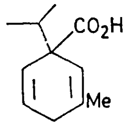
Anodic Decarboxylation of Dihydroaromatic Acids

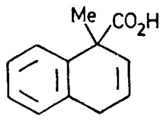
By JACOB SLOBBE

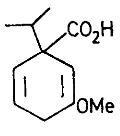
(*Research School of Chemistry, Australian National University, P.O. Box* 4, *Canberra, A.C.T.* 2600, *Australia*)

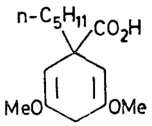
Summary Kolbe oxidation in methanol of 1-alkyl-1,4-dihydrobenzoic acids gives alkylbenzenes in good yield.

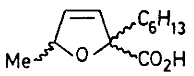
WE have recently investigated the oxidative decarboxylation of dihydroaromatic acids with lead tetra-acetate and demonstrated the use of the reductive alkylation–oxidative decarboxylation procedure in the regiospecific alkylation of some aromatic systems.[1] A consideration of the likely mechanism and comparison with the putative intermediates of the Kolbe oxidation[2,3] suggested the possibility of the reaction being performed electrochemically. We now report that this can be realized, at least for benzenoid cases, using a simple Kolbe cell[4] with an uncontrolled potential. The single literature example of a reaction of this type is the anodic bis-decarboxylation of *trans*-1,2-dihydrophthalic acid to benzene.[5]


(1)


(2)


(3)


(4)


(5)

The acids (**1**)—(**4**), prepared by the reductive alkylation procedure of van Bekkum *et al.*,[6] were treated as follows. The acid (0·01 mol) was added to a solution of NaOMe (from 100 mg Na) in MeOH (20 ml) and the solution electrolysed (current 1 A) until just alkaline (20—25 min) in a cylindrical glass cell (15 × 3 cm) fitted with two Pt foil electrodes (2 × 1·5 cm, 2—3 mm apart)[4] cooled in an ice-bath. Removal of the solvent and recovery of the neutral material gave the clean product in good yield (Table).

The previous best synthesis of *m*-cymene[7] involves acid-catalysed isomerization of *p*-cymene using liquid HF and BF_3 gas and highlights the simplicity of the procedure. Variation of the alkyl halide used to produce (**2**) potentially provides one of the few[8] general preparations of 1-alkylnaphthalenes. The final two examples illustrate its use in alkylating specifically *meta* to OMe (and to OH by demethylation) in a benzene ring.

TABLE[a]

Acid	M.p./°C	Product	Yield/%
(**1**)	66—67	*m*-Cymene	60
(**2**)	118—119	1-Methylnaphthalene	65
(**3**)	—	*m*-Isopropylanisole	65
(**4**)	91—92	1,3-Dimethyoxy-5-pentylbenzene	70

[a] Satisfactory analytical results and/or physical and spectral data have been obtained for all compounds.

The above yields were not optimized; the remainder of the material was recoverable starting material which can be recycled, though care needs to be taken during acidification with the latter two examples to prevent hydrolysis of the sensitive enol ethers. Electrolysis for 5—10 min past alkalinity gave a higher yield of product in the first two cases, though this is not recommended with the latter two owing to their ready further oxidation under similar conditions.[9] Finally the dihydrofuroic acid (**5**)[1] was slow to reach alkalinity (*ca.* 45 min) and no sign (n.m.r.) of the desired 2,5-dialkylfuran was observed in the product reflecting the much lower oxidation potential for this compound.[10]

(*Received, 2nd November* 1976; *Com.* 1218.)

---

[1] A. J. Birch and J. Slobbe, *Tetrahedron Letters*, 1976, 2079.

[2] J. H. P. Utley in 'Techniques of Electroorganic Synthesis—Techniques of Chemistry,' ed. N. L. Weinberg, Wiley, New York, 1974, Vol. V, Part I, Ch. 6.

[3] S. D. Ross, M. Finkelstein, and E. J. Rudd, 'Anodic Oxidation,' Academic Press, New York, 1975, Ch. 6 and 7.

[4] B. C. L. Weedon in 'Advances in Organic Chemistry: Methods and Results,' eds. R. A. Raphael, E. C. Taylor, and H. Wynberg, Interscience, New York, 1960, Vol. I, pp. 25—27.

[5] E. A. Pasquinelli, *Anales Asoc. quim. argentina*, 1943, **31**, 181 (*Chem. Abs.*, 1944, **38**, 5734).

[6] H. van Bekkum, C. B. van den Bosch, G. van Minnen-Pathuis, J. C. de Mos, and A. M. van Wijk, *Rec. Trav. chim.*, 1971, **90**, 137.

[7] D. E. Pearson, R. D. Wysong, and J. M. Finkel in 'Organic Synthesis,' ed. H. E. Baumgarten, Wiley, New York, 1973, Coll. Vol. V, p. 332.

[8] Elsevier's 'Encyclopaedia of Organic Chemistry,' ed. F. Radt, Elsevier, New York, 1948, Vol. 12b, pp. 93—132; H. F. Hipsher and P. H. Wise, *J. Amer. Chem. Soc.*, 1954, **76**, 1747.

[9] N. L. Weinberg and B. Belleau, *Tetrahedron*, 1973, **29**, 279.

[10] Ref. **3**, p. 84.