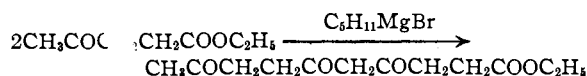
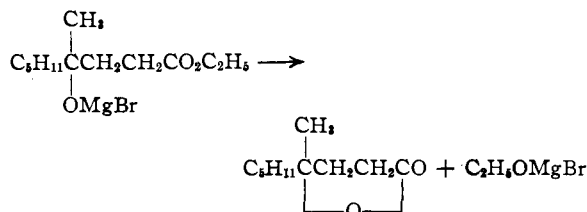


lactone: 28% for hexyl chloride, 31% for hexyl bromide,<sup>2</sup> 29% for amyl chloride<sup>3</sup> and 38% (based on crude product) for  $\beta$ -bromonaphthalene.<sup>4</sup>

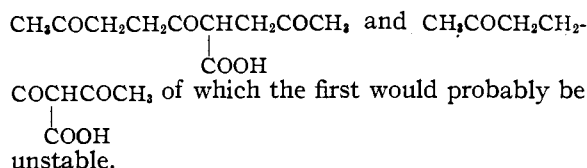
We have treated ethyl levulinate with amylmagnesium bromide and have increased the yield of lactone to 41% based on the halide, by employing a 50% excess of the ester. After the lactone had been distilled off, a large amount of material remained, which has been investigated. From this by-product a tri-keto acid, probably 4,6,9-trioxocaproic acid, m. p. 118°, was the only compound that could be isolated. This acid evidently resulted from the hydrolysis of the ester arising from the condensation of the ester group of one molecule of ethyl levulinate with the methyl group of another molecule.



It is quite possible that the actual condensation agent is ethoxymagnesium bromide which would be present by the reaction of the Grignard reagent with the ester grouping as well as by the reaction which occurs after addition of the reagent to the carbonyl group.<sup>5</sup>



Other possible structures for the acid include



That the condensation resulted in a straight-chain compound containing only one acetyl group seems highly probable from the terminal methyl determination.<sup>6</sup> The results show that on an average 66% of one acetyl group was converted to acetic acid. This figure is in agreement with the terminal methyl value observed for the semicarbazone of ethyl methyl ketone (67%).<sup>5</sup>

#### Experimental

The Grignard reaction was carried out by the inverse addition of the reagent, prepared from 302 g. (2 moles) of amyl bromide and 48 g. (2 g. atoms) of magnesium in 500 ml. of ether, to 432 g. (3 moles) of ethyl levulinate in 600 ml. of benzene. The reaction proceeded in the usual manner, and the product was distilled, yielding 140 g. (41% based on halide) of  $\gamma$ -methyl- $\gamma$ -pelargonolactone,

b. p. 110° (0.5 mm.),  $n_D^{25}$  1.4468. The higher boiling fraction, which was not distilled, amounted to 205 g.

**4,6,9-Trioxocaproic Acid.**—Twenty-five grams of the undistilled fraction was treated with 100 ml. of 10% sodium hydroxide and allowed to stand overnight at room temperature. After about 1 g. of neutral material had been removed by ether extraction, the solution was acidified with dilute hydrochloric acid, saturated with sodium chloride, and extracted with ether. The ether solution was washed free of acid with salt solution and dried, and the solvent was removed. The residue, 15.6 g., was subjected to high-vacuum distillation and yielded 2 g. of uncharacterized material. The residue was then poured into a beaker and, after about a week, crystals formed in the dark-brown mass. Trituration with cold ethyl acetate yielded 2.6 g. of crystals, which upon recrystallization from ethyl acetate melted at 118°.

*Anal.* Calcd. for  $\text{C}_{10}\text{H}_{14}\text{O}_5$ : C, 56.07; H, 6.59; neut. equiv., 214; 1  $\text{CH}_3$ , 7.0. Found: C, 56.09; H, 6.53; neut. equiv., 215;  $\text{CH}_3$ , 4.4, 4.8.

The acid yielded a monosemicarbazone, m. p. 193°.

*Anal.* Calcd. for  $\text{C}_{11}\text{H}_{17}\text{O}_5\text{N}_2$ : C, 48.70; H, 6.32. Found: C, 49.02; H, 6.29.

BUREAU OF ENTOMOLOGY AND PLANT QUARANTINE  
AGRICULTURAL RESEARCH ADMINISTRATION  
U. S. DEPARTMENT OF AGRICULTURE  
BELTSVILLE, MD. RECEIVED MARCH 10, 1947

#### Heats of Polymerization of Some Unsaturationes

BY L. K. J. TONG AND W. O. KENYON

The heats of polymerization of certain unsaturates have been measured and found to be: methyl acrylate 18.7  $\pm$  0.2, vinyl acetate 21.3  $\pm$  0.2, acrylonitrile 17.3  $\pm$  0.5, and vinylidene chloride 14.4  $\pm$  0.5 kcal./mole of monomeric unit. The unsaturates used were highly purified for these measurements. The calorimeter and the technique of its operation have been described previously.<sup>1</sup> With the exception of methyl acrylate, corrections have been made for unreacted monomers. The heat of polymerization value for methyl acrylate was determined using 0.01% of benzoyl peroxide catalyst, while vinyl acetate was determined with 0.018% and 0.035% of the catalyst. These latter values did not vary significantly. Measurements with acrylonitrile were made using catalyst concentrations of 0.05 to 0.20%, and with vinylidene chloride using 0.25 to 0.86%. The final values given above for the two latter monomers were determined by extrapolation to zero catalyst concentration. All determinations reported were at 76.8°. The  $-\Delta H$  of 21.3 kcal./mole for vinyl acetate is quite different from the value of 28.0 reported by Houwink<sup>2</sup> and 8.0  $\pm$  0.4 by Mark, *et al.*<sup>3</sup> Based on considerations of the stability of the polymerizable double bond, vinyl acetate should show a larger value of  $-\Delta H$  than do methyl acrylate or styrene, wherein the double bond is conjugated. Our value of 21.3 is close to those calculated by

(1) Tong and Kenyon. *THIS JOURNAL*, **67**, 1278 (1945); **68**, 1335 (1946); **69**, 1402 (1947).

(2) Houwink. "Chemie und Tech. der Kunststoff." Vol. I. Akad. Verlags. Leipzig, 1940, p. 60.

(3) Goldfinger, Josefowitz and Mark. *THIS JOURNAL*, **65**, 1432 (1944).

(2) Frank and co-workers, *ibid.*, **66**, 4 (1944).

(3) LaForge and Barthel, *J. Org. Chem.*, **10**, 222 (1945).

(4) Robinson and Slater, *J. Chem. Soc.*, 376 (1941).

(5) Grignard, *Compt. rend.*, **135**, 627 (1902).

(6) Barthel and LaForge, *Ind. Eng. Chem., Anal. Ed.*, **16**, 434 (1944).

Flory<sup>4</sup> for monomers in which the reacting double bond is not in resonance.

(4) Flory, *THIS JOURNAL*, **59**, 241 (1937).

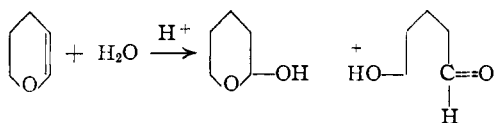
RESEARCH LABORATORIES  
EASTMAN KODAK COMPANY  
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ROCHESTER 4, N. Y.

RECEIVED JULY 2, 1947

### Dihydropyrane Addition Products

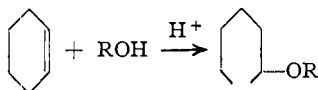
BY G. FORREST WOODS AND DAVID N. KRAMER

2,3-Dihydropyrane is the dehydration product of a hemiacetal and as such has been shown to add water<sup>1</sup> readily in the presence of a trace of mineral acid yielding an equilibrium mixture of 5-hydroxypentanal and 2-hydroxytetrahydropyrane. Paul<sup>1a</sup> observed that methyl alcohol



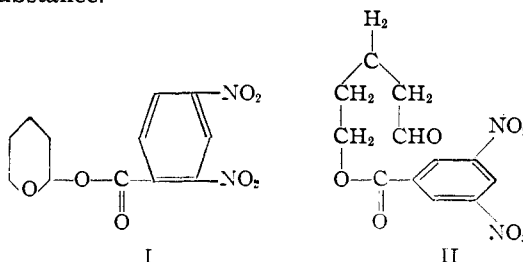
added to dihydropyrane and from this reaction 2-methoxytetrahydropyrane was obtained.

We have prepared a number of acetals from 2,3-dihydropyrane according to the equation below modifying the procedure of Paul



These acetals are stable in a basic medium and are therefore easily isolated after destruction of the acid catalyst with a strong inorganic base.

pyrane the yellow 2,4-dinitrophenylhydrazone of 5-hydroxypentanal, the hydrolysis product of dihydropyrane, has been used. We have found that 3,5-dinitrobenzoic acid when mixed with an excess of dihydropyrane forms an addition product which is excellent for characterization. This product does not form a semicarbazone when treated with free semicarbazide in methanol. Therefore, the structure (I) is preferred to that of (II) for this substance.



### Experimental

**Acetal Formation.**—Equimolar quantities of alcohol and dihydropyrane in the presence of a trace of concentrated hydrochloric acid were shaken and allowed to stand for three hours. The reaction is exothermic. A few pellets of sodium hydroxide were then added to the reaction mixture to destroy the acid, and the product isolated directly by distillation. The pure material was obtained by redistillation in the presence of a few pellets of sodium hydroxide.

The 2,4-dinitrophenylhydrazone of 5-hydroxypentanal from these acetals were prepared in the usual manner. The yellow crystalline material obtained melted at 107–109° and gave no depression in a mixed melting point determination with an authentic sample.<sup>1b</sup>

**The 3,5-Dinitrobenzoate of 2-Hydroxytetrahydropyran.**—Five grams of 3,5-dinitrobenzoic acid was dissolved with warming in a 50% excess of dihydropyrane. Upon cooling, 5 cc. of ether was added and the product slowly crystal-

TABLE I  
ACETALS FROM DIHYDROPYRANE

R -	B. p., °C.	$n_D$	Yield, %	Calcd., %		Found, %	
				C	H	C	H
Methyl <sup>a</sup>	125	1.4260	85	62.07	10.35	62.06	10.01
Ethyl <sup>b</sup>	146	1.4248	93	64.62	10.76	65.04	10.58
<i>n</i> -Propyl-	165	1.4280	91	66.67	11.11	66.27	11.00
Allyl-	126	1.4440	70	67.53	9.86	67.48	10.07
<i>n</i> -Butyl-	183	1.4312	75	68.39	11.33	68.45	11.36
Phenyl-	103 (4 mm.)	1.5290	37	74.16	7.87	73.96	7.92
Benzyl-	107 (3 mm.)	1.5128	41	75.00	8.33	74.63	8.40
Furfuryl-	124 (24 mm.)	1.4828	34	65.92	7.78	65.96	8.06
2,2'-( <i>sym</i> -Ethyleneedioxy- dihydropyrane)	164 (32 mm.)	1.4610	40	62.53	9.56	62.54	9.74

<sup>a</sup> Cf. ref. 1a. <sup>b</sup> This substance has been prepared by catalytic hydrogenation of 2-ethoxy- $\Delta^4$ -dihydropyran [Woods and Sanders, *THIS JOURNAL*, **68**, 2483 (1946)]. <sup>c</sup> In the addition of equimolar quantities of ethylene glycol to dihydropyran, mixtures of di-tetrahydropyran and mono-tetrahydropyran addition products are obtained. Ratios of two moles of ethylene glycol to one mole of dihydropyran were used to favor the preparation of the monomer which could not be obtained in a pure state. The dimer was obtained by adding two moles of dihydropyran to one mole of ethylene glycol. In each case, the two products could be separated from the initial reaction mixture by fractional distillation.

Hydrolysis of these acetals by acids in an aqueous medium in the presence of 2,4-dinitrophenylhydrazine yielded 5-hydroxypentanal-2,4-dinitrophenylhydrazone.

For purposes of identification of 2,3-dihydro-

lized as needles. After a second recrystallization from 80% dihydropyran-ether, a pale yellow solid was obtained which melted sharply at 103°. The yield was essentially quantitative.

*Anal.* Calcd. for  $C_{12}H_{12}O_7N_2$ : C, 48.65; H, 4.05. Found: C, 49.05; H, 4.46.

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(1a) R. Paul, *Bull. soc. chim.*, [5] **1**, 973 (1934).

(1b) Schniepp and Geller, *THIS JOURNAL*, **68**, 1646 (1946).

(1c) Woods and Sanders, *ibid.*, **68**, 2111 (1946).