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

Migration of Double Bonds in Olefinic and Diolefinic Hydrocarbons Catalyzed by Sodium. Dehydrogenation of *d*-Limonene to *p*-Cymene[2]

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RECEIVED JUNE 10, 1954

The catalytic isomerization of olefinic hydrocarbons in the presence of sodium and organic promoters, which are capable of reacting with the sodium to form organosodium compounds, has been investigated. It was found that 1-butene can be isomerized at 150° to 2-butene, while 1-decene on refluxing was converted to *cis*- and *trans*-decenes having the general formula $RCH{=}CHR_1$. *d*-Limonene undergoes both isomerization to conjugated menthadienes and dehydrogenation to *p*-cymene. A mechanism of the reaction is suggested.

During a study of certain reactions in the presence of sodium, it was observed that olefinic hydrocarbons present among the reactants underwent an isomerization, which involved the migration of a double bond. A more detailed study of this reaction has revealed that certain compounds capable of reacting with sodium promoted the isomerization of olefins. For that reason a more systematic study of the effect of sodium upon the isomerization of alicyclic and cyclic olefins has been undertaken.

1-Butene.—The isomerization of 1-butene was carried out in a rotating autoclave using cyclohexane or benzene as a solvent, sodium as a catalyst and *o*-chlorotoluene as a promoter. The reactants were introduced into a glass liner cooled to −78° and the latter was inserted into the autoclave. No attempt was made to eliminate air. After the autoclave was heated for the desired length of time, the recovered butenes were analyzed by means of a mass spectrograph. The experimental conditions and the results obtained are summarized in Table I. The effect of *o*-chlorotoluene as a promoter in the reaction is indicated by the increase in the rate of isomerization of 1-butene to 2-butene.

TABLE I

ISOMERIZATION OF 1-BUTENE

The following reagents were used in each experiment: 1-butene, 22 to 25 g., sodium in the form of ribbon, 3.5 g., solvent, 39 to 43 g. The duration of heating was 3.5–4.0 hours. The maximum pressure developed during the reaction was 18–21 atmospheres at 100° and 27–33 atmospheres at 150°. The amount of butenes recovered after the reaction was 90–95%.

Experiment	1	2	3	4	5	6	7	8
Solvent	←Cyclohexane→				←Benzene→			
o-Chlorotoluene, g.	0	1.0	0	1.0	0	1.0	0	1.0
Temp., °C.	100	100	150	150	100	100	150	150
2-Butene formed, %[a]	1	10	28	88	1	20	9	88

[a] Analyzed by a mass spectrograph.

The reaction is accompanied by very little of side reactions, and no skeletal isomerization of butenes was observed. The purity of reagents used seems to be of importance, since, in one experiment made under conditions described in expt. 7, but using a technical-grade benzene which was not purified by distillation over sodium, about 77% of the 1-butene isomerized to 2-butene.

***l*-Decene.**—The selection of *l*-decene as a representative of a liquid 1-alkene was governed by the ready availability of this hydrocarbon in pure form and by the fact that it distilled at 170°, making it possible to study the isomerization reaction at atmospheric pressure. The experimental data obtained were summarized in Table II.

It was found that about 99% of the 1-decene was converted to decenes of the formula $RCH{=}CHR_1$ when 1-decene containing 3% of *o*-chlorotoluene was refluxed for 20 hours in the presence of 10% by weight of sodium cut into pea size pieces. The decenes consisted of about 15% *cis* and 84% *trans* isomers. The exact position of the double bond was not investigated. The extent of isomerization was determined by infrared spectral analysis at 11.0, 14.3 and 10.3 μ, positions of maximum absorption characteristic of terminal, *cis* and *trans* double bond, respectively. The sodium, most of which was recovered unchanged, was coated with a dark brown powder-like material. A similar experiment made in the absence of *o*-chlorotoluene resulted in only 4% isomerization of the 1-decene.

Anthracene seems to be a less effective promoter than *o*-chlorotoluene, since it caused only 28% isomerization of 1-decene.

***d*-Limonene.**—The reaction of *d*-limonene in the presence of sodium was made at its reflux temperature using an apparatus and procedure similar to those employed for the study of 1-decene. Since hydrogen was evolved during the reaction, a gas collecting bottle was attached to the exit of the reflux condenser. A record of gas evolution as a function of time was kept. The experimental data are given in Table III.

Both isomerization to conjugated menthadienes and dehydrogenation to *p*-cymene took place when *d*-limonene containing 2.5% of *o*-chlorotoluene was refluxed in the presence of 8% by weight of sodium in the form of beads. For the first 4–5 hours of heating little or no hydrogen was liberated, afterwards a steadily accelerating gasification.

TABLE II

ISOMERIZATION OF *l*-DECENE

Reagents used: *l*-decene, 20 g.; sodium, cut into pea size. 2 g., promoter, 0.5 g. The flask was heated under reflux at 165–170° for 20 hours.

Experiment	1	2	3
Promoter	None	*o*-Chlorotoluene	Anthracene
Composition of decenes, %			
l-Decene	96	1	72
$RCH{=}CHR_1$	4	99[a]	28[b]

[a] *Ca.* 15% *cis* and 84% *trans* isomer. [b] *Ca.* 9% *cis* and 19% *trans* isomer.

TABLE III

ISOMERIZATION AND DEHYDROGENATION OF *d*-LIMONENE

Experiment	1	2	3	4	5
Reagents charged:					
d-Limonene, g.	40.3	44.9	41.6	23.1	22.6
Sodium, g.	3.5	3.5	3.5	3.5	
o-Chlorotoluene, g.		1.0	1.0	0.5	
Sodium hydride, g.					4.2
Duration, hr.	27	7	20	20	21
Results					
Hydrogen, l.	1.60	1.40	4.15	2.25	2.94
M_2, moles/100 moles of limonene charged	23	18	65	53	72
Hydroc. recovered, g.	36.6	32.0	37.9	20.3	21.5
Hydroc. boiling above 180°	2.9	2.7	2.8	1.8	3.3
Composition of hydroc. boiling below 180°					
Conjugated dienes, %	49	45	41	36	21
p-Cymene, %	21	17	55	57	71

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was observed. At the end of 20 hours total reaction time 4.15 liters of hydrogen was obtained, corresponding to 65 mole % based on limonene charged. Most of the sodium remained unchanged with the exception of a small amount of a powdery dark brown material. The hydrocarbon layer was also colored brown. On filtration over 90% of material boiling within limonene range was recovered. The liquid product consisted according to ultraviolet analysis of 57% *p*-cymene and of about 41% of a menthadiene having a maximum absorption peak at 244 mμ in isoöctane solution. The structure of the menthadiene by application of Woodward's rule,[3] is thought to be 3-isopropylidene-6-methyl-1-cyclohexene. The absorptivity of 67 l./g. cm. used to calculate the concentration of the methadiene was derived from an average absorptivity of 9100 l./mole cm. for semicyclic dienes.[4]

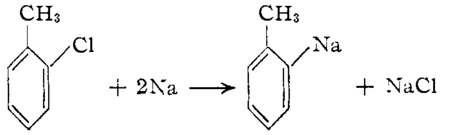
It was observed that with a reaction time of seven hours instead of 20 hours, the rate of isomerization to conjugated dienes is much greater than the rate of dehydrogenation to *p*-cymene.

In the absence of *o*-chlorotoluene as a "promoter" marked evolution of hydrogen began only after about 13 hours of refluxing. After 23 hours of total reaction time only 23 mole % of hydrogen was produced and the liquid product was composed of 21% *p*-cymene and 37% of conjugated terpenes.

Sodium hydride acts also as a catalyst for the dehydrogenation and isomerization of *d*-limonene. The liquid product obtained from the reaction, which was carried out for 21 hours at a reflux temperature, consisted of 71% *p*-cymene and 16% of conjugated menthadienes.

Discussion of Results

It was found that sodium in the presence of compounds such as *o*-chlorotoluene or anthracene acts as an efficient catalyst for the shifting of double bonds in olefinic hydrocarbons. In the case of aliphatic olefins the isomerization seems to proceed without extensive side reactions, which usually occur when acid types of catalysts are used. Although the mechanism of this reaction has not yet been studied systematically, it seems, on the basis of these and unpublished data, that the function of the "promoter" is to form a sodium organic compound which can then metalate the olefin according to the following series of reactions



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$$\mathrm{I} + \underset{\mathrm{II}}{\mathrm{RCH_2CH{=}CH_2}} \longrightarrow \mathrm{C_6H_5CH_3} + \begin{array}{c} [\mathrm{R\bar{C}HCH{=}CH_2}]\overset{+}{\mathrm{Na}} \\ \updownarrow \;\; \mathrm{IIIa} \\ \underset{\mathrm{IIIb}}{[\mathrm{RCH{=}CH\bar{C}H_2}]\overset{+}{\mathrm{Na}}} \end{array}$$

$$\mathrm{II} + \mathrm{IIIb} \longrightarrow \mathrm{IIIa} + \underset{\mathrm{IV}}{\mathrm{RCH{=}CHCH_3}}$$

Compound IV may undergo another metalation which would result in a further shift of the double bond.

The catalytic dehydrogenation of *d*-limonene by means of sodium promoted by *o*-chlorotoluene can also be explained by a series of reactions similar to those outlined above. It is probable that *d*-limonene isomerizes to endocyclic menthadiene prior to undergoing metalation and dehydrogenation.

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[3] R. B. Woodward, THIS JOURNAL, **64**, 72 (1942).

[4] H. Booker, L. Evans and A. Gillam, *J. Chem. Soc.*, 1456 (1940).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, ILLINOIS INSTITUTE OF TECHNOLOGY]

Intermediates in the Reactions of Carboxylic Acid Derivatives. IV. The Hydrolysis of Benzamide[1-3]

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RECEIVED AUGUST 11, 1954

Benzamide-O^{18} has been prepared. The kinetics of hydrolysis of benzamide under acidic and basic catalysis have been determined in aqueous solution. The oxygen exchange accompanying hydrolysis has been determined. Oxygen exchange was found to occur between benzamide-O^{18} and water during the basic hydrolysis of benzamide, but no exchange was observed during its acidic hydrolysis. The fact that $k_{\mathrm{exch}} > k_{\mathrm{hydrol}}$ in the basic hydrolysis of benzamide whereas $k_{\mathrm{hydrol}} > k_{\mathrm{exch}}$ in the basic hydrolysis of ethyl benzoate may be related to the competitive breakdown of the addition intermediate $\mathrm{RC(OH)_2X}$. The lack of oxygen exchange in the acidic hydrolysis of benzamide is attributed to the greater basicity of nitrogen relative to oxygen, which may result in a displacement reaction involving the conjugate acid of benzamide and water or in the formation of an addition intermediate from which the products of hydrolysis are formed without any appreciable back (exchange) reaction.

Introduction

A continuation of studies concerned with the elucidation of intermediates in the reactions of carboxylic acid derivatives has led to the investigation of the hydrolysis of benzamide. Earlier investigations[4] concerned with the oxygen exchange accompanying the hydrolysis of benzoate esters indicated that in those reactions a symmetrical intermediate was formed by the addition of water to the carbonyl group of the ester. In the present paper oxygen exchange data for the acid and basic hydrolysis of benzamide in aqueous solution are reported.

Kinetic investigations of amide hydrolysis[5] have indicated that amide hydrolysis is in general similar to ester hydrolysis. The rate of basic hydrolysis is proportional to the concentrations of amide and of

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[1] Previous paper: M. L. Bender, R. D. Ginger and K. C. Kemp, THIS JOURNAL, **76**, 3350 (1954).

[2] Presented at the New York Meeting of the American Chemical Society, September, 1954.

[3] This investigation was supported by a Frederick Gardner Cottrell grant from the Research Corporation.

[4] M. L. Bender, THIS JOURNAL, **73**, 1626 (1951).

[5] H. V. Euler and A. Ölander, *Z. physik. Chem.*, **131**, 107 (1928). N. V. Peskoff and J. Meyer, *ibid.*, **82**, 129 (1913); V. K Krieble and K. A. Holst, THIS JOURNAL, **60**, 2976 (1938); B. S. Rabinovitch and C. A. Winkler, *Can. J. Research*, **B20**, 73 (1942).