tablished by its melting point and that of a mixture with authentic material on hand.

Summary

The synthesis of diazo-β,β,β-triphenylethane is effected by means of a series of steps involving the preparation of ethyl N-nitroso-N-β,β,β-triphenylethyl carbamate derived from β,β,β-triphenylethylamine. This diazo compound is converted into triphenylethylene by rearrangement, when decomposed under a variety of conditions. From either diazo-β,β,β-triphenylethane or β,β,β-triphenylethylamine there is obtained by the action, under specified conditions, of nitrous anhydride, triphenylnitroethylene. The decomposition of the diazo compound in ether or ligroin solutions by acetic acid or benzoic acid leads to the formation, respectively, of benzyldiphenylmethyl acetate or benzoate, hitherto undescribed. The results of the investigation are discussed from the point of view of their bearing upon the mechanism of primary amine nitrite decompositions and the interpretation of certain molecular rearrangements.

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[COMMUNICATION FROM THE LABORATORY OF ORGANIC CHEMISTRY, UNIVERSITY OF WISCONSIN]

The Preparation, Alcoholysis and Hydrogenolysis of Nicotinyl Acyl Methanes

BY LEO F. KUICK AND HOMER ADKINS

The literature of organic chemistry contains very little information with respect to the preparation and chemical behavior of 1,3-diketones having a pyridyl or piperidyl group adjacent to one carbonyl.[1] These compounds are of especial interest to us in connection with a study of the relationships of structure to the mode of cleavage of diketones by alcohol,[2] water and hydrogen.[3] The present paper is essentially a presentation of experimental results concerning the preparation, alcoholysis and hydrogenolysis of these nitrogenous diketones.

TABLE I

PREPARATION, PROPERTIES AND ANALYSES OF NICOTINYL ACYL METHANES OR 1,3-DIKETONES $\mathrm{RC(O)CH_2C(O)C_5H_4N}$ FROM ETHYL NICOTINATE AND VARIOUS METHYL KETONES

-Nicotinyl (—)-methane	R in $\mathrm{RC(O)CH_3}$ is	Yield, %	Phys. constants B. p., °C.	Mm.	M. p. (corr.)	Molecular formula	% N_2 Calcd.	Found	Hydrochloride M. p. (corr.)	% Cl Calcd.	Found
(Acetyl)	Me	63	134–135	6	83.5	$C_9H_9O_2N$	8.59	8.62	154	17.77	17.55
(*n*-Valeryl)	*n*-Bu	46	165–168	8		$C_{12}H_{15}O_2N$	6.83	6.88	122	14.68	14.74
(Isovaleryl)	*i*-Bu	70	134–135	3	44	$C_{12}H_{15}O_2N$	6.83	6.85	128–129	14.68	14.69
(Trimethylacetyl)	*t*-Bu	42	135–136	5	44.5	$C_{12}H_{15}O_2N$	6.83	6.74	173	14.68	14.59
(*n*-Caproyl)	*n*-Amyl	47	150–152	2	29.5	$C_{13}H_{17}O_2N$	6.39	6.45	114	13.87	13.92
(Benzoyl)	Ph	70	198–200	3	121.5	$C_{14}H_{11}O_2N$	6.22	6.19	211	13.56	13.49
(*sym*-Trimethylbenzoyl)	*sym*-Mesityl	60	186–190	1	47.8	$C_{17}H_{17}O_2N$	5.24	5.44	218–219	11.68	11.74
(Nicotinyl)	3-Pyridyl	51			198	$C_{13}H_{10}O_2N_2$	12.39	12.36	240–241	23.72	23.74

Preparation of Diketones.—The nicotinyl acyl methanes were prepared by the condensation of ethyl nicotinate with a suitable monoketone in the presence of sodium ethoxide. The procedure is given in the experimental section and the yields, properties, etc., in Table I.

Eight attempted condensations were unsuccessful, *e. g.*, ethyl nicotinate and methyl tridecyl ketone or *p*-phenylacetophenone; ethyl laurate and methyl nicotinyl ketone or acetophenone, ethyl N-ethylnipecotate and acetone or acetophenone. Ethyl laurate condensed with itself and the nipecotates apparently underwent a similar type of reaction while the nicotinate was recovered unchanged.

Alcoholysis of Diketones.—In preliminary experiments the four possible products of the alcoholysis of nicotinylbenzoylmethane, and of nicotinyltrimethylacetylmethane were identified as being among the reaction products. Two analytical methods were developed and tested for estimating the proportion of the two competing reactions I and II. In the extraction

$$\mathrm{RC(O)CH_2C(O)C_5H_9N} \begin{array}{ll} \nearrow \mathrm{RC(O)CH_3 + C_5H_4NCO_2Et} & \mathrm{I} \\ \searrow \mathrm{RCO_2Et + CH_3C(O)C_5H_9N} & \mathrm{II} \end{array}$$

method the basic ketone and ester were extracted

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(1) Ferenczy, *Monatsh.*, **18**, 673 (1897).

(2) Beckham and Adkins, THIS JOURNAL, **56**, 2676 (1934).

(3) Sprague and Adkins, *ibid.*, **56**, 2669 (1934).

with acid and the amount of reaction II calculated from the amount of ester in the neutral portion. In the distillation method the lower boiling ester and ketones were separated from the ethyl nicotinate by fractionation and the amount of the lower boiling ester determined by saponification as above.

TABLE II

ALCOHOLYSIS OF NICOTINYL ACYL METHANES

Ethanol (0.187 mole), dried over lime, and a diketone (0.037 mole) reacted for eight hours at 200°. The distillation method of analysis was used for Me, *t*-Bu and *i*-Bu, and the extraction method in the other cases.

$C_5H_4NC(O)CH_2C(O)R$ R is	$C_5H_4NCO_2Et$ moles	Nicotinyl cleavage, %
Me	0.0152	41
n-Bu	.0157	42
n-Amyl	.0162	43
i-Bu	.0148	42
t-Bu	.0178	50
Ph	.0213	57

The ratio of cleavage products of the nicotinyl acyl methanes appears to be the same whether R is methyl, *n*- or *i*-butyl or *n*-amyl. However, it is evident from the data in Table II and those previously published,[2] that in a diketone $CH_3C(O)CH_2C(O)R$, the pyridyl group like phenyl, furyl and *t*-butyl increases the relative rate of cleavage at the carbonyl group more distant from R. Numerically expressed the ratios of cleavage are: Ph/Me = 4; *t*-Bu/Me = 3; pyridyl/Me = 1.5. If these groups are compared with each other in the same diketone the ratios of cleavage are as follow: Ph/*t*-Bu = 4; Ph/pyridyl = 1.3; *t*-Bu/pyridyl = 1. It may be said that while phenyl maintains its relative superiority against *t*-butyl, it does not do so against pyridyl. Similarly *t*-butyl does not maintain the superiority against pyridyl that would have been calculated from the ratio of cleavage products of the diketones containing a methyl group.

Hydrogenolysis of Diketones.—The reactions of the nicotinyl acyl methanes, with the exception of the hydrogenation of the pyridine ring, are of the same type as have been outlined in detail in an earlier paper for the hydrogenolysis of unsymmetrical 1,3-diketones.[3] These reactions are concerned with the four linkages (indicated by dotted lines) of a 1,3-diketone which react with hydrogen $C_5H_{10}NC(\underset{a}{:::}O)\ldots\underset{c}{}CH_2\ldots\underset{d}{}C(\underset{b}{:::}O)R$. Hydrogen may cleave the molecule at "a," "b," "c" and (or) "d." That all four types of cleavage occurred is established by the constitution of the products isolated and identified as recorded in Table III. The cleavage of the "c" linkage accounts for the larger portion of the products isolated. Six ketones in yields of 21 to 33% resulting from this reaction were isolated where R was *n*-Bu, *i*-Bu, *t*-Bu, *n*-amyl, Ph or mesityl. In none of the six cases was the other cleavage product (nipecotic aldehyde, C_5H_{10}-

TABLE III

PRODUCTS OF HYDROGENOLYSIS OF NICOTINYL ACYL METHANES, $C_5H_4NC(O)CH_2C(O)R$

R	Product	Yield g.	Yield %	Mol. formula	N, % Calcd.	N, % Found	Mol. wt. Calcd.	Mol. wt. Found	Hydrochloride Cl, % Calcd.	Hydrochloride Cl, % Found	Hydrochloride M. p., °C.
Me	3-*n*-Bu-piperidine	7	33				141	144[a]	19.97	20.23	148
n-Bu	*n*-Bu Me ketone	4	27								
	3-Piperidyl Me ketone	3.8	19				127	131[a]	21.68	21.36	114
	i-Bu Me ketone	3.8	25								
i-Bu	3-Piperidyl Me ketone	5.7	30								
	1-(3-Piperidyl)-5-Me-hexanone[c]	5	17	$C_{12}H_{23}ON$	7.10	6.93	197	201[a] 198[b]			
	Pinacolone	3.4	23								
t-Bu	1-(3-Piperidyl)-4,4-di-Me-pentane[d]	13	48	$C_{12}H_{25}N$	7.65	7.41			16.14	16.02	152–153
	1-(3-Piperidyl)-4,4-di-Me-pentanol[d]	6.2	21	$C_{12}H_{25}ON$	7.03				15.05	15.04	164–165
n-Amyl	*n*-Amyl Me ketone	3	21								
Ph	Ph Me ketone	6	33								
	1-(3-Piperidyl)-3-Ph-propane[e]	6.1	18	$C_{14}H_{21}N$	6.89	6.81	203	197[a]			
Mesityl	Mesityl Me ketone	6.2	32								
	3-(Piperidyl)-1-mesityl-propanone-1[f]	16	52	$C_{17}H_{25}ON$	5.43	5.56	259	254[b]	12.03	12.08	133–136

[a] From neutral equivalent. [b] From acetyl value. [c] B. p. 120–129° (2 mm.), m. p. 104°. [d] 133–135° (7 mm.) 173–175° (2 mm.). [f] 190–198° (3 mm.).

NCHO) isolated. This is not surprising since Wohl and Losanitsch[4] have shown that the aldehyde is very readily polymerized. In the cases where R was *n*-Bu or *i*-Bu, both of the ketones resulting from the cleavage of the "d" linkage were isolated in yields of 19 to 30%. The removal of one oxygen atom (cleavage of "a" or "b") with the formation of a monoketone occurred to the extent of 52% when R was mesityl and 17% when R was *i*-Bu. The removal of both oxygen atoms (cleavage of both "a" and "b") occurred to the extent of 33% when R was Me, 48% with *t*-Bu and 14% with Ph.

The assumption has been made in the above summary that saturation of the pyridine ring preceded the cleavage reactions since no product containing a pyridine ring has been isolated. Hydrogen may also add to the carbon to oxygen double bonds with or without cleavage of any of the four labile linkages. Certain products of these reactions were indicated; *i. e.*, a glycol when R was Me, alcohols when R was *i*-Bu, *t*-Bu or Ph; but none was obtained in a pure state.

The products of hydrogenation listed in Table III and summarized above do not account at all completely for the amounts of diketone undergoing reaction nor for the amount of hydrogen absorbed. The discrepancy is due to the characteristics of the products and the quantities available. Apparently some of the products interact as would nipecotic aldehyde with the formation of compounds of high molecular weight. Almost all of the products are liquids, many of them having a high boiling point even at 1–2 mm., and often two products of very similar boiling points are found in the same reaction mixture. Even when the boiling points of the substances are as far apart as those of a piperidylcarbinol and the corresponding alkylpiperidine, it is apparently impossible in some cases to separate them by fractional distillation. In several cases the products contain two or three asymmetric carbon atoms, so that the preparation of solid derivatives is not feasible because of the mixture of several stereoisomers.

Experimental Part

Preparation of Diketones.[5]—Powdered sodium (0.5 mole) and ethanol (0.5 mole) (in a 1-liter, 3-necked flask with dropping funnel, reflux condenser and stirrer) were allowed to react for several hours with stirring, and the ether then removed by distillation. Xylene (100–150 ml.) and ethyl nicotinate (0.5 mole) were added to the sodium ethoxide. The ketone (1.2 moles) was added slowly at such a rate that the reaction mixture was at a temperature between 45 and 60°. The mixture was stirred without heating for one hour after the addition of the ketone. The flask was heated on a steam-bath with stirring for one to four hours. The reflux condenser was replaced by a fractionating column and 30 to 40 ml. of ethanol and xylene distilled off. (This last step was omitted with nicotinylacetylmethane since in this case an excess of acetone (2 moles) was used.) The reaction mixture was cooled with ice and enough water (150–200 ml.) added to bring about the solution of the salt of the diketone. The mixture was extracted twice with 60-ml. portions of ether and acidified with glacial acetic acid. A saturated solution of sodium carbonate was added until there was a basic reaction toward litmus. The diketone was taken up with ether and the aqueous portion extracted once with more ether. The combined ether portions were dried over anhydrous sodium sulfate and distilled under reduced pressure in an ordinary Claisen distilling flask. Nicotinylbenzoylmethane and dinicotinylmethane were not soluble in ether, consequently they were filtered off from the aqueous solution and purified by crystallization from 95% ethanol.

The procedure of getting the sodium salt of the diketone into solution with water was modified when preparing nicotinylbenzoylmethane. One-half of the sodium salt of this diketone was only partially dissolved upon addition of 200 ml. of water. The mixture was acidified with glacial acetic acid and stirred for twenty minutes. Sodium carbonate solution was then added until there was a basic reaction toward litmus, whereupon the solid was filtered off and recrystallized from 95% ethanol.

For the preparation of the hydrochlorides the base was dissolved in anhydrous ether and the solution treated with dry hydrogen chloride gas until precipitation of the hydrochloride was complete. The hydrochlorides were obtained in a pure form by one recrystallization from an ether-alcohol solution. Since nicotinylbenzoylmethane and dinicotinylmethane are insoluble in ether, their hydrochlorides were made by dissolving the base in concentrated aqueous hydrochloric acid, evaporating off the excess acid, and recrystallizing the residue from an ether-alcohol solution.

It is important that the sodium ethoxide used for the condensation of ethyl nicotinate with a ketone or ester be of the best quality. Strong,[6] for example, obtained yields of 50 to 70% of pyridyl methyl ketone resulting (after hydrolysis) from the condensation of nicotinate with ethyl acetate. In attempting to follow his procedure we obtained even wider variations in yields with various samples of sodium ethoxide. However, when the sodium ethoxide was prepared as described above the yields of the ketone were consistently 85 to 87% in several preparations.

The 1,3 diketones which were liquids or low-melting solids were readily soluble in the usual solvents. Nicotinylbenzoylmethane and dinicotinylbenzoylmethane were only slightly soluble in the usual solvents at room tem-

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[4] Wohl and Losanitsch, *Ber.*, **40**, 4695 (1907).

[5] *Cf.* Sprague, Beckham and Adkins, THIS JOURNAL, **56**, 2665 (1934).

[6] Strong and McElvain, *ibid.*, **55**, 816 (1933).

perature. All of the diketones were readily soluble in acids and bases. Alcoholic solutions of the bases formed deep red colors upon addition of ferric chloride. The hydrochlorides of nicotinylacetylmethane, nicotinylisovalerylmethane, nicotinyltrimethylacetylmethane and dinicotinylmethane were readily soluble in water. The hydrochloride of nicotinyl-*n*-valerylmethane and nicotinyl-*sym*-trimethylbenzoylmethane precipitated the free base as an oil upon addition of water. The hydrochloride of nicotinylcaproylmethane and nicotinylbenzoylmethane precipitated the free base as a solid upon addition of water.

The diketones were analyzed for nitrogen by a "semi-micro" Dumas method. The samples taken for analysis were of such a size that they yielded 3 to 4 ml. of nitrogen gas. The combustion tube was 13 mm. inside diameter and packed as follows: 10.5 cm. of oxidized copper gauze, 9.5 cm. space for sample, 1 cm. of oxidized copper gauze, 17.5 cm. of copper oxide in wire form and 1 cm. of asbestos. This packing is unorthodox in that no reduced copper spiral was used. However, better results have been obtained in the analysis of known compounds than with the reduced spiral. The reason for this lies in the fact that in the "semi-micro" method small amounts of carbon monoxide are produced over the reduced copper spiral and thus high values are obtained. The spiral is unnecessary, apparently because sufficient reduced copper is formed near the sample to reduce oxides of nitrogen if formed.

The hydrochlorides of three of the diketones were analyzed by the gravimetric method but in some other cases the precipitated silver chloride occluded the base. Difficulty was also encountered in using the Volhard method due to colored solutions. Both of these difficulties were avoided by hydrolyzing the sample of diketone (usually three or four hours) before precipitating the silver chloride.

Neutral equivalents were determined by direct titration with hydrochloric acid, using the methyl red–methylene blue indicator. The acetyl values were determined by treating the substance with an excess of acetic anhydride and heating in a steam-bath for twelve hours in a sealed tube. Occasionally, considerable difficulty was encountered during the titration due to the color of the acetylated product. It was found that thymol blue or brom thymol blue could be used satisfactorily, unless the product was too deeply colored. In the latter case the end-point was ascertained by means of a spot plate.

Analysis of Products of Alcoholysis.—In the distillation method the contents of the bomb were carefully washed into the distillation flask by means of 15 to 20 ml. of butyl alcohol. After the distillation of the ethyl and butyl alcohols, four additional 15-ml. portions of butyl alcohol were added and distilled out. The distillate was washed into a 200-ml. volumetric flask with ethanol and made up to volume with more ethanol. Fifty-ml. aliquot portions were then saponified by means of 30-ml. portions of 0.4 *N* sodium hydroxide. (A correction was made because of the fact that a 104.5% recovery had been effected upon distillation of known amounts of ester.)

In the extraction method the contents of the bomb were carefully washed into the extraction funnel with the aid of 20 to 25 ml. of ether. The ether solution was then extracted twice with 15-ml. portions of a 20% hydrochloric acid solution. The combined acid portions were extracted with four 15-ml. portions of ether. The ether extractions were added to the original ether solution, 50 to 60 ml. of ethanol was added, and the hydrochloric acid neutralized by means of alcoholic potassium hydroxide using phenolphthalein as an indicator. Care must be exercised at this point, as the slight color and precipitation of potassium chloride may cause the appearance of the end-point to be somewhat obscure. The best procedure was to add the alcoholic potassium hydroxide (2 to 3 normal) until the end-point was passed, and then to add 0.4 *N* hydrochloric acid until the end-point was just reached.

Hydrogenolysis of Diketones.—The diketones (0.12 to 0.15 mole) were subjected to the action of hydrogen at 150–160° in ether or preferably dioxane (75 ml.) under 150–250 atm. of hydrogen over Raney nickel (5 g.). In general the duration of hydrogenation was four to five hours and the absorption of hydrogen was 4 to 5 moles per mole of diketone. Exceptions were for R equals Me, three hours and 5.5 moles, and for mesityl two hours and 3.8 moles. The reaction mixture was filtered from the catalyst in a sintered glass funnel, dried in ether over potassium carbonate and fractionated through a heated Widmer column.

The simpler products were characterized by the usual methods, *i. e.*, comparison of properties with those previously reported, analysis and preparation and comparison of solid derivatives. In most cases the foregoing and the data given in Table III are sufficient description of the experimental work. However, the following should be noted: 1-(3-piperidyl)-5-methylhexanone was separated from a fraction of b. p. 120–129° (2 mm.) by making use of its relative insolubility in ether. The acetyl value was 2.96 and is consistent with the formula for the glycol as well as for the ketone. However, the boiling point, nitrogen analysis, and neutral equivalent exclude the latter structure. There is no evidence as to whether the carbonyl group is in the 1 or 3 position.

A fraction (20 g.) of b. p. 133–135° (7 mm.) showed a nitrogen analysis and acetyl value intermediate between that for 1-(3-piperidyl)-4,4-dimethylpentane and for 1-(3-piperidyl)-4,4-pentanone or the corresponding alcohol. The fraction was treated with hydrogen chloride and the hydrochlorides of these two substances separated by virtue of the solubility of the hydrochloride of the alkyl piperidine in acetone–ether mixtures. The analytical results on nitrogen, acetyl value and chlorine content of the hydrochloride serve as basis for the calculation of yields but do not justify a conclusion as to whether the more insoluble hydrochloride m. p. 164–165° (15.04% Cl) is that of the alcohol or of the ketone or as to the position of the oxygen.

A fraction (7.3 g.) of b. p. 100–104° (2 mm.) of a substance that was apparently 1-(3-piperidyl)-butanediol-1,3 was obtained from a diketone where R was Me, but while the analysis for nitrogen gave values only slightly high, the acetyl value indicated that the supposed glycol was not pure. The same statement may also be made for a fraction (6.2 g.) of b. p. 131–137° (2 mm.) (from the diketone where R is *i*-Bu) which was apparently 1-(3-piperidyl)-5-methylhexanol and another (6.1 g.) of b. p. 176–180° (2 mm.) which was apparently 1-(3-piperidyl)-3-phenylpropanol (from the diketone where R is Ph). The hydroxyl group in the latter alcohol must be in the 1 position but in the first there is no indication as to whether it is in the 1 or 3 position.

Summary

The preparation and properties of several nicotinyl acyl methanes have been described and their reactions with alcohol and hydrogen surveyed.

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[COMMUNICATION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

Hydrogenation and Hydrogenolysis of Ethers

BY EDWARD M. VAN DUZEE AND HOMER ADKINS

Ethers react with hydrogen under suitable conditions of temperature, pressure and catalyst, *i. e.*

$$ROR' + H_2 \begin{array}{l} \nearrow R'H + ROH \\ \searrow RH + R'OH \end{array}$$

If R or R′ is unsaturated, hydrogenation may precede or follow hydrogenolysis. These reactions have been observed by Sabatier, Senderens, Mailhe, Murat and Ipatieff and others to occur over nickel and by Skita, Grave, Waser and others over platinum or palladium.[1] The rapidly increasing importance of Raney nickel made it seem advisable to survey the behavior of typical ethers toward hydrogen over this catalyst. Such a survey was desirable since the intelligent use of the catalyst in preparational and constitutional work may require a knowledge of the type of reaction (or lack of it) which may be expected to occur with a given type of ether at a given temperature.

There are summarized in Table I the data obtained in this survey. In addition, a considerable number of ethers were found to be stable toward hydrogen over Raney nickel[2] at 200°, *i. e.*, monoethyl ether of ethylene glycol, *p*-methoxycyclohexanol, monomethyl ether of ethylene glycol, duodecyl phenyl ether, di-isopropyl ether, di-*n*-butyl ether, di-cyclohexyl ether, duodecyl *n*-butyl ether, duodecyl ethyl ether, diacetone glucose, cyclohexyl ethyl ether, cyclohexyl methyl ether, 1,3-dimethoxycyclohexane, 1,4-dimethoxycyclohexane, monocyclohexyl ether of trimethylene glycol, 4-cyclohexylbutyl cyclohexyl ether, cyclohexyl *n*-butyl ether, ethyl *n*-butyl ether of ethylene glycol, 3-cyclohexylpropyl cyclohexyl ether, methyl *n*-butyl ether of ethylene glycol, *n*-butyl ether of trimethylene glycol, 3-cyclohexylpropyl *n*-butyl ether, diethyl 2-cyclohexylethylmalonate, diethyl 3-cyclohexylpropylmalonate.

Discussion of Results

The answer to three questions will be considered with respect to the behavior of an ether toward hydrogen under the conditions of catalyst and pressure underlying the data in Table I.

(a) In what temperature range will the cleavage of the ether become reasonably rapid?[3]

(b) Which of the carbon to oxygen linkages in R···O···R′ will be ruptured by the reaction indicated in (a)?

(c) In what temperature range (in case R or R′ is unsaturated) will the hydrogenation of R or R′ become reasonably rapid?

The benzyl ethers undergo hydrogenolysis at a lower temperature than do other ethers. This is in accord with previous observations and with the well-known fact that a carbon to oxygen linkage β to a double bond (C=C—C···O) is very easily broken by a variety of reagents. The benzyl ethers undergo cleavage exclusively between the benzyl group and the oxygen at temperatures of 100 to 150°. Within this range a definite conclusion cannot be drawn as to the effect of variation in R upon the temperature of cleavage of benzyl ethers since traces of impurities in various ethers may account for apparent differences in the temperature required for hydro-

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[1] Sabatier and Senderens, *Bull. soc. chim.*, [3] **33**, 616 (1905); Mailhe and Murat, *ibid.*, [4] **11**, 122 (1912); Ipatieff and Lugovoi, *J. Russ. Phys.-Chem. Soc.*, **46**, 470 (1914); Ipatieff and Philipow, *Ber.*, **41**, 1001 (1908); *ibid.*, **46**, 3589 (1913); Skita and Brunner, *ibid.*, **49**, 1600 (1916); Skita and Rolfes, *ibid.*, **53**, 1245, 1253 (1920); Skita, *ibid.*, **54**, 1560 (1921); Grave, THIS JOURNAL, **46**, 1460 (1924); Waser and Brauchli, *Helv. Chim. Acta*, **7**, 743, 746 (1924); Waser, Sommer, Landweer and Gaza, *ibid.*, **12**, 418 (1929); Marty, *Compt. rend.*, **187**, 47 (1928).

[2] Adkins and Covert, THIS JOURNAL, **54**, 1651 (1932). The volume of the water should be maintained by addition during the reaction of aluminum with sodium hydroxide, and the temperature should be 110–115° during the period of heating.

[3] That the cleavage involved hydrogenolysis and not simply disproportionation ($RCH_2OR' \longrightarrow RCHO + R'H$) followed by hydrogenation ($RCHO + H_2 \longrightarrow RCH_2OH$) was shown by the fact that benzyl *n*-butyl ether, for example, was stable at 200° over Raney nickel under 100 atmospheres of nitrogen.