

TABLE III
 MELTING POINTS AND ANALYSES^a OF (4-CH₃OC₆H₄)C₆H₅CHOOC₆H₄X

X	M.p., °C.	Carbon, %		Hydrogen, %		-% Nitrogen or Chlorine-	
		Calcd.	Found	Calcd.	Found	Calcd.	Found
H	56-59 ^b	79.22	79.36	5.70	5.71		
<i>m</i> -NO ₂	104-106	69.41	69.11	4.72	4.74	3.86	3.80
<i>p</i> -NO ₂	81-82	69.41	69.33	4.72	4.84	3.86	3.74
<i>m</i> -Cl	Oil	71.49	71.81	4.86	5.21	10.05	9.78
<i>p</i> -Cl	66-67	71.49	71.48	4.86	4.72	10.05	9.92
<i>m</i> -CH ₃	Oil	79.50	79.69	6.06	6.31		
<i>p</i> -CH ₃	46-49	79.50	79.62	6.06	6.19		
<i>p</i> -CH ₃ O	57-60	75.84	75.96	5.78	5.84		

^a Analyses by Dr. Weiler and Dr. Strauss, Oxford, England. ^b A. G. Davies and J. Kenyon, *Quart. Rev.*, **9**, 203 (1955), report 58°.

TABLE IV

RATE OF HYDROLYSIS OF 0.0226 *M* *p*-METHOXYBENZHYDRYL *m*-NITROBENZOATE IN 88.9% ACETONE AT 90.5°, [NaClO₄] = 0.0106 *M*

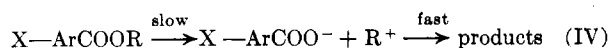
Time, sec.	0.01127 <i>M</i> NaOH, ml. ^a	10 ⁴ <i>k</i> , sec. ⁻¹
0 ^b	0.68	...
400	2.02	3.80
800	3.20	3.87
1200	4.21	3.90
1600	5.06	3.87
2000	5.79	3.88
2400	6.40	4.01
3200	7.47	3.94

Av. 3.90 ± 0.05

^a Amount of base to titrate a 5.0-ml. aliquot. ^b Zero time represents 200 sec. after a sample was immersed in the bath.

benzhydryl carbonium ion is such that improvement along this line does not appear worth pursuing.

The uncatalyzed hydrolysis of the *p*-methoxybenzhydryl esters by the B_{AL}¹ mechanism (IV) appears closely



analogous to the ionization of benzoic acids. It is, therefore, not surprising that the hydrolysis shows a good σ correlation (Table II) and that ρ , for the hydrolysis (1.8), is comparable to ρ for benzoic acid ionization^{7c} in ethanol-water.

Experimental

The esters were prepared by conventional means¹⁰ from readily available starting materials. The properties of the esters are given in Table III. The 88.9% acetone was prepared by mixing 250 ml. of redistilled water, which contained either perchloric acid or sodium perchlorate, with 2000 ml. of pure acetone¹¹ at 25°. The kinetic procedure involved standard ampoule technique, with titration of the acid present by standard base.¹² Very small corrections had to be supplied for solvent decomposition in a few runs. All runs were followed to at least 70% reaction, except for the *p*-methoxy (to 25%) and the unsubstituted, *m*-methyl and *p*-methyl esters (to 50%) in the uncatalyzed reactions at 70.5°. Good first-order plots were obtained and Table IV shows a typical example.

(10) H. L. Goering and J. P. Blanchard, *J. Am. Chem. Soc.*, **76**, 5405 (1954).

(11) J. K. Kochi and G. S. Hammond, *ibid.*, **75**, 3445 (1953).

(12) H. L. Goering and E. F. Silversmith, *ibid.*, **77**, 6249 (1955).

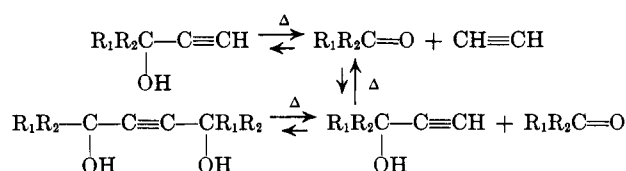
The Reaction of Alkali Metal Hydroxides with Tertiary Acetylenic Carbinols and Glycols

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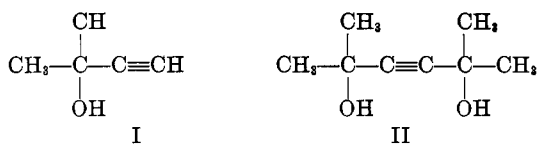
The base-catalyzed cleavage of tertiary acetylenic carbinols¹⁻³ and glycols^{4,5} to ketones and acetylene has been extensively studied. The cleavage is generally irreversible above 100° and diol cleavage proceeds through the intermediate formation of carbinol. The reverse reaction (ethynylation) also is well documented and is known as the Favorskii synthesis.^{2,6}



However, the direct, stoichiometric reaction of pure alkali metal hydroxides with tertiary acetylenic carbinols and glycols followed by isolation and characterization of the reaction products has never been reported. The closest analogy has been the preparation of potassium derivatives^{7,8} using potassium metal in which reaction with the tertiary hydroxyl groups was claimed.

Work at this laboratory now has shown that the heterogeneous reaction of essentially anhydrous, finely divided potassium hydroxide with either 3-methyl-1-butyn-3-ol (I) or 2,5-dimethyl-3-hexyne-2,5-diol (II) takes place rapidly and in high conversion in inert solvents under mild reaction conditions.

- (1) L. Henry, *Ber.*, **8**, 398 (1875).
- (2) A. E. Favorskii and M. Skossarewskii, *Zh. Fiz. Khim. Obshchestva*, **32**, 652 (1900); *Bull. soc. chim.*, **26**, 284 (1901).
- (3) Farbenfabriken Vorm. Friedr. Bayer and Co., German Patent 285,770; *Chem. Zentr.*, **II**, 508 (1915).
- (4) G. Arbuзов, *Zh. Fiz. Khim. Obshchestva*, **53**, 288 (1921); *Chem. Abstr.*, **18**, 2327 (1924).
- (5) G. Arbuзов and T. Temnikova, *Zh. Fiz. Khim. Obshchestva*, **54**, 219 (1922); *Chem. Abstr.*, **18**, 2514 (1924).
- (6) A. W. Johnson, "Acetylenic Compounds," Vol. I, "The Acetylenic Alcohols," Edward Arnold Co., London, 1946, pp. 14, 137, 147.
- (7) P. L. Salzberg and C. S. Marvel, *J. Am. Chem. Soc.*, **50**, 1737 (1928).
- (8) G. Arbuзов, *et al.*, *Zh. Fiz. Khim. Obshchestva*, **53**, 288 (1921); *Chem. Abstr.*, **18**, 2327 (1924); *Zh. Fiz. Khim. Obshchestva*, **54**, 219 (1922); *Chem. Abstr.*, **18**, 2514 (1924).



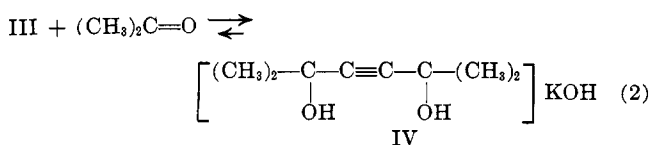
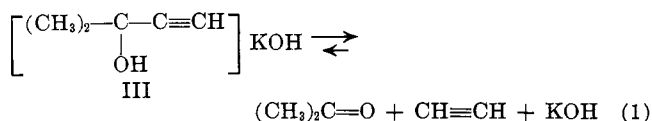
The addition of I or II to a well stirred stoichiometric amount of finely divided potassium hydroxide in dry inert solvents such as diisopropyl ether or toluene under anhydrous conditions results in the rapid formation of a thick, white reaction mass. Highly crystalline 1:1 molar adducts of either I or II and potassium hydroxide can be readily isolated under anhydrous conditions in conversions of 98–100%. The resulting reactions proceed rapidly in organic solvents at temperatures as low as -30° and are not significantly exothermic. Potassium hydroxide adducts of I and II also form rapidly (15–30 minutes) in quantitative conversion in liquid ammonia at temperatures of -50° to -60° .

The degree of reactivity of other alkali metal hydroxides with I and II is of additional interest. The following data show that conversions are highest with potassium, cesium, and rubidium hydroxides and greatly inferior with lithium and sodium hydroxides.

TABLE I
REACTION OF ALKALI METAL HYDROXIDES WITH METHYL-BUTYNOL (I) AND DIMETHYLHEXYNEDIOL (II) IN ISOPROPYL ETHER

Hydroxide	Conversion to adduct, %	
	I	II
Li	0	0
Na	3.5	0
K	100	100
Rb	100	76
Cs	52	72

A sample of dry, powdered adduct derived from I on standing at room temperature for thirty months protected from moisture was found on re-analysis to contain no methylbutynol, although it appeared visually unchanged in color or physical state. Subsequent analysis and hydrolysis of the product showed it to be composed mainly of II and potassium hydroxide. This solid phase transformation can be represented by the following route, which in turn is based on the known reactions of base-catalyzed cleavage¹⁻³ and diol formation⁶ from ethynylcarbinols and ketones in the presence of potassium hydroxide.



However, two attempts to treat adduct III with acetone in isopropyl ether were surprisingly negative. The reactions were carried out at $30-35^\circ$ (optimum diol

range) using both isolated, and freshly prepared (*in situ* at 0 to 5°) adducts as starting materials. No 2,5-dimethyl-3-hexyne-2,5-diol was isolated from either run. These observations and the fact that the transformation of III into IV takes place efficiently without the formation of acetone condensation products indicates a more complex intra-intermolecular mechanism may be involved here.

The possibility also exists that the free potassium hydroxide (equation 3) might be tied up as a 1:2 diol-potassium hydroxide adduct. An attempt to form a 1:2 adduct starting with II and potassium hydroxide gave a product which contained a large amount of free base on X-ray examination indicating a 1:2 diol-potassium hydroxide adduct was not formed in significant amount. The diol II was isolated in 77% conversion from the transformed adduct. On analysis (See Experimental section) of the adduct mixture the observed mole ratio of diol (dimethyl hexynediol) to potassium hydroxide (1.20) for equation 3 agreed fairly well with the calculated value (1.27). Further, by heating a freshly prepared sample of adduct I, as a well stirred slurry in dry isopropyl ether at $35-40^\circ$, the transformation could be markedly hastened. In six hours the diol content increased from 7 to 14% as measured by the decrease in methylbutynol present.⁹ However, at temperatures above 60° , the complete reversal of I to acetone, potassium hydroxide, and acetylene began. The latter was readily detected by a nitrogen sweep in the system, and bubbling the exit gas through 50% silver nitrate solution or Ilsovsy's reagent.

The potassium hydroxide adduct of I can be readily formed by the stoichiometric reaction of acetone, acetylene, and finely ground base in isopropyl ether at -10 to 0° in 87% conversion. Infrared and X-ray comparison of this adduct with the product formed from I and potassium hydroxide show them to be identical. Even though adduct III was stored at $0-5^\circ$ in an ice-box desiccator a slow transformation after several months into adduct IV (10% conversion) was observed. No attempt has been made to isolate adduct IV by the reaction of acetone, acetylene, and potassium hydroxide at higher temperatures ($30-35^\circ$). However, this should be comparatively simple, since the Favorskiĭ synthesis carried out at $30-35^\circ$ in solvents such as isopropyl ether or dioxane particularly with the more reactive ketones (acetone, methyl ethyl ketone), always gives high conversions (85–95%) to isolated acetylenic diol.^{8,10} The same thick characteristic reaction mass, typical of adducts III and IV, is always obtained before hydrolysis and isolation of diol II. Further, this method is a commercial process used by the Air Reduction Company, Inc., to produce acetylenic carbinols and glycols.

These adducts are now known to be the intermediate products in the Favorskiĭ² synthesis of tertiary acetylenic carbinols and glycols,⁶ as verified by chemical, infrared, and X-ray analyses in this laboratory. Hydrolysis with water yields (90–100%) the free acetylenic compound and potassium hydroxide as is always observed in the Favorskiĭ method. Likewise, treatment of the solvent-adduct slurry with dry carbon

(9) L. Barnes, Jr., and L. J. Molinini, *Anal. Chem.*, **27**, 1025 (1955).

(10) R. J. Tedeschi, T. F. Rutledge, R. K. Frantz, and J. P. Russell, unpublished work, Air Reduction Co., Inc., Murray Hill, N. J., 1953–1958.

dioxide gas yields the free acetylenic and potassium bicarbonate.

Potassium hydroxide also has been observed qualitatively to form crystalline adducts with other tertiary acetylenic carbinols and glycols. Very rapid (less than one minute) formation of thick reaction slurries of adducts, at room temperature, were observed with 1-ethynylcyclohexanol and 3-methyl-1-pentyn-3-ol, while diols such as 3,6-diethyl-4-octyne-3,6-diol, 4,7-dimethyl-5-decyne-4,7-diol, and bis-1-(1-hydroxycyclohexyl)-acetylene gave moderately rapid reactions as evidenced by the formation of crystalline slurries in ten to fifteen minutes. 3-Phenyl-1-butyn-3-ol showed only slight evidence of reaction during a fifteen-minute period, but on overnight shaking formed a moderately thick slurry.

The X-ray diffraction patterns of adducts III and IV (determined in sealed capillaries) are essentially identical, it being difficult to distinguish them without prior knowledge. A characteristic intense d spacing at 11.5–12.5 Å. is present in both III and IV. As high as twenty less intense spacings have been observed at 2–13.7 Å. Free potassium hydroxide is minor or absent as estimated by characteristic d spacings at 4.00, 3.70, 2.93, 2.68, 2.58, 2.43, 2.30, 1.98, 1.84, 1.64, 1.55 Å.

The infrared spectra (potassium bromide disk or Nujol mull) of freshly prepared adduct I show the absence of the characteristic $C\equiv C$ stretch at 4.68–4.76 μ . Further, no strong absorption at 2.96–3.08 μ typical of $\equiv CH$ is noted. In place of the characteristic $-OH$ absorption of 3-methyl-1-butyn-3-ol at 3.00–3.07 μ , a broad, weak band at approximately 3.0–4.0 μ is observed in adduct III. The typical $C-O$ stretch for tertiary acetylenic carbinols and glycols at 8.7 μ is still detectable in the adducts.

The dimethylhexynediol-potassium hydroxide adduct yields an infrared spectra similar to the parent compound except for the absence of the normal $-OH$ maxima at 3.0 μ . In its place is noted a fairly strong absorption at 4.0 μ which resembles that found in chelated or hydrogen bonded groups. The typical $C-O$ stretch also is observed at 8.7 μ , but no $C\equiv C$ is detected (or expected) at about 4.7 μ since the internal triple bond is generally infrared inactive.

The infrared spectrum of freshly prepared adduct III is observed on pressing (potassium bromide disk) to undergo slight changes compared to spectra run in Nujol. Similar changes also are noted and are much more pronounced after III has stood at room temperature for periods longer than one week. These spectra changes are due to the gradual conversion of adduct III into IV or possible decomposition of the adduct into acetone and acetylene due to the heat of pressing. Adduct IV does not show comparable changes in spectrum under similar conditions.

The complete absence of $C\equiv C$ and $\equiv CH$ stretches in adduct III together with a possible weak, broad hydroxyl group absorption indicates interaction of potassium hydroxide with both the cylindrical π shell of the triple bond and the tertiary $-OH$ group. Such bonding is suggestive of complex formation rather than the alternate possibility of an alkoxide containing a tightly bound molecule of water. The essentially quantitative conversions observed in the formation of III and IV under mild temperature conditions is not typical of the

known inertness of tertiary alcohols with alkali hydroxides to form alkoxides.

Experimental

The following methods were used to determine the composition of the adducts.

Carbon and Hydrogen.—The combustion of the adducts must be carried out in the presence of excess tungstic acid well mixed with the sample in the combustion boat. A minimum combustion of 30 min. directly over the sample should be used to ensure complete decomposition of any potassium bicarbonate and carbonate formed during the combustion.

Alkali Hydroxide.—The sample is slaked in water (preferentially boiled free of carbon dioxide) and directly titrated with standard acid.

Ethynyl Hydrogen ($C\equiv C$).—The standard titrametric method of Barnes and Moliuini⁹ was used after slaking in water and neutralization of the potassium hydroxide.

Internal Triple Bond ($C\equiv C$).¹¹—The adducts are decomposed in the presence of excess caustic in a high boiling solvent such as diethylene glycol. The evolved acetylene is absorbed in silver nitrate solution and determined volumetrically.

3-Methyl-1-butyn-3-ol-Alkali Hydroxide Adducts.—This general method can be used only for potassium, cesium, and rubidium hydroxides. A desirable reaction loading is 0.20 mole of alkali hydroxide and methylbutynol per 500 cc. of solvent. The alkali hydroxide¹² is first reduced to coarse powder in a drybox at 0% relative humidity (desiccants—anhydrous molecular sieve and granular calcium carbide) and stored until used. The required amount of alkali hydroxide is then ground *in situ* in anhydrous solvents (250 cc.) such as diisopropyl ether or toluene using a two-speed stainless steel Waring Blender equipped with a gasketed screw cap top. Solvents boiling lower than 60° are best not employed due to leakage of the blender seals caused by the heat of grinding and resultant pressure increase in the system. Grinding should not be carried out longer than 5 min. for the same reasons and, in most cases, is complete in several minutes.

The fine alkali hydroxide suspension is transferred by quantitative solvent rinses (total 250 cc.) in the drybox to a dry, 1-l. resin kettle equipped with a stirrer, entrance and exit nitrogen flush connections, and a port for methylbutynol addition. The sealed reactor is then removed from the drybox, purged with a slow current of dry nitrogen, and cooled with moderate stirring from 0° to -10° . Anhydrous conditions are maintained in all operations using nitrogen dried over potassium hydroxide pellets.

Methylbutynol (0.20 mole, 16.8 g.) dissolved in 25 cc. of the selected anhydrous solvent is added during 5–10 min. to the hydroxide-solvent slurry, and stirred rapidly enough to obtain good mixing, but slow enough to avoid excessive spattering. Within 5 min. the reaction slurry changes from a thin readily stirrable slurry to a thick, white, barely stirrable mass. The reaction temperature is maintained at -10 to 0° to avoid any conversion to the dimethylhexynediol-base adduct. After stirring 30 min. to 2 hr., the reaction with potassium or rubidium hydroxides is complete and gives conversions of 98–100% depending on the water content of the base. Actually concentrations of methylbutynol and potassium hydroxide of 0.5 mole/500 cc. can be employed successfully, but the reaction mixture becomes excessively thick and difficult to stir.

The adduct is isolated either by suction filtration in the drybox or by centrifugation (basket centrifuge) in sealed tubes. After several washings (anhydrous conditions) with dry, low boiling petroleum ether, the moist filter cake is vacuum dried (< 1 mm.) to constant weight during 6–8 hr. The dry material is powdered, and stored in sealed jars in an icebox desiccator (1-l. resin kettle) over sodium hydroxide pellets.

Although potassium hydroxide containing as high as 10% water, and coarser (40 mesh) in particle size can be used, conversions to the adducts I or II are considerably lower (as much as 50%) and more variable.

(11) Unpublished analytical method developed by L. J. Molinini at the Air Reduction Co., Inc., Central Research Laboratories, Murray Hill, N. J.

(12) Essentially anhydrous (98–99.5%) granular, potassium hydroxide can be obtained from Niagara Alkali Co., Buffalo, N. Y., while cesium and rubidium hydroxides (98% hydroxide) are available from S. McKay Co., New York, N. Y.

3-Methyl-1-butyn-3-ol-Potassium Hydroxide Reaction Product.—A 42-g. (0.50 mole) sample of methylbutynol and 28.5 g. (0.50 mole) of 98% potassium hydroxide in 800 cc. of diisopropyl ether gave 69.8 g. (99.7% conversion) of adduct.

Anal. Calcd.: KOH, 40.0; C≡CH, 17.9; C, 42.8; H, 6.4. Found: KOH, 38.3; C≡CH, 17.5; C, 42.6; H, 7.8.

2,5-Dimethyl-3-hexyn-2,5-diol-Alkali Hydroxide Adducts.—The method of preparation is identical to the methyl butynol procedure except that a higher reaction temperature (30–35°) is employed with solvents such as diisopropyl ether or toluene. Dimethylhexynediol is dissolved by warming in 300–500 cc. of one of these solvents and then adding the mixture to a 300 cc. slurry of alkali hydroxide in the same solvent. The diol adducts yield a noticeably thicker reaction mass, and dilution with solvent is generally needed to facilitate isolation.

Diol-Potassium Hydroxide Reaction Product.—A 14.2-g. (0.10 mole) sample of dimethylhexynediol and 5.7 g. (98%) of potassium hydroxide in 600 cc. of isopropyl ether gave 19.2 g. of adduct (97% conversion).

Anal. Calcd.: KOH, 28.1; C≡C, 12.1; C, 48.4; H, 7.6. Found: KOH, 27.7; C≡C, 11.1; C, 47.4; H, 8.2.

The average purity based on C and KOH values was 98.1%, and the ethynyl content (C≡CH)⁹ was less than 0.05%.

Formation of Methylbutynol-Potassium Hydroxide Adduct from Acetone, Acetylene, and Potassium Hydroxide.—Dry acetylene gas was metered (liters) into a well stirred mixture of 28.5 g. (0.50 mole) of 98% potassium hydroxide in 800 cc. of dry, alcohol-free isopropyl ether at –10 to 0°. The acetylene used was dried successively over granular (0.125 in.) calcium carbide and alumina (F-10), and the 1-l. reactor protected from the atmosphere with alumina towers. The net liters of acetylene absorbed was determined by the use of entrance and exit Weston wet test meters.

When the ether-base slurry was essentially saturated with acetylene (6 l.), the addition of 29.0 g. (0.50 mole) of dry acetone was begun. Acetone addition during 1 hr. was accompanied by the formation of a thick, but stirrable reaction mass. Acetylene was metered into the reaction to a total of 15 l., always maintaining an excess of acetylene over acetone. The reaction product was isolated in the usual manner after a total reaction time of 2 hr., and weighed 61 g. (87% conversion).

Anal. Calcd. (87% pure): KOH, 43.3; C, 37.3; H, 6.58. Found: KOH, 41.5; C, 38.0; H, 6.84.

The product was found by X-ray and infrared examination to be identical with methylbutynol-potassium hydroxide adducts prepared from methylbutynol. It also contained less than 0.05% dimethylhexynediol as determined by internal C≡C value.¹¹

Analgesics. Stereoselective Syntheses of α -(+)- and α -(-)-4-Dimethylamino-1,2-diphenyl-3-methyl-2-propionoxybutane

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The preparation of α -(+)-4-dimethylamino-1,2-diphenyl-3-methyl-2-propionoxybutane has been described.¹ By this procedure the intermediate α -(±)-4-dimethylamino-1,2-diphenyl-3-methyl-2-butanol was resolved by fractional crystallization of the (+)-camphorsulfonic acid salt and the optically active carbinol was acylated by means of propionic anhydride in pyridine. The α -(+)-isomer, *d*-propoxyphene, has found general acceptance as an analgesic. It was, therefore, of interest to find alternate synthetic routes for the preparation of this compound.

(1) A. Pohland and H. R. Sullivan, *J. Am. Chem. Soc.*, **77**, 3400 (1955).

During previous work² α -(+)-4-dimethylamino-1,2-diphenyl-3-methyl-2-propionoxybutane was hydrolyzed and dehydrated to the stilbene. Ozonization of the stilbene afforded good yields of (-)- β -dimethylamino- α -methylpropionophenone. This optically active amino ketone was found to be surprisingly stable in the salt form and also as solutions of the free base in nonpolar solvents. In light of these observations, it appeared that a stereoselective synthesis of α -(+)-4-dimethylamino-1,2-diphenyl-3-methyl-2-propionoxybutane would be feasible.

β -Dimethylamino- α -methylpropionophenone was resolved by crystallization of the dibenzoyl tartrate salts from acetone solution. The use of dibenzoyl(-)-tartaric acid yielded the insoluble salt with (-)-dimethylamino- α -methylpropionophenone, while the use of dibenzoyl(+)-tartaric acid yielded the insoluble salt with the (+)-amino ketone. It is of interest that concentration of the filtrate from the resolution causes racemization of the soluble diastereoisomeric salt and affords a nearly quantitative yield of the insoluble salt of the desired optically active ketone.

(-)- β -Dimethylamino- α -methylpropionophenone was liberated from its dibenzoyl(-)-tartrate salt by means of base and allowed to react in ether solution with benzylmagnesium chloride in the same manner as described for the racemic ketone.¹ α -(+)-1,2-Diphenyl-3-methyl-4-dimethylaminobutanol-2 was obtained in good yield indicating that little racemization of the amino ketone occurs during the Grignard reaction.

The α -(+)- and α -(-)-aminocarbinols were converted to their propionyl esters by the reported procedures.¹

Experimental³

(-)- β -Dimethylamino- α -methylpropionophenone Acid Dibenzoyl(-)-tartrate.—A solution of 26 g. (0.65 mole) of sodium hydroxide in 100 ml. of water was added to 122 g. (0.536 mole) of β -dimethylamino- α -methylpropionophenone hydrochloride. The liberated base was taken up in 150 ml. of ether, washed with water, and dried over anhydrous magnesium sulfate. The dry ether solution was concentrated *in vacuo* to yield 101.7 g. (0.53 mole) of β -dimethylamino- α -methylpropionophenone. The oily ketone and 200 g. (0.532 mole) of dibenzoyl(-)-tartaric acid monohydrate were dissolved in 4 l. of acetone. The resulting solution was allowed to stir at room temperature until crystallization had begun and for an additional 18 hr. The solid was collected on a filter and washed with acetone and dried *in vacuo* to yield 157 g. of product. Successive concentration of the combined filtrate and wash solutions to 1 l., 250 ml., and 100 ml., yielded, respectively, 100.0 g., 12.0 g., and 7.3 g. of additional product. The total yield of product was 276.3 g. (94%); m.p. 112–117°; $[\alpha]^{25}_D +52.0^\circ$ (*c* 1, methanol).

A portion was recrystallized four times from acetone solution and melted at 116–117°; $[\alpha]^{25}_D +57.2^\circ$ (*c* 1, methanol).

Anal. Calcd. for C₁₂H₁₇NO·C₁₈H₁₄O₈: C, 65.56; H, 5.69; N, 2.55. Found: C, 65.04; H, 5.84; N, 2.29.⁴

(+)- β -Dimethylamino- α -methylpropionophenone Acid Dibenzoyl(+)-tartrate.—This salt was prepared in the same manner using dibenzoyl(+)-tartaric acid in place of the dibenzoyl(-)-tar-

(2) H. R. Sullivan, J. R. Beck, and A. Pohland, *J. Org. Chem.*, **28**, 2381 (1963).

(3) Melting points are uncorrected. The authors are indebted to W. L. Brown, H. L. Hunter, and G. L. Maciak for the microanalyses.

(4) This salt crystallizes as the hemihydrate and must be dried at 110° *in vacuo* before analysis.