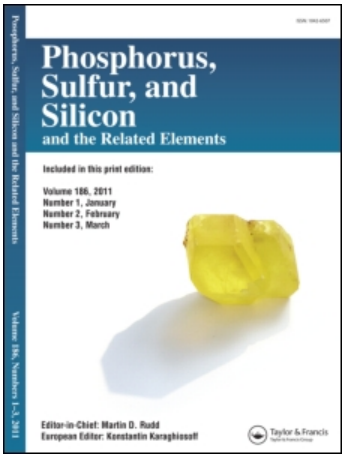

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1,1-DIANIONS OF ALKYL PHENYL SULPHONES AS SYNTHETIC INTERMEDIATES IN CYCLIZATION REACTIONS

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1,1-DIANIONS OF ALKYL PHENYL SULPHONES AS SYNTHETIC INTERMEDIATES IN CYCLIZATION REACTIONS

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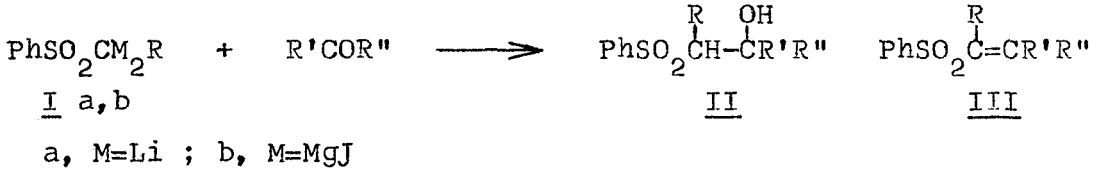
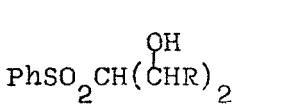
α-Sulphonyl carbanions are known to be good nucleophiles both in intermolecular and in intramolecular reactions[1]. In the same way gem-dimetalloderivatives of alkyl phenyl sulphones I a,b readily add to aldehydes and ketones to give the β-hydroxy compounds II in the case of dilithioderivatives Ia, while from dimagnesio-derivatives Ib α,β-unsaturated sulphones III are also obtained[2].



I a,b

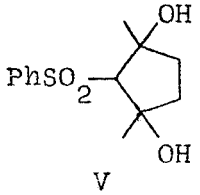
a, M=Li ; b, M=MgJ

As expected the reaction of Ia with 2 equivalents of an aldehyde gives the corresponding diol IV in good yield. Starting from these promising results we checked the possibility of preparing cyclic compounds by the reaction of Ia with molecules containing two functional groups. In fact using 2,5-hexandione as substrate the cyclic diol V was obtained together with the linear diol VI in 20 and 25% yield respectively.

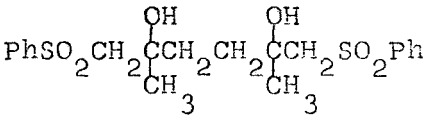


R = alkyl, phenyl

IV

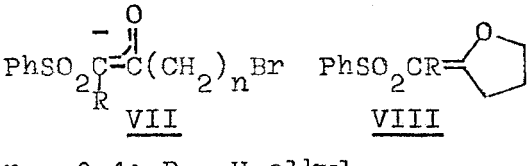


V



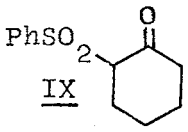
VI

Better results were obtained in the reaction with γ- and δ-bromo esters. This reaction proceeds through the attack of the dianion Ia on the carbonyl group to give the intermediate enolate VII, which successively undergoes intramolecular C- and/or O-alkylation. Only the O-alkylation product VIII was obtained from the reaction with ethyl 4-bromobutyrate, while both the C- and O-alkylation products IX and X respectively were isolated in a 30/70 ratio from the reaction with ethyl 5-bromovalerate.

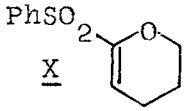


VII

VIII



IX



X

n = 3,4; R = H, alkyl

Approximately the same results were obtained when the cyclization reaction was performed on the β-ketosulphones $PhSO_2CH_2CO(CH_2)_nBr$ (n=3,4) upon treatment with the t-BuOK/t-BuOH and the phase-transfer catalyzed $NaOH/CH_2Cl_2$ systems.

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