A Free-radical Cyclisation Reaction

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A FREE-RADICAL cyclisation reaction (1) was implied by the claim[1] that pyrolysis of di-n-heptylmercury in a flow system at 340—360° c with carbon dioxide as carrier gas produced cyclohexane as a minor product.

$$\text{n-}C_7H_{15} \rightarrow \text{cyclo-}C_6H_{12} + CH_3 \qquad (1)$$

The evidence for formation of cyclohexane was based upon measurement of the refractive index of the material remaining after treatment of the first fraction of the distillate of liquid products with concentrated sulphuric acid. With the exception of brief comments by Steacie[2] and by de la Mare and Vaughan[3] no attention has been paid to this reaction.

An unsuccessful attempt was made[4] to repeat Rice and Polly's[1] experiment, but decomposition of the liquid di-n-heptylmercury ensued in the attempt to vaporise sufficient quantities of the organometallic at 120°. Recourse was made therefore to reaction (2)

$$\text{n-}C_7H_{15}Br + Na \rightarrow \text{n-}C_7H_{15} + BrNa \qquad (2)$$

An inverted sodium-flame apparatus was employed and the halide was introduced into an atmosphere of excess of sodium vapour at temperatures in the range 290—310° c, both reactants being diluted with nitrogen. The products were trapped out and analysed by gas–liquid chromatography (g.l.c.) and mass spectrometry. The n-heptyl bromide was completely consumed and a number of hydrocarbon products were obtained. One of the g.l.c. peaks was found to be entirely coincident with that for cyclohexane and this occurred both for silicone gum rubber and for $\beta\beta'$-dihydroxypropionitrile columns. Collection of the eluant corresponding to this peak and analysis by mass spectrometry confirmed the presence of cyclohexane. We conclude that it is possible for reaction (1) to occur.

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[1] F. O. Rice and O. L. Polly, *Ind. Eng. Chem.*, 1935, **27**, 915.
[2] E. W. R. Steacie, "Atomic and Free Radical Reactions," Reinhold, New York, 1954, Vol. 1, p. 250.
[3] H. E. de la Mare and W. E. Vaughan, *J. Chem. Educ.*, 1957, **34**, 10.
[4] B. H. M. Billinge and B. G. Gowenlock, unpublished experiments 1961; B. H. M. Billinge, Thesis, Birmingham, 1961.