Electrochemical Generation of a Nitrene from *NN*-Dichlorotoluene-*p*-sulphonamide

By TOSHIO FUCHIGAMI, TSUTOMU NONAKA, and KOICHI IWATA

(Department of Electronic Chemistry, The Graduate School, Tokyo Institute of Technology, Meguro-ku, Tokyo **152**, *Japan)*

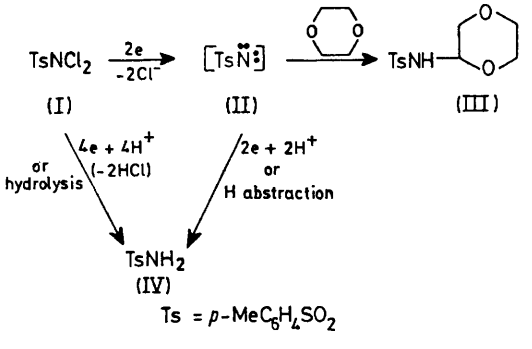
Summary Toluene-*p*-sulphonylnitrene (II) can be generated from *NN*-dichlorotoluene-*p*-sulphonamide (I) by electrolysis, as shown by the formation of 2-(*p*-tolylsulphonylamino)-1,4-dioxan (III) in the electroreduction of (I) in the presence of dioxan.

NITRENES are important electron-deficient nitrogen species which figure prominently as reactive intermediates. Breslow and Sloan[1] reported that dechlorination with zinc of the zinc complex of *NN*-dichlorotoluene-*p*-sulphonamide (I) (dichloramine-T) yielded a nitrene. In view of their work and our interest in the chemistry of *N*-halogeno-compounds[2] we have investigated the possible generation of a nitrene by the electrochemical reduction of (I).

TABLE. Results for the electrolysis of (I)[a]

Cathode material	Supporting electrolyte	Current efficiency for formation of (III) (%)	Yield of (IV) (%)
Pt	$LiClO_4 \cdot 3H_2O$	32	52
C	$LiClO_4 \cdot 3H_2O$	6	90
Pt	$LiClO_4 \cdot 2H_2O$	11	75
Pt	$LiClO_4$	—[b]	—[b]

[a] Constant-current electrolyses (1·8 A dm^{-2}) were carried out in acetonitrile–dioxan (3 : 7 v/v) at 20 °C, with a passage of 2F mol^{-1}. [b] Electrolysis could not be completed because of the extremely high cell voltage required.



We now report preliminary electrochemical results for (I). The generation of (II) was verified by the formation of (III) in the electroreduction of (I) in the presence of dioxan; it is well known that nitrenes insert easily into a C–H bond of dioxan.[3] Electrolyses were carried out in acetonitrile at platinum and carbon cathodes. The results are summarized in the Table.

Platinum formed a suitable cathode for the formation of (III). The use of anhydrous lithium perchlorate as a supporting electrolyte caused a decrease in the yield of (III), suggesting that a small amount of water is necessary for the formation of (III). Toluene-*p*-sulphonamide (IV) was a major by-product, and was also formed in the hydrolysis of (I) under electrolytic conditions. Compound (III) was also synthesized by treatment of chloramine-T with copper powder in dioxan.[3]

(*Received, 5th August* 1976; *Com.* 909.)

[1] D. S. Breslow and M. F. Sloan, *Tetrahedron Letters*, 1968, 5349.
[2] T. Fuchigami, E. Ichikawa, and K. Odo, *Bull. Chem. Soc. Japan*, 1973, **46**, 1765; T. Fuchigami and K. Odo, *Chem. Letters*, 1973, 917; 1974, 247, 1139; *J. Synthetic Org. Chem., Japan*, 1975, **33**, 66; *Tetrahedron*, submitted for publication; *Bull. Chem. Soc. Japan*, 1975, **48**, 310; *ibid.*, in the press; T. Fuchigami, T. Nonaka, and K. Odo, *ibid.*, in the press.
[3] D. Carr, T. P. Seden, and R. W. Turner, *Tetradedron Letters*, 1969, 477.

Printed by Heffers Printers Ltd Cambridge England