Tetrahedron Letters Vol. 21, pp 3339 - 3342
© Pergamon Press Ltd. 1980. Printed in Great Britain

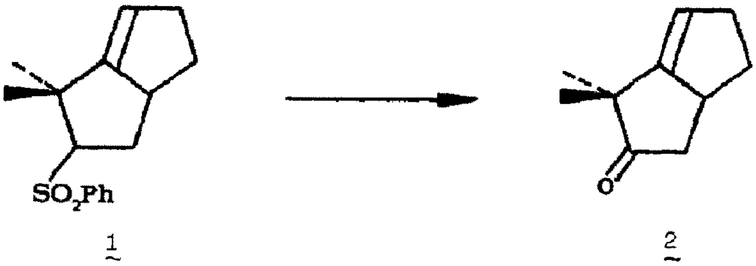
0040-4039/80/0822-3339$02.00/0

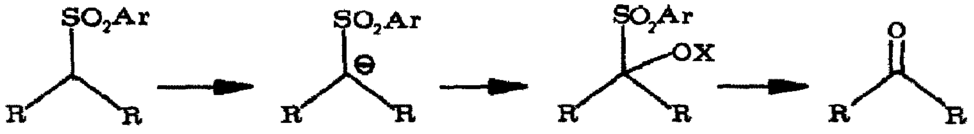
OXIDATIVE DESULFONYLATION. PHENYL VINYL SULFONE AS A KETENE SYNTHETIC EQUIVALENT

R. Daniel Little*[1] and Sun Ok Myong[2]
Department of Chemistry
University of California at Santa Barbara
Santa Barbara, CA 93106

Summary: α-Sulfonyl carbanions undergo oxidative desulfonylation to form ketones upon treatment with molybdenum peroxide MoO_5·Py·HMPA (MoOPH) in THF at -78°C.

In connection with another project involving the use of 1,3-diyls in organic synthesis, we found a need to convert sulfone 1 into ketone 2.[3a] In view of the widespread use of sulfones in synthesis,[4] we found it somewhat suprising to find that existing methodology did not provide a solution to the problem.[5] We reasoned that a viable solution could be achieved through oxygenation of an α-sulfonyl carbanion followed by desulfonylation involving elimination of an aryl sulfonyl anion, as illustrated below.





In practice, treatment of a variety of aryl α-sulfonyl carbanions with a threefold excess of MoOPH[6] in THF at -78°C leads to a rapid reaction (complete within several minutes) and to the formation of ketones in yields ranging from 50-97% (nonoptimized; note Table I). Preparation of the sulfones used in this study was accomplished either *via* a Diels-Alder cycloaddition between an appropriate diene and phenyl vinyl sulfone, or a 1,3-diyl trapping reaction between 2-isopropylidenecyclopenta-1,3-diyl and phenyl vinyl sulfone, or *via* an alkylation of an appropriate α-sulfonyl carbanion. It is apparent, therefore, that entries 1-4 of the Table I illustrate the use of phenyl vinyl sulfone as a ketene equivalent in Diels-Alder cycloadditions and in 1,3-diyl trapping reactions. This result in conjunction with the fact that phenyl vinyl sulfone has recently been shown to be the synthetic equivalent of ethylene,[7] allows the construction of the scheme illustrated below.

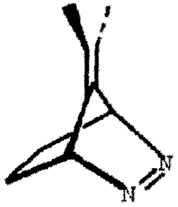
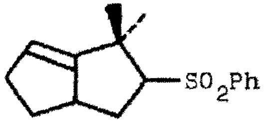
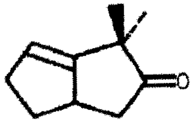
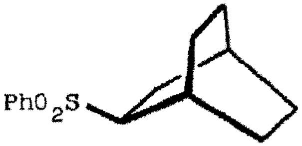
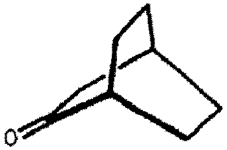
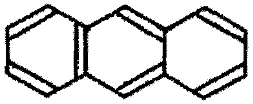
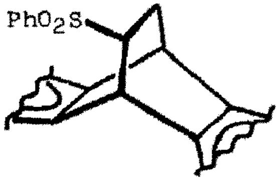
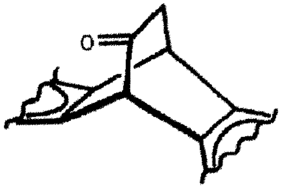
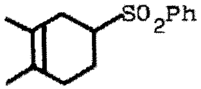
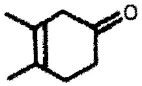
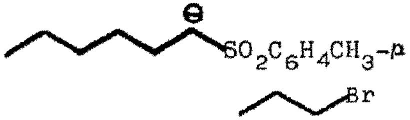
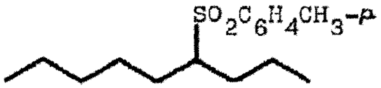
$$CH_2{=}C{=}O \equiv \underline{CH_2{=}CHSO_2Ph} \equiv CH_2{=}CH_2$$

A typical procedure is illustrated using the preparation of 4-nonanone as an example. To an oven dried, nitrogen purged 50 mL flask cooled to -78°C and containing 150 mg (0.53 mmol) of 1-propylhexyl *p*-tolyl sulfone dissolved in 15 mL of dry THF, was added 4.5 mL of 0.7 M lithium diisopropylamide (LDA). After stirring at -78°C for three minutes, 690 mg (1.59 mmol) of MoOPH dissolved in 10 mL of THF was added by using a double-ended needle; the flask containing the THF solution of MoOPH was rinsed with THF to assure complete transfer. The resulting dark red solution was stirred for one minute at -78°C, and the reaction was then quenched using 5 mL of saturated aqueous sodium sulfite. The reaction mixture was poured into 50 mL of water and the aqueous layer was extracted three times with 15 mL portions of ether. The combined extracts were washed with 50 mL of 0.6 N HCl, three times with 50 mL portions of water, once with 50 mL of brine, and dried over magnesium sulfate. The solvent was removed at atmospheric pressure and the ketone was purified *via* distillation to give 42 mg (0.29 mmol, 55%) of pure 4-nonanone.

Further studies involving the oxidative desulfonylation reaction and its applications to synthesis are in progress.

Acknowledgements: The authors would like to thank the Petroleum Research Foundation, administered by the American Chemical Society, and the National Institutes of Health (Grant No. CA 21144-02,03) for partial support of this research. S.M. thanks the University of California for a Graduate Opportunity Fellowship. We would like to thank Mr. L. Brown for the preparation of the sulfone **1**.

TABLE I. OXIDATIVE DESULFONYLATION

ENTRY	SULFONE PRECURSOR[a]	SULFONE[b]	KETONE	YIELDS (%)[c]
1				59
2	(a)  (b) H_2, Pd/C			97
3				86
4				51
5				64

a, Phenyl vinyl sulfone was used as the diylophile/dienophile for entries 1-4. b, All reactions were conducted under nitrogen. THF was freshly distilled from benzophenone ketyl. The concentration of LDA was determined by titration using phenanthroline as an indicator. In each case the ratio of sulfone to LDA to MoOPH was fixed at 1:6:3. c, The yields are not optimized and refer to ketones purified by distillation or chromatography.

References

1. Fellow of the Alfred P. Sloan Foundation, 1980-1982.

2. Graduate Opportunity Fellowship Awardee, 1978-1980.

3. (a) Little, R. D.; Brown, L. Tetrahedron Lett., 1980, accepted for publication.; (b) Little, R. D.; Bukhari, A.; Venegas, M. G. ibid., 1979, 305-308; (c) Venegas, M. G.; Little, R. D. ibid., 1979, 309-312; (d) Little, R. D.; Muller, G. W. J. Am. Chem. Soc., 1979, 101, 7129-7130.

4. See for example: (a) Magnus, P. D. Tetrahedron, 1977, 33, 2019-2045; (b) "Reactions of Organosulfur Compounds", Block, E., Academic Press, New York, 1978; (c) Field, L. Synthesis, 1978, 713; (d) Vögtle, F.; Rossa, L. Angew. Chem. Int. Ed. Engl., 1979, 18, 515-529.

5. It should be noted that Hendrickson and co-workers reported a "one-pot" method for the conversion of triflones into ketones. The sequence involves the formation of an intermediate vinyl azide or iminophosphorane and, without purification, the conversion of the intermediate to a ketone. For details, see: Hendrickson, J. B.; Bair, K. W.; Keehn, P. M. J. Org. Chem., 1977, 42, 2935-2936.

6. Vedejs, E.; Engler, D. A.; Telschow, J. E. J. Org. Chem., 1978, 43, 188-196, and references therein. The decision to use the comparatively expensive reagent MoOPH, rather than molecular oxygen was prompted by concerns for safety. We have observed that oxygen can be used to oxidize α-sulfonyl carbanions to ketones; for example, the dibenzobicyclo [2.2.2] ketone of entry 3, Table I was prepared in 45% yield; 55% of the starting sulfone was recovered. However, on one occasion, we experienced a moderate explosion and therefore, without any attempt to optimize yields, we decided to opt for the use of MoOPH. We have not encountered any problems with the use of MoOPH; however, as with the use of any oxidizing agent, the use of caution is recommended.

7. Carr, R. V. C.; Paquette, L. A. J. Am. Chem. Soc., 1980, 102, 853-855. See also: Moerck, R. E.; Harirchian, B.; Magnus, P. D. J. Am. Chem. Soc., 1978, 100, 1597-1599.

(Received in USA 2 May 1980)