

columns has been demonstrated previously.<sup>8</sup> A further advantage of the system is that there is a slight delay between the total ion current and the signal from the flame ionisation detector.<sup>7</sup> This delay (about 2 sec) permits the chromatogram to be previewed and facilitates the mass scan of partially resolved components. The GC resolution is comparable to that obtained on a corresponding F 11 instrument.

The split ratio between the mass spectrometer and the flame ionisation detector can be varied by adjusting the make-up gas flow. When the amount of make-up gas is decreased more component will pass into the separator because of the difference in pressure between separator and flame ionisation detector. A small make-up gas flow should always be maintained otherwise the hydrogen may flow into the mass spectrometer and the flame be extinguished. Since changes in the make-up gas flow alter the column flow the latter has to be re-estimated with the aid of the retention time of a known compound. In practice a constant preset split ratio is preferable.

Under normal operating conditions about 90 % of the eluate passes into the mass spectrometer, as estimated from the increase in the total ion current observed on almost closing the make-up gas valve; this eliminates the flame ionisation detector signal. The 9:1 split ratio gives about the same response on the total ion current monitor as on the flame ionisation detector.

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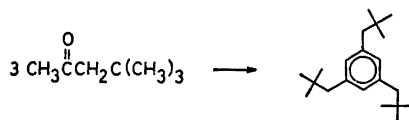
## 1,3,5-Trineopentylbenzene

### II. Synthesis by Base-Catalysed Trimerization of Methyl Neopentyl Ketone

PER MARTINSON and (in part)  
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In Part I<sup>1</sup> the multi-step synthesis of 1,3,5-trineopentylbenzene from pinacolone *via* 1,3,5-tripivaloylbenzene is described. As an alternative synthetic method we have investigated the trimerization of methyl neopentyl ketone to 1,3,5-trineopentylbenzene.



The formation of mesitylene from acetone under acidic conditions has long been well-known.<sup>2</sup> However, ethyl methyl ketone, the simplest member in the extended series of aliphatic methyl ketones, has been reported to give not a trialkylbenzene, but only products of condensation at the methylene carbon.<sup>3,4</sup> In condensations of ketones of the type  $\text{CH}_3\text{COCHR}'$  ( $\text{R}' = \text{alkyl or H}$ ;  $\text{R} = \text{alkyl}$ ) acid catalysts favour condensation at the more substituted carbon except when steric factors prevent it.<sup>5</sup> In a study of the acid-catalysed deuteration of some methyl ketones Rappe and Sachs reported that the bulky *t*-butyl group in methyl neopentyl ketone increased the rate of methyl relative to methylene deuteration.<sup>6</sup> It was expected that this diminished reactivity of the methylene group of methyl neopentyl ketone might possibly aid in the sulphuric acid-catalysed trimerization to 1,3,5-trineopentylbenzene, but all efforts were unsuccessful.

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Wirth *et al.* have reported that aromatic methyl ketones can be made to undergo cyclo-trimerization by means of ketalization reagents in the presence of gaseous hydrogen chloride.<sup>7</sup> This method also failed to give 1,3,5-trineopentylbenzene when applied to methyl neopentyl ketone.

It is generally accepted that basic conditions favour the condensation at the methyl in preference to the methylene carbon in ketones of the type  $\text{CH}_3\text{COCH}_2\text{-R}$ .<sup>4,8</sup> This opinion is also confirmed by a recent investigation of the base-catalysed enolization of some methyl ketones.<sup>9</sup> The condensation of two molecules of methyl neopentyl ketone with isopropylmagnesium chloride catalyst has been investigated by Dubois and Chastrette.<sup>10</sup> They report that the condensation is at the methyl group to an extent greater than 90%. To effect the cyclic trimerization of methyl neopentyl ketone metallic sodium was first tried as the catalyst, since Bartlett *et al.* have reported that among the products found in a reaction between pinacolone and this catalyst there was about 15% of 1,3,5-tri-*t*-butylbenzene.<sup>11</sup> The formation of a low yield of 1,3,5-trineopentylbenzene was noticed, but the method needed improvement, and we looked for another catalyst. In the paper of Bartlett *et al.*, it was also reported that sodium methoxide in toluene and potassium *t*-butoxide in *t*-butyl alcohol or without solvent were incapable of producing tri-*t*-butylbenzene from pinacolone, and we consequently expected these bases to be less effective in promoting the trimerization of methyl neopentyl ketone. Instead the possibility of effecting the trimerization by means of sodium hydride was investigated. This method proved to be very good, and at best yielded 45% of 1,3,5-trineopentylbenzene.

Sodium hydride was also found to produce a 30% yield of 1,3,5-tri-*t*-butylbenzene from pinacolone by this method. The possibility of using this method for the synthesis of other trialkylbenzenes from branched methyl ketones will be investigated.

*Experimental.* Methyl neopentyl ketone was prepared by oxidation of di-isobutylene (Fluka, techn. ~75% of 2,4,4-trimethyl-1-penten) with potassium dichromate according to Mosher and Cox.<sup>12</sup>

*1,3,5-Trineopentylbenzene.* Sodium hydride (Fluka, 50% dispersion in mineral oil, 24.0 g, 0.5 mole NaH) was placed in a 250 ml two-

necked flask equipped with a dropping funnel and a condenser fitted with a drying tube. The mineral oil was washed off twice by decantation with ligroin under nitrogen. Methyl neopentyl ketone (57.1 g, 0.5 mole) was added through the dropping funnel. Gas evolution started and the mixture was left at room temperature until it ceased. Careful heating on an oil bath (~55°C) started a vigorous reaction which sometimes had to be moderated by external cooling. The mixture soon thickened and became a voluminous paste. Another 28.5 g (0.25 mole) of methyl neopentyl ketone was added at room temperature, whereupon the temperature was raised in the course of  $\frac{1}{2}$  h to 190°C by heating. Heating was continued for 12 h at this temperature during which time a faint reflux was noticed.

After cooling, the salt-like solid was decomposed by slow addition of water and the mixture was neutralized by dilute sulphuric acid and extracted twice with ligroin. The combined extracts were washed with sodium carbonate solution, then with saturated sodium chloride solution and dried over anhydrous magnesium sulphate. After evaporation of the solvent the residue was distilled *in vacuo* (10 mm) to give 43 g (60%) of light yellow substance that crystallized in the receiver. B.p. 155–160°C. The substance was dissolved in 50 ml of carbon tetrachloride and the solution was washed several times with 10 ml portions of conc. sulphuric acid until the coloured impurities were removed. After washing with water, dilute sodium carbonate solution and saturated sodium chloride solution, in that order, the carbon tetrachloride solution was dried over anhydrous magnesium sulphate. Evaporation of the solvent left 1,3,5-trineopentylbenzene which, after one recrystallization from ethanol, weighed 32.5 g (45%) and melted at 76–77°C. It was pure according to gas chromatography. Physical properties were in accord with those reported previously.<sup>1</sup>

*1,3,5-Tri-*t*-butylbenzene.* Two portions of pinacolone (25.0 g, 0.25 mole and 12.5 g, 0.125 mole) were reacted with 12.0 g (0.25 mole) of sodium hydride (Fluka, 50% dispersion in mineral oil) in exact accord with the procedure described above. Distillation at 9 mm afforded three fractions. Fraction I: B.p. 76–88°C, 14.6 g. Fraction II: B.p. 88–110°C, 1.3 g. Fraction III: B.p. 114–118°C, 8.1 g.

Fraction II consisted of mainly one component according to gas chromatography and was redistilled in a spinning-band column yielding a colourless oil, b.p. 80–81°C (9 mm). This was shown by NMR to be a mixture of *cis*- and *trans*-2,2,5,6,6-pentamethyl-4-hepten-

3-one. This product is reported to be formed in a yield of 70 % in the treatment of pinacolone with potassium-*t*-butoxide at 200°C for 4 h.<sup>11</sup>

Fraction III crystallized in the receiver and was dissolved in carbon tetrachloride and subjected to the above-mentioned acid-washing procedure. After one recrystallization from methanol there remained 6.2 g (30 %) of 1,3,5-tri-*t*-butylbenzene, m.p. 72–73°C. Lit. 72.5–73°C,<sup>11</sup> 72–74°C.<sup>13</sup>

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## Spectrophotometric Studies on a Humic Acid Fraction

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In a study of fractionation and separation of humic acids<sup>1</sup> it was suggested that physico-chemical studies should be preceded by a careful fractionation procedure. This paper reports spectrophotometric studies on a defined (but still probably not monodisperse) humic acid fraction. The application of differential spectrophotometry to the study of humic acids was recently reported<sup>2</sup> and the absorbancy variation with pH has therefore been studied in detail.

*Experimental.* The humic acid fraction was obtained from an iron humus podsol B<sub>12</sub> (from Lerbäck, Sweden) by extraction at pH 7 with sodium pyrophosphate in 2 M NaCl (after preceding extractions with benzene and with 2 M NaCl). The humic acid was precipitated with H<sub>2</sub>SO<sub>4</sub> dissolved with NaOH to pH 7 and dialysed against distilled water. The remaining humic acid has been studied.

For the studies at different pH the following buffers (P.-H. Tamm) have been used: pH 2.00 (HCl-KCl), pH 7.00 (phosphate) and pH 11.5 (phosphate).

All spectrophotometric measurements have been made on a Zeiss PMQ II Spectrophotometer.

*Results.* Accurate determinations of the absorbancy of a humic acid solution cannot generally be obtained in the whole spectral range 13 000–40 000 cm<sup>-1</sup> from measurements on one solution, because of the steady increase of the absorbancy from low to high wave numbers. Especially at low wave numbers the shape of the absorption curve would be rather inaccurately determined. If the shape of the log *A* curve should be used as a characteristic it is further important to know that it is independent of the dilution. It is therefore suggested that absorption spectra are always measured at different dilutions in order to ascertain the constancy of the shape of the absorption curve. The same slit width should always be used for a given wave number.

In Fig. 1 the results of such measurements are given for three different pH. The