

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 propyl-

ing 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.

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 ₃012030	.012					
	Nitromethane153148	.158					
	BF ₃ ·Et ₂ O	.400400					
Experiment	1	2	3	4	5	6	7	8	9	10	
C ₃ H 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	1	5	
	<i>o</i> -Cymene	38.4	35.8	36.1	36.4	35.9	37.2	34.0	35.9	0	0
	<i>m</i> -Cymene	25.9	28.1	27.0	28.2	27.0	27.6	30.0	31.4	0	0
	<i>p</i> -Cymene	36.8	34.3	33.2	34.6	32.4	32.0	30.4	32.3	96	91
	<i>m</i> -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. %	<i>o</i> -Cymene		37.6 ± 0.6			37.5 ± 1.0			0		
	<i>m</i> -Cymene		27.5 ± 1.0			29.8 ± 1.6			0		
	<i>p</i> -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, 0.9640, 0.0130, 0.4788; at 13.75 μ : 0.0510, 0.9350, 0.0225, 0.0310, 0.0215; at 12.61 μ : 0.0200, 0.0175, 0.1240, 0.0320, 0.5755; at 12.27 μ : 0.0120, 0.0243, 0.0395, 1.3030, 0.0470; at 11.04 μ : 0.1030, 0.0243, 0.0438, 0.0165, 0.0280; (absorption maxima underlined).

ene at 65° in the presence of aluminum chloride and of benzene and nitromethane² 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.

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 dur-

Acknowledgments.—Messrs. 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.

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

RESEARCH DEPARTMENT
PHILLIPS PETROLEUM COMPANY
BARTLESVILLE, OKLAHOMA RECEIVED JANUARY 14, 1949

[CONTRIBUTION FROM THE NATIONAL BUREAU OF STANDARDS]

The Dissociation Constant of Dimethylaniline Hydrochloride in Chloroform

BY MARION MACLEAN DAVIS

Recently Moede and Curran¹ described the determination of the dissociation constant, K_c , for

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

(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).