ionic dissociation of hydrogen chloride must be practically negligible. The approximately linear relationship between $-\log K_c$ and $\sqrt{c} \times 10^2$ shown in Moede and Curran's Fig. 8 is probably fortuitous and is somewhat uncertain because of the scattering of the experimental points. A nearly linear relationship also appears to hold if $-\log K_c$ is plotted against $c \times 10^3$ or $\sqrt[3]{c}$. Moreover, these authors found that $k = 14$ in the relationship $-\log K_c = -\log K_a + 2k\sqrt{\mu}$, instead of the expected value, 32.8, and stated that the "low value appears to be due in part to the presence of a large number of $C_8H_{11}NH^+$–Cl^- ion pairs, which reduces the ionic strength below the calculated value." However, in view of the considerations outlined above, it seems more probable that in the chloroform solutions of dimethylaniline hydrochloride under discussion less than 0.6% of the salt was dissociated into $C_8H_{11}N$ and HCl, that the extent of dissociation into $C_8H_{11}NH^+$ and Cl^- was practically negligible, and that the salt existed almost entirely as hydrogen-bonded ion pairs, $C_8H_{11}NH^+$–Cl^-, in effect analogous to the amine–sulfur dioxide addition compounds. The importance of this interpretation is apparent when one observes that equilibrium (2) represents an association as well as a dissociation. More explicitly, I believe the results of Moede and Curran provide new evidence that the product of the reaction of a base with either a "Lewis" acid or a "Brønsted" acid is essentially the same thing, namely, a highly polar addition compound, when the solvent has a low dielectric constant and solvation is not a factor.

WASHINGTON, D. C. RECEIVED MAY 13, 1949

An Improvement on the Process for Making Amidone

BY JOHN W. CUSIC

One of the difficult steps in the synthesis of Amidone is the preparation of the intermediate 4-dimethylamino-2,2-diphenylvaleronitrile.

This has usually involved the use of a hazardous chemical such as sodium amide.[1] Cheney[2] has used lithium amide which, however, is a fairly expensive chemical.

I have found that the condensation of 1-dimethylamino-2-chloropropane hydrochloride with diphenylacetonitrile can be carried out with sodium hydroxide, which is both cheap and safe.

Experimental

Sixty grams (1.5 moles) of commercial sodium hydroxide flake, 77.2 g. (0.4 mole) of diphenylacetonitrile and 79.0 g. (0.5 mole) of 1-dimethylamino-2-chloropropane hydrochloride were mixed in an erlenmeyer flask and heated with occasional stirring for six to seven hours on the steam-bath.

The reaction mixture was extracted with ether and the ether in turn extracted with dilute hydrochloric acid. The acid solution was made strongly alkaline with sodium hydroxide and the liberated base extracted with ether. The ether solution was dried over anhydrous potassium carbonate, filtered and after removal of the ether the product was distilled to yield 89 g. of product, b. p. 173–174° at 1 mm. It was then crystallized from petroleum ether (60–71°) to give 49 g. (45.7%) melting at 89–90°.

Anal. Calcd. for $C_{19}H_{22}N_2$: N, 10.3. Found: N, 9.91.

G. D. SEARLE AND CO., BOX 5110
CHICAGO, ILL. RECEIVED MAY 18, 1949

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[1] Schultz, Robb and Sprague, THIS JOURNAL, **69**, 188, 2454 (1947).

[2] Cheney, Smith and Binkley, *ibid.*, **71**, 52 (1949).

Some 1,2-Dialkylcyclohexanes[1,2]

BY J. R. DICE, L. E. LOVELESS, JR., AND H. L. CATES, JR.[3]

There is a surprising paucity of data concerning 1,2-dialkylcyclohexanes where neither substituent group is methyl. Our original intention was to synthesize an extensive series of these compounds, but the poor yields encountered in many of the steps limited the number prepared.

The crucial intermediates 2-ethyl- and 2-propylcyclohexanone were prepared by the interaction of 2-chlorocyclohexanone and the appropriate Grignard reagent.[4] Propyllithium was used in one experiment. The improvement in yield was more than offset by the increased difficulty of preparation. Attempts to prepare 2-(1-methylethyl)-cyclohexanone by the Grignard method were unsuccessful, although this preparation (without any experimental details) is reported by Bouveault and Chereau.[4] Addition of cobaltous chloride did not affect the yield of 2-propylcyclohexanone. Direct alkylation of cyclohexanone using sodium amide or sodium in liquid ammonia as catalysts gave a complex mixture of products.

The addition of various Grignard reagents to 2-ethyl- and 2-propylcyclohexanone gave a series of 1,2-dialkylcyclohexanols which were dehydrated to the corresponding 1,2-dialkylcyclohexenes by distillation from iodine. The double bond was believed to be in the ring because of the difficulty of hydrogenating the unsaturated products.[5] It also has been proved[6] that the dehydration of 1,2-dimethylcyclohexanol by this method yields 1,2-dimethylcyclohexene. Hydrogenation of the dialkylcyclohexenes using Raney nickel as a catalyst gave the desired 1,2-dialkylcyclohexanes.

Experimental

2-Ethylcyclohexanone.[7]—To the Grignard reagent prepared from 25.6 g. of magnesium, 114 g. of ethyl bromide and 600 ml. of dry ether was added 122 g. of 2-chlorocyclo-

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[1] From the M.A. theses of L. E. Loveless, Jr., and H. L. Cates, Jr., The University of Texas, 1948.

[2] This work was generously supported by grants from the University of Texas Research Institute (Project 186).

[3] Present address: Department of Chemistry, The Ohio State University, Columbus, Ohio.

[4] Bouveault and Chereau, *Compt. rend.*, **142**, 1087 (1906); Vavon and Mitchtovitch, *Bull. soc. chim.*, [4] **45**, 961 (1929).

[5] Gilman, "Organic Chemistry," Vol. I, 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1943, p. 797.

[6] Signaigo and Cramer, THIS JOURNAL, **55**, 3326 (1933).

[7] For other methods for the preparation of 2-ethylcyclohexanone see (a) ref. 4; (b) Tiffeneau, Tchoubar and Le Tellier, *Compt. rend.* **216**, 856 (1943); and (c) Ruzicka and Peyer, *Helv. Chim. Acta*, **18** 676 (1935).

TABLE I

1,2-DIALKYLCYCLOHEXANOLS

Substituted cyclohexanol	Yield, %	B. p., °C.	Mm.	n^{25}_D	d^{25}_4	Formula	Composition,[a] %			
							Carbon		Hydrogen	
							Calcd.	Found	Calcd.	Found
1,2-Diethyl-[b]	83	72–73	3	1.4653	0.919	$C_{10}H_{20}O$	76.9	77.2	12.9	12.9
1-Ethyl-2-propyl-	75	60–68	2	1.4640	.907	$C_{11}H_{22}O$	77.6	77.3	13.0	12.9
1,2-Dipropyl-[c]	27	70–74	7	1.4641	.928	$C_{12}H_{24}O$	78.2	78.0	13.1	13.7
1-(1-Methylethyl)-2-propyl-	20	83–85	10	1.4605	.938	$C_{12}H_{24}O$	78.2	78.3	13.1	12.6
1-Butyl-2-propyl-	48	84–85	4	1.4642	.898	$C_{13}H_{26}O$	78.7	78.7	13.2	12.8

[a] Difficulties were encountered in adapting the semi-micro analytical procedure outlined by Horning and Horning, *Ind. Eng. Chem., Anal. Ed.*, 19, 688 (1947), to the analysis of these compounds. The use of small glass bulbs consistently led to rather vigorous "flashing" and low results. Open platinum boats were impractical due to the volatility of the compounds. Reasonably satisfactory results were finally obtained by increasing the size of the sample to approximately 40 mg. and adding 75 mg. of potassium chlorate to the open boat. [b] Ruzicka and Peyer, ref. 7c, prepared but did not isolate this compound. [c] Vavon and Barbier, *Bull. soc. chim.*, [4] 49, 4567 (1931), report a *cis-cis*-dipropylcyclohexanol. The positions occupied by the alkyl groups are not indicated, nor is the method of synthesis given.

TABLE II

1,2-DIALKYLCYCLOHEXENES

Substituted cyclohexene	Yield, %	B. p. °C.	Mm.	n^{25}_D	d^{25}_4	Formula	Composition,[a] %			
							Carbon		Hydrogen	
							Calcd.	Found	Calcd.	Found
1,2-Diethyl-[b]	85	170–175	747	1.4598	0.831					
1-Ethyl-2-propyl-	76	180–184	746	1.4559	.843	$C_{11}H_{20}$	86.8	86.3	13.2	13.4
1,2-Dipropyl-	60	162–167	748	1.4557	.868	$C_{12}H_{22}$	86.7	86.6	13.3	13.1
1-(1-Methylethyl)-2-propyl-	45	167.5–168.5	746	1.4535		$C_{12}H_{22}$	86.7	86.7	13.3	13.1
1-Butyl-2-propyl-	72	210–211	746	1.4609	.868	$C_{13}H_{24}$	86.6	86.6	13.4	13.5

[a] See footnote *a*, Table I. [b] Reported, ref. 7c, b. p. 60–61° (10 mm.).

TABLE III

1,2-DIALKYLCYCLOHEXANE

Substituted cyclohexane	Yield, %	B. p., °C.	Mm.	n^{25}_D	Formula	Composition, %			
						Carbon		Hydrogen	
						Calcd.	Found	Calcd.	Found
1,2-Diethyl-[a,b]		170–175	746	1.4453	$C_{10}H_{20}$	85.6	85.6	14.4	14.3
1-Ethyl-2-propyl-[b]	60	190–197	746	1.4448	$C_{11}H_{22}$	85.6	85.7	14.4	14.3
1,2-Dipropyl-[c]	25	225–228	748	1.4524	$C_{12}H_{24}$	85.6	86.0	14.4	14.0
1-Butyl-2-propyl-[c]	30	236–240	750	1.4531	$C_{13}H_{26}$	85.6	85.7	14.4	14.1

[a] Prelog and Zalan, *Helv. Chim. Acta*, 27, 535 (1944), prepared this compound by a different method and reported a boiling range (heating-bath temperature) of 132–197°. [b] Analysis by C. W. Beazley, Micro-Tech Laboratories, Skokie, Illinois. [c] Analysis by the authors. See footnote *a*, Table I.

hexanone[8] over a period of two hours. Most of the ether was replaced by 500 ml. of dry benzene and the mixture was refluxed for five hours. After hydrolysis the product was distilled through a 60-cm. fractionation column to yield 52 g. (41%) of a colorless liquid boiling at 42° (2 mm.) (reported[4] 67° (13 mm.)); n^{16}_D 1.4530 (reported[4] 1.4528); semicarbazone, m. p. 161–162° (reported,[4,7b] 161, 165°).

2-Propylcyclohexanone[9] using Propylmagnesium Bromide.—Using the method described previously 2-propylcyclohexanone was prepared from 13.4 g. of magnesium, 67.5 g. of 1-bromopropane and 66.7 g. of 2-chlorocyclohexanone. The colorless distillate (14 g., 20%) boiled at 80–81° (12 mm.) (reported[9a,9c] 83–84° (13 mm.) and 94–95° (25 mm.)), semicarbazone m. p. 119–120° (reported[9a] 133.5–134.0°), semicarbazide m. p. 101–103° (reported[9a] 103–104°), semicarbazide hydrochloride m. p. 146–148° (reported[9a] 146–148°).

2-Propylcyclohexanone Using Propyllithium.—To a stirred mixture of 7.6 g. of freshly-cut lithium and 300 ml. of dry ether was added a solution of 67.5 g. of 1-bromopropane in 200 ml. of dry ether over a three-hour period. The mixture turned black and was refluxed for twelve hours. To the stirred propyllithium reagent was added 61.5 g. of 2-chlorocyclohexanone over a two-hour period; a green color formed. After standing eight hours the mixture was filtered from excess lithium and the filtrate was hydrolyzed by means of an ice–hydrochloric acid slurry. The mixture was extracted with ether and the organic layer was washed with dilute sodium hydroxide and dilute hydrochloric acid and dried over sodium sulfate. The ether was removed by means of a current of air and the residue was distilled at 86–88° (16–17 mm.), yield 22.2 g. (30%), semicarbazone m. p. 119–120°, mixture m. p. with semicarbazone from Grignard method, 119–120°.

Preparation of 1,2-Dialkylcyclohexanols.—To the Grignard reagent prepared from 0.23 mole of magnesium and 0.23 mole of the appropriate alkyl halide in 200–300 ml. of dry ether was added 0.20 mole of the desired 2-alkylcyclohexanone over a period of two hours. The mixture was refluxed with stirring for twelve hours and then poured on an ice–hydrochloric acid slurry. The combined ether extracts were washed with saturated sodium bisulfite solution and twice with water. After drying over sodium sulfate and evaporation of the solvent the alcohols were distilled *in vacuo*. Yields, physical constants and other pertinent data are given in Table I.

Preparation of 1,2-Dialkylcyclohexenes.—Two to 25 g. batches of the various 1,2-dialkylcyclohexanones were distilled from 0.05 to 0.20 g. of iodine. The distillate was washed with sodium thiosulfate solution, dried over calcium chloride and then refluxed with sodium from ten to sixty minutes. Distillation from the sodium gave colorless liquids. Table II contains the data relative to these compounds.

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(8) Newman, Barbman and Hipsher, *Org. Syntheses*, **25**, 22 (1945).

(9) For other preparations of 2-propylcyclohexanone see (a) Vavon and Aziani, *Bull. soc. chim.*, [4] **41**, 1642 (1927); (b) ref. 4; (c) Cornubert and Marvel, *Bull. soc. chim.*, **49**, 1498 (1931).

Preparation of 1,2-Dialkylcyclohexanes.—Preliminary tests showed that the 1,2-dialkylcyclohexenes were resistant to hydrogenation at room temperature and 1–2 atmospheres of hydrogen using platinum as catalyst. Hydrogenation occurred smoothly in a bomb at 150° and a starting hydrogen pressure of 2400 p. s. i. using 0.5–1.0 g. of Raney nickel catalyst for 2–5 g. of cyclohexene. Absolute ethanol (30–50 ml.) was used as solvent in all cases. After filtration the solution was evaporated to approximately 10 ml. and poured into water. The mixture was extracted with benzene and the combined extracts dried over sodium sulfate. After evaporation of the solvent the residue was treated with concentrated sulfuric acid to remove any cyclohexenes. The mixture was diluted with water and was extracted with benzene which was washed with dilute sodium hydroxide and water and dried over sodium sulfate. On distillation colorless liquids were obtained. Data on the cyclohexenes prepared are given in Table III.

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RECEIVED JUNE 21, 1949

Preparation of 2-Pyridylmethanol[1]

BY WALTER M. EDWARDS[2] AND PEYTON C. TEAGUE[3]

Harries and Lenart[4] and Graf, *et al.*,[5] have reported the preparation of 2-pyridylmethanol by methods which require several steps beginning with readily obtainable derivatives of pyridine. This report describes a simple method of preparation of 2-pyridylmethanol from 2-picoline, which does not involve the isolation of any intermediate product. 2-Picolyllithium was prepared by the hydrogen–metal interchange reaction between 2-picoline and phenyllithium. The picolyllithium was oxidized with a slow current of air to form the desired 2-pyridylmethanol.

A compound, $C_{12}H_{12}N_2$, was obtained as a by-product of the reaction. This compound was not identified but is probably 1,2-dipyridylethane, which would be expected[6] as the coupling product of two pyridyl radicals.

Experimental[7]

2-Picolyllithium was prepared by the procedure of Finkelstein and Elderfield[8] from 46.5 g. of 2-picoline. When the reaction was complete, the source of nitrogen was removed. Dry, carbon dioxide-free air was drawn at the rate of 2 cc. per minute into the flask and over the surface of the solution. The oxidation was carried out with stirring and without heating or cooling for eight hours, at which time the bright red color had disappeared and the mixture was light yellow. From time to time, more anhydrous ether was added to replace that lost by evaporation.

For the separation of the product, 6 *N* hydrochloric acid was added until the solution was acid to congo red. The aqueous layer was separated, made alkaline with sodium carbonate, saturated with sodium chloride, and extracted several times with chloroform. After the chloroform layer had been dried over anhydrous calcium sulfate for twenty-four hours, the chloroform and 2-picoline was distilled from the mixture at atmospheric pressure. The picoline boiled at 128° and was identified by the melting point of its picrate (168°). It weighed 11.3 g. or 24% of the original amount added.

The mixture of free bases was then fractionally distilled under reduced pressure. The following fractions were obtained: Fract. 1 (70–103° at 3–4 mm.), 11.2 g.; fract. 2 (103–136° at 3–4 mm.), 8.0 g., fract. 3 (138–170° at 1–2 mm.), 0.9 g.; residue, 16 g.

Identification of 2-Pyridylmethanol.—Fraction 1 on redistillation boiled completely at 111–115° at 16 mm. *Anal.* Calcd. for C_6H_7NO: N, 12.84. Found: N, 12.64. The picrate melted at 150° and the chloroplatinate at 179°. These data are in agreement with the values of Harries and Lenart.[4]

The yield of 11.2 g. was 20.5% based on the 2-picoline added or 27.0% on the basis of 2-picoline consumed in the reaction.

Compound $C_{12}H_{12}N_2$.—Fraction 2 redistilled at 112–114° at 1–2 mm. The distillate solidified on standing. After recrystallization from ligroin, its melting point was 49°. *Anal.* Calcd. for $C_{12}H_{12}N_2$: C, 78.23; H, 6.57; N, 15.21. Found: C, 77.98; H, 6.67; N, 15.05. Molecular weight determination by the Rast camphor method. Calcd.: 184. Found: 197, 196, 193; av. 195. This product was not further characterized.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF GEORGIA
ATHENS, GEORGIA
RECEIVED APRIL 27, 1949

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[1] Abstracted from the thesis of Walter M. Edwards, submitted in partial fulfilment of the requirements for the M.S. degree at the University of Georgia, Athens, Georgia.

[2] Present address: Ohio State College, Columbus, Ohio.

[3] Present address: University of Kentucky, Lexington, Kentucky.

[4] Harries and Lenart, *Ann.*, **410**, 107 (1915).

[5] Graf, *et al.*, *J. prakt. Chem.*, **146**, 88 (1936).

[6] Gilman and Pacevitz, THIS JOURNAL, **61**, 1603 (1939).

[7] All melting points and boiling points are corrected.

[8] Finkelstein and Elderfield, *J. Org. Chem.*, **4**, 365 (1939).

Polyvinyl Bromide[1]

BY DAVID EDELSON AND RAYMOND M. FUOSS

In connection with our work on polyelectrolytes,[2] we attempted to prepare a polymeric quaternary compound by the addition of tertiary amines to polyvinyl bromide. The desired product was not obtained, but the results of some of our experiments seem worth reporting. Vinyl bromide is one of the earliest known vinyl compounds; Regnault[3] prepared it by treating ethylene dibromide with alkali. Staudinger[4] studied its polymerization and noted that the polymer readily loses hydrogen bromide.

We heated 0.5 cc. of 30% hydrogen peroxide and 10 g. of vinyl bromide[4a] in a bomb at 47° for twenty-four hours and obtained no polymer, although Güyer and Schütze[5] report complete conversion in twenty hours at 60°. About 30% conversion was obtained in two days at 60° from a (deoxygenated) solution of vinyl bromide (10 g.) in toluene (8 g.) saturated with benzoyl peroxide. The product was white, but darkened on drying under vacuum at 30°; Parr bomb bromine averaged to 70.2% (theoretical 74.77%). Fair results were obtained by photochemical

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[1] Project NR 054-002 of the Office of Naval Research.

[2] R. M. Fuoss and G. I. Cathers, *J. Polymer Sci.*, **2**, 12 (1947); **4**, 97 (1949); R. M. Fuoss and U. P. Strauss, *ibid.*, **3**, 246 (1948); G. I. Cathers and R. M. Fuoss, *ibid.*, **4**, 121 (1949).

[3] V. Regnault, *Ann. chim.*, [II] **59**, 358 (1935).

[4] H. Staudinger, M. Brunner and W. Feisst, *Helv. Chim. Acta* **13**, 805 (1930).

[4a] We are indebted to the Dow Chemical Company for the sample of vinyl bromide on which these experiments were made.

[5] A. Güyer and H. Schütze, *Helv. Chim. Acta*, **17**, 1544 (1934).