3. No rearranged product could be found.
4. Further evidence has been advanced that the rearrangements studied in this Laboratory do not take place by a free radical mechanism.

STATE COLLEGE, PENNSYLVANIA RECEIVED MAY 5, 1941

[CONTRIBUTION FROM THE RESEARCH DIVISION OF COMMERCIAL SOLVENTS CORPORATION]

Some Nitro and Amino Acetals Derived from Polyhydric Nitro Alcohols

BY MURRAY SENKUS

Introduction

Polyhydric alcohols which have hydroxyl groups on carbon atoms removed by one carbon atom or on adjacent carbon atoms are characterized by the ease with which they form acetals. Ethylene glycol, propylene glycol, trimethylene glycol, glycerol and erythritol are a few common polyhydric alcohols of the above types which can be converted readily to acetals.

Recent work on the nitroparaffin–aldehyde condensation has made available several nitro glycols for the first time.[1] *tris*-(Hydroxymethyl)-nitromethane, a condensation product of nitromethane and formaldehyde, had already been known.[2] These nitro hydroxy compounds have hydroxyl groups on carbon atoms removed by one carbon atom. Preliminary work showed that these nitro polyhydric alcohols also react with aldehydes in the presence of inorganic acids to form acetals. In view of the possible application of these materials in industry, a number of cyclic acetals of the three commercially available nitro polyhydric compounds, namely, *tris*-(hydroxymethyl)-nitromethane, 2-nitro-2-methyl-1,3-propanediol and 2-nitro-2-ethyl-1,3-propanediol were prepared and are reported herein. The reduction of these nitro acetals to the corresponding amino acetals and the conversion of some of these amino acetals to alkylidenimino acetals and alkylamino acetals are also described.

Experimental

Formaldehyde acetals of 2-nitro-2-methyl-1,3-propanediol and 2-nitro-2-ethyl-1,3-propanediol were prepared by heating a mixture of nitro glycol (1 mole), 36% (by weight) aqueous formaldehyde (1 mole) and 1 g. of *p*-toluenesulfonic acid in a Claisen flask until 66–68 ml. of distillate (vapor temperature 96–103°) had been obtained. The residue was cooled and washed with 200 ml. of 2% sodium bicarbonate solution. The material solidified during the washing. The mixture was filtered and the product was washed with 100 ml. of cold water. The acetals were purified by recrystallization from 50% aqueous methanol.

Other acetals were prepared by refluxing mixtures of an aldehyde (1 mole), nitro hydroxy compound (1 mole), 200 ml. of benzene and 0.2 g. of *p*-toluenesulfonic acid in a flask connected to a modified Dean and Stark moisture trap[3] which was connected to a reflux condenser. After water had ceased separating in the trap, heating was arrested and the mixtures were cooled. They were washed with 500 ml. of 2% sodium bicarbonate solution and 500 ml. of water. The benzene was removed by distillation and the products were purified by rectification *in vacuo* or by recrystallization from methanol or petroleum ether.

The reactions required from two to three hours and conversions of nitro hydroxy compounds to acetals averaged about 90% of theoretical.

The nitro acetals prepared are white crystalline solids or colorless liquids. They are entirely stable at room temperature, however they decompose slowly when heated to 150°. They are unaffected by dilute alkali and boiling water, but are rapidly hydrolyzed by hot mineral acids. The formaldehyde acetals are appreciably soluble in hot water but insoluble in cold water. All nitro acetals described herein are soluble in ether, methanol, acetone and benzene. They are entirely odorless.

The procedure for the reduction of the nitro acetals was the same in all cases. One hundred grams of nitro acetal dissolved in 300 ml. of methanol was hydrogenated for two to three hours at 60 to 75° at 1000 to 1500 lb. pressure in the presence of 5 g. of Raney nickel catalyst. The conversions of nitro acetals to amino acetals averaged about 90%.

The amino acetals are white crystalline solids or colorless liquids. Their thermal stability is comparable to that of the amino alcohols. Hot mineral acids convert them to aldehydes and salts of the corresponding amino polyhydric alcohols. The amino acetals, except those derived from α-ethylhexaldehyde and lauraldehyde, are soluble in water. All amino acetals are soluble in ether, methanol, acetone and benzene. The amino acetals derived from formaldehyde possess a faint amine-like odor. The remaining amino acetals are odorless.

5-Methylenimino-5-ethyl-1,3-dioxane was prepared by heating a mixture of 36% (by weight) aqueous formaldehyde (1 mole) and 5-amino-5-ethyl-1,3-dioxane (1 mole) until all of the water had been removed from the product. The crude material was purified by recrystallizing from ether. The other two alkylidenimino acetals were pre-

---

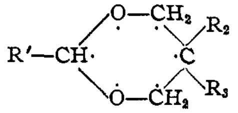
[1] Vanderbilt and Hass, *Ind. Eng. Chem.*, **32**, 34 (1940).

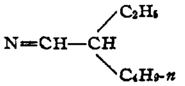
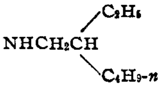
[2] Henry, *Compt. rend.*, **120**, 1265 (1895).

[3] Dean and Stark, *Ind. Eng. Chem.*, **12**, 486 (1920).

TABLE I

Acetals of the Type



R^1	R^2	R^3	M. p., °C.	B. p., °C.	Mm.	d^{20}_{20}	n^{20}_D	Formula	Nitrogen, % Calcd.	Found
H	NO_2	CH_3	71.0					$C_5H_9O_4N$	9.52	9.40
H	NH_2	CH_3		86.0	50	1.0551	1.4524	$C_5H_{11}O_2N$	11.96	12.09
H	NO_2	C_2H_5	53.2					$C_6H_{11}O_4N$	8.69	8.62
H	NH_2	C_2H_5		186.0	760	1.0481	1.4570	$C_6H_{13}O_2N$	10.69	10.76
H	$N{=}CH_2$	C_2H_5	91.6					$C_7H_{13}O_2N$	9.79	9.75
H	$NHCH_3$	C_2H_5		192.0	760	1.0253	1.4567	$C_7H_{15}O_2N$	9.66	9 81
H	 $N{=}CH{-}CH(C_2H_5)(C_4H_9\text{-}n)$	C_2H_5		139.5–141.2	10	0.9377	1.4580	$C_{14}H_{27}O_2N$	5.81	5.85
H	 $NHCH_2CH(C_2H_5)(C_4H_9\text{-}n)$	C_2H_5		146.0–147.0	10	.9340	1.4564	$C_{14}H_{29}O_2N$	5.76	5.69
C_3H_7-*n*	NO_2	CH_3	47.8					$C_8H_{15}O_4N$	7.41	7.53
C_3H_7-*n*	NH_2	CH_3		197.3	748	.9706	1.4437	$C_8H_{17}O_2N$	8.80	8.73
C_3H_7-*n*	$N{=}CHC_6H_5$	CH_3	33.0					$C_{15}H_{21}O_2N$	5.67	5.43
C_3H_7-*n*	$NHCH_2C_6H_5$	CH_3		172.5–173.0	10	1.0181		$C_{15}H_{23}O_2N$	5.62	5.49
C_3H_7-*n*	NO_2	CH_2OH	69.8					$C_8H_{15}O_5N$	6.83	6.89
C_3H_7-*n*	NH_2	CH_2OH	62.0					$C_8H_{17}O_3N$	8.00	7.95
$(C_2H_5)_2CH$	NO_2	CH_2OH	70.5					$C_{10}H_{19}O_5N$	6.01	5.96
$(C_2H_5)_2CH$	NH_2	CH_2OH	43.0					$C_{10}H_{21}O_3N$	6.89	6.77
C_6H_{13}-*n*	NO_2	CH_2OH	59.8					$C_{11}H_{21}O_5N$	5.67	5.62
C_6H_{13}-*n*	NH_2	CH_2OH	83.6					$C_{11}H_{23}O_3N$	6.45	6.33
C_2H_5—CH—*n*-C_4H_9	NO_2	CH_3		154.0–155.5	5	1.0490	1.4591	$C_{12}H_{23}O_4N$	5.71	5.74
C_2H_5—CH—*n*-C_4H_9	NH_2	CH_3		123.0–124.4	10	0.9401	1.4535	$C_{12}H_{25}O_2N$	6.51	6.45
C_2H_5—CH—*n*-C_4H_9	NO_2	C_2H_5		163.0–164.5	5	1.0413	1.4601	$C_{13}H_{25}O_4N$	5.40	5.65
C_2H_5—CH—*n*-C_4H_9	NH_2	C_2H_5		137.2–137.8	10	0.9399	1.4561	$C_{13}H_{27}O_2N$	6.11	6.14
C_2H_5—CH—*n*-C_4H_9	NO_2	CH_2OH		183.0–184.5	5	1.1156	1.4716	$C_{12}H_{23}O_5N$	5.36	5.57
C_2H_5—CH—*n*-C_4H_9	NH_2	CH_2OH		175.0–178.0	10	1.0260	1.4737	$C_{12}H_{25}O_3N$	6.06	6.22
$C_{11}H_{23}$-*n*	NO_2	C_2H_5	42.5					$C_{17}H_{33}O_4N$	4.44	4.52
$C_{11}H_{23}$-*n*	NH_2	C_2H_5		198.0–201.5	10	0.9137	1.4583	$C_{17}H_{35}O_2N$	4.91	4.80
$C_{11}H_{23}$-*n*	NO_2	CH_2OH	67.9					$C_{16}H_{31}O_5N$	4.42	4.35
$C_{11}H_{23}$-*n*	NH_2	CH_2OH	103.9					$C_{16}H_{33}O_3N$	4.88	4.83
C_6H_5	NO_2	CH_3	118.3					$C_{11}H_{13}O_4N$	6.28	6.29
C_6H_5	NH_2	CH_3	84.0					$C_{11}H_{15}O_2N$	7.25	7.23

pared by mixing the aldehyde (1 mole) and amino acetal (1 mole) and letting the mixture stand for ten hours. The non-aqueous layer was separated from the water layer and dried. 5-(2-Ethylhexylidenimino)-5-ethyl-1,3-dioxane was purified by rectification *in vacuo*. 5-Benzylidenimino-5-methyl-2-propyl-1,3-dioxane was purified by recrystallization from petroleum ether. The conversions of amino acetals to imino acetals averaged about 80%.

The alkylidenimino acetals were reduced to the corresponding alkylamino acetals. One hundred grams of the imine dissolved in 400 ml. of methanol was hydrogenated for two to three hours at 80° at 1000 to 1500 lb. pressure in the presence of 5 g. of Raney nickel catalyst. Conversions were 90%.

Nitrogen was determined by the method of Dumas. The specific gravity, refractive index and boiling point of each of the liquid nitro acetals and melting point of each of the solid nitro acetals were determined and are listed in Table I. The amino acetals, the alkylidenimino acetals and the alkylamino acetals together with certain properties are also set forth in Table I.

Acknowledgments.—The author is indebted to Mr. C. E. Watts for the determinations of nitrogen percentages, specific gravities and refractive indexes and to Dr. John A. Riddick for determinations of melting points.

Summary

1. Butyraldehyde, α-ethylbutyraldehyde, heptaldehyde, α-ethylhexaldehyde and lauraldehyde acetals of *tris*-(hydroxymethyl)-nitromethane; formaldehyde, butyraldehyde, α-ethylhexaldehyde and benzaldehyde acetals of 2-nitro-2-methyl-1,3-propanediol; and formaldehyde, α-ethylhexaldehyde, and lauraldehyde acetals of 2-nitro-2-ethyl-1,3-propanediol have been prepared and certain of their properties determined.

2. Each of these nitro acetals was converted to the corresponding amino acetal by catalytic hydrogenation. Certain properties of these amino acetals were also ascertained.

3. Three alkylidenimino acetals were prepared and then reduced to the corresponding alkylamino acetals.

TERRE HAUTE, INDIANA RECEIVED MAY 8, 1941