material melting at 154–156°.[14,15] After neutralization of the free carboxyls, a neutral equivalent of 177 was obtained, calculated 174.1.

Potentiometric Titrations.—Fifty to 100 mg. of a particular lactone was dissolved in 10 ml. of water and titrated at 28° under nitrogen with standard 0.1 *N* base, using a model G Beckman *p*H meter and external electrodes.

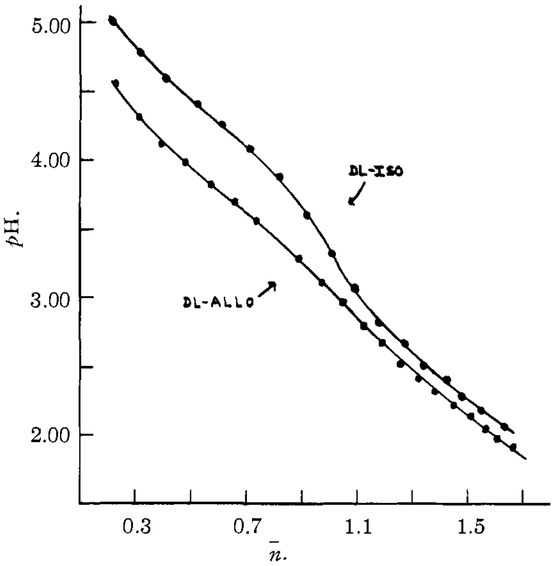


Fig. 1.—Potentiometric titration of 59.1 mg. of DL-alloisocitric lactone (neut. equiv. 88.2, theory 87.1) and of 64.8 mg. of DL-isocitric lactone (neut. equiv. 86.3, theory 87.1).

pK_A values were obtained from a plot (Fig. 1) of *p*H *vs.* $\bar{n}$, $\bar{n}$ being defined as[16]

$$\bar{n} = \frac{2(\mathrm{TA}) - (\mathrm{NaOH}) - (\mathrm{H}^+) + (\mathrm{OH}^-)}{(\mathrm{TA})} = \frac{(K_1/(H^+)) + 2}{1 + \frac{K_1}{(\mathrm{H}^+)} + \frac{K_1K_2}{(\mathrm{H}^+)^2}}$$

where

(TA) = concentration of added lactone
(NaOH) = concentration of added base
(H^+) = hydrogen ion concentration as calculated from the *p*H measurement
(OH^-) = hydroxyl ion concentration as calculated from K_W and the hydrogen ion concentration

At $\bar{n}$ equal to 1.5, the *p*H is equal to pK_1 and at $\bar{n}$ equal to 0.5, *p*H is equal to pK_2.

---

(14) Senear[13] reports 157–158.5°.

(15) Greenstein, *et al.*,[1] report 153°.

(16) Using the Bjerrum treatment and considering H^+ as the ligand. For details of this treatment see A. E. Martell and M. Calvin, "Chemistry of the Metal Chelate Compounds," Prentice-Hall, Inc., New York, N. Y., 1952, p. 78.

DEPARTMENT OF CHEMISTRY
DUQUESNE UNIVERSITY
PITTSBURGH 19, PENNA.

Dialkoxyalkanenitriles. III. Hydrogenation to α-Amino Acetals

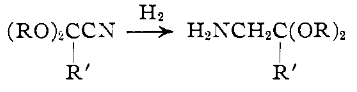
BY JOHN G. ERICKSON,[1] W. H. MONTGOMERY AND OLE RORSO

RECEIVED AUGUST 11, 1955

Of the several methods described for the preparation of acetals, the one involving reaction of an acetal of an α-haloaldehyde with ammonia or amines usually has been employed.[2] No ketone acetals appear to have been used in this reaction. The reaction also has been carried out with alkali metal derivatives of aniline and alkylanilines.[3] One disadvantage of the synthesis from ammonia and chloroacetal is the considerable amount of corrosion which may accompany the reaction unless the vessel is constructed of the proper material. It may also be difficult to obtain a pure product, since chloroacetal, aminoacetal and hydroxyacetal cannot be separated very well by distillation.

There are two less important methods of preparing α-amino acetals. One is the reduction of glycine esters with sodium amalgam and subsequent conversion of the aminoacetaldehyde so formed into its acetals.[4] The other is the reduction of acetals of nitroacetaldehyde with sodium and alcohol.[5]

We have found that hydrogenation of 2,2-dialkoxyalkanenitriles gives α-amino acetals (I) in good yields. Since the nitrile group is converted to an aminomethyl group, this method can give acetals of aminoacetaldehyde and a wide variety of α-aminomethyl ketones. We used it to prepare acetals of aminoacetaldehyde, aminoacetone and α-aminoacetophenone. By hydrogenation in the presence of primary and secondary amines, N-substituted α-amino acetals could be prepared. This phase has not been studied thoroughly.



$$\underset{\mathrm{R'}}{(\mathrm{RO})_2\mathrm{C}\mathrm{CN}} \xrightarrow{\mathrm{H_2}} \underset{\mathrm{R'}}{\mathrm{H_2NCH_2C(OR)_2}}$$

I, R = alkyl
R′ = H, alkyl or aryl

It has been shown[6] that the cyano group in dialkoxyalkanenitriles is more reactive toward dicyandiamide than it is in most other nitriles. This appears to be true in hydrogenations also. The hydrogenation reaction takes place readily under moderate conditions, giving, in general, good yields of amino acetals—from 65 to 90%. No unreacted nitrile survives to complicate the purification of the amino acetal. When no ammonia is added to the reaction mixture, the usual

---

(1) Research Department, General Mills, Inc., Minneapolis, Minn.

(2) (a) A. Wohl, *Ber.*, **21**, 616 (1888); **39**, 1951 (1906); (b) L. Wolff, *ibid.*, **21**, 1481 (1888); (c) W. Marckwald, *ibid.*, **25**, 2354 (1892); (d) R. Burtles, F. L. Pyman and J. Roylance, *J. Chem. Soc.*, **127**, 581 (1925); (e) F. A. Mason, *ibid.*, **127**, 1032 (1925); (f) W. H. Hartung and H. Adkins, THIS JOURNAL, **49**, 2517 (1927); (g) J. Boeseken and B. B. C. Felix, *Ber.*, **62**, 1311 (1929); (h) J. S. Buck and S. N. Wrenn, THIS JOURNAL, **51**, 3612 (1929); (i) A. Kirrmann, M. Goudard and M. Chahidzadeh, *Bull. soc. chim.*, **2**, 2143 (1935); (j) H. Albers, R. Kallischnigg and A. Schmidt, *Ber.*, **77**, 617 (1944); (k) R. B. Woodward and W. E. Doering, THIS JOURNAL, **67**, 860 (1945); (l) J. P. Fourneau and S. Chantalou, *Bull. soc. chim.*, **12**, 845 (1945); (m) H. H. Richmond and G. F. Wright, *Can. J. Research*, **23D**, 158 (1945); (n) E. F. J. Janetzky, P. E. Verkade and W. Meerburg, *Rec. trav. chim.*, **66**, 312 (1947); (o) C. F. H. Allen and J. H. Clark, *Org. Syntheses*, **24**, 3 (1944); (p) I. A. Kaye and I. Minsky, THIS JOURNAL, **71**, 2272 (1949); (q) R. S. Sweet, U. S. Patent 2,490,385 (Dec. 6, 1949); (r) R. G. Jones, E. C. Kornfeld, K. C. McLaughlin and R. C. Anderson, THIS JOURNAL, **71**, 400 (1949); (s) S. Senda, *J. Pharm. Soc. Japan*, **71**, 601 (1951).

(3) E. F. J. Janetzky, P. E. Verkade and W. Meerburg, *Rec. trav. chim.*, **66**, 317 (1947).

(4) E. Fischer, *Ber.*, **41**, 1019 (1908).

(5) M. S. Losanitsch, *ibid.*, **42**, 4044 (1909).

(6) V. P. Wystrach and J. G. Erickson, THIS JOURNAL, **75**, 6345 (1953).

TABLE I

HYDROGENATION OF 2,2-DIALKOXYALKANENITRILES

Nitrile Structure	Nitrile Moles	Solvent	Ml.	NH₃, moles	Temp. of reacn., °C.	Max. press., atm.	Product Structure	Yield, %
$(CH_3O)_2CHCN$	0.50	Dioxane	80	1.0	75–90	130	$H_2NCH_2CH(OCH_3)_2$	38
$(CH_3O)_2CHCN$	.50	Methylal[a]	80	1.0	75–80	135	$H_2NCH_2CH(OCH_3)_2$	56
$(CH_3O)_2CHCN$	.50	Cyclohexane	80	1.0	80–90	87	$H_2NCH_2CH(OCH_3)_2$	67
$(C_2H_5O)_2CHCN$	.39	Ethanol	80	0.7	75–125	197	$H_2NCH_2CH(OC_2H_5)_2$	10
$(C_2H_5O)_2CHCN$	.39	Methylal[b]	75	.8	75–80	197	$H_2NCH_2CH(OC_2H_5)_2$	85
$(C_2H_5O)_2CHCN$	1.16	Cyclohexane	240	2.3	75–90	100	$H_2NCH_2CH(OC_2H_5)_2$	87
$(C_2H_5O)_2CHCN$	1.16	Cyclohexane	275	0	75–80	100	$H_2NCH_2CH(OC_2H_5)_2$	67
						and	$HN(CH_2CH(OEt)_2)_2$	13
$(C_4H_9O)_2CHCN$	0.27	Cyclohexane	85	0.5	75–80	87	$H_2NCH_2CH(OC_4H_9)_2$	67
$(CH_3O)_2\underset{\displaystyle CH_3}{C}CN$	.83	Cyclohexane	300	3.0	75–115	122	$H_2NCH_2\underset{\displaystyle CH_3}{C}(OCH_3)_2$	88
$(C_2H_5O)_2\underset{\displaystyle C_6H_5}{C}CN$	.35	Cyclohexane	40	1.5	100–150	163	$H_2NCH_2\underset{\displaystyle C_6H_5}{C}(OC_2H_5)_2$	71

[a] Unpurified. [b] Purified.

TABLE II

PROPERTIES OF AMINO ACETALS

Structure	B.p., °C.	B.p., Mm.	F.p., °C.	d^{25}	$n^{25}D$	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found
$H_2NCH_2CH(OCH_3)_2$	139.5	768	<-78	0.9676	1.4144	45.71[f]	45.65	10.48	10.68	13.33	13.08
$H_2NCH_2CH(OC_2H_5)_2$	163	769	<-78	.9108[a]	1.4142[b]						
$HN(CH_2CH(OEt)_2)_2$	86	1	−30	.9419[c]	1.4250[d]						
$H_2NCH_2CH(OC_4H_9)_2$	118	17	<-78	.8835	1.4274	63.49	63.09	12.17	11.88	7.41	7.69
	78	2									
$H_2NCH_2\underset{\displaystyle CH_3}{C}(OCH_3)_2$	146	751	−70	.9620	1.4220	50.42[g]	48.68	10.92	10.05	11.76	11.69
	89	105									
$H_2NCH_2\underset{\displaystyle C_6H_5}{C}(OC_2H_5)_2$	68	0.5	−40[e]	1.0050	1.4950	68.90[h]	69.25	9.09	8.94	6.70	6.40

[a] Reported 0.9161,[2f] 0.9159.[2m] [b] Reported 1.4120,[2f] 1.4123.[2m] [c] Reported 0.9541.[2f] [d] Reported 1.4210.[2f] [e] Sets to a hard glass. [f] Calcd.: CH_3O, 59.05. Found: CH_3O, 59.02. [g] Calcd.: CH_3O, 52.10. Found: CH_3O, 43.22. [h] Calcd.: C_2H_5O, 43.06. Found: C_2H_5O, 42.10.

side reaction, yielding the secondary amine, occurs to a relatively small degree. With ammonia present, little or none of the secondary amine is formed. Suitable solvents for the hydrogenation reaction are cyclohexane and purified methylal. Unpurified methylal and dioxane are not nearly as satisfactory. The use of alcohol as solvent results in almost no product at all. This is not surprising, for it has been pointed out[7] that 2,2-dialkoxyalkanenitriles are easily cleaved by water and alcohols to hydrogen cyanide and carboxylic acids or *ortho* esters.

Acknowledgment.—Microanalyses were performed by the Microanalytical Group of these laboratories.

Experimental

Materials.—The preparation of the 2,2-dialkoxyalkanenitriles has been described elsewhere.[7]

Procedure.—The nitrile, solvent and catalyst (Raney nickel) were placed in the pressure vessel and ammonia (if it was used) was added. Agitation was started and hydrogen was introduced to a pressure of about 100 atm. in. The vessel was heated until hydrogen uptake was observed, then held at this temperature. When hydrogen absorption had ceased, the vessel was cooled and pressure vented off. The catalyst was removed by centrifuging. Fractional distillation of the reaction products yielded the aminoacetals. Table I summarizes the runs made. Table II gives the physical properties and analytical values for the products.

Despite careful fractionation, it was not possible to obtain the dimethyl acetal of aminoacetone in a completely pure state, although it is not clear what might be the impurities. None of the starting nitrile was present after the hydrogenation had been completed, since treatment with dilute $AgNO_3$–HNO_3 solution gave no precipitate of silver cyanide.

STAMFORD RESEARCH LABORATORIES
RESEARCH DIVISION, AMERICAN CYANAMID CO.
STAMFORD, CONNECTICUT

---

(7) J. G. Erickson, THIS JOURNAL, **73**, 1338 (1951).

Dioxolanones. II. Lithium Aluminum Hydride Reduction of the Diketene–Acetone Adduct[1]

BY NORMAN G. GAYLORD[2a] AND DANIEL J. KAY[2a,b]

RECEIVED JULY 14, 1955

Three possible structures were considered by Carroll and Bader[3] in their examination of the adduct $C_7H_{10}O_3$, obtained from diketene and acetone. Structure I, 2,2,4-trimethyl-6-keto-1,3-dioxene, was favored, based on ultraviolet and infrared absorption spectra, non-reactivity with reagents for preparing carbonyl derivatives and reactions with alcohols and amines. In view of the absence of degradative or synthesis evidence,

---

(1) Part I, *J. Org. Chem.*, **19**, 1991 (1954).

(2) (a) Interchemical Corporation, 432 West 45th Street, New York 36, N. Y.; (b) abstracted from the M.S. thesis of D. J. Kay, Canisius College, June, 1955.

(3) M. F. Carroll and A. R. Bader, THIS JOURNAL, **75**, 5400 (1953).