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SYNTHESIS OF SUBSTITUTED VINYL SULFONES VIA DEACYLATION

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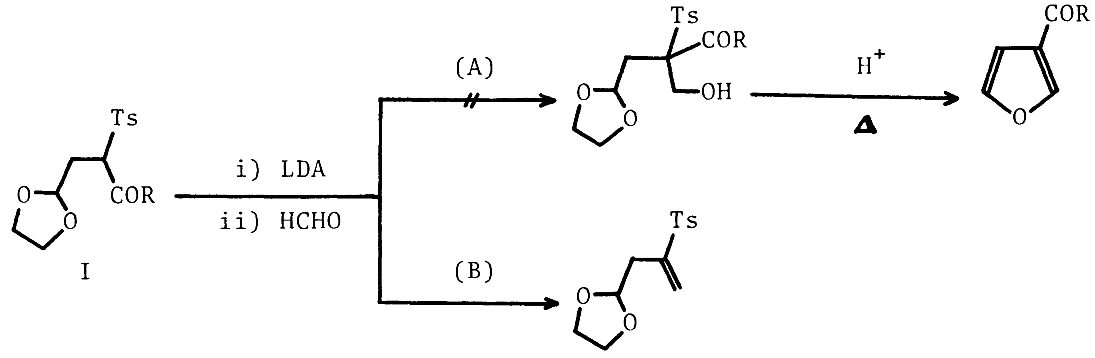
It was found that the anions of β-ketosulfones reacted with formaldehyde to give the corresponding vinyl sulfones via deacylation, which provides a new preparative method for olefinic bonds.

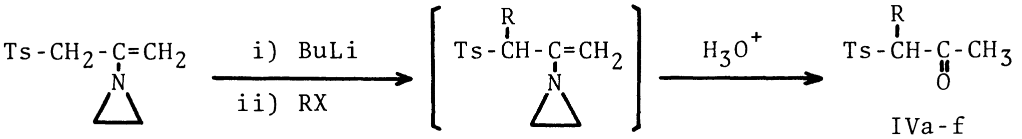
Recently, we reported the new method for the preparation of 3-substituted furans starting from 3-tosylpropanal ethylene acetal.[1] As a part of this study, we examined to prepare 3-acylfuran from 3-acyl-3-tosylpropanal ethylene acetal (I) according to the following scheme (A), however, the unexpected vinyl sulfone (II) was obtained via deacylation (B).



I

II, 66% (R=C_6H_5)

To make sure that the deacylation is general, we examined next the reaction of 1-alkyl-1-tosylpropan-2-one (IVa-f) with lithium diisopropylamide (LDA) and formaldehyde. The starting IVa-f was readily prepared from the compound III[2] according to the following scheme.[3]



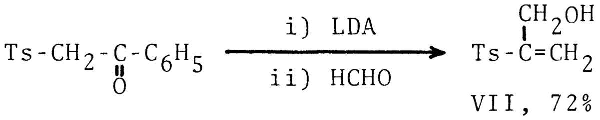
III

IVa-f

67-99%

Then the IVa-f thus prepared was lithiated with LDA in THF at −78°C followed by treatment with gaseous formaldehyde, and the reaction temperature was gradually raised to room temperature. After standing overnight, the solvent was removed, and the residue was treated with 1 M HCl and ethyl acetate. The organic layer was separated, dried over Na_2SO_4, and concentrated. The resulting residue was separated by preparative TLC to give 1-alkyl-1-tosylethylene (Va-f) produced via deacylation. The results and the probable course of this reaction are shown in the following Table.

Similarly, the lithium salt of 2-tosylpropiophenone reacted with formaldehyde to give the vinyl sulfone Va in 97% yield. In addition, it was found that 2-tosylacetophenone (VI) gave 2-tosyl-2-pentenol (VII) in 72% yield as follows.



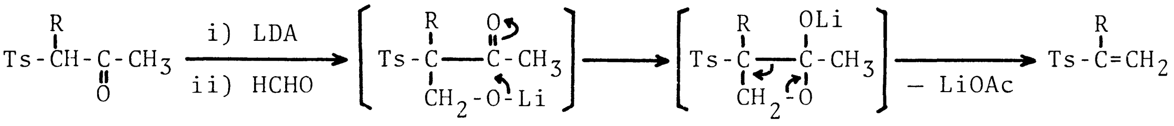
$$\mathrm{Ts\text{-}CH_2\text{-}\underset{\underset{O}{\|}}{C}\text{-}C_6H_5} \xrightarrow[\text{ii) HCHO}]{\text{i) LDA}} \mathrm{Ts\text{-}\overset{\overset{CH_2OH}{|}}{C}{=}CH_2}$$

VI

VII, 72%

We are now investigating further to elucidate the scope and the limitation of this deacylation, which provides a new preparative method for olefinic bonds.

Table. Preparation of 1-Alkyl-1-tosylethylene via Deacylation



$$\mathrm{Ts\text{-}\overset{\overset{R}{|}}{C}H\text{-}\underset{\underset{O}{\|}}{C}\text{-}CH_3} \xrightarrow[\text{ii) HCHO}]{\text{i) LDA}} \left[\mathrm{Ts\text{-}\underset{\underset{CH_2\text{-}O^-Li}{|}}{\overset{\overset{R}{|}}{C}}\text{—}\overset{\overset{O}{\|}}{C}\text{-}CH_3}\right] \longrightarrow \left[\mathrm{Ts\text{-}\underset{\underset{CH_2\text{-}O}{|}}{\overset{\overset{R}{|}}{C}}\text{—}\overset{\overset{OLi}{|}}{C}\text{-}CH_3}\right] \xrightarrow[-\ \mathrm{LiOAc}]{} \mathrm{Ts\text{-}\overset{\overset{R}{|}}{C}{=}CH_2}$$

IVa-f

Va-f

	R	Isolated yield (%) Va-f	δ (ppm from TMS)$^{a)}$ $\mathrm{>C{=}C<^{H}_{H}}$
IVa,	CH_3-	73	5.62, 6.13
IVb,	$CH_3(CH_2)_4$-	66	5.63, 6.25
IVc,	$CH_3(CH_2)_{17}$-	72	5.61, 6.25
IVd,	$CH_2{=}CHCH_2$-	75	5.62, 6.23
IVe,	$C_6H_5CH_2$-	96	5.32, 6.28
IVf,	$CH{\equiv}CCH_2$-	87	6.11, 6.37

a) in $CDCl_3$.

REFERENCES AND NOTES

1) K. Inomata, S. Aoyama, and H. Kotake, Bull. Chem. Soc. Jpn., 51, 930 (1978).

2) W. E. Truce and L. D. Markley, J. Org. Chem., 35, 3275 (1970).

3) Further detail of this reaction will be described elsewhere.

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