.1 equivalent) was added; after stirring at -78°C for 3 h, the temperature was allowed to rise to RT (1 h). The results summarized in **TABLE 1** show that this procedure B can be applied to enolizable aldehydes or ketones and to allylic or benzylic BT-sulfones.

In some experiments, the reaction mixture was quenched with a slight excess of diluted sulfuric acid, followed by the usual extraction and chromatography on silica gel which provided the olefin 3 and a crystalline compound, the physical and spectroscopical data of which were found to be identical with those described for 2(3H)-benzothiazolone [8]. The above findings allow us to propose the mechanism shown in **SCHEME** 2 involving the nucleophilic condensation of the α-lithiated BT-sulfones III with the carbonyl compound 2, addition of the thus-formed lithium alkoxide to the neighboring C=N group followed by an S to O benzothiazole transfer and simultaneous extrusion of sulfur dioxide and ejection of

2(3)-benzothiazolone anion VII yielding the olefin 3 [9].

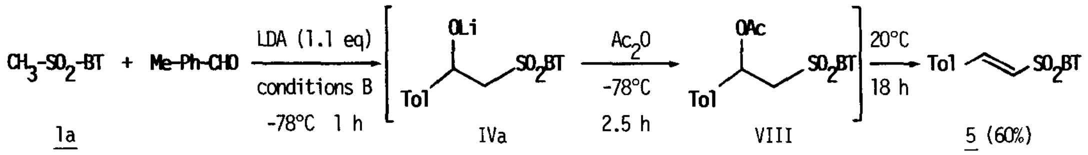
TABLE 1.

| Entry | $R^1-CH_2-SO_2-BT$ | | $R^2-\overset{O}{\overset{\|}{C}}-R^3$ | | | Conditions * |  |
|---|---|---|---|---|---|---|---|
| | $R^1$ | | $R^2$ | $R^3$ | | | Yield % |
| 1 | H | (1a) | $nC_9H_{19}$ | H | (2a) | B | 20 (3a) |
| 2 | H | (1a) | $p.MeOC_6H_4$ | H | (2b) | B | 64 (3b) |
| 3 | H | (1a) | $p.MeOC_6H_4$ | $CH_3$ | (2c) | B | 50 (3c) |
| 4 | H | (1a) | $-(CH_2)_2-CH(tBu)-(CH_2)_2$ | | (2d) | B | 21 (3d) |
| 5 | H | (1a) | Ph | Ph | (2e) | B | 55 (3e) |
| 6 | $Me_2C{=}CH$ | (1b) | $-(CH_2)_5-$ | | (2f) | A | 56 (3f) |
| 7 | | (1b) | | | (2f) | B | 68 (3f) |
| 8 | Ph | (1c) | $-(CH_2)_5-$ | | (2f) | A | 61 (3g) |
| 9 | | (1c) | | | (2f) | B | 64 (3g) |
| 10 | $Ph-CH{=}CH$ | (1d) | CH3 | $CH_3$ | (2g) | A | 51 (3h) |
| 11 | | (1d) | $-(CH_2)_5-$ | | (2f) | A | 40 (3i) |

* For conditions A or B, see text.

Concerning the transformations of **SCHEME 2**, the most interesting observations were the following:

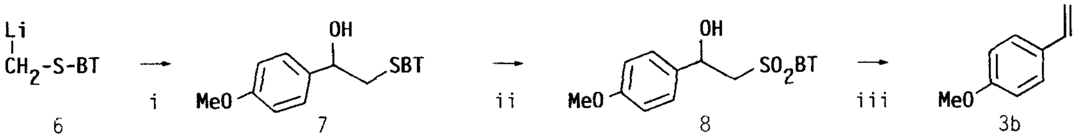
- Our attempt to trap the intermediate lithium alkoxide IVa from a reaction of sulfone 1a with p.tolualdehyde (conditions B) by acetylation led to a smooth formation of the cinnamyl BT-sulfone 5 probably via a facile elimination of acetate anion from compound VIII.



**SCHEME-3**

- Further experiments with other substrates aimed at isolation of some β-hydroxy BT-sulfones were unsuccessful owing to the instability of these compounds during purification or chromatography on silica gel.
- Proof that the lithium alkoxides IV are present as intermediates during formation of the olefins 3 was provided in the following way. According to a described procedure [10] treatment of 2-methylthio-benzothiazole with LDA in THF at -78°C yielded a solution of the lithio-derivative 6 which reacted cleanly with anisaldehyde to afford the corresponding β-hydroxy sulfide 7. After oxidation, the resulting β-hydroxy sulfone was treated with LDA (1.1 eq) in THF at -78°C for 1 h then at RT for 1 h providing

smoothly the olefin 3b with a yield comparable to that of entry 2.



i) (85%) ii) $H_2O_2$(6eq), $MoO_7(NH_4)_6$, 4 $H_2O$, EtOH, RT 65 h (96%) iii) LDA 1.1 eq, THF, -78°C then RT 1 h (63%)

SCHEME 4.

The intrinsic simplicity of the above olefination procedure of carbonyl compounds has encouraged us to explore further its scope and the interesting question of the geometry of the arising olefins will be the subject of a forthcoming report.

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