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ELECTRON-TRANSFER PROCESSES IN THE ALKYLATION OF α,β-UNSATURATED SULFONES BY ORGANOMETALLIC REAGENTS[1]

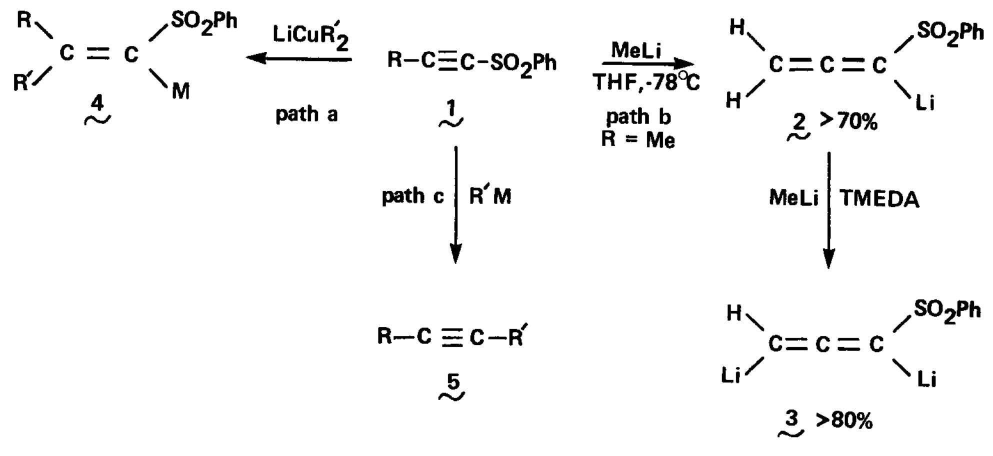
John J. Eisch,* Mohammad Behrooz
and James E. Galle
Department of Chemistry
State University of New York at Binghamton
Binghamton, New York 13901 USA

Abstract: The alkyldesulfonylation of acetylenic and vinylic sulfones by organolithium and organomagnesium reagents is shown to take place via alkyl radicals arising from electron-transfer processes.

The interaction of α,β-unsaturated sulfones with organometallic reagents can pursue a variety of pathways, with the individual reactions often occurring in a highly selective manner. For example, depending upon the nature of R in 1 and the particular organometallic R'M, the acetylenic sulfone 1 can react with R'M in three distinct ways (Scheme I): a) by Michael addition (R=alkyl[2], aryl[3] or Me_3Si[3]); b) by mono- or di-lithiation (R=CH_3 or $R'CH_2$[4]); and c) by alkyldesulfonylation (R=aryl and alkyls without α-hydrogens[5], Me_3Si[3], R'M=R'Li, R'MgX).

The last-mentioned process, alkyldesulfonylation, provides a versatile route to unsymmetrical acetylenes[5], so long as R does not contain α-hydrogens (cf. path b).

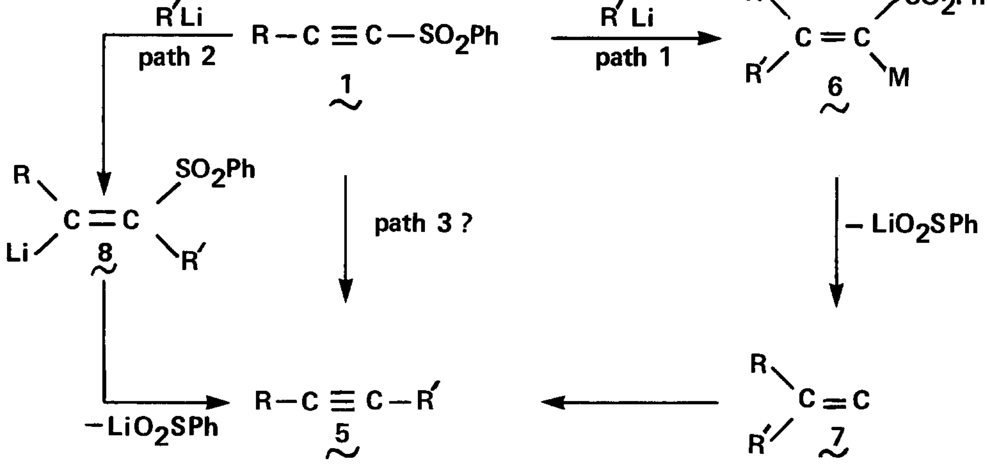
Scheme I



Since the mechanism of this reaction was puzzling, we sought to probe the electronic nature of its course. We now wish to report our findings on the intermediates involved in this reaction and to show that such alkyldesulfonylations can also be achieved with other α,β-unsaturated sulfones, such as vinylic, aryl and azaaromatic sulfones.

Based upon the known chemistry of acetylenes[6], two possible mechanisms for alkyldesulfonylation could be envisioned (Scheme II): 1) a Michael addition of R'M to 1, followed by an α-elimination of LiO_2SPh from 6 to yield vinylcarbene 7 and then by a 1,2-aryl shift to yield 5 (in essence, a Fritsch-Buttenberg-Wiechell reaction[7]); and 2) a carbometallation of 1 by R'M with the opposite regiochemistry as that in path 1, to yield 8, followed by a straightforward β-elimination to form 5.

Scheme II

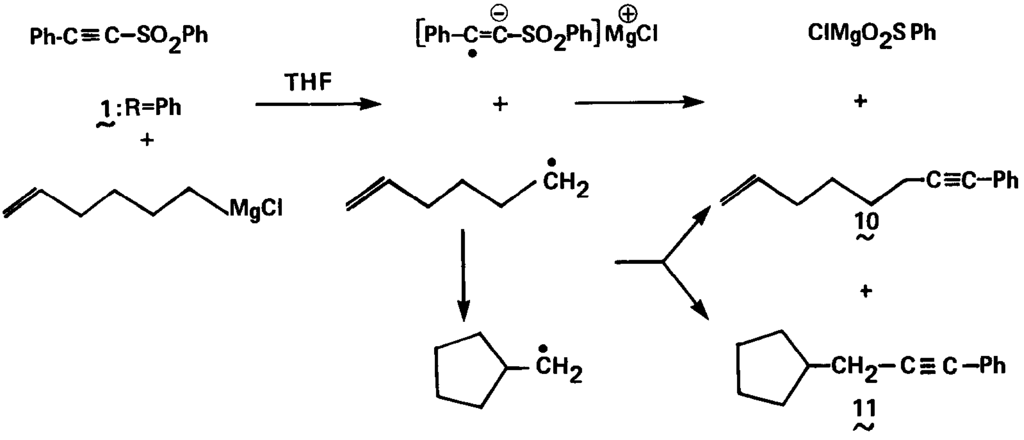


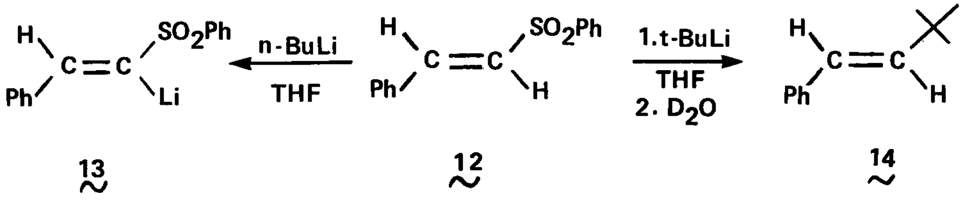
Now, path 2 is a highly improbable course, for we have shown that a variety of lithium cuprates ($LiCuR'_2$, where R'=alkyl, allyl or aryl) react with 1 (R=alkyl, aryl or Me_3Si) to give high yields of only Michael adducts (6: M=LiCuR').[3] Furthermore, we were also able to rule out the formation of 5 via path 1: intermediate 6 (R,R'=Ph; M=Li) was prepared independently, first by preparing a 2,2-diphenylethenyl phenyl sulfone (9) from $PhSO_2CH_2Li$ and $Ph_2C=O$ in 85% yield[8] and then by lithiating 9 by MeLi in THF at -95°C. Since 6 was found to be stable for over 24 h at 25°C no α-elimination took place under conditions where RLi readily converts 1 into 5.

In light of these observations, a third reaction mechanism, which would not involve an addition-elimination sequence, has to be considered: namely a polar or radical attack by R'M directly on the acetylenic carbon α to the sulfur in 1. In order to test for the possible generation of radicals[9], phenyl phenylethynyl sulfone (1: R=Ph) was treated with 1.1 molar equivalents of 5-hexenylmagnesium chloride in THF at 0°C.[8] Work-up gave 90% of alkyne 5, which was a 2:1 mixture of cyclopentylmethyl(phenyl)acetylene (11) and 5-hexenyl(phenyl)acetylene (10)[8]. The formation of 11 points to the intermediacy of the 5-hexenyl radical (which is known to undergo rapid cyclization to the cyclopentylmethyl radical[10]) and hence to the occurrence of a single-electron-transfer step in the conversion of 1 into 5 (Scheme III).

The foregoing alkyldesulfonylation of sulfones by organometallics of Groups IA and IIA is not limited to acetylenic sulfones. We have now found that vinylic sulfones undergo the same reaction, especially when allylic, benzylic or t-alkyl lithium reagents are employed. Thus, although n-butyllithium converts phenyl E-β-styryl sulfone (12) quantitatively into its α-lithio derivative (13), t-butyllithium performs an alkyldesulfonylation in high yield (N.B.: the α-hydrogen of 12 is not involved):

Scheme III

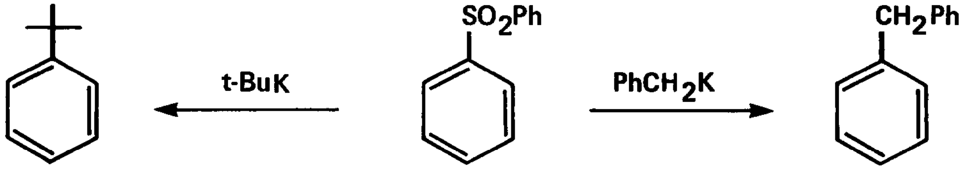




If these alkyldesulfonylations were to proceed generally via single-electron transfer, such reactions should occur most readily with those RM reagents whose anionic R groups have lower electron affinities. Particularly such R groups as t-butyl, allylic or benzylic anions ought to undergo SET processes, because the resultant radicals are relatively stable:

$$R^-M^+ + A = B \longrightarrow R^\cdot + \cdot A - B^- + M^+$$

Indeed, our recent observations with aryl and heterocyclic sulfones bear out this expectation. Thus, diphenyl sulfone (15) reacts with t-butylpotassium or with benzylpotassium to form the alkyldesulfonylation products, t-butylbenzene (**16**) or diphenylmethane (**17**), in fair to excellent yields. In contrast, n-butyllithium reacts with **15** principally by lithiation *ortho* to the sulfonyl group and **15** then is converted into dibenzothiophene.[11] Finally, the heterocyclic substrate, phenyl 2-quinolyl sulfone, undergoes alkyldesulfonation even with RLi to yield 2-alkylquinolines.[12]



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