Proportions of Cymenes from Propylation of Toluene

BY FRANCIS E. CONDON

A mechanism advanced to explain the formation of considerable *m*-dialkylbenzene in the aluminum chloride-catalyzed alkylation of a monoalkylbenzene, in apparent opposition to the well-known ortho–para directing influence of an alkyl group, is alkylation to 1,2,4-trialkylbenzene, followed by dealkylation.[1] In an experimental test of this hypothesis, as part of the present investigation of the proportions of cymenes produced by propylation of toluene under homogeneous liquid-phase conditions, pure *p*-cymene was alkylated with propylene at 65° in the presence of aluminum chloride and of benzene and nitromethane[2] as solvents, in order to determine whether any *m*-cymene would result from *p*-cymene under conditions that produced considerable *m*-cymene from toluene. The experimental data are presented in Table I.

TABLE I

PROPORTIONS OF CYMENES FROM PROPYLATION OF TOLUENE

Temperature, °C.		65		65		5		5		65	
Charge compn., mole fract.	Benzene	0.300		0.467		0.304		0.442		0.613	
	Toluene	.300		.368		.296		.380		.217[a]	
	$AlCl_3$	...		.012		...		.030		.012	
	Nitromethane	...		.153		...		.148		.158	
	$BF_3 \cdot Et_2O$	.400		...		.400		...		...	
Experiment		1	2	3	4	5	6	7	8	9	10
C_3H_6/aromatics, (mole/mole)		0.14	0.24	0.15	0.36	0.11	0.08	0.08	0.13	0.29	0.45
Cymene fraction, vol. %[b]	Cumene	0	0	0	0	0	0	0	0	1	5
	o-Cymene	38.4	35.8	36.1	36.4	35.9	37.2	34.0	35.9	0	0
	m-Cymene	25.9	28.1	27.0	28.2	27.0	27.6	30.0	31.4	0	0
	p-Cymene	36.8	34.3	33.2	34.6	32.4	32.0	30.4	32.3	96	91
	m-Diisopropylbenzene	0.5	0.0	2.9	2.5	0.5	2.9	0.7	0.0	3	4
	Total	101.6	98.2	99.2	101.7	95.8	99.7	95.1	99.6	100	100
Cymenes, average wt. %	*o*-Cymene	37.6 ± 0.6				37.5 ± 1.0				0	
	m-Cymene	27.5 ± 1.0				29.8 ± 1.6				0	
	p-Cymene	34.9 ± 0.6				32.7 ± 0.6				100	

[a] *p*-Cymene. [b] Infrared analyses. Values of log I_0/I for cumene, *o*-cymene, *m*-cymene, *p*-cymene and *m*-diisopropylbenzene, respectively, in a 0.017-mm. cell were: at 14.21 μ: 0.4700, 0.0205, $\underline{0.9640}$, 0.0130, 0.4788; at 13.75 μ: 0.0510, $\underline{0.9350}$, 0.0225, 0.0310, 0.0215; at 12.61 μ: 0.0200, 0.0175, 0.1240, 0.0320, $\underline{0.5755}$; at 12.27 μ: 0.0120, 0.0243, 0.0395, $\underline{1.3030}$, 0.0470; at 11.04 μ: $\underline{0.1030}$, 0.0243, 0.0438, 0.0165, 0.0280; (absorption maxima underlined).

No *o*-cymene and no *m*-cymene were produced when *p*-cymene was alkylated with propylene, whereas 38% *o*-cymene, 27% *m*-cymene, and 35% *p*-cymene were produced from toluene under the same conditions. These results show that all the isomeric cymenes were produced by direct alkylation of toluene at the available positions, rather than by isomerization or by alkylation-dealkylation of *p*-cymene. The considerable proportion of *m*-cymene means that a methyl group exerts a relatively feeble ortho–para orienting influence during propylation. (During nitration of toluene, only about 4% of *m*-nitrotoluene is produced.[3])

The proportions of cymenes produced at 5 and at 65° are slightly different. These differences appear real, and probably should not be considered within the experimental error (*cf.* ref. 3).

The proportions of cymenes appear to be independent of whether the catalyst is aluminum chloride or boron fluoride. Noteworthy, too, is their apparent independence of the extent of conversion (measured by the mole ratio of propylene to aromatics given in Table I). Some dependence at high conversions would be expected from inequalities in the rates of further propylation of the different isomers.

Acknowledgments.—Messers. Harold Price and Richard Sonnenfeld made the infrared analyses. Mr. Stanley Turk supplied pure isomeric cymenes for calibration of the infrared spectrometer. Phillips Petroleum Company granted permission to publish the data.

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[1] Price and Ciskowski, THIS JOURNAL, **60**, 2499 (1938); Price, "Organic Reactions," Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1946, p. 10.

[2] Schmerling, *Ind. Eng. Chem.*, **40**, 2072 (1948); Condon, THIS JOURNAL, **70**, 2265 (1948).

[3] Jones and Russell, *J. Chem. Soc.*, 921 (1947).

RESEARCH DEPARTMENT
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[CONTRIBUTION FROM THE NATIONAL BUREAU OF STANDARDS]

The Dissociation Constant of Dimethylaniline Hydrochloride in Chloroform

BY MARION MACLEAN DAVIS

Recently Moede and Curran[1] described the determination of the dissociation constant, K_c, for

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[1] J. A. Moede and C. Curran, THIS JOURNAL, **71**, 852 (1949).

the sulfur dioxide addition compounds of several amines in benzene, *n*-butyl chloride or chloroform, by measurement of dielectric properties or ultraviolet absorption spectra. The reaction assumed was

$$\text{C (addition compound)} \rightleftharpoons \text{A (amine)} + \text{B (sulfur dioxide)}$$

The correctness of this assumption was supported by the good agreement of values for K_c at various concentrations.

In the same paper, data and calculations were presented for the dissociation of dimethylaniline hydrochloride in chloroform. The equilibrium postulated in this case was

$$C_8H_{11}NH^+ + Cl^- \rightleftharpoons C_8H_{11}N + HCl \qquad (1)$$

Values obtained for K_c showed a progressive increase with dilution, varying from 0.38×10^{-6} for 0.008442 molar solution to 31×10^{-6} for 0.001203 molar solution. The salt effect of the hydrochloride was suggested as a possible explanation of the trend toward higher values of K_c as the solutions became more dilute. This interpretation of the reaction seemed erroneous to the writer, because spectrophotometric data obtained at the National Bureau of Standards for various acid–base reactions in benzene[2] and measurements of the effect of dilution on the dielectric polarization of tribenzylammonium picrate in benzene[3] have been interpreted satisfactorily on the assumption of *negligible* ionic dissociation, and the dielectric constant of chloroform (~4.7) is nearly as low as that of benzene (~2.3). Provisional calculations of the dissociation constant for dimethylaniline hydrochloride, using the data in Moede and Curran's Table V and interpolating in their Fig. 6 to obtain ϵ_C (169) and ϵ_A (11,000), but considering the reaction to be

$$C_8H_{11}NHCl \rightleftharpoons C_8H_{11}N + HCl \qquad (2)$$

gave nearly constant values with the mean value 6.0×10^{-8} for K_c at all concentrations. These provisional values for K_c were reported to Professor Curran, who graciously furnished the experimental values at 255 mμ for ϵ_C (192) and ϵ_A (10,530), and also stated that the same equilibrium (2) had originally been considered by him and Dr. Moede but that because the resulting values for K_c showed a decrease with increasing concentration, the alternative equation (1) was adopted. However, when the values for K_c computed according to both equations are compared (see Table I), it is evident that the data are more consistent with equation (2). According to either formulation, the dissociation of the salt into dimethylaniline and hydrogen chloride occurs to so slight an extent, in the range of concentrations concerned, that a small experimental error will have a large effect on the constancy of K_c. Therefore, the slight trend in the values shown in column 3 of Table I does not appear significant, particularly since the first two values correspond to transmittancies outside the range recommended by Mellon for reliable measurement.[4] The correct value for K_c thus appears to be $\sim 1.5 \times 10^{-8}$.

TABLE I

DISSOCIATION CONSTANT OF DIMETHYLANILINE HYDROCHLORIDE IN CHLOROFORM AT 24 ± 3°

c	$K_c \times 10^{6\,a}$	$K_c \times 10^{8\,b}$
0.008442	0.38	0.3
.008120	0.71	0.6
.005627	1.9	1.1
.005413	1.4	0.8
.004221	5.3	2.2
.004060	3.2	1.0
.003248	4.5	1.5
.002814	4.6	1.3
.002707	8.2	2.2
.001407	14	2.0
.001203	31	3.7
		Mean 1.5

[a] Computed by Moede and Curran according to equation (1); see ref. (1), Table V. [b] Computed by M. M. Davis, according to equation (2).

To consider that dimethylaniline hydrochloride exists mainly as an addition compound in chloroform is contrary to the rather common belief that salts are largely dissociated into the free ions in all non-aqueous solvents as well as in water. However, Kraus and his associates have found that the ionic dissociation of a salt drops off rapidly as the dielectric constant of the solvent approaches very low values.[5] Moreover, both Walden[6] and Kraus[7] have pointed out that salts which appear equally strong in water may exhibit pronounced differences in strength when dissolved in solvents of low dielectric constant and that, for example, incompletely substituted ammonium salts are distinctly weaker than quaternary ammonium salts in such solvents. This decrease in strength appears to be caused in part by the presence of a hydrogen bridge in salts of the former type.[7]

Moede and Curran report that the conductance of a 0.1 molar solution of dimethylaniline hydrochloride was observed to be about a thousand times that of hydrogen chloride in chloroform.[1] This does not necessarily imply a significant concentration of dimethylanilinium and chloride ions. Kraus has stated that hydrogen chloride in nitrobenzene, of dielectric constant ~35, is a very weak electrolyte.[7] In chloroform, therefore, the

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(2) M. M. Davis and P. J. Schuhmann, *J. Research Nat. Bur. Standards*, **39**, 221 (1947); M. M. Davis and E. A. McDonald, *ibid.*, **42**, 595 (1949).

(3) A. A. Maryott, *ibid.*, **41**, 7 (1948).

(4) M. G. Mellon, "Colorimetry for Chemists," G. Frederick Smith Chemical Co., Columbus, Ohio, 1945, p. 56.

(5) See, for example, R. M. Fuoss and C. A. Kraus, THIS JOURNAL, **55**, 1019 (1933); C. A. Kraus, *J. Chem. Education*, **12**, 567 (1935).

(6) P. Walden, "Salts, Acids, and Bases: Electrolytes: Stereochemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1929, Chapter X.

(7) C. A. Kraus, *J. Phys. Chem.*, **43**, 231 (1939); see also discussion by M. Kilpatrick and K. Fajans, *ibid.*, **43**, 288 (1939).

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.

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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] Chaney, 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).

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[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).