

protect some of the chemical bonds in starch that would otherwise enter the measured reaction.

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A New Method for the Cleavage of Unsaturated Fatty Acids¹

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The methods for the cleavage of unsaturated fatty acids reported in the literature are either by energetic oxidations or by ozonization. On account of the side reactions, the degradation products are usually complex mixtures and the yields are very low.

Lead tetraacetate has been introduced by Criegee² as a reagent for the cleavage of glycols with excellent results. This oxidizing agent should be equally effective in oxidizing polyhydroxy fatty acids which in turn can be prepared easily from the corresponding unsaturated fatty acids by means of oxidation with alkaline potassium permanganate. It was found that 9,10-dihydroxyoctadecanoic acid (from oleic acid) was oxidized completely in twenty-four hours by lead tetraacetate in glacial acetic acid. As reaction products, pelargonic aldehyde and azelaic semialdehyde were isolated in the form of semicarbazones, each in a yield of about 85%. By using benzene as a solvent, 9,10,12-trihydroxyoctadecanoic acid (from ricinoleic acid, m. p. 111–112°) oxidized in four hours and about 90% of azelaic semi-aldehyde semicarbazone and a product melting at 112–113°, the character of which has not yet been determined, were obtained. A mixed melting point with starting material indicated it was different. The supposition is it may be β -hydroxypelargonic aldehyde semicarbazone or a related compound.

A more extensive study of this method for cleavage of unsaturated fatty acids of known and unknown structure will be reported later.

Experimental

In 10 cc. of glacial acetic acid which had been distilled over phosphorus pentoxide, was suspended 0.6740 g. of 9,10-dihydroxyoctadecanoic acid and to the mixture 0.95 g. of lead tetraacetate was added. This was shaken for twenty-four hours at room temperature. The solution was fil-

tered and heated in a water-bath at 45° for five minutes. It was then treated with 15 cc. of water and a concentrated aqueous solution of 0.5 g. of semicarbazide hydrochloride and 0.6 g. of sodium acetate was added. To the reaction mixture was now introduced a few drops of methanol and it was then vigorously shaken. After standing in an ice box for twenty hours, the semicarbazones separated as a white precipitate. The precipitate was filtered and shaken with cold dilute aqueous sodium hydroxide to dissolve the azelaic semialdehyde semicarbazone. Undissolved, impure pelargonic aldehyde semicarbazone was filtered and washed with water. The alkaline filtrate was acidified with 2% hydrochloric acid. The precipitated azelaic semialdehyde semicarbazone was filtered, washed and dried, yield 0.434 g. (90%). After purification by crystallization from ethanol it melted at 163–164° (Harries and Thieme³ reported 163°).

The alkali insoluble part consisted of lead chloride and pelargonic aldehyde semicarbazone. It was dissolved in methanol and the lead chloride was filtered. On evaporating the solution to a small volume, the semicarbazone separated as fine crystals melting at 99–100.5° (Bagard and Harries and Turk⁴ reported 100°). The yield was 0.348 g. (82%).

(3) C. Harries and C. Thieme, *Ann.*, **348**, 359 (1905).

(4) P. Bagard, *Bull. soc. chim.*, **4**, I, 346 (1907); C. Harries and H. O. Turk, *Ber.*, **40**, 2756 (1907).

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Dependence of Conductance on Field Strength

BY DARWIN J. MEAD AND RAYMOND M. FUOSS

We recently reported the field dependence of the conductance of tetrabutylammonium picrate in diphenyl ether at 50° [THIS JOURNAL, **61**, 2047 (1939)]. We are indebted to Dr. L. Tonks of this Laboratory for calling to our attention a correction which we neglected. The limit approached by the Wien coefficient at zero concentration now agrees with Onsager's theoretical value, when the correction factor of $8/3\pi$ is applied.

Our measurements were made in a bridge circuit, in which balance is indicated by zero current in a detector circuit fed through a low-pass filter. Our solutions were non-linear impedances, and the detector showed balance for only the fundamental frequency. According to theory, the specific conductance κ is given by

$$\kappa(t) = \kappa_0 + A V_m |\sin \omega t| \quad (1)$$

where κ_0 is the low voltage conductance, A is Onsager's coefficient and V_m is the peak voltage of the sinusoidal input at frequency f , with $\omega = 2\pi f$. The unit current then is

$$i(t) = \kappa_0 V_m \sin \omega t + A V_m^2 \sin \omega t |\sin \omega t| \quad (2)$$

(1) Presented at the 7th Anniversary Meeting of the Chinese Chemical Society, held at Kunming, China, August 29, 1939.

(2) R. Criegee, *Ber.*, **64**, 260 (1931); *Ann.*, **481**, 263 (1930); **507**, 159 (1933).