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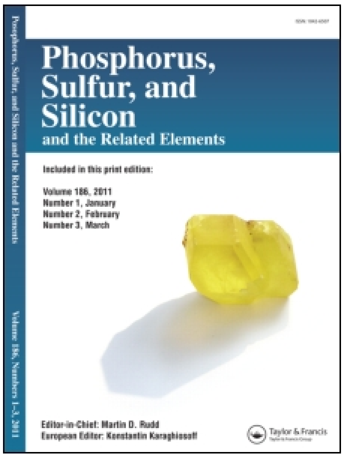

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Synthesis of α-Methylthio-Sulfones by the Sulfenylative Decarboxylation of α-Phenylsulfonyl-Carboxylic Acids

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SYNTHESIS OF α-METHYLTHIO-SULFONES BY THE SULFENYLATIVE DECARBOXYLATION OF α-PHENYLSULFONYL-CARBOXYLIC ACIDS.

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Abstract Some α-methylthio-sulfones are synthesized by reaction of α-phenylsulfonyl carboxylic acids with dimethyl disulfide or methane methylthiosulfonate, in the presence of NaH/DMSO, at room temperature. Evidences are provided for the mechanism of these reactions.

It has been reported by Trost[1] that the vic. dianions of carboxylic acids, generated utilizing 2 equiv. of LDA/THF-HMPA, can be sulfenylated by addition of dimethyl disulfide.

We presumed that in the case of α-phenylsulfonyl-carboxylic acids the reaction with a sulfenylating reagent, in the presence of a base, could lead to sulfenylative decarboxylation. However, due to the lack of solubility of the α-phenylsulfonyl-carboxylic acids in non-polar solvents, we used, instead of LDA/THF, NaH/DMSO.

When α-phenylsulfonyl-carboxylic acids (1a,b) were treated with 2 equiv. of NaH in DMSO, at room temperature, followed by addition of $MeSO_2SMe$ or MeSSMe, the corresponding monosulfenylated sulfones (2a,b) were obtained in ca 70% yields.

$$\underset{1}{PhSO_2CRR'CO_2H} \xrightarrow[MeSO_2SMe \text{ or } MeSSMe]{NaH(2equiv.)/DMSO,r.t.} \underset{2}{MeSO_2RR'C(SMe)} + CO_2$$

R=R'=H (a); R=H, R'=Me (b)

The formation of the vic. dianion as an intermediate in these reactions was evidenced by the followings results: 1) (1a,b) incorporated deuterium in α when treated with 2 equiv., but not with 1 equiv. of NaH. 2) (1a) did not give sulfenylative decarboxylation with MeSSMe, in the presence of 1 equiv. of NaH. 3) α-Phenylsulfonylisobutyric acid (1c, R=R'=Me) did not undergo sulfenylative decarboxylation.

This suggests the initial formation of the vic. dianions which, after sulfenylation, decarboxylate at room temperature. The sulfenylation, prior to decarboxylation, is in accord with the increase of the ease of decarboxylation by introduction of SR in α to the carboxylic group[2].

$$\begin{tikzcd}
PhSO_2CHRCO_2H \arrow[r, "2NaH/DMSO"] & PhSO_2\bar{C}RCO_2^- \arrow[d, "MeSSMe"] \\
PhSO_2\bar{C}R(SMe) & PhSO_2CR(SMe)CO_2^- \arrow[l, "-CO_2"']
\end{tikzcd}$$

The sulfenylative decarboxylation is a convenient method of one pot conversion of the α-sulfonyl-carboxylic acids into the α-monosulfenylated sulfones.

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REFERENCES

1. B.M.Trost and T.Tamaru, J.Am.Chem.Soc., 97, 3528 (1975).
2. K.Uneyama, W.Tagaki, I.Minamida and S.Oae, Tetrahedron, 24, 5271 (1968).