The Structure of Dibromodiethyl Ketone

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When studying the products of the bromination of laevulic acid [1] one of us (C.R.) became interested in why some ketones give only the symmetrically substituted dibromoketone on bromination, for instance laevulic acid [1] and cyclohexanone [2], while others give only the unsymmetrically substituted dibromoketone, for example methyl ethyl ketone [3] and diethyl ketone [4]. In some cases both the symmetric and unsymmetric dibromo compound are obtained, for instance with acetone [5] and methyl propyl ketone [6].

Dibromodiethyl ketone was first prepared by Pauly [7], who assigned it a symmetric structure, but without any structural evidence. Later, one of us (L.S.) [4] 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 *cf.* Reid, Gompf and Atwater [6] the possible effect of which was discussed in Ref. [4]. 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.

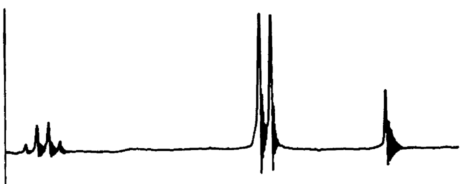

Fig. 1. The NMR-spectrum of dibromodiethyl ketone.

The compound can be obtained in good yields by both bromination in the presence of phosphorus [4] 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 τ-value similar to that of diethyl ketone ($\tau = 7.76$) and monobromodiethyl 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 [4]. The boiling point 67–69°/9 mm was obtained. Schotte gave 75–77°/10 mm. $n_D^{25} = 1.5050$.

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 $n_D^{25} = 1.5042$ were obtained.

2-Bromopentanone-3 was prepared according to Pauly [7].

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