

on the basis of statistical substitution of the tertiary positions. There can be little doubt that the faster hydrolyzing or alpha component must be 3-chloro-2,3,4-trimethylpentane (VI) and the slower hydrolyzing or beta component must be 2-chloro-2,3,4-trimethylpentane (VII). It is of particular interest that the reaction of 2,3,4-trimethyl-3-pentanol with hydrochloric acid at 25° leads to a product containing 77% of the rearranged product.

The value of the steric strain hypothesis³ is indicated by its success in predicting that the faster hydrolyzing component (alpha) would be the unrearranged tertiary chloride (VI), even though this component constitutes but a relatively small fraction of the total product obtained from 2,3,4-trimethyl-3-pentanol.

Relative Reactivity of Primary and Tertiary Hydrogen Atoms in 2,3,4-Trimethylpentane.—It was of interest to estimate the relative ease of substitution of tertiary and primary hydrogen atoms in 2,3,4-trimethylpentane. The chlorination product was analyzed for chlorine by the procedure of Rauscher.⁸ The amount of tertiary chloride present in the chlorination mixture was then determined by hydrolyzing a weighed sample of the chlorination product for 12 hours in a 50–50 ethanol–water mixture and titrating the hydrochloric acid formed with standard sodium hydroxide solution using methyl red as indicator. The essential data are summarized in Table III.

(8) Rauscher, *Ind. Eng. Chem., Anal. Ed.*, **9**, 296 (1937).

TABLE III

DETERMINATION OF THE PERCENTAGE OF PRIMARY AND TERTIARY CHLORIDES FORMED IN THE CHLORINATION OF 2,3,4-TRIMETHYLPENTANE

Theoretical % Cl in C ₈ H ₁₇ Cl	23.85	
Theoretical % Cl in C ₈ H ₁₆ Cl ₂	38.73	
Experimental % Cl in product	24.95	
Calcd. C ₈ H ₁₇ Cl in product, %	92.6	
Wt. of product hydrolyzed, g.	0.0889	0.0752
Wt. of monochloride, g.	0.0823	0.0696
Ml. 0.03771 N NaOH required	6.31	5.27
Calcd. tertiary chloride, g.	0.0354	0.0296
Tertiary chlorides in monochlorides, %	43.0	42.5

These values correspond to a relative rate of substitution (by chlorine at 25°) of primary to tertiary hydrogen atoms of 1:3.7. This value is considerably lower than the ratio of 1:5.4 or 1:5.1 previously reported for liquid isobutane at 30°.⁹ Further studies on relative reactivities are underway.⁶

Acknowledgment.—The assistance afforded by the support of a fellowship by the Standard Oil Company of Indiana is gratefully acknowledged. The donation of a pure sample of 2,3,4-trimethylpentane by the American Petroleum Institute Project No. 45 greatly facilitated the investigation.

(9) Hass, McBee and Weber, *Ind. Eng. Chem.*, **23**, 333 (1936).

LAFAYETTE, INDIANA

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Effect of Nuclear Substitution on the Rate of Silica–Zirconia–Alumina-Catalyzed Depropylation of Cumene

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A comparison was made of the relative ease of depropylation of cumene and several nuclear-substituted cumenes in the presence of silica–zirconia–alumina cracking catalyst, by flow-method, fixed catalyst bed tests. At 450°, space rate 65 moles per liter catalyst per hour, the extents of depropylation were: 1,3-dimethyl-4-isopropylbenzene, 77%; *p*-cymene, 60%; 1,3-dimethyl-5-isopropylbenzene, 57%; cumene, 39%; *p*-chlorocumene, 25%; trichlorocumene (mixture of isomers), 8%. The methyl and chlorine substituents on the aromatic nucleus were not removed under the conditions of these tests. The same relative order of reactivity was observed in experiments at 400° with *p*-cymene, cumene and *p*-chlorocumene. Relative rates predicted for electrophilic displacement of propyl by hydrogen calculated by an approximate molecular orbital method are in agreement with the observed results except in the case of 1,3-dimethyl-5-isopropylbenzene, for which the theory predicts a rate of depropylation equal to that of cumene. This correlation is taken as evidence that the dealkylation of alkylbenzenes in the presence of cracking catalysts of the silica–alumina type proceeds through formation of a polar intermediate complex between the alkylbenzene molecule and an acidic center on the catalyst.

Studies of the reactions of a large number of pure hydrocarbons in the presence of silica–zirconia–alumina and silica–alumina catalysts^{1–6} led to the proposal of a carbonium ion mechanism of catalytic cracking.⁷ Additional evidence for this

mechanism is presented here, from a comparison of the extents of depropylation of cumene and several methyl- or chloro-substituted cumenes in the presence of a silica–zirconia–alumina cracking catalyst.

Experimental Details

Apparatus and Procedure.—The experiments reported below were made in an electrically heated, 0.5 in. i.d., 18-8 chromium–nickel steel reactor tube. The procedure and equipment were essentially the same as described elsewhere.^{1,5,8} Between experiments, the catalyst was reactivated by ignition in a stream of air and the coke deposit was determined by collecting combustion products. A tube containing Ascarite was included in the product recovery system between the distillation column and the gas meter in anticipation of formation of acid gas from the

(1) B. S. Greensfelder and H. H. Voge, *Ind. Eng. Chem.*, **37**, 514 (1945) (cracking of paraffins).

(2) *Ibid.*, **37**, 983 (1945) (cracking of olefins).

(3) *Ibid.*, **37**, 1038 (1945) (cracking of naphthenes).

(4) B. S. Greensfelder, H. H. Voge and G. M. Good, *ibid.*, **37**, 1168 (1945) (cracking of aromatics); cf. also C. L. Thomas, J. Hoekstra and J. T. Pinkston, *THIS JOURNAL*, **66**, 1694 (1944).

(5) H. H. Voge, G. M. Good and B. S. Greensfelder, *Ind. Eng. Chem.*, **38**, 1033 (1946) (secondary reactions of olefins).

(6) G. M. Good, H. H. Voge and B. S. Greensfelder, *ibid.*, **39**, 1032 (1947) (cracking of structural isomers).

(7) B. S. Greensfelder, H. H. Voge and G. M. Good, *ibid.*, **41**, 2573 (1949) (mechanisms of hydrocarbon cracking); C. L. Thomas, *ibid.*, 2564 (1949).

(8) H. J. Henriques, *ibid.*, **39**, 1564 (1947).

TABLE I
CATALYTIC DEPROPYLATION OF CUMENES BY SILICA-ZIRCONIA-ALUMINA AT ATMOSPHERIC PRESSURE AND ELEVATED TEMPERATURE

Experiment	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Compound	<i>p</i> -Cymene	Cumene	<i>p</i> -Chloro-cumene	Cumene	Cumene	1,3-Dimethyl-5-isopropylbenzene	1,3-Dimethyl-4-isopropylbenzene	Cumene	<i>p</i> -Cymene	<i>p</i> -Cymene	<i>p</i> -Chloro-cumene	Trichloro-cumene	Cumene	Trichloro-cumene
Temperature, °C.	← 400 →				← 450 →									
Process period, min.	← 50 →				← 60 →									
Catalyst, cc. (sample no.)	← 50(1) →				← 10(2) →				← 10(3) →				← 50(4) →	
Space rate, moles/l./hr.	← 13 →				← 65 →									
Product recovery, wt. % charge	95.4	101.2	95.3	101.2	98.2	100.7	99.5	100.7	98.5	99.5	98.8	99.3	100.7	97.8
Composition, wt. %														
Gas	19.1	12.8	6.1	13.2	14.8	17.0	21.7	13.8	18.8	19.7	5.4	0.3	12.9	5.9
Benzene	0.1	30.2	...	29.9	23.8	22.0	18.1	...
Toluene	45.5	0.2	39.6	41.3
Xylene	38.9 ^b	54.8 ^c
Starting material and above	31.9	53.3	70.2	56.1	58.8	43.5	22.8	61.6	40.8 ^d	38.6 ^e	75.3	92.3	62.9	47.6 ^h
Coke	0.3	1.3	1.2	0.8	0.4	0.6	0.7	0.5	0.8	0.4	0.8	0.7	0.5	4.2
Other	3.1	2.2	22.5 ^a	0.0	2.2	0.0	0.0	2.1	0.0	0.0	18.5 ^f	6.7 ^g	5.6	42.3 ⁱ
Gas analysis														
Molecular weight	43	39	39	40	39	39	40	38	40	40	36	31	37	39
Composition, vol. %														
Hydrogen	0.0	...	0.0	0.0	2.6	2.6	0.7	1.5	1.2	1.0	2.4	28.6	6.3	8.3
Ethylene	0.0	...	0.0	0.0	0.4	0.0	0.0	0.6	0.2	0.2	1.2	0.0	0.0	10.7
Propylene	94.1	...	76.5	89.9	93.8	94.2	97.0	95.8	95.9	96.7	92.3	71.4	91.0	44.1
Other olefins	4.7	...	0.0	2.8
Paraffins	1.2	...	23.5	7.3	3.2	3.2	2.3	2.1	2.7	2.1	4.1	0.0	2.7	36.9
Av. C no. of paraffins	4.0	...	2.1	1.6	4.5	2.5	2.5	3.3	3.0	2.4
Conversion, wt. % charge (no-loss basis)	68.1	46.7	29.8	43.9	41.2	56.5	77.2	38.4	59.2	61.4	24.7	7.7	37.1	52.4

^a 22.1 boiling 125–146°; Cl, 30.9. Calcd. for C₉H₉Cl: Cl, 31.5. ^b *o*-3.9, *m*-79.9, *p*-xylene 8.4, ethylbenzene 0.1, other 7.7 wt. %. ^c *o*-3.9, *m*-75.5, *p*-xylene 16.7, ethylbenzene 0.1, other 3.8 wt. %. ^d Approx. analysis: *o*-13, *m*-12, *p*-cymene 70 wt. %. ^e Approx. analysis: *o*-13, *m*-18, *p*-cymene 67, other 2 wt. %. ^f 11.2 boiling 131–153°, 7.3 boiling 153–191°. ^g All boiling below 177° at 100 mm. ^h 17.0 boiling 238–252°, C, 46.6; H, 3.5; Cl, 50.0. Remainder boiling above 252°; C, 49.6; H, 4.2; Cl, 45.9. Temps. cor. to 760 mm. ⁱ 5.3 boiling 100–196°; 15.0 boiling 196–227°; 10.7 boiling 227–233°; C, 43.3; H, 2.6; Cl, 54.0. 11.3 boiling 233–238°; C, 44.3; H, 2.9; Cl, 52.9. Temps. cor. to 760 mm.

chlorinated compounds, but practically no acid gas was found.

Catalyst.—The catalyst was Universal Oil Products Company's Type B silica-zirconia-alumina cracking catalyst in the form of 1/8" cylindrical pellets with the following composition (wt. per cent. of catalyst ignited at 1000°): SiO₂, 87.0; ZrO₂, 9.1; Al₂O₃, 2.6; Na₂O, 0.009. Spectroscopic analysis gave the following results: Fe, 0.05; Cu, 0.03; Ni, Cr < 0.01; no K or Ca. The Brunauer-Emmett-Teller nitrogen adsorption area of the catalyst was 346 m.²/g. The catalytic properties of this catalyst are very similar to those of commercial silica-alumina cracking catalyst containing 10 to 12% alumina and no zirconia.

Analyses.—Liquid products from the tests at 400° were fractionated in a 20-plate column at 15:1 reflux ratio; those from tests at 450° were fractionated in a 5-plate column at 15:1 reflux ratio. Aromatic contents of certain fractions were determined by ultraviolet absorption or by refractive dispersion. Gaseous products from Experiments 1–4 were analyzed by low temperature distillation and absorption and combustion gas analysis methods⁹; the gaseous products from Expts. 5–14 were not analyzed by low temperature distillation but were subjected to absorption and combustion gas analysis only.⁹ In a few cases an infrared analysis of the C₄ fraction was made.

Cumene.—For Expts. 2 and 4, redistilled technical cumene was used: b.p. 150°, *n*_D²⁰ 1.4914. For Expts. 5, 8 and 13, Eastman Kodak Co. purest cumene was redistilled: b.p. 150–151°, *d*₄²⁰ 0.8615, *n*_D²⁰ 1.4915.

***p*-Cymene.**—For Expt. 1, *p*-cymene from Hercules Powder Co. was purified by percolation through silica gel and redistilled: b.p. 177.0°, *d*₄²⁰ 0.8569, *n*_D²⁰ 1.4906.

(9) Except for a few minor differences, the absorption and combustion methods were those given by F. R. Brooks, L. Lykken, W. B. Milligan, H. R. Nebeker and V. Zahn, *Anal. Chem.*, **21**, 1105 (1949).

For Expts. 9 and 10 Eastman Kodak Co. "terpene-free" *p*-cymene was redistilled: b.p. 176.8°, *d*₄²⁰ 0.8563, *n*_D²⁰ 1.4890.

1,3-Dimethyl-4-isopropylbenzene.—Synthesized from *m*-xylene and isopropyl alcohol with sulfuric acid catalyst by the method of Nightingale and Carton¹⁰: b.p. 197–200°, *d*₄²⁰ 0.8734, *n*_D²⁰ 1.5011.

1,3-Dimethyl-5-isopropylbenzene.—Synthesized from *m*-xylene and isopropyl chloride with AlCl₃ catalyst by the method of Nightingale and Carton¹⁰: b.p. 197°, *d*₄²⁰ 0.8621, *n*_D²⁰ 1.4956.

***p*-Chlorocumene.**—Synthesized from chlorobenzene and isopropyl chloride, with AlCl₃ catalyst by the method of Meyer and Bernhauer.¹¹ Lot for Expt. 3: b.p. 192–194°, *n*_D²⁰ 1.5149. Lot for Expt. 11: b.p. 189–191°, *d*₄²⁰ 1.0286, *n*_D²⁰ 1.5149. *Anal.* Calcd. for C₉H₉Cl: Cl, 23.0. Found: Lot for Expt. 3, Cl, 22.9; Lot for Expt. 11, Cl, 22.8.

Trichlorocumene.—One sample, used in Experiment 12, was furnished by Hooker Electrochemical Co. It was stated to be a mixture of 2,3,5-, 2,5,6- and 3,4,6-trichlorocumenes. The redistilled sample had the following properties: b.p. 179–183° (100 mm.), *d*₄²⁰ 1.2909, *n*_D²⁰ 1.5538. *Anal.* Calcd. for C₉H₅Cl₃: C, 48.3; H, 4.06; Cl, 47.6. Found: Cl, 47.5.

A second sample, used in Experiment 14, was obtained from Bios Laboratories, and a fraction having the following properties was used: b.p. 254.5–261.5° (cor. to 760 mm.), *n*_D²⁰ 1.5542. *Anal.* Found: C, 48.2; H, 4.0; Cl, 47.7.

Results and Discussion

The experimental data are presented in Table I and are summarized in the Abstract. They show

(10) D. V. Nightingale and B. Carton, Jr., *THIS JOURNAL*, **62**, 280 (1940).

(11) H. Meyer and K. Bernhauer, *Monatsh.*, **53**, 741 (1929).

that, with possible exception of trichlorocumene, the principal reaction was depropylation (as demonstrated elsewhere for cumene⁴). The several experiments with cumene and *p*-cymene establish that the activity of the catalyst was substantially the same for all the experiments.

Depropylation is reversible; therefore, if the conversions in Table I are to be regarded as a measure of the relative rates of depropylation, it must be shown that equilibrium was not attained in these experiments. Of the six compounds depropylated, cumene is the only one for which free energy data are available¹² and from these data the extent of depropylation of cumene at equilibrium is 68% at 400° and 83% at 450°. Free energy data for ethylbenzene and the three methylethylbenzenes¹² show that the extent of deethylation at equilibrium is substantially higher for the methylethylbenzenes than for ethylbenzene; by analogy, the extent of depropylation at equilibrium is presumably higher for *p*-cymene and the dimethylisopropylbenzenes than for cumene. Furthermore, for all the compounds, the extent of depropylation at equilibrium is undoubtedly higher at 450° than at 400°. Experiments 12 and 14 with trichlorocumene directly establish that equilibrium was not attained in Experiment 12—there was considerably more propylene, more trichlorobenzene, and less trichlorocumene in the product of Experiment 14 than in the product of Experiment 12. All these considerations indicate that the conversions in Experiments 5–13 at 450° were not limited by approach to equilibrium and, therefore, may be taken as a measure of the relative rates of depropylation.

The rates of depropylation decrease in the order: 1,3-dimethyl-4-isopropylbenzene, *p*-cymene, 1,3-dimethyl-5-isopropylbenzene, cumene, *p*-chlorocumene, trichlorocumene. This order of reactivities correlates well with relative activation energies for *electrophilic* displacement of propyl by hydrogen calculated by an approximate molecular orbital method¹³ and presented in Table II. In this calculation the displacing hydrogen is assumed to form a bond with the nuclear carbon atom bearing the isopropyl group, and the six, five, or four remaining π electrons are distributed over the other five nuclear carbon atoms in the case of nucleophilic, homolytic, or electrophilic displacement, respectively. In Table II α is an energy parameter associated with a methyl substituent, the corresponding parameter for chlorine being $-\alpha'$; α and α' are positive and probably approximately equal.¹⁴

The order of reactivity is opposite to that pre-

(12) W. J. Taylor, D. D. Wagman, M. G. Williams, K. S. Pitzer and F. D. Rossini, *J. Research Natl. Bur. Standards*, **37**, 113 (1946).

(13) H. C. Longuet-Higgins, *Nature*, **166**, 139 (1950); *J. Chem. Phys.*, **18**, 233 (1950).

(14) For example, relative rates of nitration at 30° are $k_{\text{toluene}}/k_{\text{benzene}} = 21$, $k_{\text{benzene}}/k_{\text{chlorobenzene}} \approx 30$. Cf. C. K. Ingold, A. Lapworth, E. Rothstein and D. Ward, *J. Chem. Soc.*, 1981 (1931); M. L. Bird and C. K. Ingold, *ibid.*, 922 (1938).

TABLE II
APPROXIMATE ACTIVATION ENERGY FOR DISPLACEMENT OF PROPYL BY HYDROGEN

Compound	Electrophilic	Nucleophilic	Homolytic
1,3-Dimethyl-4-iso-propylbenzene	$E_1 - 2\alpha/3$	$E_2 + 2\alpha/3$	E_3
<i>p</i> -Cymene	$E_1 - \alpha/3$	$E_2 + \alpha/3$	E_3
1,3-Dimethyl-5-iso-propylbenzene	E_1	E_2	E_3
Cumene	E_1	E_2	E_3
<i>p</i> -Chlorocumene	$E_1 + \alpha'/3$	$E_2 - \alpha'/3$	E_3
Trichlorocumene ^a	$E_1 + \alpha'/3$	$E_2 - \alpha'/3$	E_3
	to	to	
	$E_1 + 2\alpha'/3$	$E_2 - 2\alpha'/3$	

^a Mixture of 2,3,5-, 2,3,6- and 2,4,5-trichlorocumene.

dicted by molecular orbital theory for *nucleophilic* displacement; and the theory predicts no difference in reactivity for *homolytic* displacement (atom-free radical mechanism). The correlation with the theory for electrophilic, rather than nucleophilic or homolytic displacement, supports the carbonium ion mechanism proposed earlier.⁷

The presence of substantial quantities of *o*- and *p*-xylene in the depropylated product from 1,3-dimethyl-5-isopropylbenzene suggests the possibility of isomerization preceding depropylation. Rapid isomerization to configurations in which a methyl group is ortho or para to the isopropyl group would greatly increase the rate of depropylation, and may thus account for the apparent disagreement between experiment and theoretical prediction for electrophilic displacement in this case.

It is worthy of remark that from the point of view of the Longuet-Higgins theory, nuclear substitution of a methyl group ortho or para to the isopropyl group in cumene increases the unsaturation energy of the normal molecule and also that of the intermediate complex for electrophilic displacement. The energy of the complex is increased to a lesser extent, however, and the net effect is a decrease in activation energy relative to cumene. The increase in debutylation rate in the series *n*-butylbenzene, *s*-butylbenzene, *t*-butylbenzene (see footnote 4, first reference) is brought about in a different way. The nuclear carbon atom bearing the butyl group is not part of the conjugated system in the intermediate complex, and the unsaturation energies of the three complexes are the same, regardless of the configuration of the butyl group. The activation energy is lowered from one member to the next in this series solely by a progressive increase in the unsaturation energy of the normal molecule.

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