shoulder on the second strong maximum now appears in the curve for the *trans* form, and accordingly the modification which boils at 53.5° (746 mm.) has the *trans* configuration. It may be mentioned that the new photographs from each of the compounds show the inner maximum (near $s = 3$) with that for the *trans* form having a slightly greater s value in agreement with the curves. That this identification is not based on more extensive data is due to the fact that the two expressions for electron scattering by the *cis* and *trans* forms show only slight differences. In the chemical investigation[2] the *trans* form was identified as that one which was obtained in an optically active state and this choice is now supported by the electron diffraction result. The *cis* form is that boiling at 59.6° (746 mm.).

Accepting the chemical identification of the isomers, we see that the electron diffraction study offers proof that bending the carbon–oxygen bond in forming the three-membered ring also bends the other bonds from their "natural" or unstrained positions, since the model in which the bending effect is confined to the one bond leads to the wrong identification of the isomers.

The interatomic distances previously reported are still to be accepted since the new photographs and curves lead to the same dimensions for the molecules.

PASADENA, CALIF.
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Improved Preparation of Pentaacetyl-keto-fructose

BY FRANCIS B. CRAMER AND EUGENE PACSU

Pentaacetyl-keto-fructose, formerly designated as α-pentaacetylfructose, was first prepared by Hudson and Brauns[1] by the action of zinc chloride and acetic anhydride on fructose. The yield was less than 8% of the theoretical. Acetylation of fructose with acetic anhydride and pyridine gave rise to the same compound in less than 5% yield. When tetraacetylfructose is prepared by the improved method of Pacsu and Rich,[2] and this converted into the keto-pentaacetate by the procedure of Hudson and Brauns,[1] the yield, calculated on fructose, is increased to 36%. A procedure has now been worked out by which the keto-pentaacetate may be obtained in about 50% yield by the direct acetylation of fructose without the isolation of an intermediate compound. The production of a good yield of pentaacetyl-keto-fructose appears to take place under conditions which facilitate the preliminary formation of a large amount of β-tetraacetylfructose. As amply demonstrated by Hudson and Brauns,[1] the keto-pentaacetate, once formed, is unaffected when heated with zinc chloride and acetic anhydride in the concentrations used in our experiments.

Experimental

Preparation of Pentaacetyl-keto-fructose.—Ten grams of finely powdered fructose was added in one portion to a solution of 1 g. of fused zinc chloride in 100 cc. of distilled acetic anhydride cooled in an ice-bath. The mixture was stirred vigorously at 0° for four hours, during which time most of the sugar dissolved. The temperature was then kept at 20–25° for one hour and finally at 50° for two hours. The cooled solution was stirred with an equal volume of water for one and one-half hours, further diluted, and neutralized with an excess of sodium bicarbonate. The chloroform solution of the gummy precipitate was united with the chloroform extracts of the water solution, then dried with calcium chloride, filtered, and evaporated to a sirup *in vacuo*. The sirup was dissolved in about 50 cc. of absolute ether, and the solution on standing overnight in the ice-box deposited 10.3 g. of crystalline pentaacetyl-keto-fructose, having $[\alpha]^{20}\text{D}$ 33.5° in chloroform solution.

When half the above amount of acetic anhydride was used, the yield of the crystalline pentaacetate was 9 g. (42%). The keto-acetate was prepared more rapidly by stirring 10 g. of fructose with 50 cc. of acetic anhydride, and 1 g. of zinc chloride for one hour at room temperature and one hour at 50°. The yield was 7.5 g., or 35%. When 10 g. of fructose was stirred with the same acetylating solution at 50° for one hour and the reaction mixture worked up immediately, the yield was only 6 g., or 28%.

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[1] Hudson and Brauns, THIS JOURNAL, **37**, 2736 (1915).

[2] Pacsu and Rich, *ibid.*, **55**, 3018 (1933).

Physical Constants of Morpholine

BY V. H. DERMER AND O. C. DERMER

In preparing to study morpholine as an ionizing solvent, we have investigated its purification and measured some of its physical constants. Since the first shipment of morpholine we obtained apparently contained esters, we resorted to chemical purification through the acid oxalate. Later lots proved to be of extraordinary purity, requiring only to be dried over metallic sodium.

Table I gives the results of our measurements and calculations.

TABLE I

Constant		Value	Earlier values
Boiling point (760 mm.), °C.		128.9	128–130,[a] 128.3[b]
Freezing point, °C.		−4.9 ± 0.1	
Density, g./cc.		0.9994 20/4° vac.	1.0008 20/4°,[a] 1.0016 20/20°[b]
Refractive index, $n^{20}\text{D}$		1.4545	1.4540[a]
Molecular refraction	observed	23.60	23.54[a]
	calcd.[c]	23.72	
Viscosity, poises at 20°		0.0223	
Surface tension at 20°, dynes/cm.		37.5	
Parachor	observed	215.7	
	calcd.[d]	213.3	

[a] Knorr, *Ann.*, **301**, 1–10 (1898). [b] Wilson, *Ind. Eng. Chem.*, **27**, 870 (1935). [c] Atomic refractions from Eisenlohr, *Z. physik. Chem.*, **75**, 605 (1911); **79**, 134 (1912). [d] Atomic parachors from Bayliss, THIS JOURNAL, **59**, 444 (1937); Mumford and Phillips, *J. Chem. Soc.*, 2112 (1929).

Experimental

Commercial morpholine, purchased from Carbide and Carbon Chemicals Corporation, was added gradually to slightly more than a molar equivalent of oxalic acid dissolved in alcohol. The precipitated morpholine hydrogen oxalate was filtered out and recrystallized twice from 60% ethanol. Even then it did not melt sharply, but sintered and decomposed with effervescence at 190–195°. Titration with standard alkali gave indistinct end-points because of the morpholine liberated by hydrolysis; hence the oxalate was titrated with 0.1 *N* potassium permanganate. Molecular weight found: 178, 178; calcd. for $C_4H_8ONH(COOH)_2$, 177. Morpholine hydrogen tartrate was prepared similarly; it melts at 165–166°.

Morpholine was regenerated from the oxalate by adding the salt to concentrated aqueous potassium hydroxide. The layer of free base was separated and dried over solid potassium hydroxide and then sodium. It was then fractionally distilled from sodium through a three-ball Snyder column. After the first quarter had been set aside for further drying, the remainder had a corrected boiling point of 128.9°. This temperature was read on two thermometers, each newly calibrated with pure chlorobenzene and ethylene dibromide to avoid stem correction. Later distillations showed that it is unnecessary to subject good commercial morpholine to the oxalate method of purification; refluxing over sodium followed by fractionation gave a product of boiling point identical with that of the "purified" material.

The freezing point of freshly distilled morpholine was measured with several thermometers calibrated at 0° with pure ice. The refractive index at 20.0° was determined with a Zeiss dipping refractometer in a closed cell. At the same temperature, the surface tension relative to water was measured with Traube's stalagmometer, and the relative viscosity with an Ostwald viscometer. In all cases precautions were taken to exclude moisture and carbon dioxide from samples tested.

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The Heat of Combustion and Structure of Cuprene

BY P. J. FLORY

In a recent study of cuprene formed by alpha ray polymerization of acetylene, Lind and Schiflett[1] have reported 265.3 kcal. for the heat of combustion per structural unit $-(C_2H_2)-$. Although the structure of cuprene has never been determined, they have calculated the heat of polymerization assuming the formation of one $C{=}C$ and one $C{-}C$ bond in place of each $C{\equiv}C$ bond of acetylene and using Fajans'[2] heats of atomic linkages. The significance of the comparison of this calculated heat of polymerization with that deduced from the heats of combustion of acetylene and of cuprene was obscured by the approximate nature of Fajans' values.

A much more reliable heat of polymerization can be calculated from recent thermochemical data. In conformity with Lind and Schiflett's assumption regarding the constitution of cuprene, a chain structure in which the single and double bonds occur alternately, *i. e.*, $-(CH{=}CH)_n-$, will be assumed.

Expressing heats of combustion (*Q*) as heat

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[1] S. C. Lind and C. H. Schiflett, THIS JOURNAL, **59**, 411 (1937).

[2] K. Fajans, *Ber.*, **53**, 643 (1920).