

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

The Hydrogenation of Amides and Ammonium Salts. The Transalkylation of Tertiary Amines

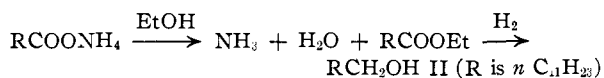
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The hydrogenation of certain unsubstituted amides and ammonium salts of acids over copper-chromium-barium oxide (I) has been reinvestigated. Contrary to previous reports, alcohols rather than amines have been isolated as the major reduction product. The transalkylation of tertiary amines with alcohols, $R_3N + R'OH \rightarrow R_2R'N + ROH$, is described. The reaction occurs under hydrogenation conditions over I or Raney nickel catalysts. The alcohol can be used as such or, when I is employed as catalyst, may be formed from an acid or ester; the transalkylation occurs under the conditions of hydrogenation of these compounds.

The hydrogenation of unsubstituted amides over copper-chromium-barium oxide (I) catalysts in dioxane has been reported to yield a mixture of primary and secondary amines.³ It was believed that a higher ratio of primary amine could be expected if the reaction were carried out more rapidly by employing higher pressures of hydrogen.⁴ To test this hypothesis the reduction of lauramide has been studied in the pressure range 300–800 atmospheres. While some amines were obtained, dodecanol-1 (II) constituted a major portion of the reduction products in all cases. The result was the same, whether I was prepared by earlier methods,^{5,6} or by improved techniques which gave more active catalysts.^{7,8} Furthermore, by lowering the temperature of the reaction, a much higher ratio of alcohol to primary amine was obtained.

A similar deviation from previously reported results was experienced in the reduction of ammonium acid laurate in dioxane. While Wojcik and Adkins³ reported that a mixture of primary and secondary amines was obtained, it was observed in the present work that dodecanol (II) constituted 38% of the reduction products; the use of ethyl alcohol instead of dioxane as a solvent gave dodecanol as the principal product, together with small amounts of *n*-dodecylamine, *n*-dodecylethylamine and ethyl laurate. The reaction in alcohol is believed to involve the intermediate formation of the ester.⁹ Presumably, the dodecylamines were



formed by the interaction of II and the ammonia from the original salt.¹⁰ When water was employed as the solvent, only a small amount of hydrogenation occurred due to the complete reductive deactivation of the catalyst.

A process for the direct catalytic hydrogenation

(1) Wisconsin Alumni Research Foundation Research Assistant, 1949–1950; Socony-Vacuum Oil Company Fellow, 1950–1951.

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(3) B. Wojcik and H. Adkins, *THIS JOURNAL*, **56**, 2419 (1934).

(4) H. Adkins, "Reactions of Hydrogen," University of Wisconsin Press, Madison, Wis., 1937, p. 113.

(5) R. Connor, K. Folkers and H. Adkins, *THIS JOURNAL*, **54**, 1138 (1932).

(6) H. Adkins and E. Burgoyne, *ibid.*, **71**, 3428 (1949), footnote 2.

(7) T. Riener, *ibid.*, **71**, 1130 (1949).

(8) H. Adkins, E. Burgoyne and H. J. Schneider, *ibid.*, **72**, 2626 (1950).

(9) Cf. E. Filachione, E. Costello and C. Fisher, *ibid.*, **73**, 5265 (1951).

(10) (a) H. Adkins and J. Paden, *ibid.*, **58**, 2487 (1936); (b) H. Adkins and C. Winans, *ibid.*, **54**, 306 (1932).

of acids to alcohols has been sought for some time with varying degrees of success.^{11–14} The carboxyl function, by virtue of its acidity, is incompatible with the basic oxide catalysts usually employed for the hydrogenation of carboxylate groups. Consequently, the methods employed for the reduction must prevent the interaction of the catalyst with the acid. It seemed that the use of a tertiary amine as a solvent for the reduction of acids would accomplish the necessary neutralization of the acid and, in contrast to ammonia, primary and secondary amines, give no further reaction with the alcohol produced by the reduction of the acid. So far as is known, no attempt to employ tertiary amines as solvents for catalytic reduction of acids has been reported.

The reduction of acids and esters proceeded smoothly in triethylamine. In four hours 0.2 mole of lauric acid was reduced over 10 g. of copper-chromium-barium oxide in 73 g. of triethylamine at 400 atmospheres and 250°. However, the yield of dodecanol was only 50%; the remainder of the acid was in the form of *N,N*-diethyldodecylamine (III). The formation of the latter product suggested that the original triethylammonium laurate had been pyrolyzed into ethyl alcohol and the *N,N*-diethylauramide,¹⁵ which then was hydrogenated to the tertiary amine (III). However, since tertiary amines were obtained only in very low yields during the reduction of *N,N*-dialkyl amides,³ it appeared that some other mechanism was operative.

It was found that alcohols and tertiary amines react at 250° to form different tertiary amines in the presence of hydrogenation catalysts such as copper-chromium-barium oxide or Raney nickel. When dodecanol and triethylamine were used, the products isolated were diethyldodecylamine and didodecylethylamine (IV). In the absence of hydrogenation catalysts the reaction did not occur. With Raney nickel¹⁶ the hydrogenolysis of the alcohol^{17,18} was a competitive reaction; for example, as much as 17% of the dodecanol was converted to undecane at 250°.

It was necessary to conduct these reactions under hydrogen pressure (270–400 atmospheres) to pre-

(11) French Patent 819,255 (1937).

(12) W. Rittmeister, U. S. Patent 2,248,465 (1941).

(13) German Patent 711,180 (1941).

(14) A. Abbey, British Patent 573,788 (1950).

(15) Cf. J. von Braun and K. Weissbach, *Ber.*, **63B**, 489 (1930).

(16) R. Mzingo, *Org. Syntheses*, **21**, 15 (1941).

(17) H. Adkins and B. Wojcik, *THIS JOURNAL*, **55**, 1293 (1933).

(18) H. Adkins and H. Burdick, *ibid.*, **56**, 438 (1934).

TABLE I
 HYDROGENATION OF AMIDES AND AMMONIUM ACID LAURATE OVER COPPER-CHROMIUM-BARIUM OXIDE AT 250°

Compound	Amount used, mole	Amount of catalyst, g.	Maximum pressure (atmospheres)	Reacn. time, hr.	Yields, %		
					RCH ₂ OH	RCH ₂ NH ₂	(RCH ₂) ₂ -NH
Lauramide	0.1 ^a	4	370	1	62	12	22
	.1 ^a	4	340	2	52	16	33
	.1 ^a	4	330	2	33	17	36
	.1 ^a	5	330	1.3	39	15	43
	.1 ^a	5	820	1	25	17	52
	.1 ^a	5	950 ^d	1	42	2.4	.. ^f
Caprylamide	.1 ^a	5	990 ^e	1	16	0.5	.. ^g
	.1 ^a	5	370	1	35	7	44
Ammonium acid laurate	.05 ^a	5	380	3	34	15	50
	.05 ^b	5	450	5	80	4.5 ^h	..
	.05 ^b	5	390	5	80	4.5 ^h	..
	.05 ^b	5	410	10	96	3.8 ^h	..
	.1 ^h	10	390	10	80	5.9 ^h	..
	.05 ^c	5	350	3	28

^a In 40 ml. of dioxane. ^b In 100 ml. of absolute ethanol. ^c In 100 ml. of water. ^d At 200°. ^e At 175°. ^f 47% lauramide recovered. ^g 80% lauramide recovered. ^h Includes N-ethyl-dodecylamine.

vent the dehydrogenation of the alcohols to esters.¹⁹ When the reaction was carried out under nitrogen pressure at 250° a gradual increase in the total pressure of the system was observed, indicating the formation of esters with liberation of hydrogen.

With copper-chromium-barium oxide the transalkylation reaction did not occur to any appreciable extent at temperatures below 250°. In a ten-hour run the conversion of dodecanol to dodecylamines III and IV dropped from 85% at 250° to 9% at 150°. Since the reaction evidently involved an equilibrium there must be an upper limit to the amount of alcohol which will interact with the triethylamine in a closed system. In general, longer reaction times and higher temperatures increased the amount of didodecylethylamine formed. The effects of temperature, time and other variables are summarized in Table II.

Two routes by which such transalkylation of tertiary amines may occur are: (1) the direct replacement of the lower alkyl group by the higher alcohol, or (2) initial interaction of water with the tertiary amine to form ethanol and the secondary and primary amines, which then react with the higher alcohol.¹⁰ When water in equimolar quantity with the alcohol was added to a copper-chromium-barium oxide catalyzed reaction of dodecanol and triethylamine, the amount of higher boiling amines formed amounted to only 65% as compared to 83% when no water was added. Moreover, the catalyst was recovered in the brick-red, deactivated form. However, diethylamine, isolated as N,N-diethylbenzenesulfonamide, was obtained in low yield by heating triethylamine alone with copper-chromium-barium oxide, at 250° under 400 atmospheres of hydrogen.²⁰ Inasmuch as copper-chromium-barium oxide catalysts contain water that cannot be removed except by destructive heating of the catalyst, and since water is produced by hydrogenolysis of the alcohols over nickel, it has not been possible to carry out the

transalkylation of a tertiary amine under rigorously anhydrous conditions. Consequently, it cannot be determined from presently available data whether water plays an essential role in this reaction.

 TABLE II
 TRANSALKYLATIONS OF TERTIARY AMINES^a IN THE PRESENCE OF COPPER-CHROMIUM-BARIUM OXIDE CATALYSTS AT 250°

R	ROH used, moles	Catalyst used, g.	Reacn. time, hr.	ROH re-covered	Yields, % (C ₂ H ₅) ₂ RN-	R ₂ -NC ₂ H ₅
n-C ₁₂ H ₂₅	0.1	0	8	96
	.2	5	3	72	22	4
	.2	10	10	28	42	10
	.2	10	10	15	66	19
	.1	5	10 ^c	91	3	..
	.1	5	10 ^d	48	37	7
	.1	2 ^e	10	.. ^f	64	5
	.1	2 ^e	10	.. ^f	63	6
n-C ₈ H ₁₇	.1 ^b	5	7	59	40	28 ^h
	.2	10	10	13	63	7
	.2 ^g	5	4.5	57	25	5

^a Unless otherwise noted, 0.37 mole of triethylamine per 0.1 mole of alcohol was used. ^b 0.09 mole of N,N-diethyl-dodecylamine/0.1 mole of alcohol. ^c At 150°. ^d At 200°. ^e Raney nickel. ^f Recovered 17% undecane. ^g Methyl caprylate instead of the alcohol used in this run. ^h A 13% yield of tridodecylamine was obtained as a higher boiling product (see Table III for properties) from this run.

Experimental

Materials.—The amides were prepared by the method of Wojcik²¹ which involved the reaction of methyl esters with a twofold molar excess of anhydrous ammonia in an autoclave at 250° for two hours. The crude material (yield 90–95%) was recrystallized from ethanol.

Ammonium acid laurate was prepared by passing ammonia gas into a stirred solution of 100 g. of lauric acid in 750 ml. of anhydrous ether. The salt was collected, washed with ether, air-dried and recrystallized from methanol to give 85–95 g. of white platelets. On the basis of earlier work,²² Wojcik had assumed this compound to be ammonium laurate³; however, the reaction of ammonia with lauric acid in ether was later shown to yield the ammonium acid salt, C₁₁H₂₃COONH₄·C₁₁H₂₃COOH.²³

The methyl esters were prepared by the methanolysis of

(19) H. Adkins and R. Burks, *THIS JOURNAL*, **62**, 3300 (1940).

(20) J. Bain and C. Pollard, *ibid.*, **61**, 2704 (1939), have obtained cyclohexanol by heating diethylcyclohexylamine in 50% aqueous dioxane over copper-chromium oxide at 270–280° without hydrogen pressure.

(21) B. Wojcik, Ph.D. Thesis, University of Wisconsin, 1934, p. 28.

(22) P. Falciola, *Gazz. chim. ital.*, **40**, II, 425 (1910).

(23) J. E. Kench and T. Malkin, *J. Chem. Soc.*, 230 (1939).

TABLE III
 COMPOUNDS USED AND REACTION PRODUCTS

Compound	Formula	M.p. or b.p., °C. (mm.)	n_D^{20}	Calcd.	N. %		Neut. or sapon. equiv.	
					Found	Calcd.	Found	
Lauramide	C ₁₂ H ₂₇ ON	99-101	7.03		7.04		
Caprylamide	C ₈ H ₁₇ ON	105-106						
Ammonium acid laurate	C ₂₄ H ₅₁ O ₄ N	74-76		3.3		3.4	417	407
Dodecanol-1	C ₁₂ H ₂₆ O	23-24	1.4409					
Lauric acid	C ₁₂ H ₂₄ O ₂	41-42					200	203
Methyl laurate	C ₁₃ H ₂₆ O ₂	87-88(1)	1.4302				214	214
Methyl caprylate	C ₉ H ₁₈ O ₂	38-42(1)	1.4160				158	158
Triethylamine	C ₆ H ₁₅ N	89-89.5	1.3987					
Dodecylamine HCl ^a	C ₁₂ H ₂₅ NCI	184-186						
Didodecylamine ^b	C ₂₄ H ₅₁ N	55-56						
Didodecylamine HCl ^b	C ₂₄ H ₅₂ NCI	205-206						
Diethyldodecylamine ^a	C ₁₆ H ₃₅ N	121-123(2)	1.4392	5.82		5.82	242	242
methiodide	C ₁₇ H ₃₈ NI	122-123		3.65		3.66		
methyl tosylate	C ₂₃ H ₄₅ O ₃ NS	128.5-129.7		3.37		3.37		
hydrochloride	C ₁₆ H ₃₆ NCI	117-119		5.03		5.13		
styphnate	C ₂₂ H ₃₈ O ₈ N ₄	57.1-58.1		11.5		11.4		
Didodecylethylamine	C ₂₆ H ₅₅ N	176-180(0.03)	1.4516	3.67		3.70	382	384
Tridodecylamine ^c	C ₃₆ H ₇₅ N	220-228(0.03)	1.4567					
Octyldiethylamine ^d	C ₁₂ H ₂₇ N	95-98(1)	1.4228	7.58		7.55	185	184
Diocylethylamine ^e	C ₁₈ H ₃₉ N	123-128(0.7)	1.4411					
Undecane ^f	C ₁₁ H ₂₄	194-194.5	1.4150					

^a O. Westphal and D. Jerchel, *Ber.*, **73B**, 1002 (1940). ^b Reference 3. ^c A. Ralston, *et al.*, *J. Org. Chem.*, **9**, 259 (1944). ^d Ref. 15. ^e E. Borrows, *et al.*, *J. Chem. Soc.*, 197-202 (1947). ^f F. Krafft, *Ber.*, **15**, 1697 (1882); C. Mabery and E. Hudson, *Am. Chem. J.*, **19**, 482 (1897).

coconut oil²⁴ and were distilled from Raney nickel before use. Dodecanol was obtained by catalytic hydrogenation of methyl laurate. The octanol employed was the commercial grade distilled from Raney nickel.

Dioxane was purified²⁵ before use. Dry ethanol was freed from catalyst poisons by distillation from Raney nickel.

Pure triethylamine was obtained by distilling 750-800 cc. of commercial grade (Sharples) through a 30-cm. Vigreux column until the overhead temperature was constant at 89° (760 mm.). The residue 650-700 cc., was refluxed with 15 g. of phthalic anhydride and then distilled slowly over a two-hour period. This distillate was distilled twice more, once from 1 g. of Raney nickel and again from 15 g. of anhydrous barium oxide. The final product was collected in a receiver protected from moisture.

Equipment.—The reactions at 400 atmospheres or lower were carried out in a chrome-vanadium steel reaction vessel.⁸ The reactor employed in experiments at pressures above 400 atmospheres was manufactured by Autoclave Engineers, Inc., Erie, Pa. It was a special high pressure vessel with a Bridgman type closure²⁶ prepared from 321 stainless steel at both ends; it was hydraulically tested to 1700 atmospheres. The main body of the vessel was 13.5 inches long, 3.0 inches o.d. and 1.5 inches i.d. It was fabricated of SAE 6140 chrome-vanadium steel. A liner of 18-8 stainless steel, eight inches in length, was sweated against the internal part of the main body. The extremes of this liner were precision machined to receive the closures. One closure was fitted with standard couplings for 1/4 inch o.d., 1/16 inch i.d. high pressure tubing both inside and out, and carried a bent tube on the inside. The second closure carried a 3/8 inch o.d. thermocouple well with standard pipe threads and sealed with a small copper gasket. Both vessels were electrically heated. The temperature was controlled by a Leeds and Northrup Model C indicating potentiometer. The autoclaves were rocked at 58 r.p.m. at 15° rocking angle.

Procedure.—The quantities of reagents used in the experiments and the conditions under which the hydrogenations

and transalkylations were conducted are summarized in Tables I and II. The physical properties of starting materials and products obtained from the reactions are listed in Table III.

In the amide and ammonium acid salt hydrogenations the products were freed from catalyst by rinsing with alcohol; in the transalkylations triethylamine was used instead of alcohol. In general, after the removal of solvents, the products were distilled at reduced pressure. When the alcohol and amine reaction products could not be separated by rectification through a 30-cm. Vigreux column, the per cent. amine was determined by potentiometric titration with dilute acid. The amine and alcohol then were separated either by (a) dissolving the fraction in anhydrous ether and saturating with hydrogen chloride to precipitate the amine hydrochloride, or (b) treating the fraction with dilute sulfuric acid and steam distilling to remove the alcohol. The separate components were then further purified and identified by preparation of derivatives. The amines were characterized by derivatives as listed in Table III. The N-phenyl- and N- α -naphthylurethans of the alcohols were prepared and compared with samples from known sources. In the transalkylations ethanol was isolated from the ethanol-water-triethylamine azeotrope,²⁷ b.p. 74.7°, by steam distillation of ethanol-water from an acid solution of the azeotrope followed by concentration and salting out with anhydrous potassium carbonate. Usually, only 50-60% of the theoretical amount of ethanol was isolated.

The following experiments are typical examples.

Hydrogenation of Lauramide.—In 40 ml. of purified dioxane 19.9 g. (0.01 mole) of lauramide and 4 g. of copper-chromium-barium oxide were heated at 250° for one hour under a hydrogen pressure of 365-340 atmospheres. The time required to reach 250° was 1.5 hours. After reaction was complete the cold pressure drop indicated absorption of 0.41 mole of hydrogen. The organic products were washed from the catalyst with methanol. After removal of the solvents the residue was distilled at 1 mm. to give the following fractions: (1) 12.3 g., 108-112°, n_D^{20} 1.4420, consisting of 15% dodecylamine in dodecanol and (2) 3.8 g. of didodecylamine which crystallized from ethanol as white platelets; the hydrochloride was prepared in anhydrous ether and recrystallized from ethanol.

Dry hydrogen chloride was passed into an anhydrous ether solution of fraction 1; the solid was separated and dried to give 2 g. of dodecylamine hydrochloride, which was

(27) L. H. Horsley, *Anal. Chem.*, **21**, 864 (1949).

(24) J. Sauer, B. Hain and P. Boutwell, *Org. Syntheses*, **20**, 67 (1940).

(25) L. Fieser, "Experiments in Organic Chemistry," 2nd ed., D. C. Heath and Co., New York, N. Y., 1941, p. 368.

(26) V. Komarewsky and C. Reisz, "Catalytic Reactions, Technique of Organic Chemistry," Vol. II, A. Weissberger, Interscience Publishers, Inc., New York, 1948, p. 48.

recrystallized from ethanol to give white, needle-like crystals. The ether solution from the hydrochloride was washed with 100 cc. of 5% hydrochloric acid, dried over anhydrous sodium sulfate and finally distilled to yield 8.1 g. of dodecanol.

Transalkylation of Triethylamine with Dodecanol.—A mixture of 37.2 g. (0.2 mole) of dodecanol, 73 g. (0.73 mole) of triethylamine and 10 g. of copper–chromium–barium oxide was heated for 10 hours under 380 atmospheres of hydrogen. On cooling, the catalyst was washed with triethylamine and dried; 10 g. of black catalyst was recovered. The triethylamine–water–ethanol azeotrope (22 g.) was separated by distillation through a 30-cm. Vigreux column. This and a similar fraction (28 g.) from another reaction were combined, neutralized to congo red with dilute sulfuric acid, distilled and the fraction, b.p. 77–83°, collected.

The ethanol was salted out with anhydrous potassium carbonate, separated and distilled to give 4.3 g., b.p. 77–78°, n_{25}^D 1.3620. The N-phenyl- and N- α -naphthylurethans were prepared and showed no depression with the same derivatives prepared from ethanol. After removal of the remaining triethylamine from the reaction products, the residue was fractionated at 2 mm. into the following fractions: (1) 11.8 g., b.p. 109–121°, n_{25}^D 1.4420, consisting of 52.5% diethyldodecylamine in dodecanol, (2) 26.3 g., b.p. 121–123°, n_{25}^D 1.4393, and (3) 5.3 g. holdup, n_{25}^D 1.4505. Fraction (2) was redistilled to give 20 g. of pure diethyldodecylamine. Fraction (3) was combined with similar material from other experiments. From 11 g. of such material, distilled in a modified Claisen flask, 7.7 g. of didodecylethylamine was obtained as a colorless oil.

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[CONTRIBUTION FROM THE RESEARCH DIVISION OF ARMOUR AND COMPANY]

The Polymorphic Behavior of Dodecylammonium Chloride with Organic Solvents

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The solubility of dodecylammonium chloride has been determined in carbon tetrachloride, carbon tetrabromide, chloroform, bromoform, ethyl acetate, "absolute" ethanol, *n*-butanol and acetonitrile. The behavior in these solvents is similar to that previously reported for the benzene system. Dodecylammonium chloride exhibits two enantiotropic forms and a monotropic variation of the lower-temperature enantiotrope.

Recent investigations^{1,2} of the behavior of dodecylammonium chloride have demonstrated that this salt exists in two crystalline modifications having an enantiotropic transition at 57.5°. Among the fatty acids and their derivatives, this enantiotropy appears to be almost unique. With very few exceptions, the aliphatic compounds exhibit monotropic polymorphism.

This transition between the two stable forms of dodecylammonium chloride has been established by determination of the respective solubility curves¹ in benzene and 95% ethanol, by the configuration of the phase diagram² of this salt with water, and by visual observation^{1,2} of the change in crystalline structure upon heating under the microscope. In both the previous investigations, it was found that the N-methyl derivatives of this salt do not exhibit enantiotropic polymorphism. Under certain conditions, the mono-, di- and trimethyldodecylammonium chlorides reveal monotropic modifications.

In connection with studies of the solubility of dodecylammonium chloride in benzene and aqueous ethanol, it was found¹ that several discontinuities in the curves occur at temperatures other than the enantiotropic transition point at 57.5°. In the benzene system there is a break in the unstable region, whereas in aqueous ethanol a break appears in the curve representing the stable system above the transition temperature. In order to ascertain whether these breaks are consequences of solvent–solute interaction, or are attributable to other factors, investigation of the behavior of dodecylammonium chloride has been extended by determination of its solubility in carbon tetrachloride, carbon tetrabromide, chloroform, bromoform, ethyl ace-

tate, "absolute" ethanol, *n*-butanol and acetonitrile.

Experimental

The dodecylammonium chloride employed herein was the material used in the previous investigations.^{1,2}

The solvents were of the best grade available and were freshly distilled in a Stedman-packed column before use, with the exception of carbon tetrabromide (Eastman Kodak Co. white-label) which was used without further treatment. The "absolute" ethanol employed herein was obtained by azeotropic distillation of 190-proof neutral grain spirits with benzene in a Stedman-packed column. The final product was estimated to be at least 99.8% ethanol by comparison of its density with values in the "International Critical Tables."³

The procedures for determining the solubilities of both the stable and metastable forms of the solute have been described in recent publications.^{1,2} Weighed portions of salt and solvent were sealed in small glass tubes, dissolved by heating, thoroughly mixed, and then cooled below the crystallization point. Solution temperatures were observed during slow heating of these samples as they were rotated in a regulated, electrically-heated water-bath (silicone-bath above 100°). Temperatures were measured by means of thermometers which were graduated in 0.1° intervals and were calibrated by the National Bureau of Standards. The solution temperatures obtained are considered accurate within $\pm 0.1^\circ$.

The solution temperatures of the metastable polymorphs were determined by observing in addition the behavior upon cooling. Homogeneous samples were cooled gradually below temperatures on the higher liquidus curve and the temperature at which precipitation occurred was noted. Solution could usually be effected by heating the samples immediately to temperatures just above the precipitation point. By repetition of this procedure it was readily possible to locate the metastable solution temperatures within $\pm 0.1^\circ$. Upon maintaining samples for a time at temperatures below their precipitation points, the metastable form converted to the stable form, the transformation being more rapid at the lower concentrations, particularly in the non-polar solvents and in those of low polarity. To effect transformation in some cases, it was necessary to chill samples for several hours.

(1) F. K. Broome and H. J. Harwood, *THIS JOURNAL*, **72**, 3257 (1950).

(2) F. K. Broome, C. W. Hoerr and H. J. Harwood, *ibid.*, **73**, 3350 (1951).

(3) "International Critical Tables," 1929, Vol. III, p. 117.