Dehydrogenation of Benzene to Biphenyl by a Potassium–Graphite Lamellar Compound (KC_8)

By FRANÇOIS BÉGUIN and RALPH SETTON

(Laboratoire de Chimie IV, U. E. R. de Sciences Fondamentales et Appliquées, 45045 Orléans, Cedex, France)

Summary The lamellar potassium–graphite compound KC_8 forms a well defined lamellar complex with benzene and tetrahydrofuran, and because of its high affinity for hydrogen causes conversion of benzene into biphenyl.

IT was shown previously[1] that solutions of polynuclear hydrocarbons in tetrahydrofuran (THF) reacted with lamellar graphite–potassium compounds to give ternary derivatives (with THF and potassium, but with no hydrocarbon, between the aromatic carbon planes of the graphite). We now report that benzene, which does not normally react with potassium, is readily adsorbed along with THF by KC_8 and, in so doing, is dehydrogenated to biphenyl.

Prolonged contact between C_6H_6 and KC_8, with complete exclusion of air and moisture (over 4 weeks), does not result in any reaction even when the temperature is raised to 50 °C, nor does THF alone react with KC_8. However, solutions of C_6H_6 in THF (1:2 v/v; *ca.* 3·7M) react even at 20 °C as shown by the swelling of the solid compound which gradually turns from golden to dark blue. The reaction is complete within 3 h, as seen by *X*-ray diffraction.

G.l.c. analysis of the filtered solution (Carbowax 20 M column) shows that it is exclusively made up of C_6H_6 and THF; it does not contain potassium in any form.

The *X*-ray powder diffraction pattern of the dried dark blue solid is made up of sharp, well defined lines. Although the spectrum has not yet been fully indexed, six lines of the $(00l)$ series, with $l = 1$—6, can easily be identified and yield a d_l value of 8·893 Å, a large increase from the original 5·4 Å, which is undoubtedly due to the penetration of benzene and/or THF between the graphite layers.

Heating the dark blue compound to 200 °C releases large quantities of gases (H_2 and CH_4, as detected by mass spectrometry) and fractions condensable at −196 °C essentially made up of THF and biphenyl.

Since it is known[2] that the action of alkali metals on aromatic hydrocarbons can give rise to condensation reactions even at fairly low temperatures and that pyrolysis of benzene also results in the formation of biphenyl and other simple molecules such as ethylene,[3] the dark blue compound (unheated samples) was also hydrolysed at 0 °C. After cessation of gas evolution, the aqueous solution was extracted with ether and the extract analysed by g.l.c. (Carbowax 20 M) or combined g.l.c.–mass spectrometry (DEGS 10%). The composition of the extract was: biphenyl (61%), 3-phenylcyclohexane (12%), 1-phenylcyclohexene (11%), 2-phenylcyclohexa-1,3-diene (11%), phenylcyclohexane (2%), 3-phenylcyclohexa-1,4-diene (2%), and 4-phenylcyclohexene (1%). Compounds with both biphenyl rings hydrogenated were not formed.

It therefore appears that biphenyl is present between the carbon planes prior to any hydrolysis or pyrolysis. Since THF is essential for the reaction with benzene to occur, the removal of hydrogen from benzene leading to dimerization to biphenyl must be brought about by a solvated potassium atom or ion (the exact status of the metal in KC_8 is still open to debate). Whether the hydrogen is then held as the hydride KH, or, as seems more likely, as an intercalated species,[4] hydrolysis in either case liberates hydrogen which can then be fixed by one or more of the available double bonds.

It is noteworthy that, in this instance, the compound KC_8, which is normally thought of as a reducer, behaves as an oxidising agent because of its high affinity for hydrogen. While the present results could be compared with those of Ichikawa and his co-workers[5] who obtained high yields of cyclohexane by hydrogenation of benzene in the presence of KC_8 or KC_{24} (250 °C; 100 kg/cm^2) and those of Podall and Foster[6] who obtained biphenyl in 19% yield, along with other products, by heating benzene in the presence of KC_8 under a high pressure of ethylene (200 °C, 63 kg/cm^2), the reaction we describe involves a fundamentally different mechanism; it is also performed under particularly mild conditions.

We thank the D.G.R.S.T. for financial support.

(*Received*, 16*th March* 1976; *Com.* 270.)

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