The Disproportionation of Paraffins Dissolved in Isobutane Catalyzed by Aluminum Chloride and Hydrogen Chloride

BY ABRAHAM SCHNEIDER

Normal and branched paraffins dissolved in excess isobutane have been found to undergo extensive disproportionation on treatment from one to three hours with aluminum chloride and hydrogen chloride at 100°. The isobutane was converted to isopentane while the higher paraffins were degraded to mixtures of predominantly branched paraffins ranging in molecular weight from isopentane to those of the starting materials. Considerable neohexane was usually formed. This reaction was observed with 2-methylpentane, n-hexane, n-heptane, n-octane, n-tetradecane, a Fischer–Tropsch gas-oil and a refined paraffin wax. The latter three materials formed products which were mainly in the C_5 to C_9 range, the weight of hydrocarbon product in each molecular weight class decreasing with increasing carbon number. A mechanism for this reaction is presented.

Introduction

Aluminum chloride and bromide, with proper activation[1] are almost unique in their capacity to cause normal paraffins higher than propane to isomerize and disproportionate.[2] Isoparaffins, on the other hand, undergo these reactions not only under the catalytic influence of the aluminum halides, but also in the presence of many combinations considered to be producers of carbonium ions such as alkyl fluoride–boron trifluoride, olefin–hydrogen fluoride, alcohol–sulfuric acid and others.[3]

Isomerization of n-butane catalyzed by aluminum halide ordinarily proceeds without side reactions[4]; however, n-pentane and n-hexane disproportionate so readily that isomerization of these paraffins to isoparaffins is secondary. In attempts to isomerize n-pentane to the iso-structure, extensive disproportionation occurred forming isobutane and a near-equilibrium mixture of hexanes.[5]

This result with aluminum halide is strikingly similar to the disproportionation of isopentane promoted by alkyl fluoride and boron trifluoride[3] and suggested that a mechanism of reaction in large part common to both types of disproportionation is operative.

In order further to test the hypothesis of a common mechanism for disproportionation initiated by aluminum halide and by combinations considered capable of producing carbonium ions, the disproportionation of normal and/or isoparaffins containing six or more carbon atoms dissolved in excess isobutane was studied using aluminum chloride–hydrogen chloride catalysis. Employing the system alkyl fluoride–boron trifluoride, it had been observed that reaction between isoparaffins of six or more carbon atoms and isobutane yields isopentane and a mixture of isomers containing one carbon atom less than the higher isoparaffin.[6]

Several patents concerning aluminum chloride-catalyzed "cracking" or "averaging" of mixtures of higher paraffins dissolved in excess isobutane have been granted,[7] but none of these give detailed analyses of the products in terms of individual compounds. In this work the products of disproportionation were rectified in highly efficient columns and the fractions analyzed by infrared spectroscopy.

Experimental

Reagents.—Isobutane and hydrogen chloride (C.P. grades) were obtained from the Matheson Co. Phillips "pure" grade of n-hexane and technical grade of 2-methylpentane (95 mole % minimum purity, n^{20}D 1.3715) were used without further purification. n-Heptane (n^{20}D 1.3877) supplied by the Westvaco Chlorine Products Corp. and n-octane and n-tetradecane (both of 95 mole % minimum purity) from the Connecticut Hard Rubber Co. were used without further purification. The Baker analyzed, C.P. anhydrous aluminum chloride employed in these experiments was taken from freshly opened bottles of the material.

The paraffin wax was a commercial sweated product, m.p. 132°F. (A.S.T.M. Method D8742), manufactured by the Atlantic Refining Co. The Fischer–Tropsch gas-oil was an 84 cetane number fuel oil obtained from a French source by the U. S. Navy. It had an initial boiling point of 178°, a 5% point of 209, 50% point of 254, and a 90% point of 308. The average molecular weight was 213. The olefin content was 10% and that of aromatics was zero. Further physical properties are n^{20}D 1.4318, d^{20}_4 0.7681, acid absorption 10%, Br. No. 72.

The Disproportionation of n-Octane Dissolved in Excess Isobutane Catalyzed by Aluminum Chloride and Hydrogen Chloride (Table I, Expt. No. 4), a Typical Experiment.—A Universal Oil Products type, one-liter, stainless steel contactor equipped with an efficient turbomixer was charged with 113.5 g. of isobutane (1.96 moles), 75 g. of n-octane (0.66 mole), 15 g. of aluminum chloride (0.11 mole) and 4 g. of hydrogen chloride (0.11 mole). The contactor was heated to 100° and stirred for 90 minutes. At the end of this period the contactor was cooled to zero and the product (165 g.) separated from a black tar-like lower layer which was slightly active toward water.

The washed and dried organic phase was distilled in a partial take-off, total condensation, glass-helix packed, silvered, vacuum-jacketed column, 4' long by $1/_2$" internal diameter; the head was refrigerated by solid carbon dioxide and acetone:

(1) -11 to $-7°$, 115 cc. at $-78°$, 72 g. largely isobutane

(2) -7 to $0°$, 7.5 cc. at $-78°$, } 8 g. largely n-butane
      0 to $+15°$, 5.0 cc. at $-78°$ }

At this point the head of the column was replaced by a water-cooled type and the distillation continued.

(3) 15 to 40°, 56 cc. at $-78°$, 37.5 g. isopentane

(4) 40 to 69°, 26 cc. at $-78°$, 15.7 g. hexanes

(5) 69 to 99°, 13 cc. at $-78°$, 8.8 g. heptanes

(1) Pertinent references in W. G. Frankenburg, V. I. Komarewsky and E. K. Rideal, "Advances in Catalysis and Related Subjects," Vol. I, Academic Press. Inc., New York, N. Y., 1948, chapter on "Isomerization of Alkanes," by H. Pines.

(2) The system hydrogen fluoride–boron trifluorides has recently been shown to possess this type of activity. E. C. Hughes and S. M. Darling, paper presented before the Petroleum Division, Am. Chem. Soc., Houston, March, 1950.

(3) Pertinent references in a paper by A. Schneider and R. M. Kennedy, THIS JOURNAL, 73, 5017 (1951).

(4) C. W. Montgomery, J. H. McAteer and N. W. Franke, ibid., 59, 1768 (1937).

(5) B. L. Evering, E. L. D'Ouville, A. P. Lein and R. C. Waugh, paper presented before the Petroleum Division, Am. Chem. Soc., Atlantic City, N. J., April, 1947.

(6) A. Schneider and R. M. Kennedy, THIS JOURNAL, 73, 5024 (1951).

(7) J. J. Owen and E. E. Stahly, U. S. Patent 2,349,458 (1944); E. L. D'Ouville and B. L. Evering, U. S. Patent 2,369,444 (1945); R. E. Burk, U. S. Patent 2,370,144 (1945).

TABLE I

EXPERIMENTAL DETAILS AND PRODUCTS OF DISPROPORTIONATION OF PARAFFINS IN ISOBUTANE CATALYZED BY ALUMINUM
CHLORIDE AND HYDROGEN CHLORIDE

Expt. No.	1	2	3	4	5	6	7
		2-Methyl-			n-	Fischer-Tropsch	Paraffin
Paraffin disproportionated	n-Hexane	pentane	n-Heptane	n-Octane	Tetradecane	Gas-oil	wax
Temperature, °C.	100	100	100	100	100	100	100
Contact time, hours	2.75	1.5	3	2.5	3	2.5	3
Reactants, g. (moles):							
Isobutane	117(2.02)	122.5(2.11)	117 (2.02)	113.5(1.96)	121 (2.09)	131(2.26)	129(2.22)
Higher paraffin	40(0.47)	57 (0.66)	69 (0.69)	75 (0.66)	100 (0.51)	88(0.41)	108(0.284)
Aluminum chloride	15(.11)	15 (.11)	15 (.11)	15 (.11)	15 (.11)	15(.11)	15(.11)
Hydrogen chloride	4(.11)	3 (.082)	5 (.14)	4 (.11)	7.5(.21)	8(.22)	6(.16)
Total, g.	176	197.5	206	207.5	243.5	242	258
Products, g. (moles):							
Isobutane[a]	97(1.67)	99.5(1.71)	82 (1.41)	80 (1.38)	66 (1.14)	64(1.10)	64(1.10)
Isopentane[b]	27(0.38)	25 (0.35)	40 (0.56)	37.5(0.52)	40 (0.56)	40(0.56)	32(0.44)
C_6	9.9	31.5	18.5(.24)	15.7(.20)	23.4	17.8	15.4
C_7			16 (.16)	8.8(.088)	12.9	11.1	9
C_8			4.9	19.5	9.0	6.8	5.7
C_9					3.6	4.0	2.7
C_{10}	5.1	7.5			1.5		
C_{11}					1.5		
C_{12}					1		
C_{13}			1.6	3	1		
C_{14}					30.0		
C_{15} plus					3	39.6	66
Wt. of hydrocarbon in aluminum chloride layer, g.[c]	18	16	23	24.5	28	[d]	
Composition of depentanized product, vol., %[e]							
C_6 2,2-Dimethylbutane		24.7	12.8	7.3		5.6	
2,3-Dimethylbutane		13.8	5.7	4.7		5.5	
2-Methylpentane		38.1	22.0	15.5		22.6	
3-Methylpentane		9.2	5.0	6.4		8.3	
n-Hexane		8.0	3.7	7.1		3.5	
C_7 2,2-Dimethylpentane			2.2	2.0		0.7	
2,2,3-Trimethylbutane			1.1	0.6		0.9	
2,4-Dimethylpentane			4.9	2.2		3.0	
2,3-Dimethylpentane			3.1	2.0		5.2	
3,3-Dimethylpentane			2.1	1.3			
2-Methylhexane			7.3	5.6		8.8	
3-Methylhexane			6.2	4.8		9.3	
n-Heptane			9.4	1.2		2.1	
C_8 2,2,4-Trimethylpentane				1.7			
2,4-Dimethylhexane				1.1		0.5	
2,5-Dimethylhexane						4.7	
2,2-Dimethylhexane						1.6	
3,4-Dimethylhexane						0.3	
2-Methylheptane				8.1		4.0	
3-Methylheptane				3.2			
4-Methylheptane				2.2		0.3	
n-Octane				10.7			
Temperature at which distillation was stopped, °C.		74	98	125		119	
Vol. % of depentanized product undistilied		7	14	12		13[f]	
Moles isopentane formed per mole higher paraffin consumed	1.07	1.16	1.05	1.07	1.55	2.30	3.90
Moles isopentane formed per mole isobutane consumed	1.07	0.87	0.91	0.90	0.59	0.48	0.40
Moles of isobutane consumed per mole paraffin consumed	1.0	1.33	1.15	1.18	2.64	4.85	9.83

[a] Includes n-butane. [b] Includes n-pentane. [c] Assumed to equal difference in weight of organic starting materials and products. [d] Loss of some product makes calculation impossible. [e] By infrared. [f] Material boiling from 41 to 150.0° (39 g.) fractionated and analyzed by infrared; 39.6 g. of higher boiling material not fractionated.

(6) 99 to 124°, 28 cc. at −78°, 19.5 g. octanes

(7) residue 3 g., n^{20}D 1.4050, mainly n-octane

Cuts 4–6 were combined and fractionated into 0.5-cc. fractions in a concentric-tube distillation column rated at approximately 100 plates.[8] The distillation was stopped before all the octane had distilled to prevent the still-pot from running dry. The spectra of the distilled fractions were obtained with a Perkin–Elmer infrared spectrometer and a method similar to that of Heigl, et al., used to calculate com-

position from the spectral data.[9] The composition of the distillate is given in Table I, Expt. No. 4.

Discussion of Experimental Details

Comparison of the Disproportionation of n-Hexane in Excess Isobutane Catalyzed by Aluminum Chloride and Hydrogen Chloride with the Dis-

(8) C. K. Donnell and R. M. Kennedy, Ind. Eng. Chem., 42, 2327 (1950).

(9) J. J. Heigl, M. F. Bell and J. U. White, Anal. Chem., 19, 293 (1947). Wave length and base-line points for the infrared analysis are given in a paper by A. Schneider and R. M. Kennedy, THIS JOURNAL, 73, 5013 (1951).

proportionation of 2-Methylpentane in Excess Isobutane Promoted by Alkyl Fluoride and Boron Trifluoride.—In studies on disproportionation of higher isoparaffins dissolved in isobutane promoted by secondary or tertiary alkyl fluorides and boron trifluoride,[6] Schneider and Kennedy observed that per mole of isohexane consumed slightly more than one mole of isopentane was formed. This was less than the two moles called for by the equation

$$i\text{-}C_4H_{10} + i\text{-}C_6H_{14} \rightleftharpoons 2i\text{-}C_5H_{12}$$
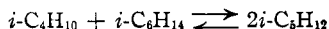
but more than enough to demonstrate the formation of isopentane by participation of isobutane as shown in the equation; accordingly, disproportionation of two molecules of the isohexane yielding a molecule of isopentane and one of isoheptane[3] was ruled out.

$$2i\text{-}C_6H_{14} \rightleftharpoons i\text{-}C_5H_{12} + i\text{-}C_7H_{16}$$
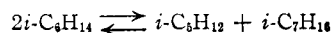
In the work at hand, n-hexane and isobutane (Table I, Expt. No. 1) underwent a reaction catalyzed by aluminum chloride and hydrogen chloride forming slightly more than one mole of isopentane per mole of n-hexane or isobutane converted. Slightly more than one mole of isopentane was formed per mole of higher isoparaffin consumed in a reaction between 2-methylpentane and isobutane with the same type of catalysis (Expt. No. 2). By analogy with the results obtained from the work with alkyl fluoride and boron trifluoride, the data for the experiments investigated here suggest interaction of isobutane and the higher paraffin in the production of isopentane.

The formation of considerable quantities of neohexane in the disproportionations catalyzed by aluminum halide is in contrast to the complete absence of this hexane in the products of disproportionations promoted by alkyl fluoride–boron trifluoride. A possible explanation lies in the slow rate of formation of neohexane from the other hexanes[10] and in its inertness once formed.[11] To illustrate, reaction of the combination alkyl fluoride–boron trifluoride in a solvent of 2-methylpentane produces 2- and 3-methylpentane and 2,3-dimethylbutane, a mixture the components of which have been shown to be interconvertible by relatively fast reactions employing aluminum chloride catalysis.[10] Short exposure of either of the singly branched hexanes or 2,3-dimethylbutane to aluminum chloride gives mixtures of the three components and no neohexane; however, longer contact forms considerable neohexane with concurrent consumption of the other hexanes.[10] Thus, because of the slow rate of formation of neohexane and its stability once formed, an isomerization catalyst of continuing activity is required for its production, a condition not extant in the alkyl fluoride–boron trifluoride combination.

Mechanism of the Aluminum Chloride–Hydrogen Chloride Catalyzed Disproportionation of n-Octane in Isobutane (Table I, Expt. No. 4).—A primary purpose of this work is to show that the disproportionation of normal and isoparaffins in excess isobutane occurs by reaction paths that are essentially the same. The work of Pines indicates
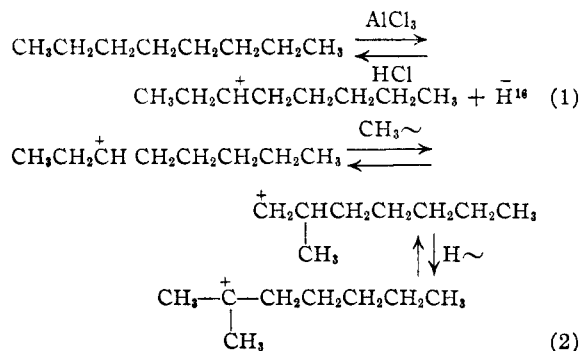
that for the isomerization of normal butane to isobutane, the normal isomer is brought into reaction by exchanging a secondary hydrogen atom with a trace amount of carbonium ion.[1] The isomerization is postulated as being a chain reaction with t-butyl ions as the chain carriers.[12] Confirmatory evidence of the ability of the trimethylcarbonium ion to abstract a secondary, negative hydrogen ion is found in the reaction[13]
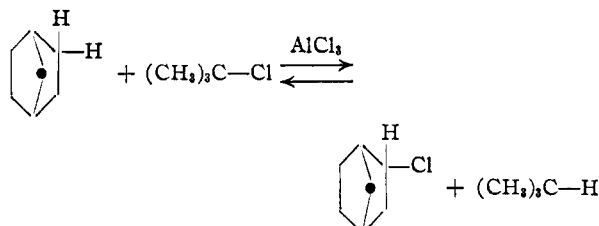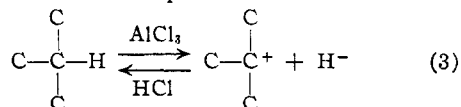

Accepting the hypothesis that properly activated aluminum halide effects the ionization of secondary and tertiary carbon–hydrogen bonds,[14] the complex phenomena taking place in these disproportionations are explicable in terms of the Whitmore carbonium ion theory.[15]

It is believed that the mechanism of the disproportionation of isobutane and normal or isoparaffins of six or more carbon atoms is not dependent on the molecular weight of the latter; consequently, a detailed discussion will be given to one example, the aluminum chloride-catalyzed disproportionation of n-octane in excess isobutane, under the assumption that the other paraffins studied can be treated in a closely similar fashion.

The first step by which n-octane enters into the disproportionation reaction with isobutane is probably its conversion to a tertiary octyl ion

$$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3 \underset{HCl}{\overset{AlCl_3}{\rightleftharpoons}}$$
$$CH_3CH_2\overset{+}{C}HCH_2CH_2CH_2CH_2CH_3 + \overset{-}{H}{}^{16} \quad (1)$$

$$CH_3CH_2\overset{+}{C}H\ CH_2CH_2CH_2CH_2CH_3 \underset{}{\overset{CH_3\sim}{\rightleftharpoons}}$$

$$\overset{+}{C}H_2CHCH_2CH_2CH_2CH_2CH_3$$
$$\underset{CH_3}{|} \quad \uparrow\downarrow H\sim$$

$$CH_3\overset{+}{-}\overset{}{C}-CH_2CH_2CH_2CH_2CH_3$$
$$\underset{CH_3}{|} \quad\quad\quad\quad (2)$$

By the same mechanism, isobutane is probably converted to the trimethylcarbonium ion with even greater ease than the C_8-paraffin

$$\begin{array}{ccc} C & & C \\ | & AlCl_3 & | \\ C-C-H & \underset{HCl}{\overset{}{\rightleftharpoons}} & C-C^+ + H^- \\ | & & | \\ C & & C \end{array} \quad (3)$$

Both the t-butyl and t-octyl ions may lose protons and be converted to the corresponding olefins

(10) B. L. Evering and R. C. Waugh, paper presented before the Petroleum Division, Am. Chem. Soc., Chicago, Ill., April, 1948.

(11) B. L. Evering and E. L. D'Ouville, THIS JOURNAL, **71**, 440 (1949).

(12) H. S. Block, H. Pines and L. Schmerling, *ibid.*, **68**, 153 (1946).
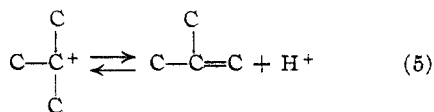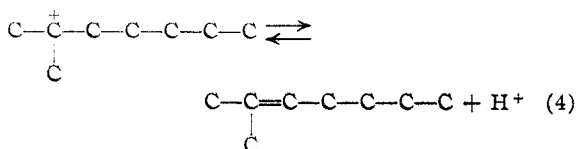
(13) L. Schmerling, *ibid.*, **68**, 195 (1946).

(14) P. D. Bartlett, F. M. Condon and A. Schneider, *ibid.*, **66**, 1531 (1944).

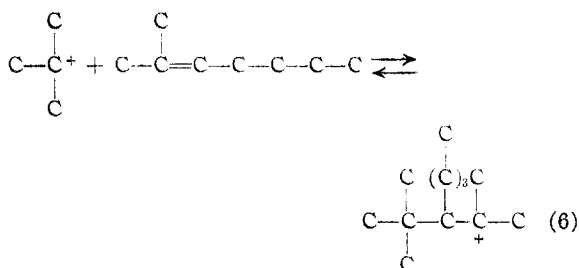(15) F. C. Whitmore, *Ind. Eng. Chem.*, **26**, 94 (1934).

(16) The hydride ion in (1) according to the chain mechanism of Block, *et al.*,[12] is removed from the paraffin by transfer to another carbonium ion.

C—$\overset{+}{\text{C}}$—C—C—C—C—C $\rightleftharpoons$
$\overset{|}{\text{C}}$

$$\text{C—C}=\text{C—C—C—C—C} + \text{H}^+ \quad (4)$$
$\overset{|}{\text{C}}$

$$\text{C—}\overset{+}{\underset{|}{\text{C}}}\text{—} \rightleftharpoons \text{C—}\overset{|}{\text{C}}=\text{C} + \text{H}^+ \quad (5)$$

The possible modes of addition of the various carbonium ions to the olefins produced from them have been previously discussed[6] and it is concluded that the addition leading to the formation of isopentane is
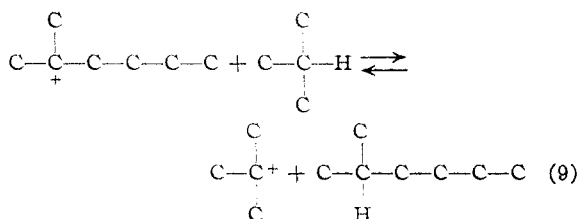
C—$\overset{+}{\underset{|}{\text{C}}}$ + C—$\overset{|}{\text{C}}$=C—C—C—C—C $\rightleftharpoons$

$$\text{C—C—}\overset{|}{\underset{+}{\text{C}}}\text{—C} \quad (6)$$

with the (C)$_3$C and C groups attached

Isomerization and cleavage of the ion on the right in (6) forms fragments of 5 and 7 carbon atoms

C—C—$\overset{+}{\text{C}}$—C $\rightleftharpoons$ C—C—$\overset{+}{\text{C}}$—C—C $\rightleftharpoons$

C—C—$\overset{+}{\text{C}}$—C $\quad (7)$

C—$\overset{+}{\text{C}}$—C—$\overset{|}{\text{C}}$—C $\rightleftharpoons$

$$\text{C—}\overset{|}{\text{C}}=\text{C—C} + \text{C—}\overset{|}{\underset{+}{\text{C}}}\text{—C—C—C—C} \quad (8)$$
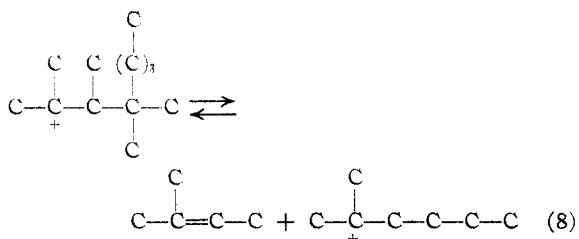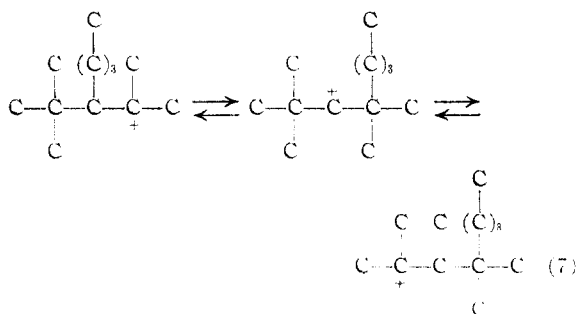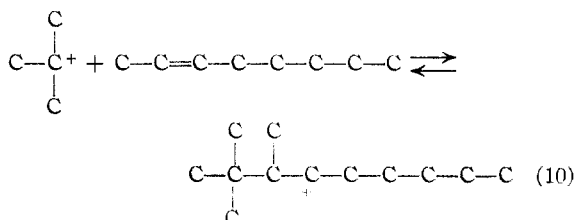
In accordance with the chain mechanism of isomerization,[12] the tertiary heptyl ion on the right in (8) is saturated by abstraction of a negative tertiary hydrogen atom from a molecule of isobutane (which is present in large concentration), thus initiating another chain

C—$\overset{+}{\underset{|}{\text{C}}}$—C—C—C—C + C—$\overset{|}{\text{C}}$—H $\rightleftharpoons$

$$\text{C—}\overset{+}{\text{C}} + \text{C—}\overset{|}{\underset{\text{H}}{\text{C}}}\text{—C—C—C—C} \quad (9)$$

The trimethylethylene in VIII is converted to isopentane in the strongly acid medium by adding a

proton to form the dimethylethylcarbonium ion which is then saturated in the same fashion as the tertiary heptyl ion.

Addition of the trimethylcarbonium ion to the olefin derived from the isomerized octyl ion rather than to normal octene is required because there is no simple sequence of rearrangements which ultimately yields isopentane from an intermediate of this sort

C—$\overset{+}{\underset{|}{\text{C}}}$ + C—C=C—C—C—C—C—C $\rightleftharpoons$

$$\text{C—}\overset{|}{\text{C}}\text{—}\overset{|}{\text{C}}\text{—C—C—C—C—C—C} \quad (10)$$

From the tabulation of products presented in Table I, Expt. No. 4, it is seen that lower molecular weight isoparaffins are produced in larger amounts than higher isoparaffins as a result of the disproportionation. Hexanes exceed heptanes which, in turn, are present in larger amount than branched octanes. This suggests that aluminum chloride-catalyzed disproportionation of isobutane with the higher, intermediary, isoparaffinic fragments (such as those produced in 8) or with the higher isoparaffins themselves proceeds at a more rapid rate than the isomerization of normal octane to the iso-structure. If this is true, the rate-determining step in the sequence of reactions is the initial isomerization of n-octane. To produce hexanes, the t-heptyl ion formed in 8 loses a proton and undergoes with the t-butyl ion a series of reactions entirely similar to 6–8. The products, trimethylethylene and the tertiary hexyl ion, are converted to the corresponding saturates by ionic hydrogenation.

The ratio of moles of isobutane consumed to that of octanes converted (1.18) is additional evidence that the intermediate products of disproportionation of n-octane with isobutane, e.g., heptyl and hexyl ions, react further with isobutane. However, the number of moles of isopentane formed per mole of isobutane reacting, which should equal or exceed one, falls short of this figure. The same deficiency of isopentane was observed in the alkyl fluoride–boron trifluoride promoted disproportionations of six and seven carbon isoparaffins in excess isobutane.[6] An explanation may be sought in the polymerization of trimethylethylene (or an isomeric olefin) catalyzed by aluminum chloride.

The mechanism developed for this type of isomerization calls for singly branched products of disproportionation, and, in general, this has been observed. Thus, singly branched paraffins constitute the major products of disproportionation and, of the isomerized octanes, 83 vol. % is singly branched. The more highly branched paraffins are probably formed as secondary reaction products by the isomerizing action of the metal halide on the primary products.

The concentrations of the various hexane isomers produced in the disproportionation of n-octane in excess isobutane do not correspond to the

equilibrium values determined at 100°.[11]   On the other hand, the amounts of 2- and 3-methylpentane and 2,3-dimethylbutane are in the proper sequence. The data indicate that insufficient time was allowed for equilibration to occur, since the concentration of neohexane is too low relative to that of 2-methylpentane.

[Contribution from the Chemistry Department of the University of Missouri]

Acylations of Phenol Ethers with Diphenoyl Chloride[1]

By Dorothy V. Nightingale, Robert L. Sublett and Robert H. Wise

Received November 29, 1951

Diphenoyl chloride reacted with phenol ethers in the presence of aluminum chloride at room temperature or at temperatures of −10 to +5° in carbon disulfide, nitrobenzene or *sym*-tetrachloroethane to form the corresponding 2,2′-diaroylbiphenyls. When the solution of diphenoyl chloride was stirred with aluminum chloride for about two hours at room temperature prior to the addition of the phenol ether, the product was a 4-aroylfluorenone and/or a 9,9-diaryl-4-aroylfluorene. Without solvent, the products were the 2,2′-diaroylbiphenyls.

In a previous publication[2] it was established that 2,2′-diphenoyl chloride reacted with some alkylbenzenes in the presence of aluminum chloride to form 2,2′-diaroylbiphenyls. When the isomerization of the diphenoyl chloride was attempted in nitrobenzene solution prior to the addition of the hydrocarbon, 4-aroylfluorenones were formed.

The study has been extended to the reaction of diphenoyl chloride with phenol ethers in the presence of aluminum chloride under similar conditions, both without solvent and in nitrobenzene, carbon disulfide and *sym*-tetrachloroethane. The types of products formed from the ethers in these solvents were largely determined by the reaction temperature and by the rate at which the reactants were mixed.

chloride, or if the phenol ether was added immediately to the cooled solution of diphenoyl chloride and aluminum chloride at such a rate that the temperature did not exceed 5°, the 2,2′-diaroylbiphenyls were obtained in good yields.

When the solution of diphenoyl chloride was cooled to 0° followed by the addition of the aluminum chloride at such a rate that the temperature did not exceed 15° and then stirred for an hour or more at room temperature prior to the addition of the phenol ether, different products were obtained. *o*-Cresol methyl ether and veratrole yielded 4-aroylfluorenones II and/or 4-aroyl-9,9-diarylfluorenes III (54–70%) while *m*- and *p*-cresol methyl ethers yielded only 4-aroylfluorenones (40–73%). Anisole yielded 4-anisoylfluorenone (47%) and 4-anisoyl-

Table I

Products Obtained from Diphenoyl Chloride and Phenolic Ethers

| | M.p., °C. | Formula | Analyses, % | | | |
| | | | Carbon | | Hydrogen | |
			Calcd.	Found	Calcd.	Found
2,2′-Bis-(3-methyl-4-methoxybenzoyl)-biphenyl	145.5–146	$C_{30}H_{26}O_4$	79.99	79.90	5.82	6.05
2,2′-Bis-(4-methyl-6-methoxybenzoyl)-biphenyl	147–148	$C_{30}H_{26}O_4$	79.99	79.92	5.82	5.98
2,2′-Bis-(5-methyl-2-methoxybenzoyl)-biphenyl	166–167	$C_{30}H_{26}O_4$	79.99	79.85	5.82	6.03
2,2′-Bis-(3,4-dimethoxybenzoyl)-biphenyl	186–186.5	$C_{30}H_{26}O_6$	74.67	74.45	5.43	5.46
2,2′-Bis-(2,4-dimethoxybenzoyl)-biphenyl	191.5–192	$C_{30}H_{26}O_6$	74.67	74.55	5.43	5.26
4-(3-Methyl-4-methoxybenzoyl)-fluorenone	141.5–142 125–126	$C_{22}H_{16}O_3$	80.47	80.38	4.91	5.07
4-(4-Methyl-6-methoxybenzoyl)-fluorenone	139.5–140 126–126.5	$C_{22}H_{16}O_3$	80.47	80.37	4.91	4.91
4-(2-Methoxy-5-methylbenzoyl)-fluorenone	114–114.5 167.5–168	$C_{22}H_{16}O_3$	80.47	80.36	4.91	4.92
4-(3,4-Dimethoxybenzoyl)-fluorenone	167–168	$C_{22}H_{16}O_4$	76.73	76.72	4.68	4.80
4-(2,4-Dimethoxybenzoyl)-fluorenone	155–156 141.5–142	$C_{22}H_{16}O_4$	76.73	76.52	4.68	4.73
4-(3-Methyl-4-methoxybenzoyl)-9,9-bis-(3-methyl-4-methoxyphenyl)-fluorene	193.5–194	$C_{38}H_{34}O_4$	82.39	82.21	6.27	6.26
4-(3,4-Dimethoxybenzoyl)-9,9-bis-(3,4-dimethoxyphenyl)-fluorene	225.5–226	$C_{38}H_{34}O_4$	75.73	75.65	5.67	5.80
4-(4-Methoxybenzoyl)-9,9-bis-(4-methoxyphenyl)-fluorene	177.5–178	$C_{35}H_{28}O_4$	82.01	82.22	5.51	5.81

If the phenol ethers and the diphenoyl chloride were first dissolved in these solvents and cooled to −10° prior to the slow addition of the aluminum

(1) Abstracted from the Ph.D. dissertation of Robert L. Sublett, 1950, and the Master's dissertation of Robert H. Wise, 1951.

(2) D. V. Nightingale, H. E. Heiner and H. E. French, This Journal, 72, 1875 (1950).

9,9-dianisilfluorene (31%) in nitrobenzene, but only 4-anisoylfluorenone (50%) in carbon disulfide.

When the phenol ether was used in excess as solvent for the reaction and the aluminum chloride was added last at room temperature, the corresponding 2,2′-diaroylbiphenyls were formed in yields of 59–77%.