lithium sulfate, which is generally kept on stock in a laboratory, might interact to give lithium azide and sodium sulfate.

The four salts in question are all soluble in water. Lithium azide is soluble and sodium azide is sparingly soluble in ethanol (0.22 g NaN_s per 100 g at 0 °C), while lithium and sodium sulfate are insoluble. Even in 75–80 % ethanol the solubilities of lithium and sodium sulfate are very small. Based on these facts the following method of preparation has been worked out:

1.30 g of sodium azide and 1.41 g of lithium sulfate, Li2SO4, H2O, which is 10 % in excess, are dissolved in 7 ml of water by shaking and gentle heating. 35 ml of ordinary 96 % ethyl alcohol are now added in a thin stream, while stirring with a spatula. After 10 min (it has been ascertained that a longer time is of no effect) the mixture is filtered. The precipitate, which consists of sodium and lithium sulfate, is washed with a few ml of ethanol, and the filtrate plus the washing liquid is evaporated on a water bath to near dryness. Finally, it is dried at 80 °C in a drying oven. The theoretical yield of lithium azide is 0.98 g, while actually 1.02-1.04 g is obtained. This raw product contains no sulfate but a few per cent of sodium. It can be purified by 2 min digestion with 10 ml 96 % ethanol at about 35 °C, filtering the undissolved sodium azide, and evaporating and drying as above. The yield is usually ca. 0.6 g lithium azide of a purity not less than 99.5 %. It contains a slight trace of organic material due to the use of ethyl alcohol.

The purified lithium azide has been analyzed by two methods. The content of azide has been determined according to Martin 1 by oxidation with Ce(IV). Analysis of two products of lithium azide gave 99.5 % and 99.5 %. The same two products were analyzed by conversion to lithium sulfate and weighing 2. The results were 100.2 % and 99.7 % lithium azide, respectively. Thus it seems that the prepared lithium azide is slightly "basic" due to loss of hydrazoic azid when evaporating.

- Martin, J. J. Am. Chem. Soc. 49 (1927) 2133.
- Fresenius, R. and Jander, G. Handbuch der analytischen Chemie III, Ia, Springer, Berlin 1940, p. 3.

Received March 20, 1957.

The Rearrangement of cis-2-en-4:6-diyn-oic Acids to αβ-Unsaturated γ-Lactones

PER KOCH CHRISTENSEN

Sintef, Norges Tekniske Høgskole, Trondheim, Norway

The so called "Composit-Cumulene I" originally reported by Sørensen and Stavholt " was given the structural formula I

$$CH_3$$
— CH_2 — CH_2 — CH_3 — CH_2 — CH =
$$C = C = CH$$
— $COOCH_3$ I

based on the UV-absorption and the hydrogenation to a hexahydro derivative with an odour of strawberry like methyl caprate.

A reinvestigation of this compound isolated from scentless mayweed (Matricaria inodora L.) showed that the substance contained a disubstituted acetylenic bond (2 190 cm⁻¹) and the carbonyl frequency (1 793 and 1 765 cm⁻¹) indicated a fivering lactone. Hydrogenation with Pd/BaSO₄ showed a consumption of 5 moles of hydrogen and the product was a saturated five-ring lactone with carbonyl frequency at 1 786 cm⁻¹. The formula accordingly had to be revised ^{2,3} and the substance was found to be the lactone II (R = cis CH₃-CH=CH-)

The formation of this type of lactone from the free 2-cis-acid III was first observed when III ($R=CH_3C=C-C=C-$) was treated with dilute sodium hydrogen-carbonate ³

On measuring the ultra-violet absorption of an alcoholic solution of cis:cis matricaria acid III (R=CH₃CH=CH-C=C-) in a UV-recorder (Beckman DK) it was noticed that on scanning the spectrum of two solutions with different concentrations, the absorption curve was markedly different the second time. The long wave-

Acta Chem. Scand. 11 (1957) No. 3

length absorption had shifted to longer wave-lengths with stronger intensity while the short wave-length absorption ($\sim 2\,576$ Å) had undergone a hypsochromic shift with lower intensity. This phenomenon was further investigated, and it turned out that on dissolving cis:cis matricaria acid in a solvent containing water, in this case 95 % ethanol, the rearrangement free acid \rightarrow lactone took place spontaneously. In absolute ethanol (~ 99.8 %) the speed of reaction was very much slower.

A solution of the free acid in dry tetrahydrofuran was stable and the UV-absorption was quite similar to a solution in hexane. Addition of distilled water to the tetrahydrofuran immediately caused rear-

rangement to the lactone.

Working in a mixture of tetrahydrofuran and buffers (1:1) the reaction took place with a measurable speed in the interval pH $\sim 4.5-11$. Above pH ~ 11 also other reactions occurred and the product was no longer pure. Measurement of reaction velocities by means of UV-absorption was impossible.

In the interval pH $\sim 6-11$ the rate of reaction was approximately constant. The reaction appeared to be of first order with half-times of ~ 3.5 min at 30 °C and ~ 11 min at 20 °C. Below pH ~ 6 the rate decreased rapidly.

The same rearrangement in water-containing solvents has been followed starting

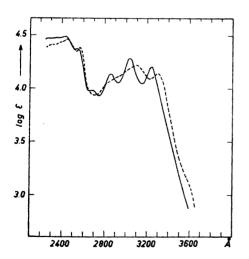


Fig. 1. 2-trans Matricaria acid, — — in dry tetrahydrofuran; — in tetrahydrofuran-water (10:1).

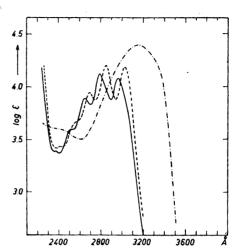


Fig. 2. trans Lachnophyllum acid, — — in dry tetrahydrofuran; — in tetrahydrofuran-water (10:1); — CH₃—CH₂—CH₂

CH—CH

C=C—CH=C

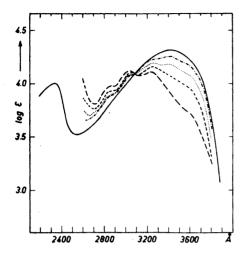
C=O from cis lach-

nophyllum acid.

with cis lachnophyllum acid (III, $R=CH_3-CH_2-CH_2-C\equiv C-$). According to Ref.³ it also takes place with cis dehydro matricaria acid (III, $R=CH_3-C\equiv C-C\equiv C-$) at pH=8.4. Other substances have not yet been tried.

When the rearrangement was followed in the UV-recorder with rapid successive scannings of the spectrum, it turned out that with the cis:cis matricaria acid no direct transformation from the free acid spectrum to the lactone spectrum took place, but some intermediate absorption with more pronounced fine structure (Fig. 3, curve 1) was observed. The transformation from the normal free acid spectrum to this spectrum took place in less than 0.5 min.

In order to be able to make a reasonable guess as to the origin of the absorption of this compound, some 2-trans matricaria acid was dissolved in tetrahydrofuran with water. This acid is incapable of forming a lactone for steric reasons and gave immediately after having been dissolved (< 0.5 min) a spectrum entirely different



from that of the acid dissolved in hexane or dry tetrahydrofuran. In these two solvents the spectrum of the 2-trans acid (Fig. 1) was very similar to the spectrum of both the 2-trans and the 2-cis-ester with no marked fine structure in the long wavelength area (2 800-3 400 Å). When dissolved in tetrahydrofuran with water (10:1) a marked fine-structure developed with bands at 2 850, 3 035 and 3 240 Å (Fig. 1). The 2-trans lachnophyllum acid gave the same overall picture with a shift from 2 690, 2 850 and 3 025 Å in dry tetrahydrofuran to 2 645, 2 790 and 2 965 Å in tetrahydrofuran-water (10:1) (Fig. 2).

The substances trans (HC=C-CH=CH-COOH and trans (-C=C-CH=CH-COOH)₂ gave the same shift to shorter wavelengths, although less pronounced.

When 2-cis-matricaria acid is dissolved in 0.01 N ethanolic H_2SO_4 , there is no formation of the fine-structure spectrum.

If samples are withdrawn at certain time intervals from a solution of the *cis*-acid in 95 % ethanol the reaction can be stopped with acid. Analysis of these samples in

UV now gives as result a set of curves where the intermediate curves between pure acid and pure lactone are mixtures of the normal acid spectrum and the lactone spectrum.

At present it is not possible to give a detailed reaction mechanism, but from the spectral studies two general routes are possible:

A: Fine-structure complex ≠ free acid
→ lactone

B: Free acid ≠ fine-structure complex → lactone

The choice between the two must await more detailed studies, the most probable is apparently B. If, in B, the equilibrium acid ≠ complex is over to the right, there would be an apparent isosbestic point 4 in the UV-curves from the reaction fine-structure complex → lactone. (Fig. 3).

Holman and Sørensen s reported in 1950 some spectral and oxidation studies on matricaria ester and the free acid. Their curve for the UV-absorption of the acid in ethanol can now be interpreted as being the curve for a mixture of the free acid and the lactone formed from it. The sharp maximum at $\sim 2\,580$ Å in the pure free acid been reduced and indicates a fairly large amount of lactone formation. The maximum at $3\,250$ Å corresponds to the rapidly developed maximum in solvents containing water.

This work is in progress and further results will be published elsewhere.

The author thanks Prof. N. A. Sørensen for his interest and Norges Teknisk-Naturvitenskaplige Forskningsråd for financial support.

- Sørensen, N. A. and Stavholt, K. Acta Chem. Scand. 4 (1950) 1080.
- Christensen, P. K. Det 9. Nordiske Kemikermøde. Aarhus 1956.
- Christensen, P. K., Sørensen, N. A., Bell, I., Jones, E. R. H. and Whiting, M. C. Festschrift Proj. Dr. Arthur Stoll, Basel 1957, p. 545.
- Schläfer, H. L. and Kling, O. Angew. Chem. 68 (1956) 667.
- Holman, R. T. and Sørensen, N. A. Acta Chem. Scand. 4 (1950) 416.

Received March 12, 1957.