[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE OHIO STATE UNIVERSITY]

OZONIZATION AND OXIDATION OF STEAROLIC ACID TO 9,10-DIKETOSTEARIC ACID

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The formation of vicinal dicarbonyl compounds as a result of the ozonization of acetylenes has been noted several times (1) but there seems to be no case in which it has been established whether the dicarbonyl compounds are formed along with ozonide or are formed on hydrolysis of the ozonide. Jacobs (2) mentions that the ozonides formed from diphenylacetylene and benzylphenylacetylene had a yellow color indicative of diketone formation. After hydrolysis, diketones were obtained (2).

Recently the ozonization of stearolic acid was studied in connection with the proof of structure and homogeneity of this acid when prepared by an improved process (3). During the rather slow ozonization a yellow color was noted. This observation prompted us to attempt to determine whether 9,10-diketostearic acid could be found prior to and subsequent to the decomposition of the ozonide. It was noted also that the yellow color decreased on prolonged ozonization.

The presence of diketoacid was indicated visually, by a yellow color, and spectrally by absorption maxima at 2750 Å and 4250 Å (4). Examination of the ozonization mixture revealed the presence of diketoacid both before and after hydrolysis. We were not able to prove that more was present after hydrolysis but a slight increase in intensity of the yellow color was noted. Since the ultraviolet spectral analyses showed conclusively that diketone was present before hydrolysis, we ran experiments to ascertain whether the diketone was formed directly by the action of ozone or in some other way.

We have shown that passage of air alone through an acetic acid solution of stearolic acid does not result in the formation of diketoacid. Similarly, the passage of ozonized air through acetic acid alone does not produce a solution which will attack stearolic acid. This provides evidence against the hypothesis that ozonized air reacts with acetic acid to produce peracetic acid (5) since peracetic acid reacts readily with stearolic acid (3).

The diketoacid formed during ozonization is gradually destroyed by the further passage of ozonized air through the reaction mixture. This is indicated by a gradual disappearance of the yellow color and the typical absorption maxima.

The chemical oxidation of acetylenic compounds to diketones has been frequently reported (6) but rarely has the yield been great. Recently (3) the oxidation of stearolic acid to 9,10-diketostearic acid in high yield by the action of neutral permanganate prompted us to study the effect of variation of acidity on the yield of diketoacid and on further oxidation of the diketoacid. We have shown that the yield of diketoacid is at a maximum (92–96%) in the range *p*H 7.0–7.5. In oxidations at a higher *p*H, 12, or a lower one, 1, no diketoacid was isolated. Experiments showed that diketoacid was destroyed oxidatively under both of these extreme conditions but was stable at *p*H 7.0–7.5.

EXPERIMENTAL

Ozonization experiments. Pure stearolic acid (3) (m.p. 46.0–46.5°, 2 g.) was dissolved in 50 cc. of acetic acid and treated with ozonized air (5–10% ozone in different experiments) for 1–2.5 hours in an apparatus of the Henne type (7). Water was then added and the mixture was heated on a steam-bath for one hour. On cooling to 0–3° 0.1 g. (4%) of fine yellow leaflets separated. The melting point after recrystallization from dilute alcohol was 84.5–85.5° and it was not depressed by admixture with an authentic sample of 9,10-diketostearic acid. The absorption spectrum in aldehyde-free alcohol showed characteristic absorption maxima at 2750 Å and 4250 Å (4).

When ozonization was conducted in carbon tetrachloride the yellow color of diketoacid appeared soon but on prolonged ozonization the yellow color faded. If the solvent was removed under reduced pressure when the yellow color was at an approximate maximum and the residue was dissolved in alcohol, ultraviolet spectroscopy revealed the absorption maxima at 4250 and 2750 Å characteristic of 9,10-diketostearic acid.

In almost all experiments it was possible to isolate azelaic acid in 69–80% from the decomposition of the ozonide in the usual way (3).

Permanganate oxidations. In a run typical of those carried out under the best conditions, 5.6 g. of stearolic acid (3) was dissolved by stirring in 3 l. of water containing 1.5 g. of potassium hydroxide. The solution was brought to *p*H 7.5 by bubbling in carbon dioxide. A solution of 6.3 g. of potassium permanganate in 300 cc. of water was added all at once. The temperature was kept at about 25° and the solution in the range of *p*H 7.0–7.5 by gradual bubbling in of carbon dioxide as the oxidation proceeded. After one hour, the excess permanganate was destroyed by the addition of sodium bisulfite and hydrochloric acid was added to precipitate the product. The diketoacid was collected and crystallized from 200 cc. of absolute alcohol at 0°. The first and second crops amounted to 5.7–6.0 g. (92–96%) of good diketostearic acid, m.p. 84.5–85.0°.

When similar experiments were carried out at about *p*H 9.0 the yield of acid was 5.4–5.6 g. When the solution was held at about *p*H 12, no diketostearic acid was obtained and over 80% of azelaic acid could be isolated. Oxidation in acid systems was difficult because of the insolubility of stearolic acid. No successful experiment was carried out in the range of *p*H 5–7.

In a typical experiment under more acidic conditions 2.8 g. of stearolic acid was dissolved in 500 cc. of pure dioxane. One liter of water was added and alkanesulfonic acids[1] to bring the solution near *p*H 1. An additional 100 cc. of dioxane was then added followed by a solution of 3.2 g. of potassium permanganate in 250 cc. of water. After one hour at 25° the excess permanganate was destroyed with bisulfite. No diketostearic acid was obtained but considerable azelaic acid was present.

All of the above experiments were repeated except that diketostearic acid was used in place of stearolic acid. The following amounts of diketoacid were destroyed at the different acidities: 100% at *p*H 1; 1–2% at 7.0–7.5; 6–7% at 9.0; and 100% at 12.0.

SUMMARY

9,10-Diketostearic acid has been isolated from the products of ozonization of stearolic acid. Evidence was obtained which proves that the diketoacid is produced during ozonization in acetic acid and in carbon tetrachloride.

The permanganate oxidation of stearolic acid to 9,10-diketostearic acid is quite sensitive to changes in *p*H. The optimum range is 7.0–7.5 and in this range no oxidative cleavage of the diketoacid occurs when using permanganate.

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[1] *Obtained from Standard Oil Company of Indiana.*

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