[Chem. Pharm. Bull. 20(8)1762—1767(1972)]

UDC 547.867.04 : 542.941.7

Catalytic Hydrogenation of Tetrahydro-4*H*-1,3-oxazin-4-ones and 4-Oxazolidinones

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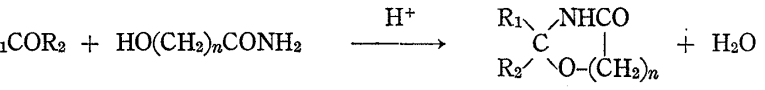
(Received January 21, 1972)

For the present investigation on catalytic hydrogenation the compounds in which both amide nitrogen and ether oxygen are bound to the same carbon were provided as several cyclic compounds such as tetrahydro-4*H*-1,3-oxazin-4-ones and 4-oxazolidinones, the former being newly prepared in the present work. Our objective was to know the condition of possible hydrogenolysis, which may proceed at either one of the two carbon bonds. The hydrogenolyses proceeded in acetic acid solvent over palladium-on-charcoal catalyst under high hydrogen pressure and, from the results of product analyses, were shown to be selectively effected at the carbon-oxygen bond of the compounds.

The catalytic hydrogenolyses of the compounds possessing two different nitrogens or both oxygen and nitrogen bound to the same carbon atom have been reported from this laboratory with series of N-(dialkylaminomethyl)amides,[2] N-(α-dialkylaminobenzyl)amides[3] and N-(α-alkoxybenzyl)dialkylamines,[3] and the bond which is susceptible to preferential hydrogenolysis has been made clear. In continuation of this study we were tempted to see which bond is initially susceptible to hydrogenolysis in the compound possessing both amide nitrogen and ether oxygen bound to the same carbon. Although several labile or specific open-chain compounds of this type have been known, for the present study we thought it preferable to select the compounds of cyclic system such as tetrahydro-4*H*-1,3-oxazin-4-ones and 4-oxazolidinones.

The preparations of 2-alkyl-substituted derivatives of tetrahydro-4*H*-1,3-oxazin-4-one and 4-oxazolidinone were performed by condensation of carbonyl compounds with hydracrylamide and glycolamide, respectively, in the presence of acid catalyst.



in the case of $n=2$
R_1 and R_2: C_6H_5, H; CH_3, H; C_6H_5, CH_3; CH_3, CH_3; $(CH_2)_5$
in the case of $n=1$
R_1 and R_2: C_6H_5, H; CH_3, CH_3; $(CH_2)_5$

Except 2,2-dimethyl-4-oxazolidinone,[4] these seven compounds have not been described previously. For most runs sulfuric acid was suitable as acid catalyst. Since the reactions were reversible, water formed during the course of the reaction was removed by the azeotropic distillation method and by the method of using Soxlet apparatus packed with solid drying agent such as anhydrous magnesium sulfate and calcium oxide. By these methods sufficient yields of the desired products were obtained in most runs, although the following side reactions were inevitable to some extent. Hydracrylamide is apt to undergo dehydration to acrylamide followed by successive polymerization in the presence of the acid catalyst. This side reaction proceeded to some extent to give gelatinous polymerization product, along with the formation of tetrahydro-4*H*-1,3-oxazin-4-ones. Partial hydrolysis of the amide also

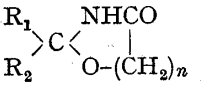
1) Location: *2-2-1 Oshika, Shizuoka.*
2) M. Sekiya and K. Ito, *Chem. Pharm. Bull.* (Tokyo), **14**, 996 (1966).
3) N. Sakura, K. Ito and M. Sekiya, *Chem. Pharm. Bull.* (Tokyo), **20**, 1156 (1972).
4) H.O.L. Fischer, G. Dangschat and H. Stettiner, *Ber.*, **65**, 1032 (1932).

occurred, where sulfuric acid was partly neutralized with the ammonia formed. An attempt to obtain unsubstituted tetrahydro-4*H*-1,3-oxazin-4-one from formaldehyde and hydracrylamide failed, resulting in the formation of the further condensation product, 3,3'-methylene-bis(tetrahydro-4*H*-1,3-oxazin-4-one).

Tetrahydro-4*H*-1,3-oxazin-4-ones and 4-oxazolidinones thus obtained showed the characteristic infrared (IR) absorption band of lactam carbonyl at 1658—1680 cm^{-1} for the former six-membered compounds and at 1692—1740 cm^{-1} for the latter five-membered compounds. The nuclear magnetic resonance (NMR) spectra of the tetrahydro-4*H*-1,3-oxazin-4-ones possessing one substituent or two different substituents at the C_2 position, such as 2-phenyl, 2-methyl, and 2-methyl-2-phenyl derivatives, exhibited the multiplet signals in deuterochloroform due to four spin system of the methylene protons at C_5 and C_6, while 2,2-dimethyl and 2,2-cyclopentamethylene derivatives exhibited the simple triplet signals for each set of the methylene protons. Among the 4-oxazolidinones, 2-phenyl-4-oxazolidinone exhibited the proton coupling between the C_5 and C_6 protons (coupling constant, 2 cps). Similar long range coupling across the five-membered heterocyclic system has been reported[5] in the NMR spectrum of 2,5-bis(trichloromethyl)-1,3-dioxolan-4-one.

Catalytic hydrogenation of the compounds thus obtained, which possess both nitrogen and oxygen bonds attached to the same carbon in ring system, was then investigated. On survey of literature there has been reported[6] the catalytic hydrogenation of 2,2-dimethyl-5-phenyl-4-oxazolidinone over copper chromite catalyst at high temperature (210—215°), but the formations of the products, mandelamide, phenylethyleneglycol, phenethyl alcohol and diisopropylamine, are not worthwhile to suggest any process of hydrogenolysis. Detailed investigation was made with tetrahydro-2-phenyl-4*H*-1,3-oxazin-4-one (I) as a model substrate. Resistance toward hydrogenation was observed in ethanol and dioxane as solvent over Raney nickel and palladium-on-charcoal catalyst, however, hydrogenation proceeded when acetic acid was used as a solvent at an elevated temperature under high pressure of hydrogen over palladium-on-charcoal catalyst. Based on the preliminary confirmation of their stability in acetic acid at elevated temperature, the other tetrahydro-4*H*-1,3-oxazin-4-ones and 4-oxazolidinones were also subjected to the hydrogenation under the same conditions, and the results are summarized in Table I.

Table I. Catalytic Hydrogenation of 2-Substituted Tetrahydro-4*H*-1,3-oxazin-4-ones and 4-Oxazolidinones

Substrate: 

n	R_1	R_2	Hydrogenation Temp. (°C)	Hydrogenation Time (min)	Yield (%)[b] of product[c] A	B	C	D	Total
2	C_6H_5	H	80— 85	240	92	—	—	—	92
2	CH_3	H	130—135	380	—	38	58	trace	96
2	C_6H_5	CH_3	125—130	350	—	2	25	68	95
2	CH_3	CH_3	155—160	160	—	—	41	52	93
1	C_6H_5	H	95—100	120	95	—	—	—	95
1	CH_3	CH_3	160—165	160	21	73	—	—	94

a) substrate: 0.04 mole; solvent: AcOH 100 ml; catalyst: 10% Pd-C 1 g; initial hydrogen pressure: 80 kg/cm² (at room temp.)

b) Yield is based on the product actually isolated.

c) A: $\frac{R_1}{R_2}$>CHNHCO$(CH_2)_n$OH; B: $\frac{R_1}{R_2}$>CHNHCO$(CH_2)_n$OCOCH$_3$; C: $\frac{R_1}{R_2}$>CHNHCOC_2H_5; D: $C_2H_5CONH_2$

5) "NMR Spectra Catalog," Vol. 2, No. 425, Varian Associates, California, 1963.

6) D.D'Ianni and H. Adkins, *J. Am. Chem. Soc.*, **61**, 1675 (1939).

As shown in Table I, among the tetrahydro-4*H*-1,3-oxazin-4-ones, I suffered hydrogenolysis exclusively at the C_2-O bond at moderate temperature to give N-benzylhydracrylamide in excellent yield. However, the other three compounds more resisted the hydrogenation, requiring higher temperature and longer reaction period. Careful fractional distillation of the reaction mixture gave three kinds of the products, N-substituted 3-acetoxypropionamide (B), N-substituted propionamide (C) and propionamide (D), and no expected hydrogenolysis product, N-substituted hydracrylamide (A), was obtained. Likely route for the formation of these products is shown in Chart 1.

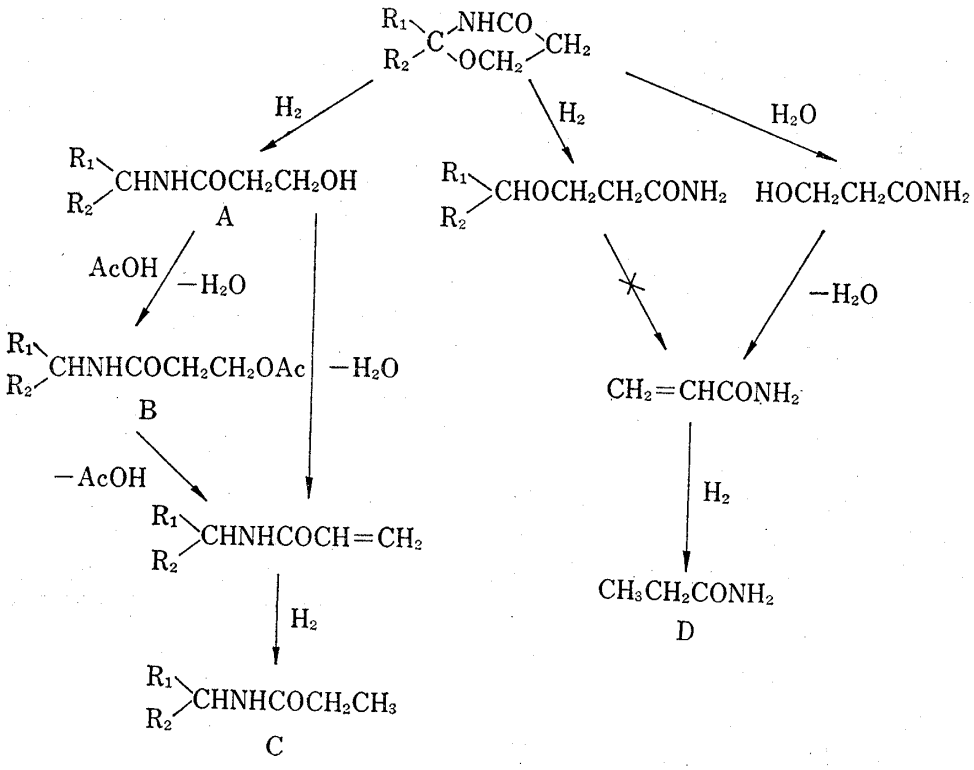


Chart 1

The products, B and C, are regarded as those formed from the direct hydrogenolysis product A by successive reactions. B may be the product formed by the acetylation of A with acetic acid solvent, and C may be the product derived by the dehydration of A and/or the elimination of acetic acid from B, followed by hydrogenation. These conversions were substantiated by the experiment using N-ethylhydracrylamide (R_1=CH_3, R_2=H) as a representative A. The catalytic hydrogenation of this compound was carried out under the same conditions as for tetrahydro-2-methyl-4*H*-1,3-oxazin-4-one (II) and gave the expected products, 3-acetoxy-N-ethylpropionamide and N-ethylpropionamide. Route of the formation of D can be considered in the following two ways; hydrolysis of the substrate and successive dehydration of the formed hydracrylamide to acrylamide followed by hydrogenation, or hydrogenolysis of the substrate at C_2-N bond to 3-alkoxypropionamide followed by elimination of alcohol to acrylamide and successive hydrogenation. However, the latter hydrogenolysis route was excluded by the following observation that 3-isopropoxypropionamide was found to be unchanged under the same hydrogenation condition as for tetrahydro-2,2-dimethyl-4*H*-1,3-oxazin-4-one (IV). For the former route the conversion from hydracrylamide to D was actually demonstrated under the same hydrogenation conditions. Thus it would be concluded that the product A, B, and C are those formed directly or indirectly through the hydrogenolysis of the carbon-oxygen bond of the substrates, tetrahydro-4*H*-1,3-oxazin-4-ones, and the product D is formed through hydrolysis of the

substrates. From the data in Table I it can be qualitatively said that 2-phenyl substituent facilitates the hydrogenolysis of the carbon-oxygen bond and 2,2-disubstituted compounds are less reactive than 2-monosubstituted ones. A trial of catalytic hydrogenation of the compound, 3,3′-methylenebis(tetrahydro-4*H*-1,3-oxazin-4-one) which is described in the foregoing, resulted in complete recovery under the same condition even at 150—160°.

Results of catalytic hydrogenations of the five-membered 4-oxazolidinones, 2-phenyl and 2,2-dimethyl derivatives, under the same conditions are also recorded in Table I. As can be seen, the hydrogenolysis at the carbon-oxygen bond occurred exclusively to give the corresponding product and its acetate.

In summary, it is concluded that catalytic hydrogenation of the compounds of such cyclic system, which possess both amide nitrogen and ether oxygen bonds bound to the same carbon, proceeds in acetic acid solvent over palladium-on-charcoal catalyst at elevated temperature under high hydrogen pressure, where the hydrogenolysis at the carbon-oxygen bond is effected selectively.

Experimental[7]

Tetrahydro-2-phenyl-4*H*-1,3-oxazin-4-one (I)——To a solution of 60 g of benzaldehyde in 90 ml of benzene 4.5 g of hydracrylamide was dissolved and 0.45 g of H_2SO_4 was added. The mixture was refluxed for 2.5 hr, where water formed was removed from distilled benzene azeotrope. After removal of small amount of gelatinous polymer by decantation, H_2SO_4 was removed by treatment with $BaCO_3$. Concentration under reduced pressure gave the solid residue, which was washed with ether and dried. Recrystallization from benzene gave prisms, mp 121—122°. Yield, 4.5 g (51%, based on hydracrylamide). *Anal.* Calcd. for $C_{10}H_{11}O_2N$: C, 67.78; H, 6.26; N, 7.91. Found: C, 67.93; H, 6.36; N, 7.82. IR ν_{max}^{KBr} cm^{-1}: 3145, 1660 (CONH), 1094 (ether). NMR τ: 2.54 (5H, singlet, C_6H_5), 4.25 (1H, singlet, -CH<), 5.55—6.28 (2H, multiplet, $-OCH_2-$), 7.29—7.80 (2H, multiplet, $-COCH_2-$).

Tetrahydro-2-methyl-4*H*-1,3-oxazin-4-one (II)——To a solution of 11.2 g of hydracrylamide and 33.3 g of paraldehyde dissolved in 400 ml of dioxane was added 2.5 ml of conc. HCl. The mixture was placed in Soxlet apparatus packed with anhyd. $MgSO_4$ as drying agent and refluxed for 8 hr with constant stirring. After gelatinous polymer was removed by decantation, anhyd. K_2CO_3 was added to remove HCl. After filtration the resultant solution was concentrated under reduced pressure and the residue was extracted with dry warm benzene. Colorless crystals obtained by evaporation were recrystallized from benzene to prisms, mp 124—125°. Yield, 5.5 g (43%, based on hydracrylamide). *Anal.* Calcd. for $C_5H_9O_2N$: C, 52.16; H, 7.88; N, 12.17. Found: C, 52.15; H, 7.90; N, 12.17. IR ν_{max}^{KBr} cm^{-1}: 3155, 1660 (CONH), 1100 (ether). NMR τ: 1.62 (1H, broad singlet, NH), 5.08 (1H, quartet, $J=5$ cps, -CH<), 5.61—6.42 (2H, multiplet, $-OCH_2-$), 7.04—7.95 (2H, multiplet, $-COCH_2-$), 8.59 (3H, doublet, $J=5$ cps, CH_3).

Tetrahydro-2-methyl-2-phenyl-4*H*-1,3-oxazin-4-one (III)——In a three-necked flask provided with a water separator 25 g of hydracrylamide, 460 g of acetophenone and 500 ml of benzene were placed. The mixture was refluxed with stirring and 1 ml of H_2SO_4 was carefully added in small portions. Stirring and refluxing were continued for 11 hr until removal of water formed, by azeotropic distillation, was almost ceased. After decantation, H_2SO_4 was removed by treatment with $BaCO_3$. The solution was concentrated to remove benzene and under reduced pressure excess of acetophenone. The oily residue was washed with dry ether until solidified in a refrigerator. Recrystallization from iso-Pr_2O gave prisms, mp 122—123°. Yield, 5.2 g (10%, based on hydracrylamide). *Anal.* Calcd. for $C_{11}H_{13}O_2N$: C, 69.09; H, 6.85; N, 7.33. Found: C, 69.21; H, 6.81; N, 7.23. IR ν_{max}^{KBr} cm^{-1}: 3150, 1677 (CONH), 1079 (ether). NMR τ: −0.70 (1H, broad singlet, NH), 2.44 (5H, singlet, C_6H_5), 5.82—6.51 (2H, multiplet, $-OCH_2-$), 7.07—7.98 (2H, multiplet, $-COCH_2-$), 8.21 (3H, singlet, CH_3).

Tetrahydro-2,2-dimethyl-4*H*-1,3-oxazin-4-one (IV)——In Soxlet apparatus packed with anhyd. $MgSO_4$ a mixture of 9 g of hydracrylamide, 130 g of acetone and 0.8 g of H_2SO_4 was refluxed with stirring for 10 hr. After decantation, H_2SO_4 was removed by treatment with $BaCO_3$. The solution was concentrated and the resultant oily residue was distilled under reduced pressure to give a fraction of bp 122—149° (0.5 mmHg), which was gradually solidified on standing. Recrystallization from iso-Pr_2O gave prisms, mp 91—93°. Yield, 4.1 g (32%, based on hydracrylamide). *Anal.* Calcd. for $C_6H_{11}O_2N$: C, 55.79; H, 8.58; N, 10.85. Found: C, 55.35; H, 8.61; N, 10.89. IR ν_{max}^{KBr} cm^{-1}: 3172, 1658 (CONH), 1088 (ether). NMR τ: 2.15 (1H,

7) All melting points are uncorrected. IR spectra were determined on a Hitachi EPI-G2 grating spectrophotometer. NMR spectra were taken at 60 Mc in $CDCl_3$ solution with a JEOL JNM-C-60H spectrometer using tetramethylsilane as the internal standard.

broad singlet, NH), 6.00 (2H, triplet, J=6 cps, -OCH_2-), 7.60 (2H, triplet, J=6 cps, -$COCH_2$-), 8.52 (6H, singlet, 2×CH_3).

1-Oxa-5-azaspiro[5,5]undecan-4-one (V)——To a solution of 4.5 g of hydracrylamide, 49 g of cyclohexanone and 75 ml of benzene, 0.45 g of H_2SO_4 was added and the mixture was refluxed with stirring for 4 hr, where water formed was removed from distilled benzene azeotrope. The same treatment of the reaction mixture as described for I gave colorless crystals, which were recrystallized from benzene to prisms, mp 158—160°. Yield, 5.2 g (61%, based on hydracrylamide). *Anal.* Calcd. for $C_9H_{15}O_2N$: C, 63.88; H, 8.94; N, 8.28. Found: C, 64.18; H, 8.98; N, 8.33. IR ν_{max}^{KBr} cm^{-1}: 3195, 1680 (CONH), 1093 (ether). NMR τ: 1.88 (1H, broad singlet, NH), 6.05 (2H, triplet, J=6 cps, -OCH_2-), 7.58 (2H, triplet, J=6 cps, -$COCH_2$-), 7.90—8.90 (10H, multiplet, $(CH_2)_5$).

2-Phenyl-4-oxazolidinone(VI)——To a mixture of 159 g of benzaldehyde, 7.6 g of glycolamide and 225 ml of benzene, 0.9 g of H_2SO_4 was added and the whole was refluxed with stirring for 5 hr, where water formed was removed from distilled benzene azeotrope. The reaction mixture was treated by the same manner as described for I to give colorless crystals, which were recrystallized from benzene to prisms, mp 94—96°. Yield, 9.9 g (58%, based on glycolamide). *Anal.* Calcd. for $C_9H_9O_2N$: C, 66.24; H, 5.56; N, 8.58. Found: C, 66.36; H, 5.63; N, 8.81. IR ν_{max}^{KBr} cm^{-1}: 3085, 1692 (CONH), 1060 (ether). NMR τ: 1.52 (1H, broad singlet, NH), 2.56 (5H, singlet, C_6H_5), 3.86 (1H, triplet, J=2 cps, -CH<), 5.69 (2H, doublet, J=2 cps, -CH_2-).

2,2-Dimethyl-4-oxazolidinone(VII)——In Soxlet apparatus packed with CaO a mixture of 7.5 g of glycolamide, 116 g of acetone and 0.8 g of H_2SO_4 was refluxed with stirring for 8 hr. H_2SO_4 was removed by treatment with $BaCO_3$. The solution was concentrated to dryness under reduced pressure and the solid residue was extracted with $CHCl_3$. After dried over $MgSO_4$, removal of $CHCl_3$ gave crystals of crude VII, which were recrystallized from benzene to leaves, mp 98—100° (lit.[4] mp 104—105°). Yield, 9.0 g (78%, based on glycolamide). *Anal.* Calcd. for $C_5H_9O_2N$: C, 52.16; H, 7.88; N, 12.17. Found: C, 51.97; H, 7.90; N, 12.45. IR ν_{max}^{KBr} cm^{-1}: 3075, 1740 (CONH), 1073 (ether). NMR τ: 1.30 (1H, broad singlet, NH), 5.70 (2H, singlet, -CH_2-), 6.48 (6H, singlet, 2×CH_3).

1-Oxa-4-azaspiro[4,5]decan-3-one (VIII)——To a mixture of 1.9 g of glycolamide, 35 g of cyclohexanone and 50 ml of benzene, 0.23 g of H_2SO_4 was added and the whole was refluxed with stirring for 5 hr, where water formed was removed from distilled benzene azeotrope. The reaction mixture was treated by the same manner as described for I to give crystals, which were recrystallized from benzene to leaves, mp 150—151°. Yield, 2.5 g (64%, based on glycolamide). *Anal.* Calcd. for $C_8H_{13}O_2N$: C, 61.91; H, 8.44; N, 9.03. Found: C, 61.62; H, 8.26; N, 8.94. IR ν_{max}^{KBr} cm^{-1}: 3065, 1740 (CONH), 1073 (ether). NMR τ: 0.65 (1H, broad singlet, NH), 5.69 (2H, singlet, -CH_2-), 7.90—8.75 (10H, multiplet, $(CH_2)_5$).

3,3′-Methylenebis(tetrahydro-4*H*-1,3-oxazin-4-one)——In Soxlet apparatus packed with anhyd. $MgSO_4$ a mixture of 13.5 g of hydracrylamide, 22.5 g of paraformaldehyde, 450 ml of dry dioxane and 0.7 g of H_2SO_4 was refluxed with stirring for 8 hr. After decantation, H_2SO_4 was removed by treatment with $BaCO_3$. The oily residue obtained by concentration under reduced pressure gradually solidified and was washed with dry ether. Recrystallization from benzene gave prisms, mp 149—150°. *Anal.* Calcd. for $C_9H_{14}O_4N_2$: C, 50.46; H, 6.59; N, 13.08. Found: C, 50.39; H, 6.63; N, 12.88. IR ν_{max}^{KBr} cm^{-1}: 1658 (CONH), 1112 (ether). NMR τ: 5.00 (4H, singlet, -OCH_2N<), 5.08 (2H, singlet, >NCH_2N<), 5.95 (4H, triplet, J=6 cps, -OCH_2-), 7.42 (4H, triplet, J=6 cps, -$COCH_2$-).

3-Isopropoxypropionamide——A mixture of 17.0 g of 3-isopropoxypropionitrile,[8] 150 g of 10% H_2O_2 and 12 ml of 5% NaOH solution was warmed with vigorous stirring at 50—60° for 5 hr. After the reaction, excess H_2O_2 was decomposed by warming with MnO_2. After filtration, the filtrate was neutralized with 5% HCl and concentrated under reduced pressure to dryness. After extraction with iso-PrOH and evaporation, distillation of the oily residue under reduced pressure gave a solid fraction of bp 107—108° (3 mmHg). Recrystallization from iso-Pr_2O gave leaves, mp 54—56°. Yield, 15.5 g (79%). *Anal.* Calcd. for $C_6H_{13}O_2N$: C, 54.94; H, 9.99; N, 10.68. Found: C, 55.05; H, 9.88; N, 10.71. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3476, 3340, 1670, 1590 ($CONH_2$), 1125, 1082 (ether).

Catalytic Hydrogenation of 2-Substituted Tetrahydro-4*H*-1,3-oxazin-4-ones and 4-Oxazolidinones——As summarized in Table I, the four tetrahydro-4*H*-1,3-oxazin-4-ones and the two 4-oxazolidinones were catalytically hydrogenated by the following general procedure.

General Procedure——In an autoclave 0.04 mole of the substrate, 100 ml of AcOH and 1.0 g of freshly prepared 10% Pd-C catalyst were placed. Under 80 kg/cm^2 of initial hydrogen pressure at room temperature the whole was heated and then constant shaking was started at the requisite temperature and, after drop of hydrogen pressure was nearly ceased, shaking and heating were continued for additional 30 min. Reaction temperature and hydrogenation period are indicated for each run in Table I.

After removal of the catalyst by filtration, the filtrate was concentrated under reduced pressure. Product isolation from the resultant residue was carried out by the following usual procedures. In the runs with I and VI the simply hydrogenolyzed product was obtained by the treatment, where crystalline material

8) J.H. McGregor and C. Pugh, *J. Chem. Soc.*, **1945**, 535.

was obtained by washing the residue with dry ether containing small amount of Et_3N and recrystallized. In the runs with II, III, IV, and VII the residue, which was composed of more than two products, was subjected to rectification under reduced pressure. The followings are the products obtained in each run. Yields of these products are recorded in Table I.

Run with I——N-Benzylhydracrylamide: mp 61—63° (lit.[9] mp 63—64°), identified by noting exact correspondence of its IR spectrum with that of authentic sample and by mixed melting point test. *Anal.* Calcd. for $C_{10}H_{13}O_2N$: C, 67.01; H, 7.31; N, 7.81. Found: C, 66.85; H, 7.52; N, 7.89.

Run with II——N-Ethylpropionamide: bp 103—104° (14 mmHg), n_D^{24} 1.4333, identified by comparison of its IR spectrum with that of authentic sample. 3-Acetoxy-N-ethylpropionamide: bp 113—114° (0.08 mmHg), n_D^{27} 1.4481. *Anal.* Calcd. for $C_7H_{13}O_3N$: C, 52.81; H, 8.23; N, 8.80. Found: C, 52.76; H, 8.36; N, 8.68. IR ν_{max}^{liquid} cm^{-1}: 3370, 1747, 1652, 1555, 1240. NMR τ: 3.00 (1H, broad, NH), 5.62 (2H, triplet, $J=7$ cps, $-CH_2O-$), 6.70 (2H, octet, $>NCH_2C<$), 7.44 (2H, triplet, $J=7$ cps, $-COCH_2-$), 7.95 (3H, singlet, CH_3CO), 8.84 (3H, triplet, $J=7$ cps, $CH_3C<$).

Run with III——Propionamide: bp 107—109° (20 mmHg), mp 75—77°, identified by comparison of its IR spectrum with that of authentic sample and by mixed melting point test. N-(α-Phenylethyl)propionamide: bp 125—128° (0.07 mmHg), mp 58—59° (lit.[10] mp 58—60°), identified by noting exact correspondence of its IR spectrum with that of authentic sample and by mixed melting point test. *Anal.* Calcd. for $C_{11}H_{15}ON$: C, 74.54; H, 8.53; N, 7.90. Found: C, 74.70; H, 8.55; N, 8.11. 3-Acetoxy-N-(α-phenylethyl)-propionamide: bp 139—142° (0.02 mmHg), n_D^{27} 1.4890. *Anal.* Calcd. for $C_{13}H_{17}O_3N$: C, 66.36; H, 7.28; N, 5.95. Found: C, 66.09; H, 7.18; N, 6.14. IR ν_{max}^{liquid} cm^{-1}: 3382, 1730, 1651, 1562, 1236.

Run with IV——Propionamide: bp 110—113° (21 mmHg), mp 75—76°. N-Isopropylpropionamide: bp 132—135° (21 mmHg), mp 47—48° (lit.[11] mp 49°), identified by comparison of its IR spectrum with that of authentic sample. *Anal.* Calcd. for $C_6H_{13}ON$: C, 62.57; H, 11.38; N, 12.16. Found: C, 62.32; H, 11.50; N, 11.96.

Run with VI——N-Benzylglycolamide: mp 102—103° (lit.[12] mp 103—104°), identified by comparison of its IR spectrum with that of authentic sample and by mixed melting point test. *Anal.* Calcd. for $C_9H_{11}O_2N$: C, 65.44; H, 6.71; N, 8.48. Found: C, 65.28; H, 6.77; N, 8.37.

Run with VII——N-Isopropylglycolamide: bp 107—109° (0.07 mmHg), n_D^{24} 1.4559, identified by noting exact correspondence of its IR spectrum with that of authentic sample prepared from ethyl glycolate and iso-$PrNH_2$. *Anal.* Calcd. for $C_5H_{11}O_2N$: C, 51.26; H, 9.46; N, 11.96. Found: C, 51.29; H, 9.71; N, 12.06. IR ν_{max}^{liquid} cm^{-1}: 3300, 1647, 1542, 1080. 2-Acetoxy-N-isopropylacetamide: bp 128—130° (0.05 mmHg), n_D^{24} 1.4711. *Anal.* Calcd. for $C_7H_{13}O_3N$: C, 52.81; H, 8.23; N, 8.80. Found: C, 53.02; H, 8.23; N, 8.73. IR ν_{max}^{liquid} cm^{-1}: 3325, 1741, 1650, 1555, 1228.

Catalytic Hydrogenations of N-Ethylhydracrylamide and of Hydracrylamide in Acetic Acid——In an autoclave 4.7 g of N-ethylhydracrylamide,[9] 100 ml of AcOH and 1.0 g of 10% Pd-C were placed. Under 80 kg/cm^2 (at room temperature) of initial hydrogen pressure the whole was heated and constant shaking was started at 130°. Shaking and heating were continued at 130—135°. After 6 hr hydrogen absorption was almost ceased before uptake of equimolar amount of hydrogen. After removal of the catalyst by filtration, the filtrate was concentrated under reduced pressure. The oily residue was subjected to distillation under reduced pressure to give two fractions of distillate. The first distillate, bp 103—104° (13 mmHg), weighing 2.1 g, was identified as N-ethylpropionamide. Yield, 52%. The second distillate, bp 113—114° (0.08 mmHg), weighing 2.7 g, was shown to be 3-acetoxy-N-ethylpropionamide. Yield, 42%. Both the products were identified by noting exact correspondence of their IR spectra with those of authentic samples.

Catalytic hydrogenation of hydracrylamide was carried out by the same procedure as described above, where 4.5 g of hydracrylamide and 100 ml of AcOH were used and one hour was required for hydrogenation. Treatment of the reaction mixture gave 3.3 g (90%) of propionamide.

Acknowledgement The authors are indebted to the members of the Analytical Center of this college for the elemental analyses and for NMR measurement.

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