TABLE I

ACID-CATALYZED ALKYLATION OF ISOPARAFFINS WITH ALCOHOLS

Expt.	1	2	3	4	5
Catalyst	HF	HF	HF	HF	H_2SO_4
Isoparaffin	*i*-BuH	*i*-BuH	*i*-BuH	*i*-BuH	*i*-AmH
Alcohol	*t*-BuOH	*i*-PrOH	*i*-PrOH	*n*-BuQH	*t*-BuOH
Weights used, grams					
Catalyst	160	150	150	154	930
Isoparaffin	145	145	145	142	216
Alcohol	93	75	75	93	111
Isoparaffin/alcohol (mol.)	1.98	2.00	2.00	1.96	2.00
Temp., °C.	19–26	20–22	49–51	48–50	20
Pressure (max.), atm.	4.5	4.5	9.5	8.6	1.0
Stirring time, min.					
Alcohol addition	56	60	45	49	155
Subsequent	64	65	80	87	30
Alkylation product					
Yield, ml.	184	14	142	0	256
% of theory	89	7.9	78	0	95
Specific gravity (20°/4°)	0.6913	0.7073	0.6868	....	0.7153
Refractive index (20°)	1.3947	1.3945	1.3895	....	1.4028
Olefin content, wt. %	0.0	1.8	0.14	....	0.6

TABLE II

PROPERTIES OF ALKYLATE FRACTIONS

Expt.	Fraction	B. p., °C.	Vol. %	d^{20}_4	n^{20}_D	Olefin, wt. %
1	C_{5-6}	23–75	10.2	0.6332	1.3630	0.0
	C_7	75–95	7.3	.6805	1.3880	.0
	C_8	95–125	64.4	.6971	1.3958	.0
	C_9	125–150	4.3	.7186	1.4069	.6
	C_{10}	150–177	5.4	.7383	1.4168	1.1
	C_{11-12}	177–212	6.9	.7538	1.4247	2.0
	Residue	.....	1.5	.6941	1.4454	...
3	C_6	23–75	10.4	.6481	1.3712	0.12
	C_7 (low)	75–85	22.4	.6740	1.3842	.0
	C_7 (high)	85–95	41.7	.6885	1.3920	.14
	C_8	95–125	11.7	.7012	1.3977	.3
	C_9	125–150	3.3	.7218	1.4064	.17
	C_{10}	150–175	7.9	.7358	1.4152	.54
	Residue	.....	2.6	.7614	1.4260	...
5	C_6	40–77	12.8	.6566	1.3725	.0
	C_7	77–95	7.1	.6817	1.3870	.0
	C_8	95–120	15.7	.7070	1.3989	.0
	C_9 (low)	120–125	17.9			
	C_9 (high)	125–152	11.0	.7231	1.4069	.0
	C_{10}	152–180	25.8	.7363	1.4132	.0
	C_{11-12}	180–210	5.3	.7561	1.4239	1.3
	Residue	.....	4.4	.7866	1.4405	19

In experiments 1–4, the alcohol was pumped at a uniform rate into a vigorously stirred mixture of isobutane and anhydrous hydrofluoric acid in a water-cooled 625-ml. steel reactor. The reaction mixture was treated successively with ice, water, and 50% sodium hydroxide, was dried, and was debutanized and fractionated in a 5-foot glass column, 0.5 inch in diameter, packed with 6-mm. glass helices.

In experiment 5, the alcohol, diluted with an equal volume of isopentane, was added from a graduated separatory funnel to a vigorously stirred mixture of isopentane and concentrated sulfuric acid in a 3-liter flask provided with an ice-water-cooled reflux condenser. The reaction mixture was separated into two layers; the hydrocarbon layer was washed, dried, debutanized and fractionated.

The main product in each experiment was of the expected number of carbon atoms per molecule; however, the alkylate from experiment 5, made with isopentane and tertiary butyl alcohol, had a noteworthily large decane fraction. During the fractionation in experiment 3, made with isobutane and isopropyl alcohol, a few crystals of apparently triptane were collected at Dry-Ice temperature, at a pressure corresponding to a boiling point of 79°; the amount was so small that it indicated that this heptane was not a major product.

Whereas *t*-butyl alcohol resembled a butylene in reactivity, the non-*t*-alcohols were less reactive than the corresponding olefins—due allowance being made for dilution of acid by by-product water.

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The Preparation of ε-Aminocaproic Acid

BY ALEXANDER GALAT AND SHIRLEY MALLIN

The preparation of ε-aminocaproic acid according to the procedures described in the literature is rather long and tedious. Thus, ε-caprolactam is hydrolyzed with hydrochloric acid, the excess of acid is removed in vacuum and the ε-aminocaproic acid hydrochloride which remains as residue, is repeatedly treated in a very dilute, aqueous solution with several portions of litharge freshly precipitated lead hydroxide, silver oxide and finally with hydrogen sulfide.[1]

This procedure proved to be very inconvenient and time consuming for the preparation of reasonably large amounts of ε-aminocaproic acid. A much simpler method has been found in the ammonolysis of ε-caprolactam under pressure, which

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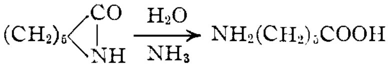
[1] "Organic Syntheses," Coll. Vol. 11, John Wiley and Sons, New York, N. Y., p. 28.

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.



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

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; β = 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 $2C_{10}H_{21}SO_3Na\cdot H_2O$ 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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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).