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COMPETING REACTIONS WITH THE RECOVERY OF ALCOHOLS FROM ARENESULPHONATES BY CATHODIC REDUCTION

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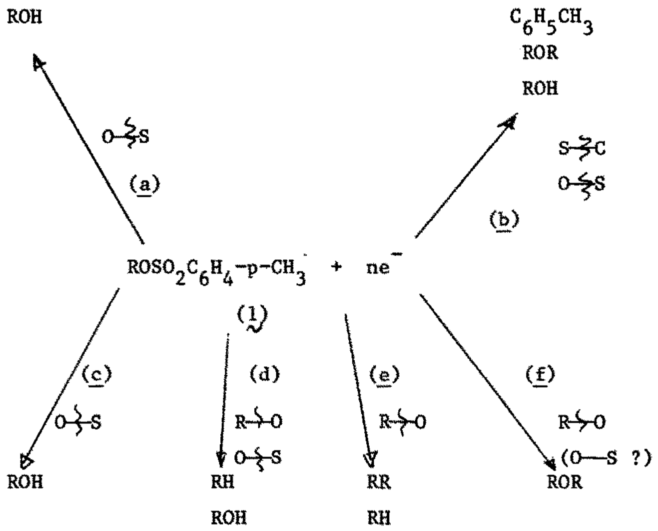
Cathodic reduction of tosylates (1, Scheme) has entered the practice of organic synthesis because, owing to selective O-S bond breaking, there is no loss of optical activity in the case of chiral RO groups[1] (Scheme, path a), in contrast with solvolytic methods where racemization or inversion occur.



SCHEME *a* *(R = Me,* $PhCH_2$*, Ph, cyclo-*C_6H_{11}*, l-menthyl, in EtOH, ref. 1);* *b* *(R = Me, Et, n-Bu,* Me_3CCH_2*, cyclo-*C_6H_{11}*, in* CH_3CN*, ref. 1);* *c* *(R = Ph, p-*$NO_2C_6H_4$*, 2- and 4-troponyl, in* CH_3CN*);* *d* *(R = allyl in DMF, p-*$CH_3C_6H_4CH_2$ *in* CH_3CN*);* *e* *(R = p-*$NO_2C_6H_4CH_2$ *in* CH_3CN*);* *f* *(R =* Ph_2CH*, in* CH_3CN*)*

However, the electrochemical method has some limitations. In fact, it has been reported that S-C bond breaking, leading to toluene, and formation of ethers by reaction of the alkoxide RO^- with unreacted tosylate compete with the normal formation of alcohols for cathodic reduction in aprotic media for simple alkyl tosylates[1] (Scheme, path b).

More serious, from the above synthetic point of view, appears to be the competing rupture of the R-O bond of (1), leading to hydrocarbons, which we report here for controlled potential cathodic reduction of certain tosylates at a mercury pool in acetonitrile (a medium which is very amenable to product isolation) or in dimethyl formamide, with added tetraethylammonium perchlorate).

Thus, continuing our work on the generation of radical anions from aromatic and polyenone systems in non polar media,[2] we have found that with phenyl-, p-nitrophenyl-, 2-pyridyl-, and 2-, or 4-troponyl tosylates straightforward formation of ROH products[3] occurs in high yields (Scheme, path c). This follows the rule above[1] for cathodic reduction of tosylates in protic media. Also, in contrast with the results for cathodic reduction of simple alkyl tosylates in non protic media,[1] in our cases above toluene was not detectable at the sensitivity level of v.p.c., which rules out S-C bond breaking. However, going to allyl tosylate, cathodic reduction in acetonitrile gave propene (25%) besides allyl alcohol (15%) and diethyl ether (15%), whilst, again, toluene was not detectable.[3]

With the idea that propene was the result of allyl-O bond breaking of $(1)^{\overline{\cdot}}$, driven by the stabilisation of the allyl radical, we examined the case of another similarly stabilised radical. It was rewarding to find that also with p-methylbenzyl tosylate R-O bond breaking occurs, leading to p-xylene in 30% yield, besides p-methylbenzyl alcohol (70%) (Scheme, path d).[3]

According to the above idea, R-O bond breaking in $(1)^{\overline{\cdot}}$ is expected to become the more prevalent path, the more the radical $R^{\cdot}$ stabilised is. This was nicely proved by the cathodic reduction of p-nitrobenzyl tosylate where, besides 1,2-di-p-nitrobenzylethane (78%), only p-nitrotoluene (13%) was detectable (Scheme, path e).[3] Prevalent formation of the ethane derivative in this case is most likely attributable to dimerisation of $R^{\cdot}$ which, being formed far from the cathode, owing to the relatively high stability of $(1)^{\overline{\cdot}}$ in this case (as proved by cyclic voltammetry), is not easily reduced to the carbanion.

Finally, going to another stabilised radical, such as the benzydryl one, it was surprising to find dibenzydryl ether[3] as the main product of the cathodic reduction of benzydryl tosylate. The ether is not the mere result of RO^- attack on (1) since sulphinate was not detectable among the products in this case and diphenylmethane was formed in a 12% yield when the electrolysis was carried out with guanidinium perchlorate as supporting electrolyte.

Clearly cathodic reduction of tosylates is more complex than previously thought, thus deserving further attention.

REFERENCES

1)L. Horner and H. Lund, in "Organic Electrochemistry", M.M. Baizer, Ed., M. Dekker, N.Y. 1973.

2)M. Cavazza, M.P. Colombini, M. Martinelli, L. Nucci, L. Pardi, F. Pietra, and S. Santucci, *J. Amer. Chem. Soc.*, in the press.

3)Compounds were isolated and their identity was established by spectral (i.r., n.m.r., mass) comparison with authentic samples prepared according to literature.