

SYNTHESIS AND REACTIONS OF 3,4-DIHYDROANISOLE

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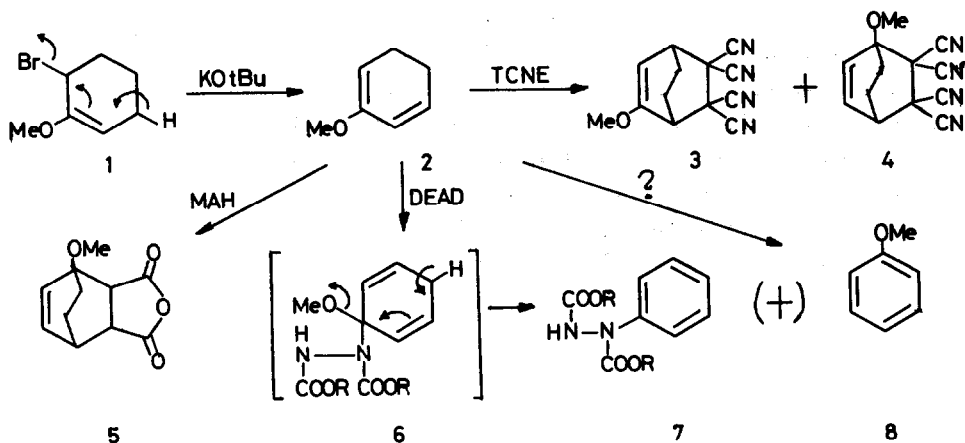
E.R. de Waard*, J. Kattenberg and H.O. Huisman,
 Laboratory for Organic Chemistry, University of Amsterdam,
 Nieuwe Achtergracht 129, Amsterdam, The Netherlands.

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Dissolving metal reduction of anisole leads to 2,5-dihydroanisole^{1,2} which has been isomerized to 2,3-dihydroanisole by base³ and transition metal complexes⁴. The presence of 3,4-dihydroanisole 2 has never been demonstrated in these equilibria. In situ isomerization Diels-Alder experiments with 2,5-dihydroanisole failed to give products derived from 2 as was the case with pyrolytic decarboxylation of 1,4-dihydro-2-methoxybenzoic acid⁵. Enol-etherification experiments on cyclohex-2-enone followed by Diels-Alder reaction have given indications of products derived through the intermediacy of 2⁵.

We now wish to report a smooth synthesis of the hitherto unknown 3,4-dihydroanisole 2 and some of its reactions.

Treatment of 1⁶ with KOtBu in DME during fifteen hr. at r.t. followed by filtration of the precipitated KBr and distillation of the filtrate gave pure 2 in 70% yield (b.p. 78-84°/90 mm, n_D^{20} 1.4843). The structure of 2 is confirmed by the spectral data. IR (neat), sharp and strong absorptions at 1640, 1590, 1235, 1195 and 1160 cm^{-1} . NMR (60 MHz, CCl_4), narrow multiplet at δ 2.10 (C_3 and C_4 -H), singlet at δ 3.45 (CH_3O), broad singlet at δ 4.55 (C_2 -H) and a narrow multiplet at δ 5.75 (C_5 and C_6 -H). UV ($\text{C}_2\text{H}_5\text{OH}$) λ_{max} 268 nm (ϵ 2230), (cyclohexane) λ_{max} 268 nm (ϵ 2380).



The diene 2 can be stored at -30° indefinitely and the solution in non protic solvents is stable for several days at r.t. When dissolved in chloroform commonly used for IR spectroscopy a fast decomposition takes place to a mixture containing anisole, 2,5- and 2,3-dihydroanisole and at least two other products of higher degree of saturation, presumably arising from acid catalyzed disproportionation and polymerization. The presence of the 2,5-dihydroisomer - easily recognizable by its characteristic signals in NMR - is significant, since it sheds some light on the relative stabilities of the dienes.

Diels-Alder reaction of 2 with TCNE in DME at r.t. gave a crystalline precipitate after twelve hr. containing the adducts 3 and 4 in a ratio of 10 : 1 in addition to coprecipitated TCNE. Recrystallization from chloroform gave the main product 3 in an almost pure state (m.p. $135-140^{\circ}$, 68%), IR (KBr), 1645 cm^{-1} (enol-ether). NMR (100 MHz, CDCl_3), quartet at δ 5.20 ($\text{C}_3\text{-H}$), singlet at δ 3.70 (CH_3O), multiplets at δ 3.57 and δ 3.32 (C_4 and $\text{C}_1\text{-H}$) respectively. The minor adduct 4 could not be obtained free from 3 but could be recognized in the NMR spectrum of the mixture : multiplet at δ 6.70 (C_2 and $\text{C}_3\text{-H}$), singlet at δ 3.60 (CH_3O), and a multiplet at δ 3.6 ($\text{C}_4\text{-H}$).

The reaction of 2 with maleic anhydride in refluxing benzene gave the adduct 5 derived from 2,3-dihydroanisole in moderate yield in addition to polymeric material from which it could be separated by column chromatography.

Reaction of 2 with diethyl azodicarboxylate at -20° in pentane gave a reaction mixture which could be separated by column chromatography into 7, 8 and hydrazodicarboxylate, all three in ca. 20% yield. A reasonable explanation for the formation of 7 seems to be an addition abstraction mechanism leading to 6 followed by loss of methanol. No compounds derived from other modes of addition⁷ of the azodicarboxylate have been detected. The anisole may have been formed from the same intermediate or by direct oxidation of 2.

Further properties of 2 are under investigation.

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* To whom correspondence can be addressed.

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