

Short Communications

An Anodic Synthesis of 2,5-Dimethyl-2,5-diphenyltetrahydrofuran

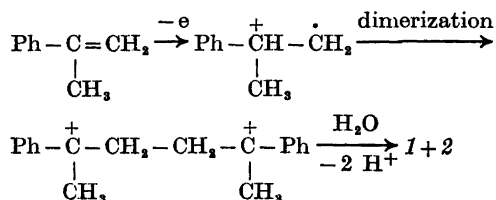
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The anodic oxidation of aromatic hydrocarbons with at least one benzylic hydrogen partly results in the formation of the corresponding olefin *via* proton loss from an intermediate benzylic cation. Since the olefin formed is oxidized at a lower potential than the starting material, further oxidation takes place — possibly in the adsorbed state — with formation of the two-electron oxidation product from the olefin, as has been shown in the case of indan.¹ If cumene is oxidized according to the same mechanism it should under suitable conditions give α -methylstyrene as the primary product. This might then be oxidized further to phenylacetone by analogy with the known behaviour of α -methylstyrene upon lead tetraacetate oxidation.^{2,3} Hence, it might be possible to realize a direct route from cumene to this important intermediate.

The oxidation of cumene in acetonitrile/water (volume ratio 98:2) with sodium perchlorate or tetrabutylammonium tetrafluoroborate as supporting electrolyte gives, however, 2-phenylpropanol-2 as the main product. To see if it was possible to obtain phenylacetone from α -methylstyrene itself, this compound was oxidized under identical conditions, but no trace of phenylacetone was detectable. GLC analysis of the reaction product showed, besides starting material, only two well-resolved peaks (retention times 5.1 and 5.8 min on a 5 % neopentylglycol succinate column (2 m \times 0.3 mm) at 170 °C, ratio 52:48), with identical mass spectra. After distillation, the product partly crystallized on standing. Recrystallization from ethanol gave crystals which on GLC analysis were found to correspond to one of the peaks in the gas chromatogram (with retention time 5.8 min). From the mother liquor, the second compound could be isolated as an oil. NMR and elemental analysis led to the identification of the two compounds as the *cis* (1) and *trans* (2) isomers of 2,5-dimethyl-2,5-diphenyltetrahydrofuran. The formation of these compounds is in ac-

cordance with earlier mechanistic work on the additive dimerization of arylelefins.⁴



The NMR spectra of 1 and 2 have been reported⁵ and agree well with those given in the experimental section.

Experimental The concentric capillary gap cell used has been described in a recent paper.⁶ Analytical procedures were as described earlier.⁷

Oxidation of cumene. Cumene (120 g, 1 mol), NaClO₄·H₂O (2.8 g, 0.01 mol) and water (18 ml, 1 mol) were dissolved in acetonitrile (1000 ml). At the beginning of the electrolysis the applied voltage was 13 V. The current was kept at 25 A throughout the experiment. The voltage increased slowly and as soon as it reached 30 V, 4.5 ml of a solution of NaClO₄·H₂O (2.8 g) in water (36 ml) was added. After passing a charge of 2.70 F the electrolysis was interrupted and the solvent removed by evaporation *in vacuo*. Ether was added to the residue and the solution washed with water and dried over MgSO₄. After removing the ether, the residue (57.7 g) was distilled to give the following fractions: 1, b.p. 87 °C/11 mmHg (11.0 g); 2, b.p. 87–92 °C/11 mmHg (28.1 g); 3, residue (13.4 g). Fraction 2 was found to be pure 2-phenylpropanol-1 by comparison with an authentic sample.

Oxidation of α -methylstyrene. α -Methylstyrene (118 g, 1 mol), NaClO₄·H₂O (2.8 g, 0.02 mol) and water (18 ml, 1 mol) were dissolved in acetonitrile (1000 ml). The electrolysis was run at 50 A until 1 F had passed. The applied voltage rose from 12 to 26 V during the run. The reaction solution was worked up as above. The residue after evaporation of the ether (100.5 g) was distilled to give the following fractions: 1, 103 °C/0.4 mmHg (8.7 g); 2, 103–128 °C/0.4 mmHg (4.8 g); 3, 128–143 °C (30.6 g); 4, residue (43.3 g). GLC of fraction 3 showed two well-resolved peaks with an integral ratio of 52:48. On standing this fraction partly crystallized. A sample of the solid compound was recrystallized from ethanol giving colourless

crystals, m.p. 74–75 °C (lit.⁵ 75 °C). By suction of fraction 3 the oily isomer was obtained contaminated with 20 % of the solid isomer. NMR of the crystalline isomer:⁵ δ 1.53 ppm (s, 6, methyl protons), 2.15 (an AA'BB' spectrum centered at 2.15 ppm, 4, methylene protons), 7.12–7.63 (m, 10, aromatic protons). NMR of the liquid isomer:⁵ δ 1.60 ppm (s, 6, methyl protons), 2.20 (s, 4, methylene protons), 7.00–7.58 ppm (m, 10, aromatic protons). The two isomers showed identical mass spectra, m/e (% of base peak): 238(15), 237(100), 219(7), 117(21), 105(95), 91(11), 77(16), 43(15). (Found: C 85.3; H 7.97; O 6.49. Calc. for $C_{18}H_{20}O$: C 85.7; H 8.00; O 6.34).

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4-Chlorobuten-3-yne: a Spectrochemical Characterization

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True acetylenic hydrogens are generally replaced by halogen by action of alkaline hypohalites. This reaction has been applied to vinylacetylene with different halogen atoms by Carothers and Jacobson.¹ We prepared 4-chlorobuten-3-yne by adding monovinylacetylene to a potassium hypochlorite solution.

The substance was isolated and purified with gas liquid chromatography at a temperature of 100 °C. The column was packed with diethylhexyl sebacate (15 %) absorbed on Chromosorb.

The identification is primarily based on the mass spectrum obtained by using a combined GLC–MS. After correction for background, the largest peaks are: m/e (rel. intensity), 49(19.5), 50(46.5), 51(100.0), 52(4.5), 60(10.5), 62(3.5), 84(10.5), 85(12.0), 86(98.5), 87(8.5), 88(30.5) and 89(1.5).

The occurrence of chlorine is demonstrated by the intensity relation 3:1 of the mass numbers 86:88 corresponding to the molecular ions with ^{35}Cl and ^{37}Cl and the mass numbers 60:62 probably corresponding to the ions $CHC^{35}Cl^+$ and $CHC^{37}Cl^+$. The molecular weight is consequently 86.5. The relation $^{13}C:^{12}C$ in the substance appears most evident from the intensity relation 4.5:100.0 between the mass numbers 52:51, corresponding to the ions $^{13}CC_4H_3^+$ and $C_4H_3^+$. Hence the assumption of four carbon atoms is confirmed.

A UV-spectrum of the substance was run between 340 and 200 nm. An absorption at 277–278 nm was observed.

For monovinylacetylene, absorption at 221 nm and 227.5 nm has been reported by Georgieff *et al.*²

The IR-spectrum of gaseous 4-chlorobuten-3-yne is given in Fig. 1. A theoretical calculation of the frequencies, from a normal coordinate analysis using a simple diagonal valence force field, shows good agreement with the obtained spectrum for some of the peaks.^{3,4}

At 3120 cm^{-1} we observed the asymmetric hydrogen stretch for the vinyl group. The peak at 3035 cm^{-1} belongs either to the symmetric hydrogen stretch for the vinyl group or a stretch of the remaining hydrogen. At 2220 cm^{-1} the characteristic stretching of $-C\equiv C-$ was observed and at 1600 cm^{-1} the $-C=C-$ stretch. There is no strong absorption around 3300 cm^{-1} which shows the purity of the substance and eliminates the isomeric chlorobutenyne structures.^{5,6}