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STUDIES ON THE HYDROLYSIS OF THE SODIUM–POTASSIUM–BIPHENYL ADDUCT*

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SUMMARY

The hydrolysis of the sodium–potassium–biphenyl adduct in 1,2-dimethoxyethane has been investigated. Phenylcyclohexane, 1-phenylcyclohexene and biphenyl were identified in the products by GLC. Preparative GLC led to isolation of 3 components, which on the basis of their UV and NMR spectra are thought to be 3-phenylcyclohexene, 3-phenyl-1,4-cyclohexadiene and 2-phenyl-1,3-cyclohexadiene.

INTRODUCTION

The formation of anion radicals[1–4] by reaction of alkali metals with aromatic hydrocarbons in the presence of solvents such as 1,2-dimethoxyethane (glyme) and tetrahydrofuran (THF) and liquid ammonia[5,6] has been known for some time. The reactions of the sodium adducts with carbon dioxide and active hydrogen compounds have been known since 1928[1–3, 7–10], and these adducts are also known to react with organic halides, the carbon bonded halogen being converted quantitatively into halide ion[11–15].

The chemistry and electronic structure of such mononegative ions of aromatic hydrocarbons have been a field of active investigation[4,16–18] but conclusive evidence on the identities of the end products has been lacking. Recently Grisdale *et al.*[19] examined the published methods for reduction of the biphenyl via the alkali metal adducts, and showed that in most of the cases studied such reduction leads to a complex mixture of products. This complexity no doubt contributed to incorrect product assignments in earlier work.

We have now established the composition of the products obtained by hydrolysis of an adduct formed from sodium–potassium alloy and biphenyl in glyme as solvent. A previous report from this laboratory described the use of this adduct as a dehalogenating reagent, and its advantages in analysis of organic halides[13].

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EXPERIMENTAL

Reagents

1,2-Dimethoxyethane (Merck, Darmstadt) was dried over Na and distilled. Biphenyl (BDH Chemicals Ltd.) was dried at 50° and used as a 2.6 *M* solution in dry glyme. The Na–K alloy (22% Na+78% K) was prepared under dry toluene[13].

Pure samples of phenylcyclohexane, 1-phenylcyclohexene (Aldrich Chemical Co.), dimethyl oxalate, dimethyl malonate, dimethyl succinate and methyl benzoate (Eastman Kodak Co.) were used as standards for GLC.

CCl_4 (BDH for spectroscopy) was used as solvent for NMR with TMS (Aldrich Chemical Co.) as internal standard.

Cyclohexane (Riedel de Haen) was used as solvent for the UV analysis.

Reactions

All the experiments were carried out in special weighing bottles[13], the adduct being prepared shortly before use. Glyme (2.5 ml) and 0.16 ml of alloy were shaken until a fine dispersion was obtained, 2.5 ml of biphenyl solution were then added, and shaking was continued for some minutes to give a dark green solution.

In the hydrolysis, water (0.2–5 ml) was added slowly with shaking. The organic layer was separated and dried with anhydrous Na_2SO_4, and the solvent evaporated off in a current of nitrogen. On cooling the residue, biphenyl was precipitated, and was removed by centrifugation. The residue was an oil.

Gas chromatographic (GLC) analysis of the hydrolysis products

The oil produced was diluted with glyme and the solution injected into a Wilkens Aerograph 1522-B gas chromatograph. The instrument operated isothermally at 145°. The column used was 6 feet × $\frac{1}{8}$ inch stainless steel packed with 15% FFAP on 60/80 Chromosorb W, with a nitrogen flow of 20 ml/min. A flame ionization detector was used. The injection system and the detector were kept at 230° and 225°, respectively.

Separation of the components of the reaction mixture

The hydrolyzed products were separated by preparative GLC with a Varian Aerograph Autoprep 700 gas chromatograph, fitted with a thermal conductivity detector. A 6 feet × $\frac{3}{8}$ inch column packed with 15% FFAP on 60/80 Chromosorb W was used, with hydrogen as carrier gas. The column was kept at 145° and the injection system at 230°. The fractions were collected in special tubes (provided by Varian) closed with silanized glass wool (Analabs Co.) and cooled at −30° and −40°. The homogeneity of each sample was checked on the analytical GLC column.

Oxidation analysis of the reaction products

An aliquot of the oil produced was treated by the usual procedures with $KMnO_4$ and the acids obtained were esterified with 14% BF_3 in CH_3OH (BDH Chemicals Ltd.)[20].

The methyl esters were identified by comparison of their retention times with those of pure samples (from Eastman Kodak Co.).

The oxidation with ozone was carried out as described by Beroza and Bierl[21] and esterification was as before.

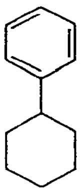
Chromatographic analysis was carried out with a 6 feet × $\frac{1}{8}$ inch stainless steel column packed with 15% Carbowax 20M on 60/80 Chromosorb W at 100°, with nitrogen as carrier gas and a flame ionization detector.

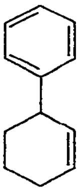
Nuclear magnetic resonance (NMR) and ultraviolet (UV) spectroscopic analysis

Except for compounds (I) and (VI), the products isolated by preparative GLC were studied by NMR and UV spectroscopy. The NMR spectra were recorded with a Varian T-60 spectrometer, using TMS 1% as internal standard, CCl_4 as solvent and a microkit for 20–30 μl samples. UV data were recorded in cyclohexane with a Zeiss PMQ II spectrometer, using 0.5 cm quartz cells and variable slit.

RESULTS AND DISCUSSION

The mixture produced by hydrolysis of the adduct consisted of six main compounds, (I)–(VI), with retention times (relative to biphenyl) given in Table 1. The retention times of (I), (IV), and (VI) were identical with those of pure samples of phenylcyclohexane, 1-phenylcyclohexene and biphenyl respectively.


(I)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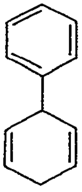
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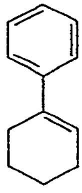
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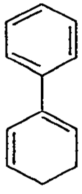
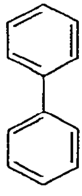

(V)


(VI)

The NMR spectrum of compound (II) showed protons in the ratios of 2 olefinic (δ 5.7 ppm), 1 benzylic (δ 3.3 ppm), 2 allylic (δ 2.0 ppm), 2 methylenic (δ 1.7 ppm) to 5 aromatic (δ 7.1 ppm). The UV spectrum had λ_{max} 247 nm, ε 540 $l \cdot mole^{-1} \cdot cm^{-1}$, in agreement with published data[15] for 3-phenylcyclohexene.

TABLE 1

RETENTION TIMES FOR THE COMPONENTS OF THE REACTION MIXTURE

Compound	*RRT*[a] *(min.)*
(I)	0.37
(II)	0.46
(III)	0.57
(IV)	0.66
(V)	0.80
(VI)	1.00

[a] Relative to biphenyl.

The NMR spectrum for compound (III) showed protons in the ratios of 4 olefinic (δ 5.8 ppm), 1 benzylic (δ 3.8 ppm), 2 allylic (δ 2.8 ppm), to 5 aromatic (δ 7.2 ppm). The absence of conjugated double bonds suggested that the compound was 3-phenyl-1,4-cyclohexadiene.

The NMR spectrum for compound (IV) showed protons in the ratios of 1 olefinic (δ 6.0 ppm), 4 allylic (δ 2.3 ppm), 4 methylenic (δ 1.7 ppm) to 5 aromatic (δ 7.2 ppm). The absence of benzylic protons, the similarity in the UV spectra (λ_{max} 247 nm; ε 11300 $l \cdot mole^{-1} \cdot cm^{-1}$) and the refraction index n_D^{20} 1.5690 as reported in literature[15] suggested that it was 1-phenylcyclohexene. Comparison with a pure sample of (IV) showed that they were identical in all these properties.

The chemical behaviour of compound (V) suggested that it might be a conjugated diene. It was very unstable on contact with air. Its NMR spectrum showed protons in the ratios of 3 olefinic (δ 6.0 ppm), 4 allylic (δ 2.3 ppm) to 5 aromatic (δ 7.2 ppm). The absence of benzylic protons indicated that it was 2-phenyl-1,3-cyclohexadiene.

We were not able to get useful information about the structure of the reaction products because of their oxidation and the esterification of the resulting acids; the same products are obtained from all starting compounds. With ozone when oxidation times were long or when an excess of $KMnO_4$ was used, only benzoic acid was obtained. After short oxidation time, oxalic, malonic and succinic acids were detected by GLC.

When the mixture was decomposed with different amounts of water, the same products were obtained, but the relative concentrations changed; *e.g.* with 0.2 ml of water compound (III) did not appear, while with 5 ml compound (V) could not be detected.

When the reaction mixture was decomposed with methanol, butanol, phenol, or glacial acetic acid instead of water, the same products were formed.

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