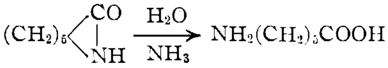
leads directly to the free and pure ε-aminocaproic acid in a single step. The conversion after five days at 80° was about 20%, but the unreacted ε-caprolactam can be simply and quantitatively recovered, so that the actual yield is close to the theoretical. Undoubtedly speedier and higher conversions can be obtained with higher temperatures and pressures but this was not investigated.


$$(\mathrm{CH_2})_5\left<\begin{matrix}\mathrm{CO}\\ |\\ \mathrm{NH}\end{matrix}\right. \xrightarrow[\mathrm{NH_3}]{\mathrm{H_2O}} \mathrm{NH_2(CH_2)_5COOH}$$

### Experimental

**ε-Aminocaproic Acid.**—Eleven and three-tenths grams (0.1 mole) of ε-caprolactam[2] was heated in an oven with 55 ml. of concentrated ammonia in a pressure-bottle for five days at 80°. The contents of the bottle were then evaporated to dryness, treated with 30 ml. of *i*-propanol, the precipitated ε-aminocaproic acid filtered off, washed with *i*-propanol and dried: yield 2.6 g.; m. p. 201–202° (dec.). On distillation to dryness, the mother liquors yielded an oily residue which promptly crystallized; it had a m. p. of 65–68° and thus proved to be pure ε-caprolactam.

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[2] ε-Caprolactam was generously supplied by E. I. du Pont de Nemours & Co., Inc.

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## X-Ray Crystallographic Data for Sodium 1-Decanesulfonate Hemihydrate

BY L. H. JENSEN AND E. C. LINGAFELTER

X-Ray crystallographic data for the hemihydrates of sodium 1-dodecane-, 1-tetradecane-, 1-hexadecane- and 1-octadecanesulfonate have been reported.[1] The hemihydrate of sodium 1-decanesulfonate was now been obtained as extremely small single crystals suitable for X-ray diffraction studies.

Conditions for the growth of sodium 1-decanesulfonate hemihydrate differ from those for the hemihydrates previously reported. Sodium 1-decanesulfonate hemihydrate crystallized from a solution of approximate composition 15% water, 85% 1,4-dioxane at *ca* 5°. Work is in progress at the present time to delineate the temperature and solvent conditions for the formation of this and the other hydrates of the sodium 1-alkanesulfonates.

In addition to the habits observed for the other hemihydrates, sodium 1-decanesulfonate hemihydrate crystallizes as rhomb-shaped tablets, extremely thin parallel to {001} and outlined by (12 *l*).

X-Ray crystallographic data were obtained as previously reported.[1] Cell constants for the monoclinic unit cell are: $a_0$ = 6.82 kX; $b_0$ = 15.36 kX; $c_0$ = 25.69 kX; $\beta = 90° 45'$.

The X-ray value for $a_0/b_0$ is 0.4440. The goniometric value of $a/b$ is 0.4402. The density calculated from the unit cell constants assuming four molecules of $2\mathrm{C_{10}H_{21}SO_3Na\cdot H_2O}$ per unit cell is 1.261 g./cc. From the size of the unit cell and the intensity distribution of the diffraction effects, the structure of sodium 1-decanesulfonate hemihydrate seems identical with the other members of the hemihydrate series.

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[1] Jensen and Lingafelter, THIS JOURNAL, **68**, 1729 (1946).

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RECEIVED SEPTEMBER 23, 1946

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## Electron Microscopic Structure of Cellulose Powder from Wood Pulp Ground in Very Dry Condition*

BY P. H. HERMANS

In a previous paper[1] we have shown that on grinding of very dry cellulose fibers in a vibrating ball mill two characteristic types of disintegration product are observed, fibrillar ones still showing a crystalline nature on X-ray examination and an amorphous powder without clearly recognizable structure. The former disappears more and more on prolonged grinding and the latter apparently represents the final product, probably consisting of crumpled or otherwise deformed fibrillar elements admixed with porcelain powder from mill abrasion. The electron micrograph reproduced in Fig. 5 of the paper cited showed powder from ramie fibers containing about 20% of porcelain.

Using balls of a harder ceramic material it was possible to reduce the ash content of the grinding products considerably. Powder from woodpulp fibers ground five hours and containing less than 3% ash was used for the recrystallization experiments referred to in our previous paper. In the present note we shall briefly deal with a further electron microscopic study on the morphological structure of this product in the original and in the recrystallized state.

As stated before, the particle size of the powder largely depends on the method of previous treatment. In order to get the best possible dispersion for examination with the electron microscope, a suspension of the powder in water was exposed to ultrasonic radiation (200,000 cycles). Particles ranging between about 1–10 μ were so obtained.

Figure 1 shows a typical particle of the original powder so dispersed in water and then dried on the collodion film. Figures 3 and 4 show typical particles of the same powder which had previously been heated in water at 100° (recrystallized sample). There is no observable difference between the original and the recrystallized preparations. Both consist of rather compact aggregates whose actual structure is difficult to recognize. Since there is only 3% ash present, their substance must be almost entirely cellulose. It will be seen that there are some indications of a distorted and crumpled fibrillar structure. Figure 2 shows a

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[1] P. H. Hermans and A. Weidinger, THIS JOURNAL, **68**, 2547 (1946).

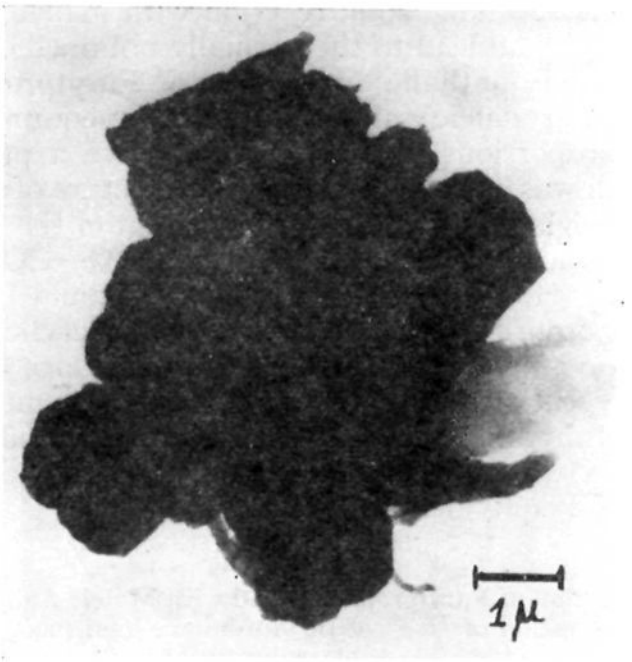

Fig. 1.—10,000 ×.

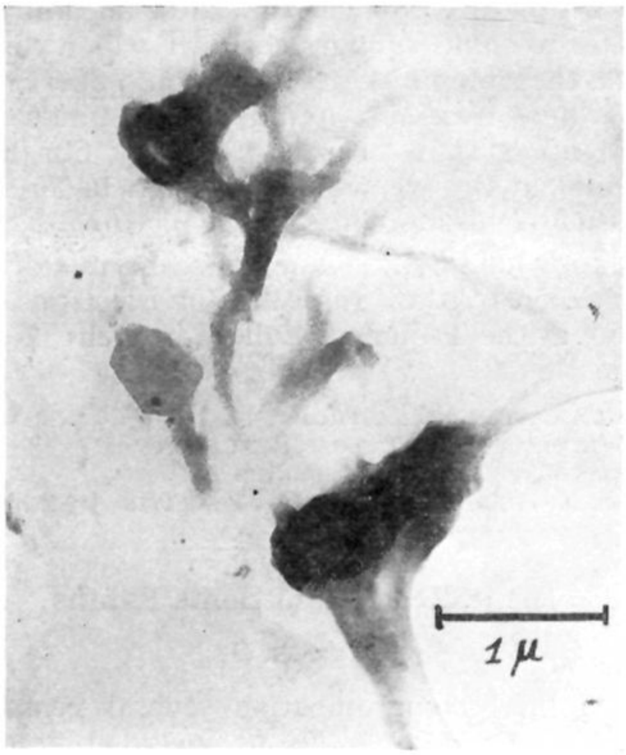

Fig. 2.—20,000 ×.

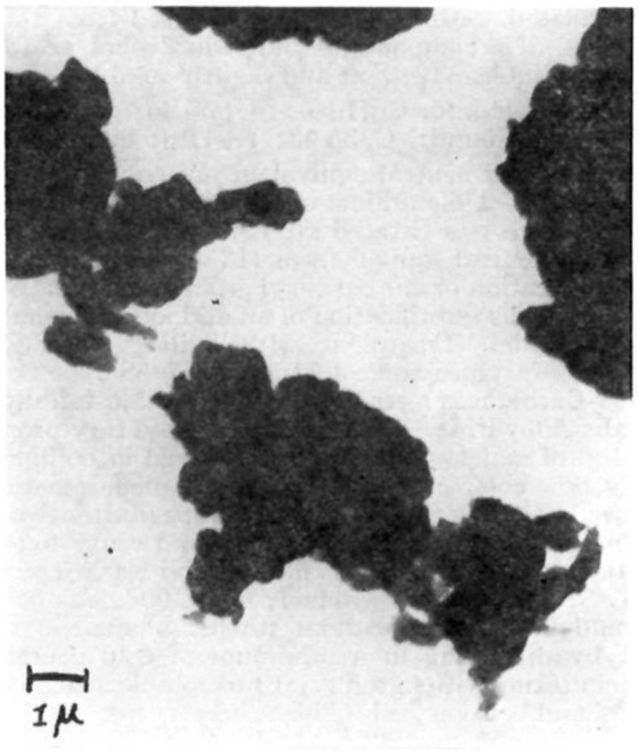

Fig. 3.—6400 ×.

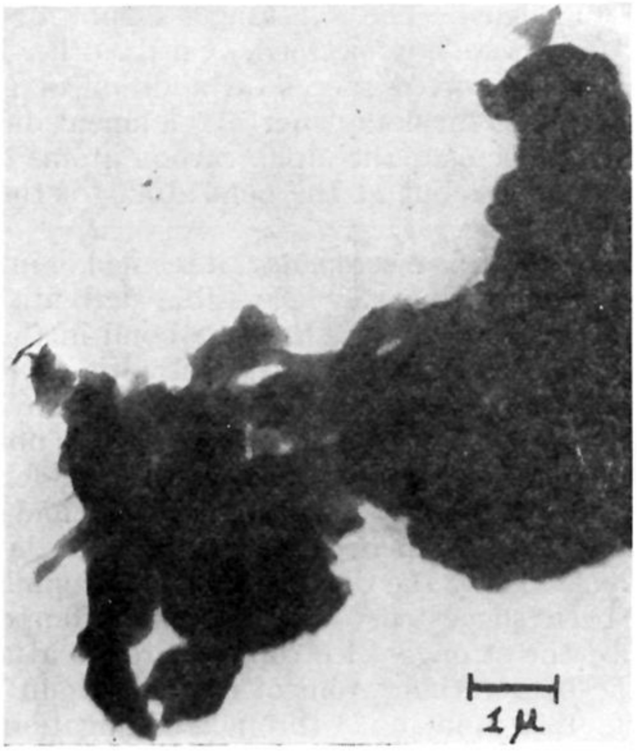

Fig. 4.—10,000 ×.

Particles of woodpulp fibers ground five hours in the very dry state and dispersed in water with the aid of ultrasonic radiation. Figures 1 and 2 from original powder, Figs. 3 and 4 from recrystallized powder (Fig. 2 represents an exceptional case; see text).

| | | Fig. 1 | Fig. 2 | Fig. 3 | Fig. 4 |
|---|---|---|---|---|---|
| Kilovolt | | 88 | 88 | 100 | 100 |
| Enlargement | Electronic | 2000 | 4000 | 1280 | 2000 |
| | Photographic | 5 | 5 | 5 | 5 |
| Total magnif. | | 10000 | 20000 | 6400 | 10000 |

single case of an exceptionally clear fibrillar structure found after a long search among the particles as shown in Fig. 1.

In no case a distinct splitting up into "elementary fibrils," as in the picture published by Hess and co-workers,[2] has been found and we agree with Husemann[3] in her suggestion that the single

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[2] E. Husemann, *J. makrom. Chem.*, **1**, 118 (1943).

[3] K. Hess, H. Kiessig and J. Gundermann, *Z. physik. Chem.*, **B49**, 64 (1941); compare W. Wergin, *Kolloid. Z.*, **98**, 131 (1942).

relevant picture published by these authors seems to refer to some foreign substance which contaminated their preparation of wood pulp fibers.

We have invariably found with all kinds of cellulose fibers that, in order to study fibrillation, grinding in the wet condition is to be preferred and then yields more interesting pictures.

**Acknowledgment.**—The electron micrographs were taken by the "Institute for Electron-microscopy" at the Technical College in Delft, Netherlands.

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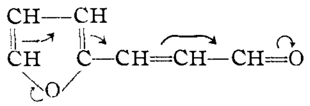
## Diene Reaction of Some Furans

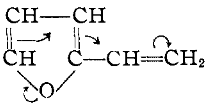
BY WERNER HERZ

In a brief communication several years ago, Van Campen and Johnson[1] included among a number of furans which did not undergo the Diels–Alder reaction with maleic anhydride compounds containing an ethylenic group attached to the furan nucleus. The substances exhibiting such inactivity were not specified. On the other hand, Paul[2] has reported successful addition of maleic anhydride to furylethylene. Attachment did not, however, occur at the alpha carbon atoms of the furan nucleus, but at the beta atoms of the side chain and ring.

In view of this discrepancy, it seemed of interest to subject some easily accessible derivatives of furfural containing an ethylenic bond in the side chain to the action of maleic anhydride. Furylacrolein, furylacrylic acid and 2-(β-nitrovinyl)-furan were found to be inactive. This is not surprising if it is assumed that the Diels–Alder synthesis is initated by an anionoid–cationoid reaction in which the diene is nucleophilic and the beta carbon atom of the dienophile is electrophilic, as has been suggested.[3] In the three compounds named the strongly electrophilic groups attached to the beta carbon atom of the side chain deactivate this atom and, through conjugation, the nucleus (I). In furylethylene, on the other hand, extended conjugation favors attack of the dienophile on the beta carbon atom of the side chain (II), as actually observed by Paul.



I



II

According to this concept, if the conjugation in the three compounds cited is destroyed by saturation of the side chain, reaction with maleic anhydride should lead to the normally obtained epoxytetrahydrophthalic anhydrides. Furylpropionic acid and maleic anhydride, mixed in equimolecular proportions in boiling ether, gave a product which was assumed to have the structure of a normal Diels–Alder adduct and not that of the mixed anhydride $C_4H_3O—CH_2CH_2CO—O—COCH{=}CHCO_2H$, as no similar anhydride could be isolated from the reaction mixture furylacrylic acid–maleic anhydride. To obtain a substance of unequivocal structure, furylpropionic ester and maleic anhydride reacted under identical conditions and yielded a compound having the correct neutral equivalent and analysis.

### Experimental[4]

**Reaction of Furylpropionic Acid with Maleic Anhydride.** To a solution of 13 g. of furylpropionic acid in 50 ml. of ether was added 11 g. of maleic anhydride with boiling until completely dissolved. At intervals, the mixture was shaken vigorously; crystals soon appeared and the mixture became a solid crystalline mass in two hours. The product was separated by filtration, washed with a little ether and purified by dissolving in acetone, treating with charcoal and diluting with benzene. Eleven grams of the substance in the form of white needles melting at 96° were isolated. More could be recovered from the ether washings. The compound is soluble in alcohol, acetone and water, insoluble in benzene and slightly soluble in ether.

*Anal.* Calcd. for $C_{11}H_{10}O_6$: C, 55.46; H, 4.20; neut. equiv., 79. Found: C, 55.43; H, 4.18; neut. equiv., 79.

Analysis and neutral equivalent are equally correct for either a Diels–Alder adduct or a mixed anhydride. When the substance was titrated after having been dissolved in alcohol, a neutral equivalent of 113 was obtained, indicating esterification of one carboxyl group. This may be due to spontaneous esterification of an adduct or alcoholysis of an anhydride. Treatment with boiling water yielded crystals of furylpropionic acid, m. p. 57–58°.

**3-(β-Carbethoxy)-ethyl-3,6-epoxy-1,2,3,6-tetrahydro-*o*-phthalic Anhydride.**—Nine grams of ethyl furylpropionate and 4 g. of maleic anhydride were mixed in boiling ether. The yellow color characteristic of the diene reaction was observed and long needles began to appear after two hours. The mixture was allowed to stand for twenty-four hours and the separated solid was filtered and washed with cold ether. Nine grams of product, m. p. 90°, was obtained. It could be purified without further change in melting point by dissolving in a minimum of cold acetone and reprecipitating with ligroin. It was soluble in acetone, hot alcohol and benzene, dilute base, acetic acid, ethyl acetate and chloroform, partially soluble in carbon tetrachloride and insoluble in ligroin and dilute acid. Boiling in water regenerated the constituents.

*Anal.* Calcd. for $C_{13}H_{14}O_6$: C, 58.65; H, 5.26; neut. equiv., 133. Found: C, 58.59; H, 5.22; neut. equiv., 130.

No compound, other than the reactants, could be isolated after two weeks of standing from mixtures containing furylacrylic acid, furylacrolein or 2-(β-nitrovinyl)-furan, each with an equivalent amount of maleic anhydride in boiling ether. Refluxing in benzene solution for eight to ten hours gave similar results. A solution of equivalent quantities of furylacrylic acid and maleic anhydride in ether, allowed to stand at room temperature for two months, gave no precipitate upon being chilled in the refrigerator for several days and on removal of the solvent yielded only a mixture of the reactants.

UNIVERSITY OF COLORADO
BOULDER, COLORADO RECEIVED SEPTEMBER 6, 1946

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(1) Van Campen and Johnson, THIS JOURNAL, **55**, 430 (1933).

(2) Paul, *Compt. rend.*, **208**, 1028 (1939); *Bull. soc. chim.*, **10**, 163 (1943).

(3) Hudson and Robinson, *J. Chem. Soc.*, 715 (1941); Remick, "Electronic Interpretations of Organic Chemistry," John Wiley and Sons, New York, N. Y., 1943, p. 131.

(4) Melting points are uncorrected.