Tetrahedron Letters,Vol.30,No.24,pp 3187-3188,1989 0040-4039/89 $3.00 + .00
Printed in Great Britain Maxwell Pergamon Macmillan plc

ANODIC OXIDATION OF ALKYLATED BIPHENYLS. SYNTHETIC ROUTES TO CERTAIN CYCLOHEXA-1,4-DIENES

Isidoro Barba*, Rafael Chinchilla and Cecilia Gómez

División de Química Orgánica, Universidad de Alicante,
P.O. Box 99, Alicante, Spain

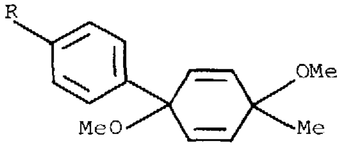
Abstract: The anodic methoxylation of 3-phenyltoluene, 4-phenyltoluene and 4,4'-dimethylbiphenyl carried out under constant current intensity afforded a number of new cyclohexa-1,4-dienes.

Functionalization of biphenyl systems is an interesting matter in organic chemistry since they have been utilized for the preparation of various kinds of natural products.[1] In the last years, a few number of works have focused on the electrosynthesis of biphenylic cyclohexadiene rings,[2,3] but always through the anodic oxidation of oxygenated biphenyl systems. Neverthless, nothing is known about the anodic oxidation chemistry of alkylbiphenyls. We report now the preliminary electrochemical oxidation of a number of methylbiphenyls giving cyclohexadiene rings.

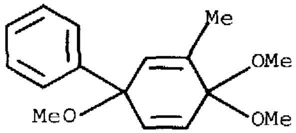
Our investigation of the oxidation of alkylbenzenes by electrochemical methoxylation[4,5,6] led us to conclude that nuclear addition products as the cyclohexa-1,4-dienes could not be only obtained when the original substrates are activated benzenes.

Anodic oxidation of 3-phenyltoluene, 4-phenyltoluene and 4,4'-dimethylbiphenyl (0.3 g) was carried out in a cell without separated compartments, with a constant current intensity of 1 amp and with a solvent supporting electrolyte system prepared by adding sodium methoxide (0.2 g) to dry methanol (70 mL) and using a carbon-paste plate as anode and a stainless-steel plate as cathode. The reaction was followed by TLC and judged to be completed after 45 minutes. In the electrolysis of 4-phenyltoluene and 4,4'-dimethylbiphenyl, conventional workup afforded an oil wich was separated by flash chromatography. In this way were isolated or detected compounds **1** to **4**, not described previously in the literature[7]. Comparison of the ^{1}H NMR spectral data of the isolated dienes **1**, **2** and **4** with those of the trans-3,6-dimethoxy-3,6-dimethyl-cyclohexa-1,4-diene, unequivocally identified by X-ray diffraction[8], let us assign the cis and trans structures of these compounds. In the case of 3-phenyltoluene, workup was realized using a buffer solution KH_2PO_4/Na_2HPO_4 (0.025 M) during the extraction process instead of water and the crude extract was chromatographed on a neutral carbon-celite column because the lability of the new cyclohexadienes **5** and **6** to the slight acid medium. The acidic hydrolysis of these compounds leads to the new dienones **7** and **8** in quantitative yield.

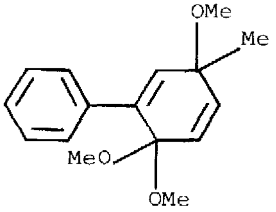
The anodic oxidation of 3-phenyltoluene afforded only nuclear addition compounds, whereas the electrolysis of the p-methyl biphenyls studied also gave side-chain methoxylation products. This side-chain versus nuclear attack is well known in the electrooxidation of p-alkylated methoxybenzenes[9]. The studies concerned with other alkylbiphenyls are now in progress and will be reported in near future.



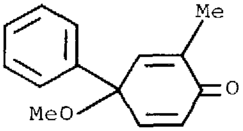
1, R = H (20%)
2, R = Me (25%)
3, R = CH_2OMe (5%)
4, R = $CH(OMe)_2$ (13%)



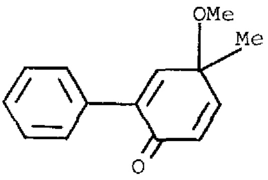
5, (52%)



6, (6%)



7



8

References and notes

1) M. Sainsbury, Tetrahedron, **1980**, 36, 3327.
2) M. P. Capparelli, R. E. DeSchepper and J. S. Swenton, J. Org. Chem., **1987**, 52, 4953.
3) R. E. DeSchepper and J. S. Swenton, Tetrahedron Lett., **1985**, 26, 4831, and references cited therein.
4) F. Barba, A. Guirado and I. Barba, J. Org. Chem., **1984**, 49, 3022.
5) F. Barba, A. Guirado and I. Barba, J. Chem. Research (S), **1986**, 228.
6) I. Barba, C. Gómez, M. Tornero and F. Barba, Chem. Scr., **1988**, 28, 419.
7) All new compounds were characterized by ^{1}H NMR, IR, MS (EI and CI) and satisfactory combustion analysis (C, H).
8) F. Alonso, I. Barba and F. Florencio, J. Org. Chem., in press.
9) K. Yoshida, "Electrooxidation in Organic Chemistry", Wiley (1984), p. 177, and references cited therein.
10) Yields were obtained by gas chromatography, using cyclohexanone as internal standard.

(Received in UK 28 April 1989)