

CONVENIENT DESULFONYLATION REACTIONS OF CYCLIC SULFONES
WITH ULTRASONICALLY DISPERSED POTASSIUM

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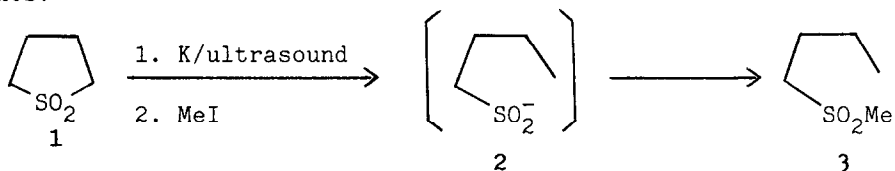
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Summary: Ultrasonically dispersed potassium, generated in toluene with an ultrasonic cleaning bath, was found to be efficient and regioselective for desulfonylation of cyclic sulfones.

Sulfone functionality is of considerable synthetic importance.² Most of its uses in synthesis ultimately involve the reductive cleavage of the sulfur-carbon bond to remove the sulfur atom from the target molecules. While various conventional reagents, including alkali metal amalgam, lithium in amines, Raney nickel, are effective for this purpose on aryl and some tertiary sulfones,^{2,3} there are only limited reports in literature about the desulfonylation of dialkyl or cyclic sulfones with low regioselectivity.⁴ We now report that ultrasonically dispersed potassium is very convenient, efficient and regioselective for the reductive cleavage of C-S bond of cyclic sulfone systems. Cyclic sulfones were used in this study because, after the cleavage of C-S bond, the oxidation state of the sulfur could be easily examined and the results should be applicable to dialkyl sulfones.

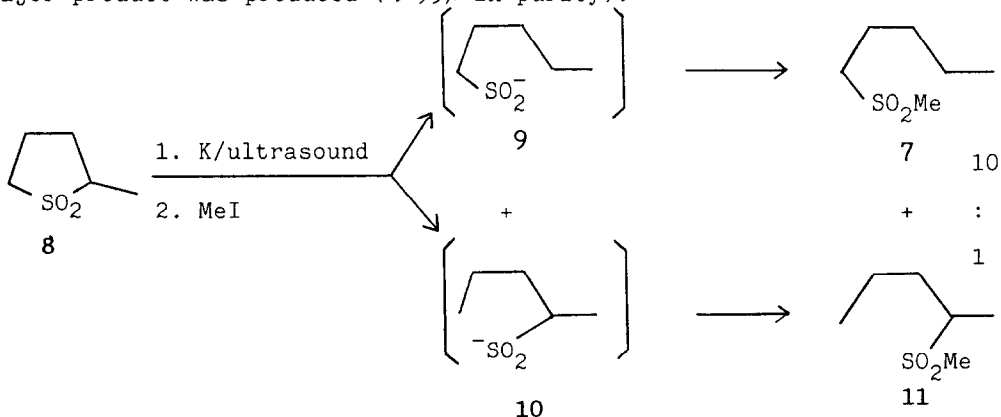
Attempted desulfonylation of sulfolane 1 by treatment with metal potassium, Raney nickel, sodium amalgam, sodium dithionite,⁵ or K/graphite,⁶ in this laboratory resulted in no reaction within reasonable period of time. While product from reaction with Li/EtNH₂ was inconvenient to work up. It was later found that when 1 was treated with excess of ultrasonically potassium, generated in toluene in an ultrasonic bath⁷ the reaction took place immediately and the starting material was consumed in less than 4 hours. The reaction was then quenched with excessive MeI to give cleanly methyl butyl sulfone 3. Although butyl sulfinic acid 2 was assumed to be formed during the stage of the reductive stage, no efforts were made to isolate it owing to its high solubility in water. In addition to its high efficiency, this reaction is

extremely convenient to handle. In practice, a small piece of potassium was added to dry toluene and submitted to ultrasonic irradiation⁸ under nitrogen. A blue color appeared immediately and K was consumed completely within 10 min and the reagent was ready for use. There is no complicated procedure involved. When benzene was used instead of toluene as the reaction solvent, potassium could also be dispersed giving the blue color albeit at a much slower rate. However, the reduction was so sluggish that it was not completed even after a period of 8 hr of reaction time and it gave only complex mixture with no major components.

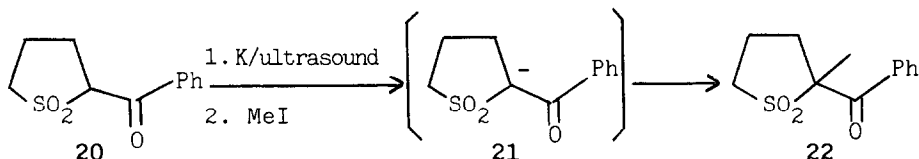


Cyclic sulfones of different ring sizes behaved similarly. For example, when trimethylene sulfone 4 and pentamethylene sulfone 6 were treated with ultrasonically dispersed potassium and quenched with MeI, the ring-opened products 5 and 7 were produced, respectively.


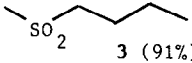

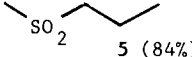

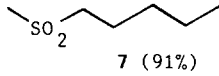

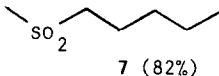
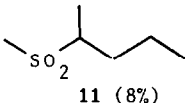
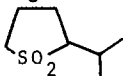
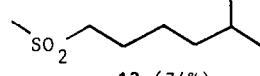
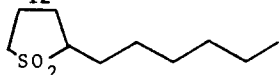
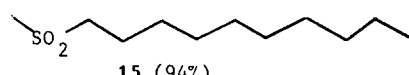
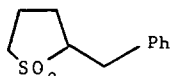
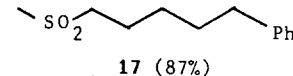
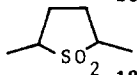
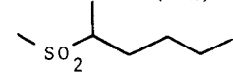
The reduction reaction was found to be highly regioselective on unsymmetrical sulfolane systems. When 2-methyl sulfolane 8 was subjected to the reaction sequence, sulfone 7 and its isomer 11 were formed in about 10:1 ratio. Products 7 and 11 should be produced via the sulfinate intermediates 9 and 10, respectively meaning that the reductive cleavage of C-S bond took place preferably at the carbon with more substitution. For sulfolanes substituted with larger alkyl groups, the selectivity of the reaction was even higher. As can be seen in the table that, for 2-isopropyl sulfolane 12, 2-n-hexyl sulfolane 14, and 2-benzyl sulfolane 16, only the bond between sulfone and the more substituted carbon was selectively cleaved in each case and only one major product was produced (>95% in purity).



2-Benzoyl sulfolane **20** failed to undergo desulfonylation reaction under the same reaction conditions. Instead, 2-methyl-2-benzoyl sulfolane **22** was produced in 87% yield. This result suggested the electron-transfer from the dispersed potassium to the C-H bond of the α -carbon bearing acidic proton to be more favored than that to the sulfone functionality.⁸



The procedure described herein represents a general, convenient, efficient, and regioselective desulfonylation reaction for non-aryl sulfones. It is therefore believed that this reaction is highly synthetically useful. Further application of this reaction is under study in this laboratory.

reactants	time for reduction (hr)	products and yields ^{a, b}
 1	4	 3 (91%)
 4	3	 5 (84%)
 6	4	 7 (91%)
 8	2	 +  7 (82%) + 11 (8%)
 12	3	 13 (74%)
 14	2.5	 15 (94%)
 16	1.5	 17 (87%)
 18	2	 19 (83%)

a. isolated yields after purification by HPLC. b. all products gave satisfactory spectral (NMR, IR, MS) and/or analytical data.

Typical procedure Small pieces of K (3 equiv) suspended in anhydrous toluene was subjected to ultrasonic irradiation at 0°C under nitrogen for 10 min. The K was dispersed completely and a blue color formed. Cyclic sulfone (1 mmol) in toluene was then added dropwise to the solution and the irradiation continued at 0°C for 0.5-4 hr until the complete consumption of the starting material. The ultrasound bath was removed and MeI (3 equiv) was added and the resulting mixture was stirred at room temperature for another 30 min. With the presence of the precipitate, saturated NH₄Cl was added, and the product, the methyl sulfone, was extracted from the mixture with CHCl₃ and purified with HPLC (LiChrosorb, hexane/ethyl acetate).

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REFERENCES AND NOTES

1. Partial contribution from the Providence College, Taichung, Taiwan.
2. T. Durst in "Comprehensive Organic Chemistry", D. H. R. Barton and W. D. Ollis, Ed., Pergamon Press, (1979). vol. 3, pp181-193.
3. E. Vedejs and G. A. Krafft, Tetrahedron, 38, 2857 (1982).
4. (a) Y. Ueno, A. Kojima, and M. Okawara, Chem. Lett., 2125 (1984). (b) W. E. Truce, D. P. Tate, and D. N. Burdge, J. Am. Chem. Soc., 82, 2872 (1960). (c) W. E. Truce and F. J. Frank, J. Org. Chem., 32, 1918 (1967). (d) D. B. Hope, C. D. Morgan, and M. Walti, J. Chem. Soc. (C), 270 (1970). (e) K. Takaki, K. Nakagawa, and K. Negoro, J. Org. Chem., 45, 4789 (1980).
5. J. Bremner, M. Julia, M. Launay, and J.-P. Stacino, Tetrahedron Lett., 23, 3265 (1982).
6. J. M. Lalancette, G. Rollin, and A. P. Giraitis, Can. J. Chem., 50, 3058 (1972).
7. The active species involved in the reaction medium is unclear. Luche described it as the "colloidal potassium": J. L. Luche, C. Petrier, and C. Dupuy, Tetrahedron Lett., 25, 753 (1984).
8. A common ultrasound cleaning bath (Bransonic 220) filled with soap water and crushed ice was used.

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