The Structure of Dibromodiethyl Ketone
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When studying the products of the bromination of laevulic acid one of us (C.R.) became interested in why some ketones give only the symmetrically substituted dibromoketone on bromination, for instance laevulic acid and cyclohexanone, while others give only the unsymmetrically substituted dibromoketone, for example methyl ethyl ketone and diethyl ketone. In some cases both the symmetric and unsymmetric dibromo compound are obtained, for instance with acetone and methyl propyl ketone.

Dibromodiethyl ketone was first prepared by Pauly, who assigned it a symmetric structure, but without any structural evidence. Later, one of us (L.S.) proposed the unsymmetric structure on the basis of its hydrolysis reactions. Unfortunately, this method is not quite unambiguous as a rearrangement may take place during the hydrolysis. The possible effect of which was discussed in Ref. This uncertainty has prompted a reinvestigation of the structure using modern techniques.

The structure may be determined by means of nuclear magnetic resonance spectroscopy. The NMR-spectrum of dibromodiethyl ketone has been recorded and is given in Fig. 1. The spectrum shows two peaks at \( \tau = 4.96 \) ppm and \( \tau = 8.20 \) ppm with the relative intensities of 1:3. The methyl resonance is a doublet and the hydrogen band a quartet with the intensity ratio 1:3:3:1. The symmetry of the spectrum, the chemical shifts and the multiplicities are in accordance with the expected spectrum of the symmetric dibromoketone; thus its real structure is 2,4-dibromopentanone-3.

The compound can be obtained in good yields by both bromination in the presence of phosphorus and by acid catalyzed bromination. No traces of the unsymmetric dibromoketone could be detected by means of NMR-spectroscopy in the twice distilled product, indicating that the amount of this isomer (if any) is less than a few percent. This unsymmetric ketone would have a CH\(_2\)-band with a \( \tau \)-value similar to that of diethyl ketone (\( \tau = 7.76 \)) and mono-bromodiethyl ketone (\( \tau = 7.18 \)), and two different methyl resonances.

Experimental. The NMR-spectra were recorded on a Varian Associates Model A 40 spectrometer.

2,4-Dibromopentanone-3. I. Diethyl ketone was brominated as described by Schotte. The boiling point 67–68°/9 mm was obtained. Schotte gave 75–77°/10 mm. \( n_D^{28} = 1.5050 \).

II. 320 g of bromine were added dropwise to 86 g of diethyl ketone mixed with 100 ml of hydrobromic acid (48 %) and chilled in an ice bath. The product was washed with water, sodium carbonate, and sodium bisulfite solutions and distilled. A fraction, b.p. 65–70°/8 mm, was collected, 182.5 g (75 %). On redistillation the b.p. 67–68°/8 mm and \( n_D^{28} = 1.5042 \) were obtained.

2-Bromopentanone-3 was prepared according to Pauly.

Acknowledgements. The authors wish to express their thanks to Professor Arne Fredga for his interest in this work and for all facilities put at their disposal. The NMR-spectra were recorded by Dr. Ragnar A. Hoffman.

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Received September 14, 1962.

Acta Chem. Scand. 16 (1962) No. 8