Tetrahedron Letters Vol. 21, pp 5055 - 5056

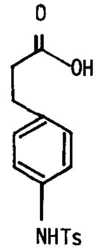
0040-4039/80/1222-5055$02.00/0

SPIRODIENONES IV[1] THE SYNTHESIS OF N-SULPHONYLCYCLOHEXADIENIMINES AND RELATED DIENONES

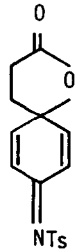
Ian G. C. Coutts*, Mark Edwards, Donald R. Musto and David J. Richards
Department of Physical Sciences, Trent Polytechnic, Burton Street, Nottingham. NG1 4BU.

Summary: Oxidation of N-4-toluenesulphonylanilines bearing appropriate para substituents gives good yields of spirocyclic N-sulphonylcyclohexadienimines; these compounds may be selectively hydrolysed to the corresponding spirodienones.

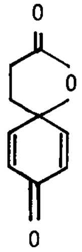
The spirolactone (3) which we required in large quantities for another investigation has previously been prepared[2] by chemical or anodic oxidation of 3-(4-hydroxyphenyl)propanoic acid but in low (6-22%) yield. Since secondary aromatic sulphonamides may act as phenol equivalents in oxidative coupling reactions[1], it seemed logical to examine their use in the synthesis of compounds such as (3). Electrochemical oxidation of sulphonamide (1) at 1.4v versus S.C.E. (carbon felt anode, acetonitrile) gave the N-sulphonylimine (2) in 65% yield; on passage down a neutral alumina (Grade II activity) column this imine was smoothly converted to dienone (3) in 45% overall yield. This synthetic sequence was applied to the preparation of a range of dienones (see Table). From the imine derived from (5) only p-benzoquinone was obtained, probably because of the hydrolytic instability[3] of the dienone. The overall yield of dienones obtained from (4) (6) and (7) compares favourable with those reported for oxidation of phenolic precursors. The application of this cyclohexadienone synthesis to more complex systems is being examined, as is the chemistry of the sulphonylimines.



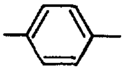
(1)

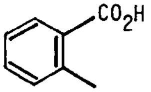
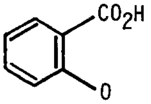
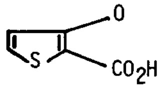


(2)



(3)

Conversion of R  NHTs to N-sulphonylimine and dienone.

Compound	R	Sulphonylimine (% yield)	Dienone (% overall yield)	Lit. Yield (%) from phenol
(4)	$HOCH_2CH_2O$	80	54	50[a]
(5)	HO_2CCH_2O	68	-	-
(6)		80	56	25[b]
(7)		81	42	35[c]
(8)		82	36	-

Satisfactory analytical and spectral data were obtained for all new compounds a) P. Margaretha & P. Tissot, Helv. Chim. Acta, 1975, 58, 933. b) D. H. Hey, J. A. Leonard & C. W. Rees, J. Chem. Soc., 1963, 5263. c) C. W. Hassall & J. R. Lewis, J. Chem. Soc., 1961, 2312.

REFERENCES

1. I. G. C. Coutts, and M. R. Hamblin, J.C.S. Chem. Comm. in the Press, is considered to be Spirodienones III.

2. H. Iwasaki, L. A. Cohen and B. Witkop, J. Amer. Chem. Soc., 1963, 85, 3701; A. I. Scott, P. A. Dodson, F. McCapra and M. B. Meyers, ibid., 1963, 85, 3702; H. S. Davies, C. H. Hassa and J. A. Schofield J. Chem. Soc., 1964, 3126; I. Saito, Y. Chujo, H. Shimazu, M. Yamane, T. Matsuura and H. J. Cahnmann, J. Amer. Chem. Soc., 1975, 97, 5272.

3. M. B. Meyers, M. J. Gallagher and F. F. Orr, Proc. Roy. Irish Acad., 1977, 77B, 507.

(Received in UK 6 October 1980)