By recrystallization twice from ethyl acetate–ligroin there was obtained one-half gram of 4,6-dichlorodiphenic acid (I) white needles, m. p. 216–217°.

Anal. Calcd. for $C_{14}H_8O_4Cl_2$: Cl, 22.8; neut. equiv., 155.5. Found: Cl, 23.0; neut. equiv., 154.

Because of the difficulties in isolating this material the quantitative determination of its formation was carried out by treatment of the original crude with concentrated sulfuric acid (see below).

A number of experiments were performed in which mixtures of diazotized anthranilic acid and diazotized *o*- or *p*-nitroanilines were reduced. The only acidic product was pure diphenic acid.

2,4-Dichlorofluorenone-5-carboxylic Acid (II).—Three-tenths gram of 4,6-dichlorodiphenic acid was heated with 2 cc. of concentrated sulfuric acid for ten minutes at 150° or for two days at 80°. The resulting solution was poured on ice and the yellow solid dissolved in warm dilute bicarbonate solution (in some experiments the sodium salt crystallized if the solution was cooled). After reprecipitation with dilute hydrochloric acid it was recrystallized from benzene–alcohol as yellow needles, m.p. 240–242°.

Anal. Calcd. for $C_{14}H_6O_3Cl_2$: Cl, 24.2; neut. equiv., 293. Found: Cl, 24.2, 24.3; neut. equiv., 293, 294.

The formation and isolation of this substance proved to be a convenient method for estimating the amount of 4,6-dichlorodiphenic acid when the latter was mixed with both diphenic acid and 4,6,4′,6′-tetrachlorodiphenic acid as in the crude reduction product. In a typical run 14 g. of crude was heated with 45 cc. of concentrated sulfuric acid at 150° for ten minutes or at 80° for three days. The solution was cooled and 2.6 g. (28% yield) of *d,l*-4,6,4′,6′-tetrachlorodiphenic acid filtered off. The filtrate was poured on ice and the resulting yellow solid dissolved in warm dilute bicarbonate solution and filtered free from a small amount of non-acidic material. Reprecipitation with dilute hydrochloric acid gave 6 g. of mixed fluorenone carboxylic acids. There was evidence for the presence of water soluble sulfonation products which were removed at this point. Separate experiments showed that they were derived chiefly but not entirely from the diphenic acid. The acid mixture was recrystallized from a mixture of nine parts of benzene and one part of alcohol. The first fractions were pure 2,4-dichlorofluorenone-5-carboxylic acid, m. p. 240–242°. A total of 2.5 g. melting in the range 235–241° was obtained in some runs. A separate experiment showed that when mixtures of diphenic acid and tetrachlorodiphenic acid were heated in concentrated sulfuric acid no dichlorofluorenone carboxylic acid was formed. Thus the 2.5 g. isolated above corresponds to an 18% yield of 4,6-dichlorodiphenic acid in the reduction reaction.

Summary

1. By reduction with cupro-ammonia ion in dilute ammonium hydroxide the diazotized forms of the following amines are converted to biaryls in yields of 20–90%: the nitroanilines, the nitrotoluidines, anthranilic acid, a variety of halogeno- and nitroanthranilic acids, a number of aminonaphthalene carboxylic acids, *o*-aminobenzenesulfonic acid.

2. The following yield azo compounds in yields of 20–50%: aniline, the toluidines, *p*-aminophenol, *p*-aminoacetanilide, *m*- and *p*-aminobenzoic acids.

3. Reduction of a mixture of diazotized anthranilic and 3,5-dichloro-2-aminobenzoic acids produces the unsymmetrical biaryl 4,6-dichlorodiphenic acid (I) in addition to the usual symmetrical products.

4. 4,6-Dichlorodiphenic acid is converted to 2,4-dichlorofluorenone-5-carboxylic acid (II) by heating with concentrated sulfuric acid.

DURHAM, N. H. RECEIVED JULY 14, 1945

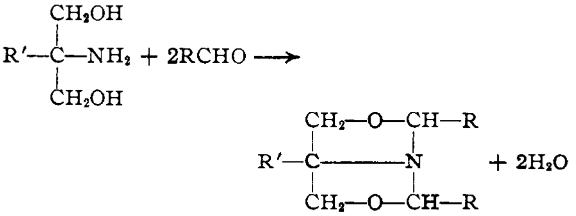
[CONTRIBUTION FROM THE RESEARCH AND DEVELOPMENT DEPARTMENT OF THE COMMERCIAL SOLVENTS CORP.]

Some New Derivatives of Amino Hydroxy Compounds[1]

BY MURRAY SENKUS

Amino alcohols which have an amino group or a monosubstituted amino group and an alcohol group attached to adjacent carbon atoms are known to react with aldehydes to form oxazolidines. A large number of new amino alcohols have recently become available from the hydrogenation of nitro alcohols that can be prepared by allowing one mole of a nitroparaffin to react with one mole of an aldehyde.[2] Some of these amino alcohols have been converted to oxazolidines and the new compounds are reported herein.

A study was also made of the reaction of aldehydes with amino polyhydric alcohols that can be prepared by the hydrogenation of nitro polyhydric alcohols derivable from normal nitroparaffins and formaldehyde.[2] Two types of products were obtained from the above reactions. The reaction of one mole of an aldehyde with one mole of an amino polyhydric alcohol gave an oxazolidine. The reaction of two moles of an aldehyde with one mole of an amino polyhydric alcohol gave substituted 1-aza-3,7-dioxabicyclo-[3.3.0]octanes according to the scheme



The structures chosen for the new compounds are supported by analytical data and by the observation that in each reaction one mole of amino polyhydric alcohol and 2 moles of an aldehyde yielded 2 moles of water and the amount of product calculated according to the above equation.

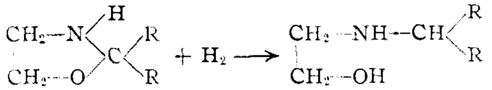
---

[1] The portion of this article describing the reactions of aldehydes with the amino polyhydric alcohols was originally received by us on September 7, 1943.—*The Editor.*

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

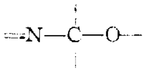
Further confirmation of the new structure was obtained by studying the hydrogenation of these compounds as well as their reaction with Grignard reagents.

Cope and Hancock[3] had shown that hydrogenation of oxazolidines derivable from 2-aminoethanol gave 2-alkylaminoethanols according to the equation



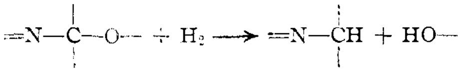
We studied the hydrogenation of other oxazolidines derived from 2-aminoethanol as well as other amino alcohols and isolated the expected N-alkylamino alcohol in each experiment. The N-alkylamino alcohols were allowed to react with aldehydes. This reaction gave N-substituted oxazolidines. The N-substituted oxazolidines were also hydrogenated. These hydrogenations yielded the expected dialkylamino alcohols.

An examination of the structures of oxazolidines and the 1-aza-3,7-dioxabicyclo[3.3.0]octanes will reveal that the grouping



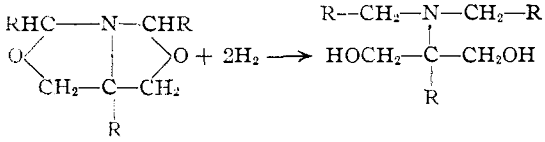
$$=N-\overset{|}{\underset{|}{C}}-O-$$

is common to both structures. During the hydrogenation of the oxazolidines the grouping at hand is split as set forth below

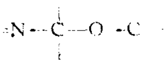


$$=N-\overset{|}{\underset{|}{C}}-O- + H_2 \longrightarrow =N-\overset{|}{\underset{|}{C}}H + HO-$$

A similar splitting of this grouping in the 1-aza-3,7-dioxabicyclo[3.3.0]octanes would be expected to take place if these compounds were hydrogenated. The hydrogenation of these compounds was tried and the expected dialkylamino polyhydric alcohol was isolated in each experiment. This reaction is represented by the equation



The grouping



$$=N-\overset{|}{\underset{|}{C}}-O-C$$

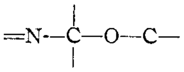
which is common to oxazolidines and 1-aza-3,7-dioxabicyclo[3.3.0]octanes is also present in compounds of the type

$$R_2N-CH_2-O-R$$

Robinson and Robinson[4] had found that these compounds will react with Grignard reagents according to the scheme

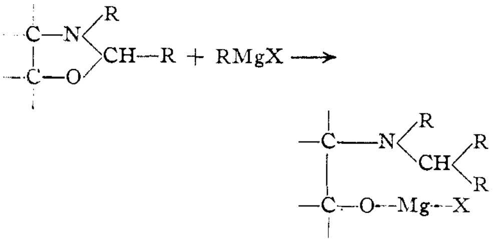
$$R_2N-CH_2-O-R + RMgCl \longrightarrow R_2N-CH_2-R + R-O-Mg-Cl$$

In view of the above reaction the Grignard reagent would be expected to effect a similar splitting of the

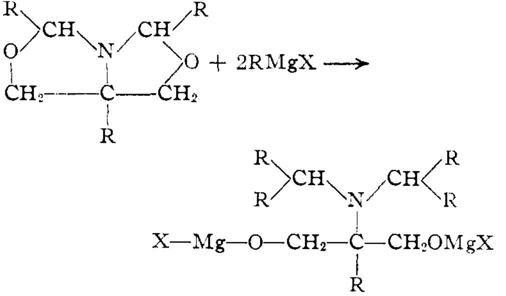


$$=N-\overset{|}{\underset{|}{C}}-O-C-$$

grouping in the N-substituted oxazolidines and in the 1-aza-3,7-dioxabicyclo[3.3.0]octanes. These reactions were tried and the expected dialkylamino hydroxy compound was isolated from each experiment. These reactions are set forth in the equations below.



(1)



(2)

Experimental

Preparation of Oxazolidines and 1-Aza-3,7-dioxabicyclo[3.3.0]octanes.—The oxazolidines were prepared by refluxing mixtures of one mole of aldehyde, one mole of amino alcohol and 150 ml. of benzene in a flask connected to a Dean and Stark moisture trap[5] which was connected to a condenser. The 1-aza-3,7-dioxabicyclo[3.3.0]octanes were prepared by refluxing mixtures of two moles of aldehyde, one mole of amino polyhydric alcohol and 200 ml. of benzene. After water had ceased separating in the above reactions, the benzene was removed by distillation. The crude products were purified by rectification *in vacuo* or by recrystallization from a suitable solvent. The new oxazolidines are listed in Table I. The 1-aza-3,7-dioxabicyclo-[3.3.0]octanes are listed in Table II.

Hydrogenation of Oxazolidines to Alkylamino and Dialkylamino Alcohols.—The procedure for the hydrogenation of oxazolidines and N-monosubstituted oxazolidines to alkylamino alcohols and dialkylamino alcohols, respectively, with the exception of 4,4-dimethyl-2-phenyloxazolidine was as follows:

One hundred grams of an oxazolidine dissolved in 100 ml. of methanol was hydrogenated in the presence of 5 g. of 1% palladium charcoal at 100° and 1000 lb./sq. in. The mixture was filtered and the filtrate was rectified through a laboratory column. The conversions of oxazolidines to alkylamino or dialkylamino alcohols averaged about 90%.

The hydrogenation of 4,4-dimethyl-2-phenyloxazolidine according to the above method gave toluene and 2-amino-2-methyl-1-propanol but no 2-benzylamino-2-methyl-1-propanol. Debenzylations of this type have been reported by Peyer[6] and by Baltzly and Buck.[7] However, at 35-

---

[3] Cope and Hancock, THIS JOURNAL, **64**, 1503 (1942).

[4] Robinson and Robinson *J. Chem. Soc.*, **123**, 532 (1923).

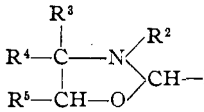
[5] Dean and Stark, *Ind. Eng. Chem.*, **12**, 486 (1920).

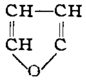
[6] Peyer, U. S. Patent 2,243,977.

[7] Baltzly and Buck, THIS JOURNAL, **65**, 1984 (1943).

TABLE I

SOME OXAZOLIDINES OF THE TYPE

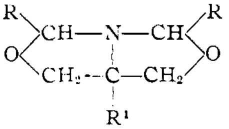


No.	R¹	R²	R³	R⁴	R⁵	Conversion	B. p., °C.	B. p., mm.	n^{20}_D	d^{20}_{20}	Formula	Nitrogen, % Calcd.	Nitrogen, % Found
1	$(CH_3)_2CH$	H	H	H	H	92	62.0- 62.5	30	1.4463	0.9215	$C_6H_{13}NO$	12.16	12.15
2	H	$(CH_3)_2CHCH_2$	H	H	H	80	66 - 68	30	1.4352	0.9066	$C_7H_{15}NO$	10.84	10.76
3	$(CH_3)_2CH$	$(CH_3)_2CHCH_2$	H	H	H	90	72 -73	10	1.4358	0.8700	$C_{10}H_{11}NO$	8.18	8.19
4	C_6H_5	H	CH_3	H	C_6H_5	84	99.5[a]				$C_{16}H_{17}NO$	5.85	5.81
5	C_6H_5	$C_6H_5CH_2$	CH_3	H	C_6H_5	79	190 -193	0.2	1.5873	1.12	$C_{21}H_{23}NO$	4.25	4.29
6	$(C_2H_5)_2CH$	H	CH_3	CH_3	H	65	78 - 79	10	1.4424	0.8895	$C_{10}H_{21}NO$	8.18	8.09
7	H	$(C_2H_5)_2CHCH_2$	CH_3	CH_3	H	94	93 - 95	10	1.4464	0.8898	$C_{11}H_{23}NO$	7.56	7.33
8	C_6H_5	H	CH_3	CH_3	H	99	66.0[a]				$C_{11}H_{15}NO$	7.90	7.82
9	C_3H_7	H	CH_3	CH_3	C_3H_7	65	80	2.7	1.4418	0.8884	$C_{11}H_{23}NO$	7.56	7.19
10	H	C_4H_9	CH_3	CH_3	C_3H_7	89	97	5	1.4477	0.8829	$C_{12}H_{25}NO$	7.03	7.06
11	C_6H_5	H	CH_3	CH_3	C_3H_7	87	90 - 92	0.1	1.4515	0.9876	$C_{14}H_{21}NO$	6.39	6.15
12	H	$C_6H_5CH_2$	CH_3	CH_3	C_3H_7	84	111	0.3	1.5079	0.9776	$C_{15}H_{23}NO$	6.00	6.03
13	H	$C_6H_5CH_2$	CH_3	CH_3	H	96	110.0-110.5	4	1.5166	1.0134	$C_{12}H_{17}NO$	7.32	7.30
14	$\begin{matrix}C_4H_9\\C_2H_5\end{matrix}\!>CH$	H	CH_3	CH_3	H	98	89 - 90	4	1.4460	0.8780	$C_{12}H_{25}NO$	7.03	6.94
15		H	CH_3	CH_3	H	60	73.0[a]				$C_8H_{13}NO_2$	8.38	8.37
16	C_3H_7	H	CH_3	CH_2OH	H	80	65.0[a]				$C_8H_{17}NO_2$	8.80	8.64

[a] Melting point.

TABLE II

SOME 1-AZA-3,7-DIOXABICYCLO[3.3.0]OCTANES OF THE TYPE



R	R¹	Conversion	B. p., °C.	B. p., mm.	n^{20}_D	d^{20}_{20}	Formula	Nitrogen, % Calcd.	Nitrogen, % Found
H	H	77	66.5	10	1.4715	1.1850	$C_5H_9NO_2$	12.17	12.17
H	CH_3	97	60.0	10	1.4590	1.1088	$C_6H_{11}NO_2$	10.85	11.05
H	C_2H_5	94	74.5	10	1.4618	1.0829	$C_7H_{13}NO_2$	9.78	9.79
H	C_3H_7	95	90-91	10	1.4604	1.0522	$C_8H_{15}NO_2$	8.91	8.85
H	$(CH_3)_2CH$	90	84-85	10	1.4631	1.0602	$C_8H_{15}NO_2$	8.91	8.92
H	CH_2OH	90	65[a]				$C_6H_{11}NO_3$	9.65	9.86
C_3H_7	CH_3	94	94-95	10	1.4494	0.9594	$C_{12}H_{23}NO_2$	6.60	6.63
C_3H_7	C_2H_5	81	104.5	10	1.4544	0.9599	$C_{13}H_{25}NO_2$	6.16	6.37
$\begin{matrix}C_4H_9\\C_2H_5\end{matrix}\!>CH$	CH_3	70	114-118	0.5	1.4601	0.9276	$C_{20}H_{39}NO_2$	4.30	4.32
C_6H_5	CH_3	95	123.0[a]				$C_{18}H_{19}NO_2$	4.98	5.04

[a] Melting point.

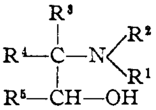
45° debenzylation did not occur. The solution from the low temperature hydrogenation was distilled to remove the methanol. The residue from this distillation solidified on cooling. The crude 2-benzylamino-2-methyl-1-propanol was purified by recrystallization from cyclohexane. The new alkylamino and dialkylamino alcohols are listed in Table III.

Hydrogenation of 1-Aza-3,7-dioxabicyclo[3.3.0]octanes to Dialkylamino Polyhydric Alcohols.—One hundred grams of 1-aza-3,7-dioxabicyclo[3.3.0]octane dissolved in 400 ml. of methanol was hydrogenated at 100° and 1000 lb./sq. in. in the presence of 10 g. of Raney nickel catalyst. The mixture was filtered and the filtrate was distilled to remove the methanol. The residue was purified by rectification *in vacuo* or by crystallization from a suitable solvent. The dialkylamino polyhydric alcohols are listed in Table IV.

Reaction of Grignard Reagents with N-Substituted Oxazolidines.—The procedures for the reaction of Grignard reagents with N-substituted oxazolidines were all similar. The reaction of methylmagnesium iodide with 3-isobutyl-2-isopropyloxazolidine is described below to serve as an example. The Grignard reagent was prepared from 8 g. (0.33 mole) of magnesium turnings and 40 g. (0.31 mole) of methyl iodide in 300 ml. of ethyl ether. While this solution was stirred, 51.5 g. (0.31 mole) of 3-isobutyl-2-isopropyloxazolidine in 300 ml. of ether was added at such a rate that the mixture in the reaction flask refluxed gently. The mixture was allowed to stand in the room for twenty-four hours, and then while it was stirred 20 ml. of water was added dropwise to hydrolyze the Grignard addition product. A further 130 ml. of water was added and stirring was continued for three hours. The mixture was allowed to settle for fifteen minutes and the top ether layer was separated from the thick aqueous layer by decantation. The aqueous layer was extracted with two 200-ml. portions of ether. The ether solutions were combined and the composite was rectified. This distillation yielded 54 g. of N-isobutyl-N-(1,2-dimethylpropyl)-2-aminoethanol, b. p. 104.5–105.0° at 10 mm.; conversion, 96%.

It is noteworthy that in one experiment of the above type a side reaction occurred. Hydrolysis of the product from the reaction of isopropylmagnesium bromide with 3-

TABLE III

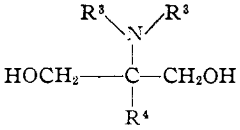
SOME AMINO ALCOHOLS OF THE TYPE 

$$R^4-\overset{\displaystyle R^3}{\underset{\displaystyle R^5-CH-OH}{C}}-N\begin{matrix}R^2\\R^1\end{matrix}$$

Starting materials: Oxazolidine reference no.	Starting materials: Reducing reagent	R¹	R¹	R¹	R⁴	R⁵	Conversion	B. p., °C.	B. p., mm.	$n^{20}D$	d^{20}_{20}	Formula	Nitrogen, % Calcd.	Nitrogen, % Found
1	H	$(CH_3)_2CHCH_2$	H	H	H	H	85	81 - 82	10	1.4370	0.8844	$C_6H_{15}NO$	11.95	11.85
2	$(CH_3)_2CHMgCl$	$(CH_3)_2CHCH_2$	$(CH_3)_2CHCH_2$	H	H	H	75	89[a]	10	1.4355	.8433	$C_{10}H_{23}NO$	8.08	7.96
3	H	$(CH_3)_2CHCH_2$	$(CH_3)_2CHCH_2$	H	H	H	92	89[b]	10					
3	$(CH_3)_2CHMgBr$	$[(CH_3)_2CH]_2CH$	$(CH_3)_2CHCH_2$	H	H	H	35	112.5-113.0	4	1.4600	.8819	$C_{13}H_{29}NO$	6.50	6.40
3	CH_3MgI	$(CH_3)_2CH(CH_3)CH$	$(CH_3)_2CHCH_2$	H	H	H	96	104.5-105.0	10	1.4462	.8647	$C_{11}H_{25}NO$	7.48	7.45
4	H	$C_6H_5CH_2$	H	CH_3	H	C_6H_5	70	100.5[c]				$C_{16}H_{19}NO$	5.80	5.80
5	CH_3MgI	$C_6H_5CH_2$	$(C_6H_5)(CH_3)CH$	CH_3	H	C_6H_5	90	190 -193	0.2	1.5845	1.06	$C_{24}H_{27}NO$	4.05	4.21
6	H	$(C_2H_5)_2CHCH_2$	H	CH_3	CH_3	H	85	89 - 90	4	1.4526	0.8751	$C_{10}H_{23}NO$	8.08	8.06
7	C_2H_5MgBr	$(C_2H_5)_2CHCH_2$	C_3H_7	CH_3	CH_3	H	80	105	4	1.4538	.8746	$C_{13}H_{29}NO$	6.50	6.48
8	H	$C_6H_5CH_2$	H	CH_3	CH_3	H	85	67.6[c]				$C_{11}H_{17}NO$	7.81	7.86
9	H	C_4H_9	H	CH_3	CH_3	C_3H_7	86	63	0.3	1.4475	.8685	$C_{11}H_{25}NO$	7.48	7.52
10	C_3H_7MgCl	C_4H_9	C_4H_9	CH_3	CH_3	C_3H_7	75.	86.5- 87.0	.2	1.4529	.8634	$C_{15}H_{33}NO$	5.75	5.79
11	H	$C_6H_5CH_2$	H	CH_3	CH_3	C_3H_7	80	112	.3	1.5100	.9733	$C_{14}H_{23}NO$	6.33	6.33
12	CH_3MgI	$C_6H_5CH_2$	C_2H_5	CH_3	CH_3	C_3H_7	86	110 -112	.2	1.5082	.9617	$C_{16}H_{27}NO$	5.62	5.63

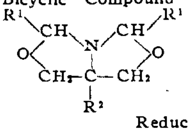
[a,b] Melting points of picrates and of a mixture of these picrates, 122.5°. [c] Melting point.

TABLE IV

SOME AMINO POLYHYDRIC ALCOHOLS OF THE TYPE 

$$HOCH_2-\overset{\displaystyle R^3\diagdown_{N}\diagup R^3}{\underset{\displaystyle R^4}{C}}-CH_2OH$$

Starting materials
Bicyclic Compound



R¹	R²	Reducing reagent	R³	R⁴	Conversion	B. p., °C.	B. p., mm.	d^{20}_{20}	$n^{20}D$	Formula	Nitrogen, % Calcd.	Nitrogen, % Found
H	H	C_4H_9MgCl	C_5H_{11}	H	80	132-134	0.2	0.9260	1.4620	$C_{11}H_{11}NO_1$	6.00	6.11
H	CH_2OH	C_4H_9MgCl	C_4H_{11}	CH_2OH	70	170	0.2	.9919	1.4752	$C_{14}H_{31}NO_1$	5.32	5.57
C_1H_7	CH_1	C_2H_1MgBr	$\begin{matrix}C_1H_7\\C_1H_6\end{matrix}>CH$	CH_3	50	152-153	1	.9493	1.4777	$C_{15}H_{15}NO_2$	5.12	5.22
H	CH_1	C_3H_7MgCl	C_4H_9	CH_1	82	123	1	.9440	1.4665	$C_{12}H_{27}NO_1$	6.44	6.54
C_1H_7	CH_1	H	C_4H_9	CH_3	18	123	I	.9487	1.4659	$C_{12}H_{17}NO_1$	6.44	6.47
H	CH_1	C_6H_5MgBr	$C_6H_4CH_2$	CH_3	71	121[a]				$C_{18}H_{22}NO_2$	11.09[b]	11.19[b]
H	CH_2OH	H	CH_3	CH_2OH	85	90[a]				$C_6H_{15}NO_3$	9.39	9.55
H	CH_1	H	CH_3	CH_1	79	56[a]				$C_6H_{15}NO_2$	10.52	10.80
H	C_2H_5	H	CH_3	C_2H_5	93	32[a]				$C_7H_{17}NO_2$	9.51	9.45

[a] Melting point. [b] Chlorine content of hydrochloride.

isobutyl-2-isopropyloxazolidine yielded besides the expected product some 2-diisobutylaminoethanol. This reducing reaction of some Grignard reagents has been observed by Conant[8] and by Kharasch[9] in their work on the reaction of Grignard reagents with some highly branched ketones. The dialkylamino alcohols prepared by this method are listed in Table III.

Reaction of Grignard Reagents with 1-Aza-3,7-dioxabicyclo[3.3.0]octanes.—The procedures for the reaction of Grignard reagents with 1-aza-3,7-dioxabicyclo[3.3.0]octanes and the isolation of products were the same as in the above reaction, except that the molar ratio of Grignard reagent to bicyclic compound was 2:1 in the experiments in which a 5-alkyl-1-aza-3,7-dioxabicyclo[3.3.0]octane or 1-aza-3,7-dioxabicyclo[3.3.0]octane was used and 3:1 in the experiment in which 5-hydroxymethyl-1-aza-3,7-dioxabicyclo[3.3.0]octane was used. The dialkylamino polyhydric alcohols that were prepared by this method are listed in Table IV.

Discussion

The identity of the products from the hydrogenation of oxazolidines has been established by Cope and Hancock. The structures of the products from the reaction of Grignard reagents with N-substituted oxazolidines are supported by analytical data. Comparison of 2-diisobutylaminoethanol which was obtained by hydrogenating 3-isobutyl-2-isopropyloxazolidine with the product which was obtained by hydrolyzing the Grignard addition product from the reaction of isopropylmagnesium chloride with 3-isobutyloxazolidine reveals that the two materials are identical. Each product boiled at 89° at 10 mm., and the picrate of each product as well as a mixture of the two picrates melted at 122.5°. This additional datum adds further proof to the mechanism of the reaction of Grignard reagents with N-substituted oxazolidines.

The structures of the products from hydrogenation of 1-aza-3,7-dioxabicyclo[3.3.0]octanes as well as the structures of the products from the reaction of Grignard reagents with these bicyclic compounds are supported by analytical data. These data in turn support the proposed structures of the 1-aza-3,7-dioxabicyclo[3.3.0]octanes. The preparation of 2-dibutylamino-2-methyl-1,3-propanediol by the Grignard method (from *n*-propyl chloride and 5-methyl-1-aza-3,7-dioxabicyclo[3.3.0]octane) and by the hydrogenation method (hydrogenation of 2,8-dipropyl-5-methyl-1-aza-3,7-dioxabicyclo[3.3.0]octane) provides further proof of the structures of the 1-aza-3,7-dioxabicyclo[3.3.0]octanes and the mechanism of the reactions of these compounds which are proposed earlier in the paper and reported herein.

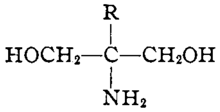
Summary

Some new oxazolidines have been prepared from aldehydes and amino alcohols as well as N-alkylamino alcohols.

Some of the oxazolidines that were prepared were hydrogenated to N-alkylamino and N-dialkylamino alcohols.

The reaction of Grignard reagents with N-substituted oxazolidines was studied. A N-dialkylamino alcohol was isolated from each of these experiments. The mechanism for this reaction is discussed.

1-Aza-3,7-dioxabicyclo[3.3.0]octanes were prepared from some amino polyhydric alcohols of the type



$$HOCH_2-\underset{NH_2}{\overset{R}{C}}-CH_2OH$$

and some aldehydes. Catalytic hydrogenation of these compounds gave dialkylamino polyhydric alcohols. The reaction of Grignard reagents with 1-aza-3,7-dioxabicyclo[3.3.0]octanes gave addition products which on hydrolysis yielded dialkylamino polyhydric alcohols. Mechanisms of these reactions are discussed.

TERRE HAUTE, INDIANA RECEIVED JUNE 13, 1945

---

(8) Conant and Blatt, THIS JOURNAL, **51**, 1227 (1929).

(9) Kharasch and Weinhouse, *J. Org. Chem.*, **1**, 209 (1936).

[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY AT CORNELL UNIVERSITY]

Polymerization of Nitroölefins. The Preparation of 2-Nitropropene Polymer and of Derived Vinylamine Polymers

BY A. T. BLOMQUIST, W. J. TAPP AND JOHN R. JOHNSON

Despite the large variety of synthetic high polymers recorded in the chemical literature, there is no description of a polymeric amine with recurring primary amino groups attached directly to a long carbon chain, such as $(-CHNH_2-CH_2-)_n$. Polymers of acyl derivatives of vinylamine, such as N-vinylimide and vinyl isocyanate polymers, have been described but efforts to obtain a vinylamine polymer from these acyl derivatives or by other routes have failed.[1]

The reported polymerization of nitroethylene[2] and 1-nitropropene[3] suggested a possible indirect synthesis of a vinylamine polymer by reduction of an appropriate nitroölefin polymer.

$$(-CHNO_2-CH_2-)_n \xrightarrow{H} (-CHNH_2-CH_2-)_n$$

Attempts to reduce nitroethylene polymer to vinylamine polymer have not succeeded,[1] but this may be due to the circumstance that nitroethylene polymer is probably highly cross-linked

---

(1) Jones, Zomlefer and Hawkins, *J. Org. Chem.*, **9**, 500 (1944). This paper surveys various methods for obtaining vinylamine polymers.

(2) Wieland and Sakellerios, *Ber.*, **52**, 898 (1919).

(3) Schmidt and Rutz, *ibid.*, **61**, 2142 (1928).