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SYNTHESIS OF α-PHENYLSULFONYL CYCLOPENTANONES BY INTRAMOLECULAR CARBENOID CYCLIZATION OF α-DIAZO-β-KETO PHENYLSULFONES

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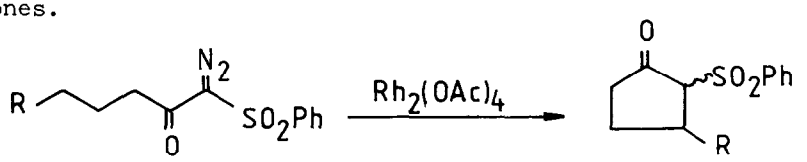
Summary: Acyclic α-diazo-β-keto phenylsulfones undergo smooth intramolecular carbenoid cyclizations under rhodium (II) catalysis to afford α-phenyl sulfonyl cyclopentanones.

Substituted α-arylsulfonyl cyclopentanones 2 are potentially important intermediates in the synthesis of natural cyclopentanoids.[1] We have examined the carbenoid intramolecular cyclization of α-diazo-β-keto sulfones 1 as one of the possible routes to these compounds, which were required in connection with a project under investigation in our laboratory. We now wish to report herein the preliminary results of our work.

The intramolecular carbenoid cyclization of α-diazo carbonyl compounds to give carbocyclic rings is a well documented reaction.[2] The formation of 5-membered rings is particularly facile under rhodium (II) catalysis,[3] and the reaction has been extremely useful in the preparation of several α-carboalkoxy cyclopentanones from the corresponding acyclic α-diazo-β-keto esters.

The intramolecular cyclization of α-diazo-β-keto sulfones 1 has, however, received comparatively little attention. To our knowledge, the only reported study was that of Kuwajima and co-workers[4] who investigated the thermal and copper catalyzed decomposition of some acyclic γ,δ- and δ,ε-unsaturated α-diazo-β-keto phenylsulfones. However, they were able to isolate only poor yields of the α-phenylsulfonyl cyclopentanones expected from addition and C-H insertion of the intermediate keto sulfonyl carbenes. Very recently, a rhodium (II) catalyzed intramolecular aromatic C-H insertion has been used by Durst[5] in the preparation of 1-carboalkoxy-1,3-dihydrobenzo [b]thiophene 2,2-dioxides from α-diazo-β-arylsulfonyl esters.

We have recently described an efficient preparation of α-diazo-β-keto sulfones 1 from the readily available β-keto sulfones through the use of an in situ generated azidinium salt as a diazo transfer reagent.[6] We have now found that treatment at room temperature of a dichloromethane solution of the crude α-diazo derivatives with catalytic amounts (1 mol %) of rhodium (II) acetate induces their smooth cyclization to the α-phenylsulfonyl cyclopentanones.



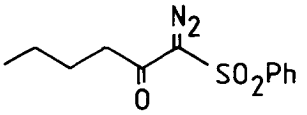
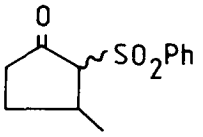
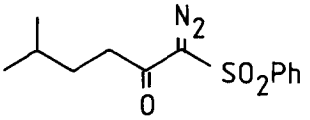
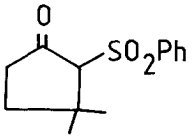
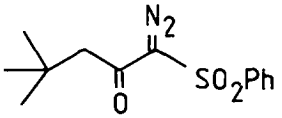
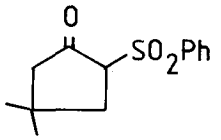
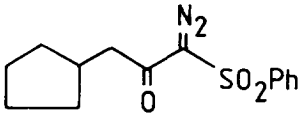
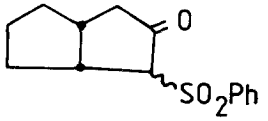
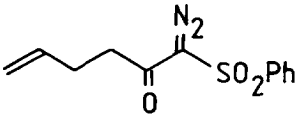
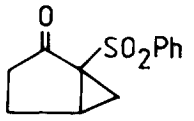
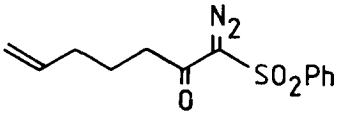
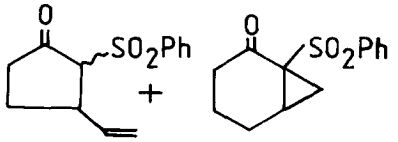
1 2

As the examples given in the Table show, the reaction is very useful for the preparation of a veriety of substituted α-phenyl sulfonyl cyclopentanones. As expected, a cyclopentane ring is formed preferentially over a cyclohexane, even when double bond addition is possible (entry 6). The reactivity actually parallels that observed in the rhodium (II) catalyzed cyclization of α-diazo-β-keto esters described by Taber.[3b,g] The yields quoted have not been optimized, being based upon crystalline products isolated from reactions done with the crude α-diazo derivatives.[6]

A few practical points deserve mention. Due to their rather acidic nature and relative stability to base,[7] most of the cyclic products can be easily isolated from the reaction mixtures by extraction with dilute NaOH followed by precipitation with solid NH_4Cl. Furthermore, the α-phenylsulfonyl cyclopentanones are generally solids and are readily purified by crystallization. Finally, the sulfonyl activating group can be easily removed under mild conditions at a later stage,[1,8] a property which should be of value in sensitive molecules.

In a typical experiment, a solution of 266 mg (1 mmol) of α-diazo-β-ketohexyl phenylsulfone (1, R = Me) in 10 ml CH_2Cl_2 was treated at room temperature with 4.5 mg (1 mol %) of rhodium (II) acetate, and the progress of the reaction monitored by TLC. After completion of the reaction (~ 1 hr) the solvent was evaporated, the residue redissolved into 15 ml Et_2O, and the solution extracted with 1N NaOH (3 x 3 ml). Immediate neutralization of the basic phase with solid NH_4Cl, followed by extraction with CH_2Cl_2 gave a

TABLE*

Entry	α-Diazo-β-keto sulfones (1)	α-Sulfonyl cyclopentanones(2) (isolated yield, m.p.)
1		 (67%, 124-125°)
2		 (53%, 94-96°)
3		 (68%, 80-81°)
4		 (75%, 104-105°)
5		 (65%, 96-97°)
6		 (40%, 89-90°) (25%, 146-147°)

* All compounds gave analytical and spectral data in agreement with the assigned structures.

resin which crystallized on standing. Recrystallization from Et_2O afforded 160 mg (67%)of 2-phenylsulfonyl-3-methyl cyclopentanone (2, R = Me), m.p. 124-125°.

REFERENCES AND NOTES

1. M.J. Kurt and M.J. O'Brien, J. Org. Chem., 50, 3846 (1985).
2. S.D. Burke and P.A. Grieco, Org. Reactions, 26, 361 (1979).
3. a) E. Wenkert, L.L. Davis, B.L. Mylari, M.F. Solomons, R.R. da Silva, S. Shulman, R.J. Warnet, P. Ceccherelli, M. Curini, and R. Pellicciari, J. Org. Chem., 47, 3242 (1982);
   b) D.F. Taber and E.H. Petty, J. Org. Chem., 47, 4808 (1982);
   c) D.F. Taber and K. Raman, J. Am. Chem. Soc., 105, 5935 (1983);
   d) D.F. Taber, E.H. Petty, and K. Raman, J. Am. Chem. Soc., 107, 196 (1985);
   e) D.F. Taber and J.L. Schuchardt, J. Am. Chem., 107, 5289 (1985);
   f) D.F. Taber and R.E. Ruckle, Jr., Tetrahedron Lett., 26, 3059 (1985);
   g) D.F. Taber and R.E. Ruckle, Jr., J. Am. Chem. Soc., 108, 7686 (1986);
   h) D.E. Cane and P.J. Thomas, J. Am. Chem. Soc., 106, 5295 (1984).
4. I. Kuwajima, Y. Highuchi, H. Iwasawa, and T. Sato, Chem. Lett. 1271 (1976).
5. M. Hrytsak, N. Etkin, and T. Durst, Tetrahedron Lett., 27, 5679 (1986).
6. H.J. Monteiro, Synth. Commun., in press.
7. Although α-sulfonyl cyclopentanones are prone to ring cleavage on extended exposure to alkali [see for instance J. Ficini and G. Stork, Bull. Soc. Chim. Fr., 723 (1964)], rapid work-up has not presented any problems.
8. B.M. Trost, H.C. Arndt, P.E. Stage, and T.R. Verhoeven, Tetrahedron Lett., 3477 (1976) and references therein.

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