

## Notes

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### The pyrolysis and hydrogenation of alkylbenzenes

The identification of isomeric methylalkanes by combined pyrolysis and hydrogenation followed by gas chromatographic separation of the products, using hydrogen as carrier gas, has recently been described<sup>1</sup>. Using this procedure the pyrolysis/hydrogenation products of a series of alkylbenzenes have been studied, and the results are presented herein.

WOLF AND ROSIE<sup>2</sup>, in a study on the pyrolysis of simple organic compounds, found that benzene when pyrolysed (in the presence of helium) between 700° and 1000° gave four hydrocarbons, *viz.* propane, propylene, hexane and 1-hexene. The identification of alkyl groups attached to aromatic rings has formed the subject of a recent paper<sup>3</sup>. The compounds were subjected to catalytic hydrogenation cleavage and the products separated by gas chromatography. Interference from functional groups was minimised by pretreatment of the compounds by decarboxylation or desulphonation as appropriate. Dealkylation of the aromatic compounds was carried out at 620° in a chamber directly attached to a gas chromatograph, and the resulting aliphatic hydrocarbons detected by flame ionisation.

In the present work pyrolysis was carried out at a significantly lower temperature (400°) with the object of maintaining the benzene ring intact, and forming a series of alkylbenzenes by the successive removal of carbon atoms from the side chain of the compound. The products were subsequently subjected to hydrogenation to ensure saturation of the side chain, thus limiting the number of standards required for identification. Quantitative conversion of the benzene ring itself did not occur, so that for any alkylbenzene two series of compounds would be formed, an alkylbenzene series and an alkylcyclohexane series. By forming these compounds rather than only simple aliphatic hydrocarbons it is possible to deduce with less ambiguity the structure of the parent compound.

#### *Experimental*

The pyrolysis and hydrogenation chambers were combined in a single length of 1/8 in. O.D. stainless steel tube to minimise diffusion of pyrolysis products prior to entering the gas chromatograph, and to eliminate leakage at joints subjected to high-temperature operation. The pyrolysis chamber contained 60–80 BS mesh acid-washed sand and the hydrogenation chamber palladium on Chromosorb W. The chambers were indirectly electrically heated<sup>1</sup>. GC operating conditions were chosen such that the paraffins formed by breakdown of the side chain itself were eluted rapidly and that the alkylbenzenes were resolved from the alkylcyclohexanes. Satisfactory conditions were achieved using an 18 ft. × 1/8 in. O.D. stainless steel column containing 10% EGSP-Z (silicone gum) on Chromosorb P. The column temperature was 100° and the hydrogen carrier gas flow rate 12 ml min<sup>-1</sup>.

TABLE I

ALKYLBENZENE REACTION PRODUCTS<sup>a</sup>

Product	Parent							
	Benzene	Toluene	Ethylbenzene	n-Propylbenzene	Iso-propylbenzene	n-Butylbenzene	tert.-Butylbenzene	tert.-Amylbenzene
Toluene		+	+					
Ethylbenzene			+		+			
n-Propylbenzene				+		+		
Isopropylbenzene					+			
n-Butylbenzene						+		
sec.-Butylbenzene								
tert.-Butylbenzene							+	
tert.-Amylbenzene								+
Cyclohexane	+	+		+	+	+	+	+
Methylcyclohexane		+		+		+	+	+
Ethylcyclohexane			+	+	+	+	+	+
n-Propylcyclohexane				+		+		
Isopropylcyclohexane					+			
n-Butylcyclohexane						+		
sec.-Butylcyclohexane								
tert.-Butylcyclohexane							+	
tert.-Amylcyclohexane								+

<sup>a</sup> + = compound present.

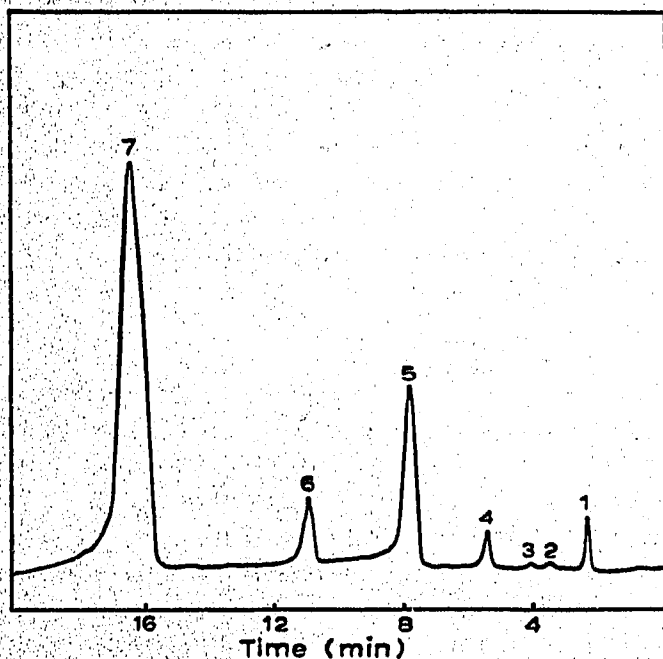


Fig. 1. Chromatogram of reaction products of *n*-propylbenzene. 1 = Propane; 2 = cyclohexane; 3 = methylcyclohexane; 4 = ethylcyclohexane; 5 = propylcyclohexane; 6 = ethylbenzene; 7 = propylbenzene.

### Results

All compounds were resolved except benzene from ethylcyclohexane, *n*-propylcyclohexane from isopropylcyclohexane, and *sec.*-butylcyclohexane from *n*-butylcyclohexane. Since by simple fragmentation none of the alkylbenzenes studied could give both of these unresolved cyclohexane pairs, lack of resolution was of little consequence. A separate study showed that benzene is only formed in very small relative amounts, so that the detection of products with this retention time was attributed predominantly to ethylcyclohexane. The alkylbenzenes studies are listed in Table I, together with the major reaction products. In all compounds the predicted behaviour was observed, and it was found that, in general, for a given parent compound, the ratio of the amount of an alkylbenzene to the corresponding cyclohexane increased with the number of carbon atoms on the side chain. For example *n*-propylbenzene gave rise to small amounts of cyclohexane and methylcyclohexane, and somewhat greater quantities of ethyl- and propylcyclohexane, ethylbenzene and unreacted parent compound. A chromatogram is shown in Fig. 1.

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## The gas chromatography of alkyldinitrophenols and the corresponding anisoles

A recent paper by HRIVŇÁK *et al.*<sup>1</sup> on the GLC separation of nitrophenols and nitroanisoles on polyester columns reports a greater retention time for certain dinitroanisoles than for the corresponding dinitrophenol. Similar behaviour has already been reported by us for some alkyldinitrophenols and alkyldinitroanisoles<sup>2,3</sup>.

### Experimental

The gas chromatographic separations were carried out as previously described<sup>3,4</sup> using DNOC (6-methyl-2,4-dinitrophenol\*) as standard, except that mononitrophenols were examined on the DEGA column at 155° using 2-nitroanisole as standard.

### Results and discussion

The three important types of hydrogen bonding in the GLC separation of nitro-

\* To simplify discussion this and similar compounds are designated 2,4-dinitrophenols even when the alkyl group is such that 2-alkyl-4,6-dinitrophenol is correct.