

Fig. 1. Separation of acids formed by reduction of acid contained in Band SO.

Resin bed:  $6 \times 715$  mm, Dowex 1-X8; 17–20  $\mu\text{m}$ .

Eluent: 0.08 M NaAc, pH 5.9

Flow rate:  $4.0 \text{ ml} \cdot \text{min}^{-1} \cdot \text{cm}^{-2}$ .

1, Chromic acid oxidation; 2, Carbazole method; 3, Periodate-formaldehyde method.

methylsilylated 1,4-lactones on a QF-1 column confirmed the identity of the aldonic acids.<sup>4</sup> The results show that the acid contained in band SO was *ribo*-4-hexulosonic acid not described previously in the literature.

It is reasonable to assume that the absolute configurations at C-2 and C-3 are the same as in the corresponding positions C-5 and C-4 in the starting material, D-glucuronic acid, and that the new acid is *L-ribo*-4-hexulosonic acid. This assumption is corroborated by the fact that no products with inverted configuration in these positions were observed on isomerization of D-glucuronic acid.<sup>1</sup>

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## Synthesis of <sup>14</sup>C-Pentachlorophenol

INGA JAKOBSON and SVEN YLLNER

National Institute of Occupational Health,  
S-104 01 Stockholm 60, Sweden

<sup>14</sup>C-Pentachlorophenol was synthesized by chlorination of <sup>14</sup>C-phenol. Quinoline was used as catalyst,<sup>1</sup> and the crude 2,3,4,4,5,6-hexachloro-2,5-cyclohexadiene-1-one ("hexachlorophenol") was reduced with zinc and hydrochloric acid.<sup>2</sup>

The uniformly labelled <sup>14</sup>C-phenol, (0.1 mC, 25.0 mC/mM, The Radiochemical Centre, Amersham, England) was diluted with 20 mg of inactive phenol (analytical grade) dissolved in 0.5 ml of ether, and transferred to a 30 ml Pyrex test tube. The ether was evaporated at room temperature, and 0.4  $\mu\text{l}$  of quinoline, dissolved in carbon tetrachloride (0.15 ml) added. Dry chlorine was led into the solution through a thin polyethylene tube. When the solution was saturated and the air in the tube replaced by chlorine, the tube was sealed and placed in an oven at 120°C. After 24 h the reaction solution was once again treated with chlorine and kept at 120°C for a further 24 h.

The reaction mixture was diluted with 10 ml of ethanol and transferred to a 25 ml Erlenmeyer flask. Granular zinc (1 g) and conc. hydrochloric acid (1 ml) were added. The mixture was kept at 60–70°C for 30 min, and then poured into 100 ml of water, yielding a crystalline precipitate. The crystals were filtered, washed with water and dried. The product was then purified by sublimation (0.001 torr) in a 10 cm glass tube (i.d. 4 mm) at 120°C for 72 h. White, needle-formed crystals were obtained; m.p. 188–189°C (uncorrected); yield 44 %. The specific activity was 1.6  $\mu\text{C}/\text{mg}$ .

Isotope dilution analysis was performed with inactive pentachlorophenol (prepared from a commercial product by repeated recrystallization, m.p. 188–190°C, no impurity found by gas chromatography of the methylated compound, see below). By recrystallization from isooctane, constant specific activity was obtained, corresponding to 97 % of the starting mixture.

Two dimensional thin layer radiochromatograms were prepared with about 5  $\mu\text{g}$  of <sup>14</sup>C-pentachlorophenol on a silica gel

plate, previously dried 30 min at 100°C. The plate was first developed with chloroform and then with benzene-ethyl acetate 10:1.<sup>3</sup> The silica gel layer was divided into squares of 1–4 cm<sup>2</sup>, and each of these was scraped into a counting vial and analysed with a liquid scintillation spectrometer (Packard Tri-Carb, Model 3314). One spot, separate from pentachlorophenol, was detected, corresponding to 3–4 % of the activity.

The purity of inactive pentachlorophenol, synthesized as described above, was checked by gas chromatography after methylation with diazomethane. An Aerograph Hy-Fi Fractometer, Model 600, supplied with an Electron Capture Detector was used. The column was packed with 20 % SE 30 on Chromosorb W and the temperature was 200°C. The only impurity found was 2,3,4,6-tetrachlorophenolether, corresponding to 1 % of the product.

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## Thermal Fragmentations

### II.\* *N*-Isothiocyanatoamines from 4,4-Disubstituted Thiosemicarbazides

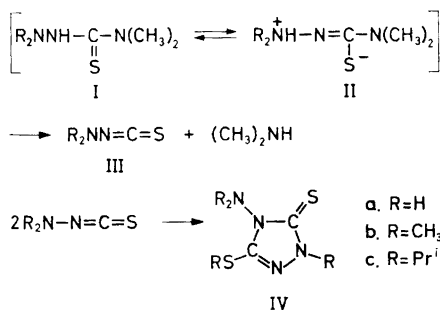
CH. LARSEN, U. ANTHONI and  
P. H. NIELSEN

*Chemical Laboratory II (General and Organic Chemistry), University of Copenhagen, The H. C. Ørsted Institute, Copenhagen, Denmark*

In part I<sup>1</sup> of this series it was shown that heating 4,4-dimethylthiosemicarbazide (Ia) resulted in the evolution of dimethylamine, together with hydrogen

\* Ref. 1 "The Decomposition of 4,4-Dialkyl-substituted Thiosemicarbazides" should be considered part I.

sulfide. The residue was shown to consist partly of the dimethylammonium salt of 4-amino-3,5-dimercapto-1,2,4-triazole, from which 4-amino-3-mercapto-1,2,4-triazol-2-ine-5-thione (IVa) was liberated on treatment with acid. It has previously been found<sup>2</sup> that the closely related 4-dimethylamino-1-methyl-3-methylthio-1,2,4-triazol-2-ine-5-thione (IVb) is the most stable product from dimerization of the unstable *N*-isothiocyanatodimethylamine (IIIb). This suggested that IVa was formed *via* the unknown isothiocyanatoamine (IIIa) by dimerization, *i.e.*



Preliminary experiments showed that detection of IIIa by gas chromatography or mass spectrometry of the gaseous products from pyrolysis of Ia could not be achieved with certainty, the main problem being that if Ia was heated at 10<sup>-3</sup> mm Hg sublimation occurred prior to fragmentation. Attempts to solve this problem by heating the inlet system to the pyrolysis temperature were unsuccessful presumably because, under these conditions, any IIIa formed would dimerize immediately.

From infrared and NMR spectroscopic investigations,<sup>3</sup> it can be concluded that Ia and Ib exist in the non-polar form both in the solid state and in solution. Therefore, if pyrolysis of Ib can be shown to yield IIIb and dimethylamine it is reasonable to assume that Ia on pyrolysis breaks down into IIIa and dimethylamine.

When Ib was pyrolyzed in a reaction vessel directly connected to the inlet system of the mass spectrometer, a mass spectrum was obtained consisting of the mass spectrum of IIIb (molecular ion at *m/e* 102) on which was superimposed the mass spectrum of varying amounts of a substance C<sub>5</sub>H<sub>9</sub>N<sub>3</sub>S<sub>2</sub> [*m/e* 175]. The