

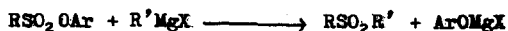
CLAISEN CONDENSATION TYPE REACTION IN A SULFONIC ESTER.
REACTIONS OF PHENYL BENZYL SULFONATE WITH PHENYL LITHIUM.

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The reactions of the derivatives of alkanesulfonic acids such as alkanesulfonyl halides or alkanesulfonic esters with such organometallic reagents as RMgX , RLi or RNa were of interest in view of the formation and reactivity of α -sulfonyl carbanion intermediates since they had acidic hydrogens α to the sulfone group. In previous publications^{1,2} we reported the reaction of benzylsulfonyl halides with phenyllithium. We now wish to report the reactions of phenyl benzylsulfonate with phenyllithium or with phenylmagnesium bromide and describe the differential comparison between phenyllithium and phenylmagnesium bromide.

It has been well known that some aryl esters of arylsulfonic acids react with a Grignard reagent to form sulfones.³ A few alkanesulfonic esters are also reported to undergo a similar sulfone formation with a Grignard reagent as is formulated below.⁴



However, very little work had been done on the reactions with lithium reagents. We have found that phenyl benzylsulfonate reacts with phenylmagnesium bromide in a similar manner to that of already known ethanesulfonic esters,⁴ but that its behavior toward phenyllithium is quite different.

When phenyl benzylsulfonate was treated with equimolar phenyllithium in diethyl ether at $18\sim 20^\circ$, α -benzylsulfonyl- α -benzenesulfonyl toluene (I) and phenyl [α -benzylsulfonyl]-benzylsulfonate (II) were formed in 17.1% and 13.7% yield respectively

in addition to phenol. α -Benzylsulfonyl- α' -benzenesulfonyl dibenzyl sulfone (trisulfone) was also obtained in 3.5% yield. The same reaction in THF-ether (1:1) at 18~20° gave 9.7% of I and 24.7% of II together with phenol. The striking increase in yield of II (84.5%) was observed when the above reaction was carried out at -60~-70° in THF-ether. In sharp contrast, however, to the reaction with the lithium reagent, the reaction of phenyl benzylsulfonate with phenylmagnesium bromide under comparable conditions gave only benzyl phenyl sulfone (III) in a high yield in addition to a corresponding yield of phenol. In this case neither I nor II was obtained. These results are presented in Table I.



Table I

Reactions	Conditions		Products (yields ^a %)		
	solvent	temp.(°C)	I	II	III
1 $\text{C}_6\text{H}_5\text{CH}_2\text{SO}_2\text{OC}_6\text{H}_5 + \text{C}_6\text{H}_5\text{Li}^b$	Ether	18~20	17.1	13.7	0
2 $\text{C}_6\text{H}_5\text{CH}_2\text{SO}_2\text{OC}_6\text{H}_5 + \text{C}_6\text{H}_5\text{Li}$	THF-Ether	18~20	9.7	24.7	0
3 $\text{C}_6\text{H}_5\text{CH}_2\text{SO}_2\text{OC}_6\text{H}_5 + \text{C}_6\text{H}_5\text{MgBr}$	Ether	18~20	0	0	84.0
4 $\text{C}_6\text{H}_5\text{CH}_2\text{SO}_2\text{OC}_6\text{H}_5 + \text{C}_6\text{H}_5\text{MgBr}^c$	THF	18~20	0	0	69.0
5 $\text{C}_6\text{H}_5\text{CH}_2\text{SO}_2\text{OC}_6\text{H}_5 + \text{C}_6\text{H}_5\text{Li}$	THF-Ether	-60~-70 ^d	0	84.5	0

a. The yields are based on reacted phenyl benzylsulfonate.

b. In addition small amount of the trisulfone formed.

c. Phenylmagnesium bromide was prepared in THF.

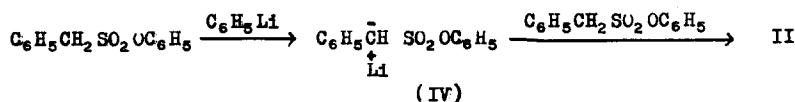
d. After stirring for 5 hr., the reaction mixture was allowed to stand overnight and then warmed to 20°, followed by hydrolysis.

All these reactions were conducted under Argon atmosphere and ethereal phenyllithium or phenylmagnesium bromide was slowly added to the solution of phenyl benzylsulfonate dissolved in diethyl ether or THF over 10 to 20 min. The reaction mixture was stirred for additional 3 to 5 hr. and then hydrolyzed with dilute hydrochloric acid.

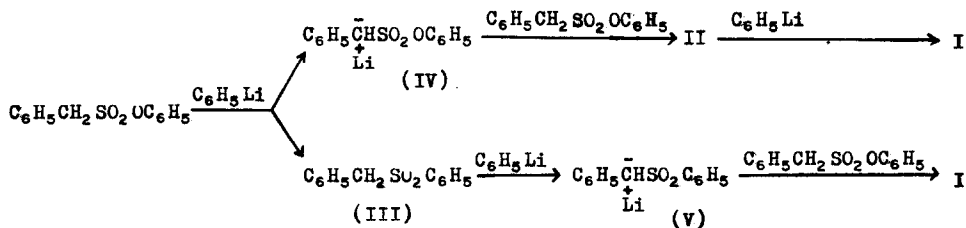
The structure of II, m.p. 174~5°, was confirmed on the basis of the infrared spectrum, n.m.r. spectrum and the elemental analysis. The infrared spectrum shows strong sulfone bands at 1330 cm^{-1} and 1135 cm^{-1} . Its n.m.r. spectrum is in agreement

with the structure, showing peaks centered at τ 2.75 (multiplet, aromatic protons, 15H), at τ 4.62 (singlet, methine proton, 1H) and at τ 5.35 (quartet, $J_{AB} = 13.8\text{c/s}$, $\int_{AB} = 0.455$ ppm, methylene protons, 2H). Found : C, 59.48; H, 4.33; S, 15.87; $\text{C}_{20}\text{H}_{18}\text{O}_5\text{S}_2$ requires : C, 59.68; H, 4.51; S, 15.93%. The identification of I, III and the trisulfone was made by comparison of their infrared spectra with those of authentic samples^{1,2} and mixed m.p. methods.

The formation reaction of phenyl [α -benzylsulfonyl] -benzylsulfonate (II), which is favored by THF solvent, is correspondent to Claisen condensation reaction in carboxylic esters. The following mechanism via the α -sulfonyl carbanion intermediate (IV) represents likely pathway.



For the formation of I the following alternative mechanisms may be proposed and from the data now available the latter path via benzyl phenyl sulfone (III) may be more probable,* since the treatment of II with phenyllithium did not give appreciable amount of I and much amount of II was recovered after working up.



As shown above, while the reaction with the lithium reagent proceeded via the α -sulfonyl carbanion intermediate, only nucleophilic displacement occurred on the

* Although benzyl phenyl sulfone (which easily undergoes metalation) was not isolated in the reaction, phenyl methanesulfonate allowed the isolation of small amount of phenyl methyl sulfone by treatment with phenyllithium in ether. In the case of benzylsulfonyl halides the disulfone (I) were formed through this process.²

sulfur atom of phenyl benzyisulfonate in the reaction with the Grignard reagent. In addition, that the metalation did not take place with the Grignard reagent appears to be regardless of its structure in solution, namely, dimeric forms or a monomeric form.**

It is also interesting to compare the reactivity of phenyl benzyisulfonate with that of benzyisulfonyl halides toward phenyllithium. For example, benzyisulfonyl halides partially undergo an initial α -hydrogen attack to give t-stilbene. On the other hand, phenyl benzyisulfonate yielded II instead of the olefin. Under the conditions of low temperature and THF solvent, benzyisulfonyl halides gave polysulfones,⁶ but phenyl benzyisulfonate did not. Further work is in progress with regard to scope and limitation.

References

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** It has been reported that Grignard reagents exist predominantly as a monomeric form, "RMgX" in THF and mainly as dimeric forms in diethyl ether.⁵