Flory[4] for monomers in which the reacting double bond is not in resonance.

(4) Flory, This Journal, 59, 241 (1937).

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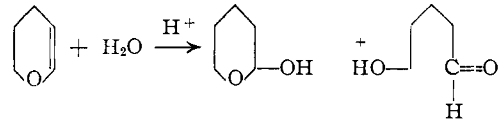
Dihydropyrane Addition Products

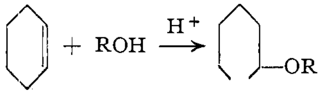
BY G. FORREST WOODS AND DAVID N. KRAMER

2,3-Dihydropyrane is the dehydration product of a hemiacetal and as such has been shown to add water[1] readily in the presence of a trace of mineral acid yielding an equilibrium mixture of 5-hydroxypentanal and 2-hydroxytetrahydropyrane. Paul[1a] 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.

TABLE I

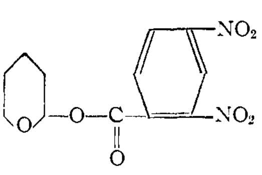
ACETALS FROM DIHYDROPYRANE

R =	B. p., °C.	N_D	Yield, %	Calcd., % C	Calcd., % H	Found, % C	Found, % H
Methyl-[a]	125	1.4260	85	62.07	10.35	62.06	10.01
Ethyl-[b]	146	1.4248	93	64.62	10.76	65.04	10.58
n-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
n-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′-(*sym*-Ethylenedioxy-ditetrahydropyrane)	164 (32 mm.)	1.4610	40	62.53	9.56	62.54	9.74

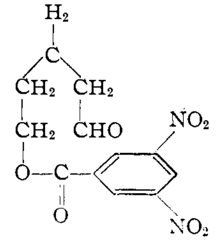
[a] *Cf.* ref. 1a. [b] This substance has been prepared by catalytic hydrogenation of 2-ethoxy-Δ^3-dihydropyrane [Woods and Sanders, This Journal, **68**, 2483 (1946)]. [c] In the addition of equimolar quantities of ethylene glycol to dihydropyrane, mixtures of di-tetrahydropyrane and mono-tetrahydropyrane addition products are obtained. Ratios of two moles of ethylene glycol to one mole of dihydropyrane 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 dihydropyrane 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-dihydropyrane 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.



I



II

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.[1c]

The 3,5-Dinitrobenzoate of 2-Hydroxytetrahydropyrane.—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 crystallized as needles. After a second recrystallization from 80% dihydropyrane–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).