analysis[23] showed the presence of 49.9% nitrogen and 50.1% nitrous acid.

Solubility of Nitrous Oxide in Potassium Hydroxide Solution.—In order to correct the mass spectrometer analysis for the solubility of nitrous oxide in 50% potassium hydroxide solution under the conditions used for the measurement of the volume of the gaseous decomposition products, measured volumes of pure nitrous oxide were bubbled through the azotometer (in the absence of carbon dioxide). The average loss of the nitrous oxide after bubbling through approximately 110 ml. of 50% potassium hydroxide solution was 2.15%.

Acknowledgment.—The interest and support of the U. S. Naval Ordnance Test Station, China Lake, California, under Research Contract N 1235-61517, Task Order No. 1 is gratefully acknowledged.

CHICAGO, ILLINOIS RECEIVED OCTOBER 30, 1950

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[23] By Consolidated Engineering Corporation, Pasadena, California.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF PURDUE UNIVERSITY]

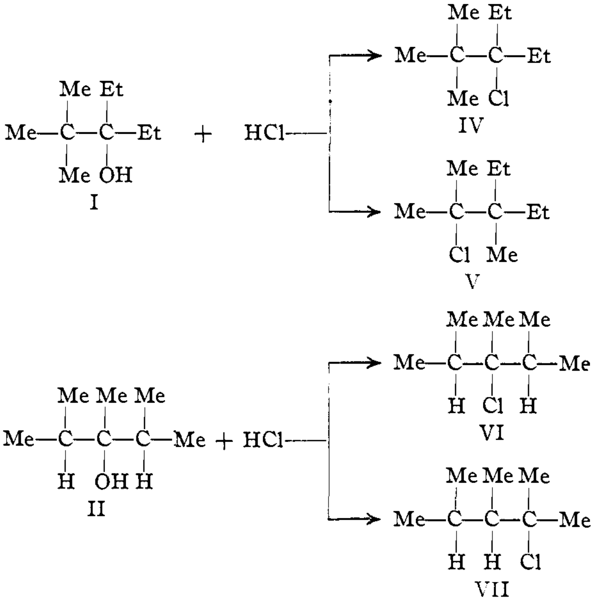
Rearrangement in the Reaction of 2,3,4-Trimethyl-3-pentanol with Hydrochloric Acid; Chlorination of 2,3,4-Trimethylpentane[1]

BY HERBERT C. BROWN AND ROSLYN SILBER FLETCHER[2]

Hydrochloric acid reacts at room temperature with 2,3,4-trimethyl-3-pentanol to give a product, presumably 3-chloro-2,3,4-trimethylpentane. However, hydrolysis of the product in 80% ethanol results in complex kinetic data which can be analyzed into two first order rate constants, $k_1^\alpha = 0.481$ hr.$^{-1}$ and $k_1^\beta = 0.0315$ hr.$^{-1}$. The product is therefore postulated to contain two components. The alpha component constitutes 22.9% of the reaction mixture; the beta, 77.1%. Photochemical chlorination of 2,3,4-trimethylpentane at 25° yields a product which also shows the existence of two isomeric tertiary chlorides: $k_1^\alpha = 0.460$ hr.$^{-1}$, $k_1^\beta = 0.0299$ hr.$^{-1}$. In this case the alpha component constitutes 33.1% of the reaction mixture; the beta, 66.9%. Assuming statistical chlorination of the available tertiary hydrogen atoms, the alpha component must be 3-chloro-2,3,4-trimethylpentane; the beta component, 2-chloro-2,3,4-trimethylpentane. The ratio of primary to tertiary substitution in the hydrocarbon is 1:3.7.

In an earlier investigation a series of twelve tertiary alkyl halides was prepared for examination of the postulated effect of steric strain on the rates of hydrolysis.[3] In the course of this study it was observed that the tertiary chlorides prepared from highly branched tertiary alcohols did not exhibit the simple first order kinetics usually observed in the solvolysis of tertiary halides.[4]

Thus the alkyl chlorides derived from 2,2-dimethyl-3-ethyl-3-pentanol (I) and from 2,3,4-trimethyl-3-pentanol (II) yielded rate data which could be analyzed into two simultaneous first order reactions. It was postulated that treatment of each of the highly branched tertiary alcohols with hydrochloric acid led to the formation of two different tertiary chlorides, the expected product (IV, VI) and a rearranged product (V, VII).



$$\mathrm{Me{-}\underset{Me}{\overset{Me}{C}}{-}\underset{OH}{\overset{Et}{C}}{-}Et} + \mathrm{HCl} \longrightarrow \mathrm{Me{-}\underset{Me}{\overset{Me}{C}}{-}\underset{Cl}{\overset{Et}{C}}{-}Et}\ (\mathrm{IV}) + \mathrm{Me{-}\underset{Cl}{\overset{Me}{C}}{-}\underset{Me}{\overset{Et}{C}}{-}Et}\ (\mathrm{V})$$

I, IV, V

$$\mathrm{Me{-}\underset{H}{\overset{Me}{C}}{-}\underset{OH}{\overset{Me}{C}}{-}\underset{H}{\overset{Me}{C}}{-}Me} + \mathrm{HCl} \longrightarrow \mathrm{Me{-}\underset{H}{\overset{Me}{C}}{-}\underset{Cl}{\overset{Me}{C}}{-}\underset{H}{\overset{Me}{C}}{-}Me}\ (\mathrm{VI}) + \mathrm{Me{-}\underset{H}{\overset{Me}{C}}{-}\underset{H}{\overset{Me}{C}}{-}\underset{Cl}{\overset{Me}{C}}{-}Me}\ (\mathrm{VII})$$

II, VI, VII

It was the purpose of the present investigation to study this phenomenon in more detail and to examine the validity of the proposed interpretation by establishing structures for the postulated isomeric halides.

Attempts to separate the isomeric tertiary chlorides into pure components offered great experimental difficulties. The isomers apparently boil quite close together. They are relatively unstable and cannot be subjected to long exposure to elevated temperatures such as are encountered in highly efficient fractionation columns. Classical methods of structure determination were therefore abandoned in favor of another, simpler approach—the photochemical chlorination of 2,3,4-trimethylpentane (III).

There is ample evidence that the chlorination of aliphatic hydrocarbons does not lead to rearrangement of the carbon skeleton.[5] Therefore the chlorination of 2,3,4-trimethylpentane should yield the same two tertiary chlorides, 3-chloro- (VI) and 2-chloro-2,3,4-trimethylpentane (VII), previously postulated to be present in the product obtained from 2,3,4-trimethyl-3-pentanol.

Since the relative ease of chlorination of tertiary hydrogen atoms is essentially constant in paraffinic hydrocarbons,[6] the two chlorides should be present in the ratio VI : VII = 1:2. Thus, a study of the hydrolysis of the chlorinated product should indicate the presence of two tertiary chlorides whose rate constants should agree with those obtained

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[1] Chemical Effects of Steric Strains. V.

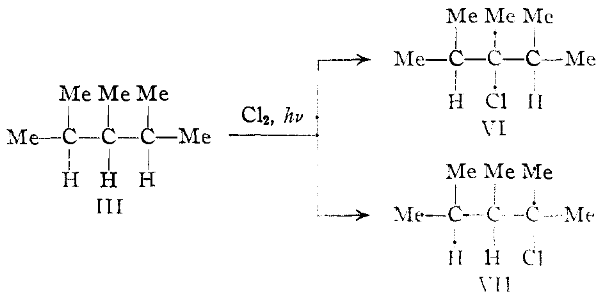
[2] Standard Oil Company (Indiana) Fellow at Purdue University, 1947-1949.

[3] Brown and Fletcher, THIS JOURNAL, **71**, 1845 (1949).

[4] Hughes, *J. Chem. Soc.*, 968 (1946).

[5] Whitmore and Fleming, THIS JOURNAL, **55**, 4161 (1933); Hass, McBee and Weber, *Ind. Eng. Chem.*, **27**, 1190 (1935).

[6] Unpublished work with Mr. Glen Russell.



in the hydrolysis of the product obtained from the tertiary alcohol (II). Moreover, since analysis of the rate data permits calculation of the concentration of each isomer, it should be possible to associate each rate constant with a particular isomer, VI or VII.

Chlorination of the hydrocarbon should result in the simultaneous formation of a considerable quantity of primary chlorides. However, since primary halides do not undergo hydrolysis under the reaction conditions at any significant rate, their presence should not raise serious difficulties.

Hydrolysis of the Chlorides from 2,3,4-Trimethyl-3-pentanol.—2,3,4-Trimethyl-3-pentanol was synthesized by the reaction of methylmagnesium iodide on diisopropyl ketone. The tertiary alcohol (b.p. 76–78° at 46 mm., $n^{25}D$ 1.4326) was converted into the chloride by treatment with concentrated hydrochloric acid by the general procedure previously described.[7] The tertiary chloride (b.p. 54° at 16 mm., $n^{25}D$ 1.4390) was hydrolyzed in 80% aqueous ethanol and the rate followed by the usual procedure.[7] Rate data for a typical experiment are given in Table I. It will be observed that k_1, determined from the usual expression for a first order reaction

$$k_1 = \frac{2.303}{t} \log \frac{a}{a - x}$$

decreases markedly with time.

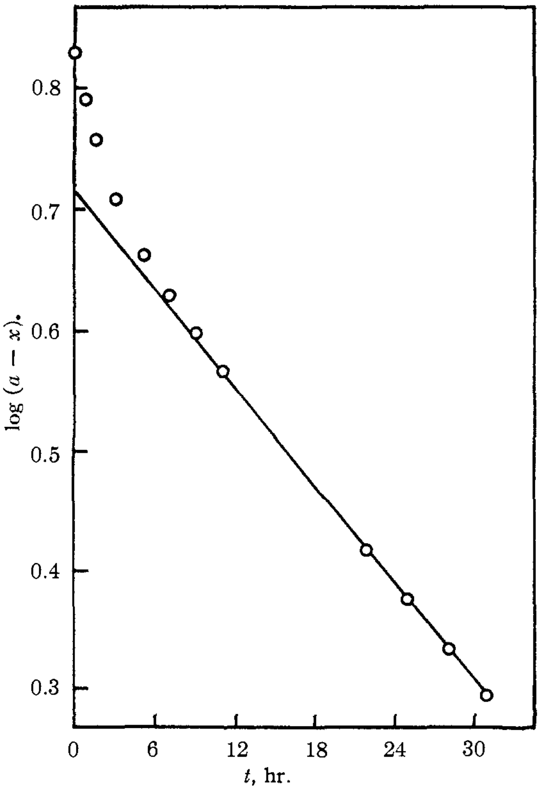


Fig. 1.—Hydrolysis of the product of the reaction of 2,3,4-trimethyl-3-pentanol and hydrochloric acid.

TABLE I

RATE DATA FOR THE HYDROLYSIS OF THE CHLORIDES FROM 2,3,4-TRIMETHYL-3-PENTANOL AT 25° IN 80% ETHANOL[a]

Time, hr.	x ml. NaOH ($x_\alpha + x_\beta$)	k_1 (hr.$^{-1}$)	$\beta - x_\beta$	k_1^β (hr.$^{-1}$)	$\alpha - x_\alpha$	k_1^α (hr.$^{-1}$)
0	0		5.21 = β		1.55 = α	0
0.25	0.22		5.17	0.0313	1.37	0.494
.50	.41	0.125	5.13	.0313	1.22	.479
.75	.59		5.09	.0316	1.08	.482
1.00	.75		5.05	.0315	0.96	.479
1.50	1.04		4.97	.0315	.75	.484
2.00	1.28	.105	4.89	.0315	.59	.483
3.00	1.65		4.74	.0315	.37	.478
5.00	2.17	.0774	4.45	.0315	.14	.481
7.00	2.51		4.18	.0315		
9.00	2.80		3.92	.0315		
10.00	2.94	.0571	3.80	.0315		
11.00	3.07		3.68	.0315		
22.00	4.15		2.60	.0315		
25.00	4.38	.0418	2.37	.0315		
28.00	4.60		2.15	.0315		
31.00	4.79		1.96	.0315		
∞	6.76 = a		Average[b]	0.0315	Average[b]	0.482

[a] d^{25}_4 0.8494. [b] The values obtained from the graphical analysis are k_1^α = 0.481 and k_1^β = 0.0315 hr.$^{-1}$.

The data are plotted in Fig. 1. It will be observed that the data do not give the usual linear graph. However, after 10 hours the points do define a straight line. It was assumed that at this time one of the two postulated components (alpha) had hydrolyzed completely and the hydrolysis of the less reactive component (beta) was under observation. From the slope of this line one of the components of k_1, namely, k_1^β, could be obtained. Extrapolation of the line to zero time gave β, the original concentration of the beta component. It was then possible to determine α, the original concentration of the alpha component, from the relationship $\alpha + \beta = a$, the total original concentration of tertiary chloride. The ratios α/a and β/a give the fraction of each of the two components present in the original product. The rate data can be corrected for the hydrochloric acid contributed by the hydrolysis of the beta component and the new data used to calculate k_1^α, the rate constant of the alpha component.

The results of this treatment are indicated in Table I and in Fig. 2. The excellent first order constants which are obtained strongly support the interpretation. The more reactive component, alpha, forms 22.9% of the chloride mixture and k_1^α is 0.481 hr.$^{-1}$; the less reactive component, beta, forms 77.1% of the original mixture and k_1^β is 0.0315 hr.$^{-1}$.

From the postulated effect of steric strain on the rate of hydrolysis,[3] the alpha component may be tentatively assigned the structure, VI; the beta component, VII.

Hydrolysis of the Chlorides from 2,3,4-Trimethylpentane.—The 2,3,4-trimethylpentane, cer-

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(7) Ref. 3, p. 1853.

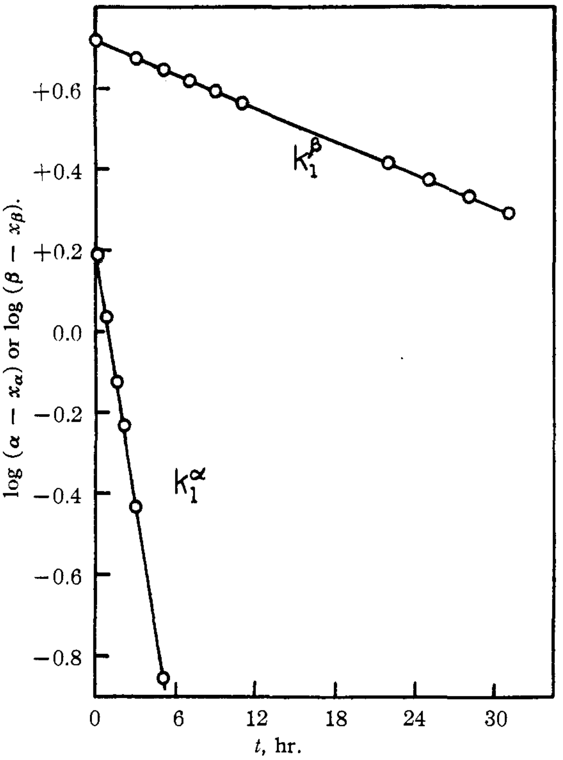

Fig. 2.—Separation of the data for the hydrolysis of the product of the reaction of 2,3,4-trimethyl-3-pentanol and hydrochloric acid into two components.

tified to be 99.35 ± 0.10% pure, was obtained from the American Petroleum Institute Research Project No. 45. The refractive index, $n^{20}\text{D}$ 1.4040, was in excellent agreement with literature values. One-half mole of the hydrocarbon was chlorinated photochemically at 25°. A molar ratio of hydrocarbon to chlorine of 6 to 1 was used to minimize formation of polychlorides. The excess hydrocarbon was removed by distillation under reduced pressure and the product was then removed and utilized without further treatment.

Approximately 1.6 ml. of the product was added to 230 ml. of the 80% ethanol and 10-ml. aliquots were removed and titrated for hydrochloric acid in the usual manner. The determination of the initial concentration of tertiary halide by the usual "infinity" titration was complicated by the slow hydrolysis of the other chlorides present in the reaction mixture. It was necessary to resort to the following expediency. Several 10-ml. samples of the reaction mixture were placed in flasks containing 100 ml. of 50% aqueous ethanol. At measured intervals the acid liberated was determined by titration with standard sodium hydroxide. A plot of the sodium hydroxide titer against time gave a straight line. Extrapolation of the line to zero time gave the titer corresponding to the initial concentration of tertiary chloride.

The hydrolysis was studied in the manner previously described and the data handled similarly. Rate data are listed in Table II.

The data lead to the value of 0.460 hr.$^{-1}$ for the faster hydrolyzing component and 0.0299 hr.$^{-1}$ for the slower hydrolyzing component (Fig. 3). Although these two values are approximately 5% lower than $k_1^α$ and $k_1^β$ obtained in the hydrolysis of the product from the tertiary alcohol (II), the agreement may be considered satisfactory in view of the difficulties involved in the indirect determination of the two rate constants. The low values are probably the result of the presence of small quantities of dichlorides in the chlorination product. As mentioned earlier, these dichlorides also complicated the precise determination of the "infinity titer."

TABLE II

RATE DATA FOR THE HYDROLYSIS OF THE CHLORIDES FROM 2,3,4-TRIMETHYLPENTANE AT 25.0° IN 80% ETHANOL[a]

Time, hr.	x ml. NaOH ($x_α + x_β$)	k_1 (hr.$^{-1}$)	$β - x_β$	$k_1^β$ (hr.$^{-1}$)	$α - x_α$	$k_1^α$ (hr.$^{-1}$)
0	0		3.01 = β		1.49 = α	
0.25	0.18		2.99	0.0295	1.33	0.454
.50	.34	0.157	2.97	.0299	1.19	.450
.75	.49		2.95	.0298	1.06	.454
1.00	.63		2.92	.0299	0.95	.450
1.50	.86		2.88	.0299	.76	.449
2.00	1.06	.134	2.84	.0299	.60	.455
3.00	1.37		2.75	.0299	.38	.456
5.00	1.76	.0993	2.59	.0299	.15	.459
7.00	2.01		2.44	.0299		
9.00	2.18		2.30	.0299		
11.00	2.33	.0663	2.17	.0299		
20.00	2.86		1.66	.0299		
23.00	2.99	.0475	1.51	.0299		
28.00	3.21		1.30	.0299		
31.00	3.31		1.19	.0299		
∞	4.50 = a		Average[b]	0.0299	Average[b]	0.453

[a] d^{25}_4 0.8494. [b] The values obtained from the graphical analysis are $k_1^α$ = 0.460 and $k_1^β$ = 0.0299 hr.$^{-1}$.

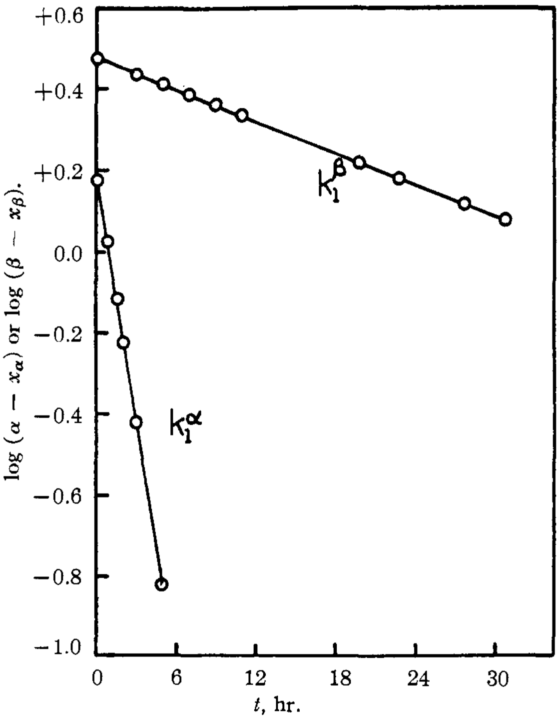

Fig. 3.—Separation of the data for the hydrolysis of the chlorination product of 2,3,4-trimethylpentane into two components.

The faster hydrolyzing component constitutes 1.49/4.50 or 33.1% of the reaction mixture; the slower hydrolyzing component, 66.9%. This is in excellent agreement with the 2 to 1 ratio predicted 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 hypothesis[3] 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.

TABLE III

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

Theoretical % Cl in $C_8H_{17}Cl$	23.85	
Theoretical % Cl in $C_8H_{16}Cl_2$	38.73	
Experimental % Cl in product	24.95	
Calcd. $C_8H_{17}Cl$ 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.

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

(9) Hass, McBee and Weber, *Ind. Eng. Chem.*, **28**, 333 (1936).

LAFAYETTE, INDIANA RECEIVED AUGUST 28, 1950

[CONTRIBUTION FROM THE SHELL DEVELOPMENT COMPANY]

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

BY RICHARD M. ROBERTS AND GEORGE M. GOOD

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

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(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).