

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 Cheney² 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

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

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

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 $C_{19}H_{23}N_2$: N, 10.3. Found: N, 9.91.

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RECEIVED MAY 18, 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 proved⁶ 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-

(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).

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(4) Bouveault and Chereau, *Compt. rend.*, **142**, 1087 (1906); Vavon and Mitchovitch, *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).