

Preparation of 1,1,3,3-Tetraiodoacetone

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In connection with studies in the Favorsky rearrangement of tetrahalo-ketones,^{1,2} it was of interest to prepare 1,1,3,3-tetraiodoacetone (I). This compound has previously been obtained by Gupta *et al.* by the oxidation of citric acid with potassium permanganate in the presence of iodine. From 100 g of citric acid they obtained 1 g of crude I.³ In their discussion of the reaction mechanism, they claimed that acetonedicarboxylic acid, which is one of the oxidation products of citric acid, failed to give I upon iodination. A literature search revealed, however, that I previously has been synthesized by the simultaneous action of iodine and an oxidizing agent, *i.e.* periodic acid, on acetonedicarboxylic acid (II). In 1893, Angeli and Levi obtained a low yield of I when they oxidized II with periodic acid,⁴ and in 1956 Brown reported that I was formed when a solution of potassium triiodide and II was added alternately to a concentrated solution of periodic acid or similar oxidant; no yield of product was given.⁵

Another method for the preparation of I, not referred to by Brown or Gupta, was found in a patent pending by Lederer from 1896.⁶ Therein he claimed patent on the preparation of iodo derivatives of acetone by the action of iodine on acetonedicarboxylic acid in the presence of agents which could destroy the hydriodic acid formed. By using periodic acid or potassium perbromate, Lederer claimed to get hexaiodo- and pentaiodoacetone, respectively.

The syntheses described by Gupta *et al.* and by Lederer, have now been thoroughly studied by the present author. I was obtained in a 40 % yield from II, when periodic acid was used as an oxidant. Several attempts to prepare penta- and hexaiodoacetone according to Lederer have failed. The only products observed in MNR and MS were I and small amounts of 1,3-diiodoacetone.

The melting point of I was reported as 114°C by Gupta *et al.* It seems, however,

to have at least two allotropic forms. Thus, a melting point of 142–143°C was obtained when the synthesis was performed at the Institute of Chemistry, Uppsala. On repeating the synthesis at the Institute of Chemistry, Umeå, a melting point of 155.0–156.0°C was observed. Several attempts to get the lower melting form back have failed.

In the synthesis of I from citric acid according to Gupta *et al.*, concentrated aqueous solutions of potassium permanganate and citric acid (excess) are reacted, followed by addition of iodine in ethanol to the resulting reddish orange coloured solution. In this way these authors obtained 1 g of crude I from 100 g citric acid. By a reverse addition, *i.e.* addition of aq. potassium permanganate to an aqueous solution of citric acid, potassium iodide and iodine, the yield of I from 100 g citric acid could be raised to 8–12 g, calculated on recrystallized product.

Experimental. 1,1,3,3-Tetraiodoacetone prepared from (a) acetonedicarboxylic acid. A solution of 9 g periodic acid in 20 ml water was periodically added to a stirred mixture of 10 g acetonedicarboxylic acid and 20 g iodine in 100 ml water. The reaction was started by adding a few drops of oxidant, which resulted in discolouration of the reaction mixture and the evolution of carbon dioxide commenced. The mixture was kept close to colourless by adding the solution of oxidant continuously. Too fast an addition of oxidant resulted in an exothermic reaction and decomposition of the product. A yellowish precipitate soon appeared. On completion of the oxidant addition (10 min) the reaction mixture was kept stirred for another 20 min; 200 ml of water was then added and the mixture left for 1 h without stirring. The precipitate was filtered off and washed with 50 ml glacial acetic acid. It was further purified by recrystallization from boiling glacial acetic acid (10 ml/g). Yellow needles, 15 g (14 %), m.p. 155.0–156.0 (d) were obtained. The mother liquor contained some 1,3-diiodoacetone. IR (KBr): 2995, 1704, 1242, 1170, 1050, 1010, and 732 cm⁻¹. NMR (DMSO); 1 singlet at 6.06 ppm. Quantitative analyses with internal standard: 0.2024 g (0.504 mmol) 1,1,3,3-tetrabromopentanone-2⁷ and 0.2809 g (0.500 mmol) 1,1,3,3-tetraiodoacetone in DMSO, $CHBr_2/2 \times CHI_2 = 56/108$. MS: Molecular peak at 562, 10 % of parent peak (254). Purified in this way the substance is stable for months in a dark place.

(b) *Citric acid*. 100 g citric acid, 10 g potassium iodide, and 5 g iodine was dissolved in 150 ml of water. During 10 min, 5 g potassium permanganate in 100 ml water was added. A yellowish precipitate soon appeared. To complete the precipitation the reaction mixture was left at room temperature for 2 h without being stirred. The precipitate was filtered, washed carefully with 200 ml water and dried by suction. It was then dissolved in acetone (100–150 ml) and filtered into water (1–1.5 l) while being stirred. A yellowish precipitate immediately formed which was collected by filtering and washed with 50 ml glacial acetic acid. It was further purified by recrystallization from boiling glacial acetic acid (10 ml/g). 8–12 g of 1,1,3,3-tetraiodoacetone was obtained, m.p. 155.0–156.0°C (d).

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On the Stability of the Rotational Isomers of 2-Furalaldehyde

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2-Furalaldehyde (F) can exist in two rotational isomers, as shown in Fig. 1. Microwave investigation¹ showed that isomer I in the gas phase is more stable than isomer II, and that the energy difference is 0.99 ± 0.20 kcal/mol.

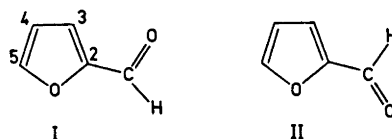


Fig. 1. The two stable rotational isomers of 2-furalaldehyde.

IR and Raman spectra of F show significant dependence on the solvent used.^{2–4} This fact is interpreted as indicating changes in the molar fractions of the two isomers.

No examination of the influence of solvents on the NMR spectrum of F has previously been performed. The most significant change produced in the NMR spectrum of F by variation of solvent or concentration is a change in $J_{\text{CHO}-4}$ and $J_{\text{CHO}-5}$, the coupling constants between the aldehyde proton and the ring protons in 4 and 5 positions, respectively. The coupling constants that we have calculated from the spectra are given in Table 1.

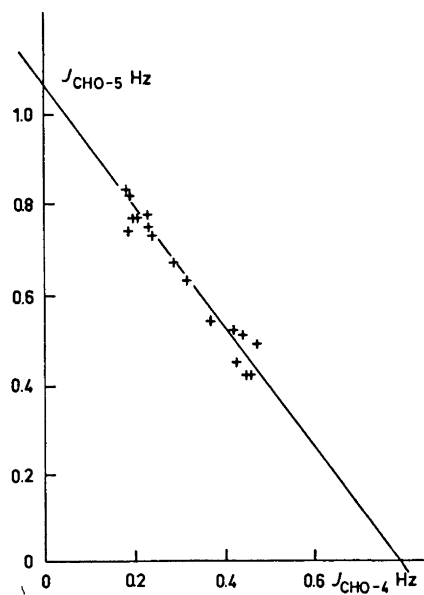


Fig. 2. Plot of the observed coupling constants $J_{\text{CHO}-4}$ against $J_{\text{CHO}-5}$ for 2-furalaldehyde at 31.4°C. The straight line represents the least squares fit.