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DESULFONYLATION OF ARYL ALKYL SULFONES

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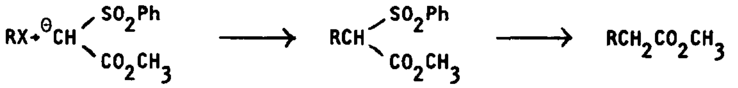
The use of sulfide[1] and sulfone[2,3] stabilized anions in organic synthesis depends upon the ease of removal of these activating groups. The most important transformation is the replacement of the C-S bond with a C-H bond. Several methods have been developed--the most important being Raney nickel, lithium in amines, and sodium amalgam. In the case of allylic sulfones, two problems are noteworthy--elimination to diene and migration of the double bond.[3,4] Reduction of the aromatic ring without cleavage of the alkyl sulfur bond has also complicated these reactions. In this letter we wish to report a simple modification that allows desulfonylation of a cross-section of sulfones that appear to obviate the previous problems and extends the utility of this reaction.

Treatment of 1 eq of sulfone with excess 6% Na(Hg) in methanol in the presence of 4 eq of disodium hydrogen phosphate at -20° to room temperature, depending upon substrate, led to good yields of desulfonylation product in every case. The individual cases are summarized in the Table. Control of the pH of the medium by addition of the acid phosphate buffer is the key. In the case of the α-phenylsulfonyl esters, this method is far superior to the alternatives and makes the use of methyl phenylsulfonylacetate as an alternative to malonate in the overall transformation represented by equation 1 an attractive strategy. By this approach strong acid, strong base, and/or high temperatures normally required for the decarboxylations of the alkylated malonates are avoided.

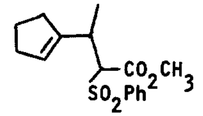
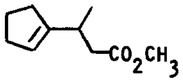
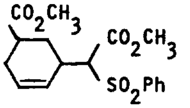
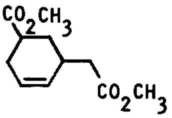
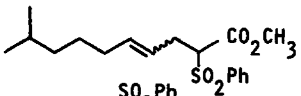
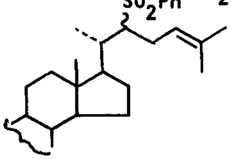
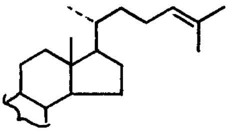
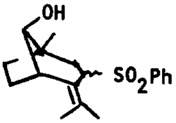
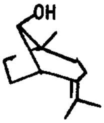
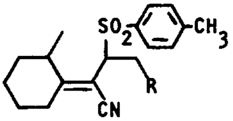
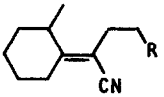
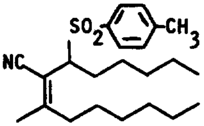
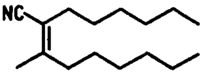


$$RX + {}^{\ominus}CH\begin{matrix}\diagup SO_2Ph\\ \diagdown CO_2CH_3\end{matrix} \longrightarrow RCH\begin{matrix}\diagup SO_2Ph\\ \diagdown CO_2CH_3\end{matrix} \longrightarrow RCH_2CO_2CH_3 \qquad \text{Eq. 1}$$

The chemospecificity of this approach is highlighted by the selective desulfonylation of the allylic sulfones incorporated into α,β-unsaturated nitriles (Table, entries 6a, 6b, 7) which do not show saturation of the double bond, nor nitrile, nor any detectable amount of double bond migration. A generalized experimental procedure follows. To a solution of 1.0 mmol of sulfone and 4 mmol of anhydrous disodium hydrogen phosphate in 10 ml of dry methanol cooled to the desired temprature (-20°, -10°, 0°, or room temperature, see Table) was added 1.5 g of pulverized 6% sodium amalgam. The solution was stirred from 7 min to 1 hr as determined by tlc. The mixture was poured into water and extracted with ether. After the usual work-up, the product was isolated by chromatography.

It is interesting to note that β-ketosulfides are desulfurized under these conditions in high yields as exemplified by eq. 2. In this case, Al(Hg) gave recovered starting material and

Table. Desulfonylation of Aryl Alkyl Sulfones

Entry	Sulfone	Temp	Time(min)	Product[a]	% Yield[b]
1		0°	60		88
2		0°	60		93
3		0°	60		Q[d]
4		RT[c]	35		82
5		-10°	60		71
6	 a) R=$\underline{n}$-C_4H_9 b) R=$\underline{s}$-C_4H_9	-20° -10°	4 20		49 58
7		-10°	7		66

a)All new compounds have been fully characterized spectrally and by elemental composition. b)All yields are for isolated pure compounds. c)RT=ambient temperature. d) Quantitative Yield.

90% Eq. 2

sodium amalgam (unbuffered) and calcium in lq ammonia gave irreproducible results.

References

1)T. Hayashi and H. Midorikawa, Synthesis, 100 (1975) and earlier references; T. Nakai, H. Shiono, and M. Okawara, Tetrahedron Letters, 4027 (1975) and earlier references; J. F. Biellman and J. B. Ducep, Tetrahedron, 27, 5861 (1971). 2) M. Julia and B. Badet, Bull Chem. Soc. France, 1363 (1975) and earlier references cited therein. K. Kondo, E. Saito, and P. Tunemoto, Tetrahedron Letters, 2275 (1975) and earlier references cited therein. 3)For leading references see M. Julia and D. Uguen, Bull Soc. Chim. France, 513 (1976); T. Nakai, H. Shiono, and M. Okawara, Chem. Lett., 249(1975). 4) We have found that α-sulfonyl esters are desulfonylated by calcium in refluxing liquid ammonia but that procedure is inferior to the buffered sodium amalgam method.