TABLE I

HYDROGENATION OF 2,2-DIALKOXYALKANENITRILES

Nitrile: Structure	Moles	Solvent	Ml.	NH_3, 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
$(CH_3O)_2CCN$ | CH_3	.83	Cyclohexane	300	3.0	75–115	122	$H_2NCH_2C(OCH_3)_2$ | CH_3	88
$(C_2H_5O)_2CCN$ | C_6H_5	.35	Cyclohexane	40	1.5	100–150	163	$H_2NCH_2C(OC_2H_5)_2$ | C_6H_5	71

[a] Unpurified. [b] Purified.

TABLE II

PROPERTIES OF AMINO ACETALS

Structure	B.p., °C.	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									
$H_2NCH_2C(OCH_3)_2$ | CH_3	146	751	-70	.9620	1.4220	50.42[g]	48.68	10.92	10.05	11.76	11.69
	89	105									
$H_2NCH_2C(OC_2H_5)_2$ | C_6H_5	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.

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

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.

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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,

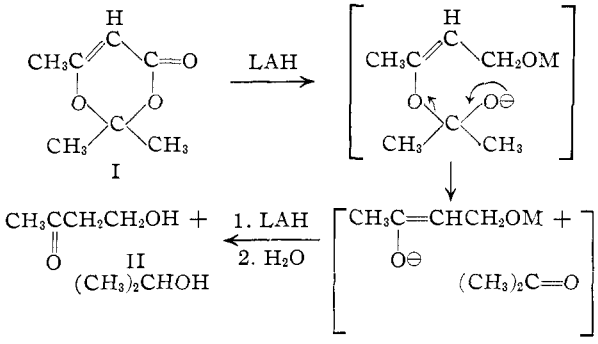
(1) Part I, *J. Org. Chem.*, **19**, 1991 (1954).

(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).

the reduction of the adduct with lithium aluminum hydride was carried out in order to obtain further evidence relating to the structure.

It has been shown[1,4] that the reduction of a dioxolanone with lithium aluminum hydride yields cleavage products, *i.e.*, a glycol and an alcohol. Since structure I is analogous to that of a dioxolanone the following reduction mechanism was postulated



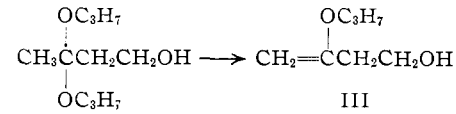
The reaction between the diketene–acetone adduct and lithium aluminum hydride gave two fractions: (a) b.p. 82–84°, and (b) b.p. 42–48° (30 mm.), $n^{25}D$ 1.419. The lower boiling fraction (a) was identified as the expected propanol-2 by its physical properties and the identity of its phenylurethan with an authentic sample.

The higher boiling fraction (b) was shown not to be the expected 3-keto-1-butanol (II) but was identified as 3-isopropoxy-3-buten-1-ol (III) by its analysis, infrared absorption spectrum and its physical and chemical properties. The absorption spectrum contained a band characteristic of a hydroxy group and bands characteristic of a vinyloxy group.[5]

The reactions between fraction (b) and the appropriate reagents gave an α-naphthylurethan and a 2,4-dinitrophenylhydrazone whose analyses were in agreement with those of the corresponding derivatives of II. The preparation of the carbonyl derivative is of interest in view of the report that the reaction of II with phenylhydrazine yields 2-phenyl-5-methylpyrazoline rather than the phenylhydrazone.[6] Fraction b gives a positive haloform reaction.

The vinyl ether structure III for fraction b is supported by the fact that vinyl alkyl ethers react with reagents for determining carbonyl groups and, in fact, these reactions are the basis for the analytical determination of such compounds.[7]

It has been reported that the dimethyl ketal of II is unstable and upon distillation reverts to 3-methoxy-3-buten-1-ol.[8] It is therefore logical to postulate that the expected reduction products, isopropyl alcohol and 3-keto-1-butanol (II), react to form the diisopropyl ketal of II which undergoes thermal decomposition to yield III.



Since none of the other structures postulated for the diketene–acetone adduct[3] would be expected to yield the indicated reduction products, structure I appears to be correct for the adduct.

Experimental

A solution of 50 g. (0.35 mole) of the diketene–acetone adduct[9] in 50 ml. of ether was added over one hour to 15 g. (0.39 mole) of lithium aluminum hydride in 500 ml. of ether. The mixture was refluxed for an additional 1.5 hours and decomposed by the successive addition of 15 ml. of water, 15 ml. of 15% sodium hydroxide and 45 ml. of water. The mixture was filtered, the filter cake extracted with ether and the ether layers combined. The filter cake contained a white crystalline solid, not further identified, intermixed with the inorganic salts. The combined ether extracts were dried over magnesium sulfate and distilled through a Vigreux column to yield two fractions: (a) 10 g. (48% yield) of isopropyl alcohol, b.p. 82–84°, identified through the phenylurethan, and (b) 11 g., b.p. 42–48° (30 mm.), $n^{25}D$ 1.419.

Anal. Calcd. for $C_7H_{14}O_2$: C, 64.61; H, 10.77. Found: C, 65.01; H, 11.11.

The α-naphthylurethan of fraction b was the derivative of 3-keto-1-butanol.

Anal. Calcd. for $C_{15}H_{15}NO_3$: C, 70.04; H, 5.84. Found: C, 69.96; H, 5.69.

The 2,4-dinitrophenylhydrazone of fraction b was the derivative of 3-keto-1-butanol.

Anal. Calcd. for $C_{10}H_{12}N_4O_5$: C, 44.78; H, 4.48. Found: C, 45.18; H, 4.22.

(4) N. G. Gaylord and J. A. Snyder, *Chemistry & Industry*, 1234 (1954).

(5) R. L. Adelman, THIS JOURNAL, **77**, 1669 (1955).

(6) K. von Auwers and H. Broche, *Chem. Ber.*, **55**, 3907 (1922).

(7) M. G. Voronkov, *Zhur. Anal. Khim.*, **1**, 218 (1946); *C. A.*, **41**, 3714 (1947); M. F. Shostakovskiĭ and E. N. Prilezhaeva, *J. Gen. Chem. (U.S.S.R.)*, **17**, 1129 (1947); *C. A.*, **42**, 3633 (1948); M. F. Shostakovskiĭ and N. I. Uvarova, *Zhur. Anal. Khim.*, **6**, 348 (1951); *C. A.*, **46**, 2963 (1952).

(8) G. F. Hennion and W. S. Murray, THIS JOURNAL, **64**, 1220 (1942).

(9) Aldrich Chemical Company, Inc., Milwaukee, Wis.

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Conjugative Effects of Cyclopropane Rings. III. Spectroscopic Properties of 1-Acetyl-2,2-dimethyl-3-(2-methyl-1-propenyl)-cyclopropane[1]

BY RICHARD H. EASTMAN[1] AND STANLEY K. FREEMAN[2]

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Attachment of a cyclopropane ring to a carbonyl group modifies the ultraviolet absorption characteristics in two ways: the intensity of the weak $n \rightarrow \pi$ band[3] near 280 mμ is increased about twofold and the position of maximum absorption of the N_1, V_1 band[3] is shifted from its position at *ca.* 190 mμ in simple ketones to 210–215 mμ. Attachment of a vinyl group to the carbonyl group produces similar modifications in the spectrum of the carbonyl group and the electronic effect of the cyclopropane ring has been likened[4] to that of the vinyl group on this basis. It has been of interest to inquire to what extent the unsaturation electrons of the cyclopropane ring[5] partake of the character of π-electrons

(1) Work done in the Department of Chemistry and Chemical Engineering, Stanford University, Stanford, California.

(2) Benzol Products Company, Newark 5, N. J.

(3) Harden McConnell, *J. Chem. Phys.*, **20**, 700 (1952).

(4) For references to earlier work see Papers I and II of this series: R. H. Eastman, THIS JOURNAL, **76**, 4115 (1954), and R. H. Eastman and J. C. Selover, *ibid.*, **76**, 4118 (1954).

(5) The unsaturation electrons of the cyclopropane ring share the property of π-electrons in general of forming complexes with metal ions; C. F. H. Tipper, *J. Chem. Soc.*, 2045 (1955).