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1,3-DIANION OF DIMETHYL SULFONE AND 1,1-DIANION OF BENZYL PHENYL SULFONE.*

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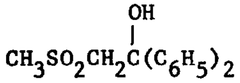
Sulfones such as dimethyl sulfone (I) have routinely been converted to monoanions, for example I', by a variety of basic reagents including methylmagnesium bromide (1), n-butyllithium (2), potassium t-butoxide (3), sodium hydride (4), and lithium amide (5). Formation of these monoanions was evidenced by condensation with an electrophilic compound; thus, treatment of I' with benzophenone afforded II (2).

$CH_3SO_2CH_3$

I

$CH_3SO_2\overset{-}{C}H_2$

I'



$$CH_3SO_2CH_2\overset{\displaystyle OH}{\overset{|}{C}}(C_6H_5)_2$$

II

However, only one convenient preparation of a 1,3-dianion of sulfones has been reported (6). Treatment of dibenzyl sulfone (III) with two molecular equivalents of potassium amide in liquid ammonia afforded 1,3-di-

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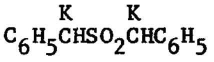
potassio salt III'' which was similar to the corresponding 1,3-dipotassio salt of dibenzyl ketone IV'' (6). On the other hand, phenylacetone (V) failed to form a dianion (6). This suggested that a 1,3-disposition of phenyl groups (or other electron withdrawing groups) was required for 1,3-diionization of at least ketones by an alkali amide.


$C_6H_5\overset{K}{C}HSO_2\overset{K}{C}HC_6H_5$

III''

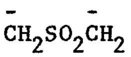

$C_6H_5\overset{K}{C}HCO\overset{K}{C}HC_6H_5$

IV''

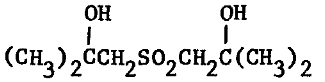
$C_6H_5CH_2COCH_3$

V

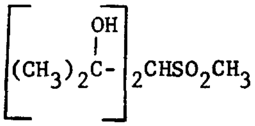
It is not surprising, therefore, that a satisfactory preparation of the 1,3-dianion of dimethyl sulfone (I'') has not been accomplished previously since the negative charges in this molecule would be stabilized only by the sulfonyl moiety. Dimethyl sulfone has been converted by ethylmagnesium bromide to a dimagnesium derivative which was condensed with acetone to give VIa or VIb, but the yield was only 15% and structure VIa was not established (1).


$\overset{-}{C}H_2SO_2\overset{-}{C}H_2$

I''

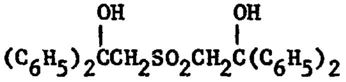

$(CH_3)_2\overset{OH}{\overset{|}{C}}CH_2SO_2CH_2\overset{OH}{\overset{|}{C}}(CH_3)_2$

VIa


$\left[(CH_3)_2\overset{OH}{\overset{|}{C}}-\right]_2CHSO_2CH_3$

VIb

We now wish to report that the 1,3-dianion I'' can be prepared readily and conveniently by means of two molecular equivalents of lithium amide in liquid ammonia, as evidenced by two-fold condensation with benzophenone to form the 1,3-derivative VII in 80% yield. Similar results were obtained with sodium amide in liquid ammonia and with n-butyllithium in tetrahydrofuran (THF)-hexane. The structure of the product was established as VII by dehydration to give VIII in 44% yield. The structures of VII and VIII were supported by analyses and by their infrared and n.m.r. spectra. Also, I'' underwent dialkylation with n-butyl bromide to afford the corresponding 1,3-di-n-butyl derivative in good yield.



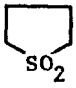
$(C_6H_5)_2\overset{OH}{C}CH_2SO_2CH_2\overset{OH}{C}(C_6H_5)_2$

VII

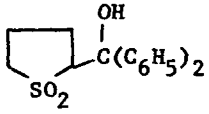
$(C_6H_5)_2C{=}CHSO_2CH{=}C(C_6H_5)_2$

VIII

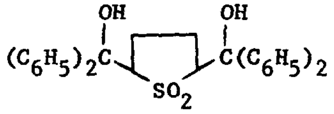
On the other hand, treatment of tetrahydrothiophene-1,1-dioxide (IX) with two equivalents of lithium amide in liquid ammonia followed by two of benzophenone afforded only monohydroxysulfone X in 85% yield. However, when IX was treated with two equivalents of sodium amide in ammonia followed by two of this ketone, di-adduct XI was obtained in 41% yield accompanied by mono-adduct X in 48% yield.



IX



X

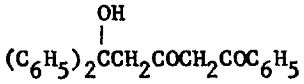


XI

The condensation of both the nucleophilic centers of dianions I'' (M = Li, Na) and IX'' (M = Na) with benzophenone to form the di-adducts VII and XI, respectively, is novel, since only one of the nucleophilic centers of other 1,3-dianions enter into such carbonyl additions with this ketone; for example, 1,3-dianion XII'' affords exclusively the mono-adduct XIII (7).

$\overset{-}{C}H_2CO\overset{-}{C}HCOC_6H_5$

XII''



$(C_6H_5)_2\overset{OH}{C}CH_2COCH_2COC_6H_5$

XIII

Interestingly, attempts by us to effect a two-fold carbonyl addition reaction, or even a single carbonyl addition of dilithio-, disodio-, or dipotassiodibenzyl sulfone (III'') with benzophenone was unsuccessful. Apparently, the equilibrium of such a reaction is on the side of III'' and the ketone.

Studies are in progress on the reactions of not only 1,3-dianions I'' and IX'', but also of certain related ones including 1,3-dicarbanions of unsymmetrical sulfones such as α-methyl-α'-butyldibenzyl sulfone which might be expected to possess preserved asymmetry similar to that of mono-carbanions of various sulfones(8).

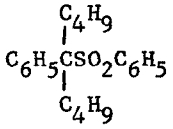
We also wish to report that benzyl phenyl sulfone is converted by *n*-butyllithium in THF-hexane to the 1,1-dilithio salt XIV'' as evidenced by deuteration with deuterium oxide and alkylation with *n*-butyl bromide to form the 1,1-derivatives XV and XVI in yields of 95 and 72%, respectively. Recently, 1,1-dilithiophenylacetonitrile has been prepared similarly(9).

$C_6H_5CLi_2SO_2C_6H_5$

XIV''

$C_6H_5CD_2SO_2C_6H_5$

XV



$$C_6H_5\overset{C_4H_9}{\underset{C_4H_9}{C}}SO_2C_6H_5$$

XVI

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