Ready Conversion of 1,1-Diphenylethylene into Benzophenone and 1,1-Diphenylethane over a Synthetic Hectorite

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Summary Synthetic fluorohectorite serves as an efficient agent for the conversion of 1,1-diphenylethylene into benzophenone and 1,1-diphenylethane.

ATTENTION has recently been drawn to the ease with which many novel organic reactions may be effected through the agency of sheet silicates, there being strong indications that intercalation of the reagent is a prerequisite for reaction. We have, in particular, demonstrated that diphenylethylene may be efficiently converted into 1-methyl-1,3,3-triphenylindan using a cation exchanged montmorillonite that serves as a Brønsted acid.[1] By taking a synthesized sheet silicate (a fluorohectorite prepared according to the procedure given by Barrer[2]) which is almost completely devoid of acidic hydroxy groups we have shown that diphenylethylene is converted, again with great efficiency, into a totally different range of products.

1,1-Diphenylethylene did not react with the synthetic hectorite at temperatures below 300 °C, but above that temperature it was consumed without producing any of the methyltriphenylindan. Instead there was formed a mixture of compounds separable into two fractions by chromatography on alumina. The faster-running (hydrocarbon) fraction consisted of a mixture of starting material, 1,1-diphenylethane, and diphenylmethane; the slower-running component consisted of benzophenone (50%) and an as yet unidentified fourth product(s). These products were identified by g.l.c. retention time ($6' \times \frac{1}{8}''$ column of 3% OVI silicone on Chromosorb G) and also by i.r. and n.m.r. spectroscopy. The unknown product had no carbonyl or hydroxy absorptions in the i.r. spectrum and only aromatic hydrogen absorptions in the n.m.r. spectrum.

The yields of products varied somewhat between runs; typically the yield of diphenylethane rose to a maximum, *ca.* 25%, over a 24 h reaction time and then declined while yields of benzophenone and diphenylmethane continued to increase up to 18 and 15%, respectively. Separate experiments showed that diphenylethane was also consumed by the hectorite catalyst, though more slowly than was diphenylethylene, with benzophenone as the sole isolated product. It was thought that diphenylmethanol, a possible intermediate *en route* to benzophenone, might have been the immediate source of hydrogen for the reduction of diphenylethylene to diphenylethane. However, when diphenylmethanol was added to the reaction mixture the yield of diphenylethane during a 24 h reaction period decreased from 25 to 19% and that of diphenylmethane increased from 15 to 30%. It was subsequently discovered that diphenylmethanol and diphenylethane react together at these temperatures, even in the absence of clay, to form diphenylmethane and diphenylethylene.

Although the mechanism of the reaction is not yet clear we do know from *X*-ray studies that substrate does enter the interlamellar spaces and also that a weight change, corresponding in all probability to loss of water, occurs in a T.G.A. run at a temperature close to that at which reaction freely ensues. However, the water content of the clay cannot be the source of either hydrogen or oxygen incorporated into the product molecules, amounting as it does, only to some 10% of the requisite amount. Using certain clays it is conceivable that water could be abstracted from hydroxy groups attached to octahedrally co-ordinated cations; however this is not a tenable view in the present instance since the hydroxy groups are substituted solely by fluoride. The oxygen incorporated into the benzophenone is atmospheric oxygen, since in an atmosphere of nitrogen and in the presence of the fluorohectorite catalyst diphenylethylene is converted smoothly into diphenylethane (33% based on consumed substrate) accompanied by only trace amounts of diphenylmethane. The only source of hydrogen, then, is the diphenylethylene itself; it could lose some hydrogen, being converted into fused ring aromatic hydrocarbons in the process. There is indeed formed a non-crystalline fraction, of such hydrocarbons, eluted from a chromatograph column after the diphenylethane. The fluorohectorite catalyst thus mediates both in a hydrogen exchange reaction and in the atmospheric oxidation of diphenylethane and diphenylethylene. Diphenylmethane, however, was unaffected under the same conditions, although in liquid phase oxidations it reacts more rapidly than does 1,1-diphenylpropane.[3]

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