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ORGANIC SYNTHESIS WITH SULFONES XXXII.
A CONVENIENT ROUTE TO α,β-UNSATURATED SULFONES FROM SATURATED SULFONES.

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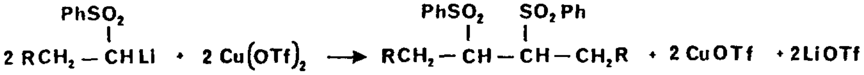
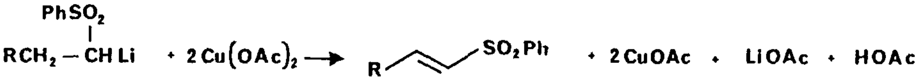
Abstract : α-sulfonyl lithiated anions are oxidized by cupric carboxylates into α,β-unsaturated sulfones. Primary sulfones lead to pure trans-vinylic sulfones.

It has recently been shown (1) that treatment of α-sulfonyl carbanions with copper(II) trifluoromethanesulfonate (1 équivalent) gives dimers of the original sulfone (1). (Scheme 1)



$$2\,RCH_2-\overset{PhSO_2}{\overset{|}{CH}}Li + 2\,Cu(OTf)_2 \longrightarrow RCH_2-\overset{PhSO_2}{\overset{|}{CH}}-\overset{SO_2Ph}{\overset{|}{CH}}-CH_2R + 2\,CuOTf + 2LiOTf$$

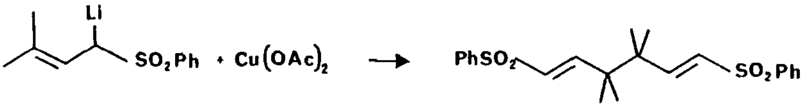
It has now been found that changing the counter ion in the copper salt dramatically alters the result : with cupric acetate α-lithiated sulfones were converted into the corresponding vinylic sulfones (scheme 2) :



As required by the stoichiometry, two equivalents of cupric salts were necessary for efficient conversion. Yields higher than 50% can be obtained, despite the fact that one equivalent of acetic acid is produced during the reaction (Table 1).

With primary sulfones yields of 60 to 85% were observed (entries 1,3,4). The stereochemistry of the new double bound is clearly E as shown by ^1H NMR and comparison with authentic samples by capillary G.L.C. Using one equivalent of copper the yield decreased from 85% to 50% (entries 1,2). Secondary sulfones proved to be more difficult to oxidize (entries 5,6). A homoallylic sulfone was easily dehydrogenated to the corresponding diene sulfone (entry 4). Here again the stereochemistry is E.

Prenyl sulfone which could have given the same dienic sulfone was treated in the same way but led to the 3,3'-dimer (scheme 3), already obtained in the reaction with copper(II) trifluoromethanesulfonate :



(70%)

TABLE 1 :

Reaction of α-lithiated sulfones with cupric carboxylates [a]

entry	substrate	Yield [b]	Stereochemistry
1	$nC_7H_{15}SO_2Ph$	85 [d]	E [c]
2	$nC_7H_{15}SO_2Ph$	50 [e]	E [c]
3	$PhCH_2CH_2SO_2P_h$	75	E [c]
4	$CH_2=CH(CH_3)CH_2CH_2SO_2Ph$	60	E [c]
5	cyclo-$C_6H_{11}SO_2Ph$	10	E
6	$(CH_3)_2CHSO_2Ph$	10	-

[a] reaction conditions : lithiated sulfone anion (2mmol) (from sulfone and n-BuLi/Hexane) THF (3ml),cupric acetate (5,3 mmol), -78°C, 30 mn, quenching with NH_4^+, CH_3COO^- ;

[b] isolated yield; [c] better than 98/2 E/Z capillary G.L.C. ; [d] same yield on a 10 mmol scale.

[e] only one equivalent of cupric acetate.

The above results provide a new access to vinyl and dienyl sulfones which have recently been used for the stereoselective synthesis of olefins and dienes (2,3,4,5). This nicely complements the previously known methods (6,7,8,9).

A related reaction involving autoxidation of cupric carboxylate at high temperature has been described (10).

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REFERENCES

(1) M. Julia, G. Le Thuillier, Ch. Rolando and L. Saussine, Tetrahedron Letters, 1982, 2453.
(2) J. Bremner, M. Julia, M. Launay and J.P. Stacino, Tetrahedron Letters, 1982, 3265.
(3) J.L. Fabre, M. Julia and J.N. Verpeaux, Tetrahedron Letters, 1982, 2469.
(4) J.L. Fabre and M. Julia, Tetrahedron Letters, 1983, 4311.
(5) T. Cuvigny, J.L. Fabre, C. Hervé du Penhoat and M. Julia, Tetrahedron Letters, 1983, 4319.
(6) P.D. Magnus, Tetrahedron, 33, 2019 (1977) and references cited therein.
(7) T. Durst, Polyfonctional sulfones in Comprehensive Organic Chemistry, Sir D.H.R. Barton and W.D. Ollis, Edr. Pergamon Press, Oxford, 1979.
(8) W.E. Truce, A.W. Borel and P.J. Mark J. Org. Chem., 41, 401 (1976).
(9) M. Julia, M. Launay, J.P. Stacino and J.N. Verpeaux, Tetrahedron Letters, 1982, 2465.
(10) L. Giuffre, E. Montoneri, M. Fornaroli, E. Tempesti, C. Bossi and M.P. Spaziante, Nouv. J. Chimie, 5, 353 (1981).

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