

(29%) was obtained, m. p. 138–142°. After several recrystallizations from isopropyl alcohol the colorless needles melted at 141–142.5° to a cloudy liquid, clear at 147°. On another run in which four moles of hydrogen was absorbed the yield of solid was only 25 mg. (12%).

*Anal.*²¹ Calcd. for C₁₈H₂₂O₂ (octahydro derivative): C, 80.0; H, 8.2; for C₁₈H₂₄O₂ (decahydro derivative): C, 79.4; H, 8.9. Found: C, 79.7, 79.6; H, 8.6, 8.9.

With the ordinary type of Raney nickel catalyst prepared according to the directions of "Organic Syntheses"²² reduction did not proceed at room temperature and atmospheric pressure. However, in a bomb at 80° and 2500 pounds pressure for four hours, reduction did occur, giving a mixture from which 19 mg. of solid, m. p. 75–145°, was isolated.

Methyl $\Delta^{1,1'-2'}$ -Keto-2-methyl-3,4-dihydro-1,2-cyclopentenophenanthrene-3'-glyoxalate (IX).—The general method of Bachmann, Cole and Wilds²⁷ was used. A mixture of 1.16 g. of dimethyl oxalate, 5 cc. of dry, thiophene-free benzene and the methanol-free sodium methoxide prepared from 0.23 g. of sodium was refluxed for one-half hour under nitrogen, cooled and a solution of 0.5 g. of the unsaturated ketone III in 7.5 cc. of benzene was added. The yellow sodio derivative of the product soon started to precipitate and an additional 5 cc. of benzene was added after one-half hour and after four hours. At the end of six hours at room temperature water was added and the benzene layer was extracted thoroughly with 2% sodium hydroxide. By acidification and filtration 0.617 g. (92%) of the yellow glyoxalate was obtained; m. p. 164–168°. After recrystallization from acetone-methanol the yellow prisms had the m. p. 168.5–170° (Pyrex m. p. tube). The compound gave a deep red-brown color with ferric chloride in alcoholic solution, and gave a dark red color with concentrated sulfuric acid.

*Anal.*²³ Calcd. for C₂₁H₁₈O₄: C, 75.4; H, 5.4. Found: C, 75.0; H, 5.5.

Methyl $\Delta^{1,1'-2'}$ -Keto-2-methyl-3,4-dihydro-1,2-cyclopentenophenanthrene-3'-carboxylate (XI).—The glyoxalate did not lose carbon monoxide very quickly even in the presence of soft glass.²⁷ The following conditions were

(26) Mozingo, "Organic Syntheses," **21**, 15 (1941). For examples of reduction of the carbonyl group in steroidal ketones by means of Raney nickel at atmospheric pressure see Strassberger and Schwenk, U. S. Patent 2,223,393 (Dec. 3, 1940).

(27) Bachmann, Cole and Wilds, *THIS JOURNAL*, **62**, 831 (1940).

found to give fair results. Undoubtedly further study will result in improved yields. An intimate mixture of 300 mg. of the pure glyoxalate (m. p. 168–169°) and an equal volume of ground soft glass was heated for one hour in an oil-bath at 190–200° under a nitrogen atmosphere. The cooled residue was dissolved in benzene, decanted from the glass and washed with 2% sodium hydroxide. This treatment removed some unchanged glyoxalate. After washing with dilute acid and water, the benzene solution was evaporated and the dark colored oil treated with Norit in methanol. The latter was then concentrated to 2 cc. and the solution allowed to stand in the refrigerator for a day. Yellow crystals of the keto-ester (82 mg., or 30% yield) were obtained with the m. p. 130–145°. The second crop of 26 mg., m. p. 137–167°, still contained some glyoxalate as shown by the ferric chloride test. Several recrystallizations of the first crop from methanol gave yellow prismatic needles which softened at 145° and melted at 150–157° (uncor.). Despite the wide melting point range the analytical results were satisfactory. The compound gave a green color with alcoholic ferric chloride and an orange colored solution with concentrated sulfuric acid.

*Anal.*²³ Calcd. for C₂₀H₁₈O₃: C, 78.4; H, 5.9. Found: C, 78.8; H, 6.1.

Summary

The method previously employed for the synthesis of $\Delta^{1,1'-2'}$ -keto-3,4-dihydro-1,2-cyclopentenophenanthrene has now been extended to the preparation of the related compound carrying an angular methyl group in the 2-position. By reduction this unsaturated ketone was converted into 16-equilenone.

The unsaturated ketone can be used to prepare derivatives of equilenane substituted in the 17-position, of which the 16,17-diketone (through the 17-oximino derivative) is of particular interest. Some attempts to convert this diketone into the desoxyequilenin analog of estriol by reduction are described.

2-Methyl-1-phenanthrol and derivatives have been synthesized.

MADISON, WISCONSIN

RECEIVED JULY 7, 1944

[CONTRIBUTION FROM THE RESEARCH AND DEVELOPMENT LABORATORIES, UNIVERSAL OIL PRODUCTS CO.]

Hydrocarbon Reactions in the Presence of Cracking Catalysts. IV. Removal of Side Chains from Aromatics

BY CHARLES L. THOMAS, JAMES HOEKSTRA AND JOHN T. PINKSTON

One of the major differences between the catalytic and the thermal cracking of hydrocarbons lies in the greater selectivity shown by the catalytic method. This fact was clearly demonstrated for aliphatic hydrocarbons by Egloff, Morrell, Thomas and Bloch.¹ It was found that in the presence of synthetic catalysts of the silica-alumina type, the tendency was to split such compounds as octane, cetane, octene, and cetene mostly into C₃ and larger molecules, with but little hydrogen, methane, ethane, and ethylene being formed. In the thermal cracking of such materials

substantial proportions of hydrocarbons smaller than C₃ are produced. In view of these results, it became a matter of interest to study the catalytic cracking of phenyl substituted alkanes and to determine whether or not, in this case, similar selectivity obtained.

Experimental

Materials.—The cumene and the ethylbenzene were obtained from the Dow Chemical Company and were purified by fractionation in a Bruun column² of twenty-six theoretical plates. The cumene had n_D^{20} 1.4911, in excellent agreement with the values n_D^{20} 1.4911 of Troyan³ and

(1) G. Egloff, J. C. Morrell, C. L. Thomas and H. S. Bloch, *THIS JOURNAL*, **61**, 3371 (1939).

(2) J. H. Bruun, *Ind. Eng. Chem., Anal. Ed.*, **8**, 224 (1936).

(3) J. E. Troyan, *THIS JOURNAL*, **64**, 3056 (1942).

TABLE I
 CATALYTIC CRACKING OF ALKYL BENZENES

Alkyl-aromatic chgd.	Ethylbenzene	Cumene	Cumene	Cumene ^a	Butylbenzene	Amylbenzenes ^a
Temperature, °C.	500	400	450	500	500	500
Vol. liq. chg./hr./gross vol. of cat.	5	5	5	5	5	4
Process per., hr.	0.5	1.0	1.0	1.0	0.5	1.0
Ylds., wt. % chg.						
% C ₆ H ₆	3.0	21.9	34.5	39.8	17.3	34.4
% C ₆ H ₁₂	..	0.4	1.3	1.3
% C ₆ H ₁₀	28.7
% Unchanged charge	95.4	63.1	45.0	35.0	68.2	27.0
% Higher boiling material	0.4	4.5	1.4	3.6	5.5	4.2
% Total gas	1.2	10.2	17.8	20.3	7.1	5.4
Propylene	..	9.4	16.8	19.0	0.76	..
Propane	..	0.4	0.9	1.0	0.31	..
Butenes	..	0.2	0.1	0.3	2.69 ^b	..
Butanes	..	0.2	3.32	..
Moles C ₆ H ₆ /Mole of reacted charge	0.885	0.913	0.967	0.945	0.934	0.895

^a A technical mixture. ^b 2.47% *n*-C₄H₈; 0.27 *i*-C₄H₈.

1.4912 of Smittenberg, Hoog and Henkes.⁴ The ethylbenzene used had *n*_D²⁰ 1.4960, in agreement with the value of *n*_D²⁰ 1.4959 of Timmermans.⁵

The butylbenzene was obtained from the Eastman Kodak Company and was redistilled in the Bruun column. The portion used had a refractive index of 1.4899, comparing well with the value of 1.4900 of Timmermans.⁶

The amylbenzene was a commercial product of the Sharples Solvents Corporation, and was very probably a mixture of several isomers.

Apparatus and Procedure.—The apparatus and general procedure were similar to those already reported.¹

Catalysts.—The catalyst used in the amylbenzene experiment was a synthetic silica-alumina-zirconia⁷ whereas a synthetic silica-alumina⁸ was used in the other tests. The same general procedure is used in making the silica-alumina catalyst as has been described for making the silica-alumina-zirconia catalyst.

Results

The catalytic cracking of alkyl-aromatics at temperatures of 400–500° proved to be the most selective hydrocarbon reaction, excluding some hydrogenations, that we have encountered. In Table I the results of the cracking of ethylbenzene, cumene, *n*-butylbenzene, and a technical mixture of amylbenzenes are summarized.

These data show the remarkable ability of this type of cracking catalyst to sever the side chain selectively at the aromatic nucleus. The yields of benzene were generally over 90% of the theoretical based on the alkylbenzene reacted. Actually, the differences between these values and 100% are probably due to errors in the analyses of the prod-

(4) J. Smittenberg, H. Hoog and R. A. Henkes, *THIS JOURNAL*, **60**, 17 (1938).

(5) J. Timmermans and F. Martin, *J. Chim. Phys.*, **23**, 747–787 (1926).

(6) J. Timmermans and F. Martin, *ibid.*, **25**, 411–451 (1928).

(7) H. S. Bloch, C. L. Thomas, *THIS JOURNAL*, **66**, 1589 (1944).

(8) U. S. Patents (to Universal Oil Products Co.). C. L. Thomas and J. E. Ahlberg, U. S. 2,229,353 (January 21, 1941); 2,285,314 (June 2, 1942); 2,329,307 (September 14, 1943). J. E. Ahlberg and C. L. Thomas, U. S. 2,282,922 (May 12, 1942). C. I. Thomas and H. Bloch, U. S. 2,242,553 (May 20, 1941). C. L. Thomas and J. D. Danforth, U. S. 2,287,917 (June 30, 1942). C. L. Thomas, U. S. 2,270,090 (January 13, 1942).

ucts, for in no case was there any evidence of carbon-carbon bond scission to give alkylbenzenes with shorter side chains. No toluene, styrene, etc., was found in any product in this study. The extent of carbon deposition on the catalyst was small.⁹

The alkenes formed apparently underwent subsequent reactions to some extent, for some hexenes were formed in the cumene tests, presumably by polymerization of the initially formed propylene. The olefinic products from butylbenzene clearly underwent the hydrogen transfer reaction since butanes were formed. Of the hydrocarbons given in Table I, ethylbenzene was by far the most resistant to reaction, *n*-butylbenzene was next and cumene was most susceptible. The mixed amylbenzenes seemed to be about as susceptible as cumene.

These results obtained with the silica-alumina type catalyst bear a resemblance to those obtained with anhydrous aluminum chloride. Ipatieff and Pines⁹ have shown that aluminum chloride in the presence of a hydrogen donor effects the scission of the side chain at the nucleus to form the aromatic hydrocarbon and an alkane. Alkyl groups of three or more carbon atoms were removed cleanly from the benzene nucleus by aluminum chloride in the presence of either cyclohexane or decalin to give the corresponding alkane and benzene. Ethylbenzene and toluene did not react under their conditions.

The contrast between the results obtained by thermally cracking *vs.* catalytically cracking the alkyl aromatic is noteworthy. At 600–650°, A. F. Dobryanskii, E. K. Kanep and S. V. Katsman¹⁰ found that the liquid product from the thermal cracking of cumene was mainly styrene, with some

(9) V. N. Ipatieff and H. Pines, *THIS JOURNAL*, **59**, 56–60 (1937).

(10) A. F. Dobryanskii, E. K. Kanep and S. V. Katsman, *Trans. Exptl. Research Laboratory "Khemgas," Materials on Cracking and Chem. Treating of Cracking Products* (U. S. S. R.), **3**, 1–9 (1936); *C. A.*, **31**, 5334¹ (1937).

benzene and a trace of toluene. The conversions of the butyl- and amylbenzenes were to rather complex mixtures, with the reactions following no clear-cut course and being affected by the configuration of the alkyl group. A summary of their results is given in Table II. The data are not strictly comparable owing to the fact that in the thermal study it was necessary to go to a considerably higher temperature to obtain appreciable conversion than in the catalytic study.

TABLE II

THERMAL CRACKING OF ALKYL BENZENES BY DOBRYANSKII, KANEP AND KATSMAN

Compound Cracked	% C ₆ H ₆	% Toluene	% Styrene	% Gas
Ethylbenzene	14.0	1.4	17.0	18.5
<i>n</i> -Propylbenzene	0.3	36.5	2.4	7.3
<i>i</i> -Propylbenzene	6	0.5	44	9.1
<i>t</i> -Butylbenzene	2.4-8	2.0-1.4	6.0	6.0-19.7
Butylbenzene	0.8	8.4	14.5	32
Amylbenzene	0.5	11.0	10.2	34.1
<i>i</i> -Amylbenzene	0	16.5	3.6	25

It is evident that the thermal and catalytic reactions are different, for the reaction products are

different. Further, the catalytic reaction is much more selective.

Summary

During the cracking of ethylbenzene, cumene, *n*-butylbenzene and technical amylbenzene in the presence of synthetic catalysts of the silica-alumina type at 400-500° and atmospheric pressure, benzene and the corresponding alkene are formed with ease and great selectivity when the side chain contained three or more carbon atoms, the yield of benzene being at least 90% in each case. The order of decreasing susceptibility to cracking is cumene, the technical amylbenzene, *n*-butylbenzene, and, in a lower order of magnitude, ethylbenzene. No toluene, styrene, etc., was found in any product in this study.

The alkenes formed apparently undergo subsequent reactions to some extent for some hexenes are formed in the cumene tests, presumably by polymerization of the initially formed propylene. The olefinic products from butylbenzene undergo the hydrogen transfer reaction; some butanes are formed.

CHICAGO, ILLINOIS

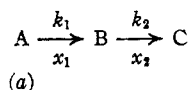
RECEIVED APRIL 7, 1944

[CONTRIBUTION FROM GIBBS CHEMICAL LABORATORY, HARVARD UNIVERSITY]

The Kinetic Analysis of Consecutive Irreversible First Order Reactions

BY C. GARDNER SWAIN

The rate constants of one-step irreversible first or second order reactions are so readily obtained that an attempt is generally made in chemical kinetics to find limiting conditions of reactant concentrations, *pH*, solvent, *etc.*, under which the rate will obey one of these simple laws. Perhaps the most frequently encountered mechanism of higher complexity not in practice reducible to a simple one-step process is one involving two consecutive irreversible first order reactions



Here A, B, and C represent starting material, intermediate product, and final product; k_1 and k_2 represent the rate constants of the two steps; x_1 and x_2 the extents of reaction (moles per unit volume) along them at any time, t ; and a the initial concentration of A.

The concentrations of A, B, and C can be readily calculated if the rate constants are known. The expressions were first obtained by Esson.¹

$$[A] = ae^{-k_1 t} \quad (1)$$

$$[B] = \frac{ak_1}{k_1 - k_2} (-e^{-k_1 t} + e^{-k_2 t}) \quad (2)$$

$$[C] = a \left[1 + \frac{1}{k_1 - k_2} (k_2 e^{-k_1 t} - k_1 e^{-k_2 t}) \right] \quad (3)$$

(1) W. Esson, *Phil. Trans. Roy. Soc. (London)*, **156**, 220 (1866); cf. A. Rakowski, *Z. physik. Chem.*, **57**, 321 (1907).

However, the converse problem of obtaining the rate constants rapidly and accurately from a set of experimental data has not received an adequate solution. This is the practical problem with which we are concerned below.

Let us first define F as a function equal to the sum of x_1 and x_2 . It is then a function of time and equal to $[B] + [C]$. Using equations (2) and (3)

$$F = a \left[2 - \left(\frac{k_1 - 2k_2}{k_1 - k_2} \right) e^{-k_1 t} - \left(\frac{k_1}{k_1 - k_2} \right) e^{-k_2 t} \right] \quad (4)$$

Now it very frequently happens that the only analytical method available to follow two consecutive reactions measures the function F directly, this therefore constituting the entire data from which the rate constants k_1 and k_2 must be obtained. This is true, for example, when one measures a common by-product or effect produced in each step, *e. g.*, hydrogen or halide ion from the hydrolysis of a dihalide, an α -particle produced by radioactive decay, a one-electron oxidation change, or a heat or volume change associated with each step. The function F is then equal to the concentration of this by-product, or the fraction of the total magnitude of this effect multiplied by $2a$. Experimental data on the decline in concentration of a reagent consumed in each step and present in large excess (or in small excess but not entering into the rate