heated with 50 ml. of 1 *f* sulfuric acid under a reflux condenser until it dissolved. Then the liquid was cooled to room temperature, 3.0 g. of paraformaldehyde was added and the formal was removed as the azeotrope with water by distillation through a fractionating column. The formal was dried and distilled.[23]

Basic Hydrolysis.—This was similar to acid hydrolysis except that the reagent was 2 *f* potassium hydroxide, which was neutralized, using some excess of sulfuric acid, before conversion to the formal.[23]

It is noted from Table II that hydrolysis of carbonate, sulfite, chlorophosphite, methoxyphosphite, ethoxyphosphite, and diethylaminophosphite gave active formal of high optical purity. Therefore, hydrolysis under either acidic or basic conditions gives the original glycol without any change in configuration. In some cases the rotation actually was improved, which may indicate that in the preparation of the ester some purification was effected.

Hydrolysis of the sulfate under acid conditions gave a formal which, from boiling point and refractive index, was largely *meso* formal. Had the amount of D- or DL-formal been significant it would have been detected during distillation. The refractive index of 1.4041 at 25° probably corresponds closely to 1.4055 at 20° for d*n*/d*t* usually is about − 0.0004 per degree.[2]

Basic hydrolysis of the sulfate gave largely DL-glycol, with about 15% *meso*, calculated from the refractive index, and 2% of D-glycol, calculated from the rotation of the formal. The range of boiling point also indicates a mixture, largely DL.

Summary

A number of cyclic acetals and esters of D(−)-2,3-butanediol have been prepared and a study has been made of the steric changes on hydrolysis. The cyclic sulfate was the only one to show abnormal behavior. In acid solution it gives *meso* glycol almost exclusively and in basic solution, DL-glycol mainly, with some *meso* and a very little D(−)-glycol.

Calcium permanganate is an excellent reagent for oxidizing the glycol sulfite to the glycol sulfate.

Molecular refractivities, *M*D have been obtained for the following: SO_4, 11.13; SO_3, 10.98; P, 6.8 to 7.4.

PASADENA 4, CALIFORNIA RECEIVED AUGUST 30, 1949

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMICAL ENGINEERING OF ILLINOIS INSTITUTE OF TECHNOLOGY]

Reactions of Paraffin Hydrocarbons in the Presence of Sulfuric Acid

BY V. I. KOMAREWSKY AND W. E. RUTHER[1]

The use of sulfuric acid as an isomerization catalyst for certain paraffin hydrocarbons has been reported in the literature.[2-6]

This article presents the results of the reactions of *n*-octane, 2,4-dimethylpentane, 2,2,4-trimethylbutane (triptane) and 2,2-dimethylbutane (neohexane) in the presence of 96 and 98% sulfuric acid as catalyst at the boiling point temperatures of the respective hydrocarbons.

Experimental

Materials.—Baker and Adams C. P. grade sulfuric acid was used. Its concentration was varied from 96–100%. The paraffins, with the exception of triptane, were obtained from the Phillips Petroleum Company. They were pure grade with a guaranteed purity of 99 mole per cent. The triptane was obtained from the Ethyl Corporation with a purity of 97%. Each of these paraffins was redistilled in a Podbielniak column. The physical constants are as follows: *n*-octane, b. p. 125.6°, $n^{25}\text{D}$ 1.3952; 2,4-dimethylpentane, b. p. 80.5°, $n^{25}\text{D}$ 1.3789; 2,2-dimethylbutane, b. p. 49.6°, $n^{25}\text{D}$ 1.3660; 2,2,3-trimethylbutane, b. p. 80.7°, $n^{25}\text{D}$ 1.3869.

Apparatus and Procedure.—The experiments were performed in a standard closed system apparatus with a Dry Ice trap for condensable gases and a gas collecting bottle. A wide-blade stirrer maintained at seven hundred r. p. m. violently agitated the contents of the creased reaction flask. Upon completion of the reaction the hydrocarbon layer was separated, stabilized, washed and dried. It was the distilled over metallic sodium in a one hundred theoretical plate Podbielniak column. The compositions of the fractions were determined by physical constants and infrared spectra. The infrared absorption spectra

TABLE I

2,4-DIMETHYLPENTANE

Temperature, °C.	25	80
Time, hr.	10	
Sulfuric acid concn., %	96%	98%
Materials charged (g.)		
Sulfuric acid	175.0	181.0
Hydrocarbon	87.5	90.5
Products obtained (g.)		
Acid layer	174.0	181.0
Hydrocarbon layer	86.5	86.0
Gas	...	2.0
Composition of hydrocarbon layer (wt. %)		
Lower boiling compounds	...	0.5
Unreacted 2,4-dimethylpentane	87.6	51.3
Isomers	11.7	47.4
Higher boiling compounds	0.6	0.8

Composition and constants of the hydrocarbon layer from 98% acid experiment

Boiling range, °C.	Weight, %	$n^{25}\text{D}$	Composition
35–80	0.5	1.3706	...
80–81	51.3	1.3790	2,4-Dimethylpentane
89–90.5	47.4	1.3880	2,3-Dimethylpentane 2-Methylhexane (minor) 3-Methylhexane (minor)
Above 90.5	0.8	1.4095	...

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(1) Standard Oil Company (Indiana) Fellowship 1948-1949.

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(3) J. H. McAteer, paper presented at Meeting of Am. Assoc. for Advancement of Science, June 17, 1940.

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(6) G. S. Gordon and R. L. Burwell, THIS JOURNAL, **71**, 2355 (1949).

Table II

2,2,3-Trimethylbutane

Temperature, °C.	50	80
Time, hr.	10	
Sulfuric acid concn., %	96	98
Materials charged (g.)		
Sulfuric acid	160.5	175.0
Hydrocarbon	81.5	84.5
Products obtained (g.)		
Acid layer	160.0	176.0
Hydrocarbon layer	79.0	79.5
Gas	0.1	2
Composition of hydrocarbon layer (wt. %)		
Lower boiling compounds	...	0.7
Unreacted 2,2,3-trimethylbutane	92.3	86.4
Isomers	6.6	12.3
Higher boiling compounds	...	0.6

Composition and constants of the hydrocarbon layer from 98% acid experiment

Boiling range, °C.	Weight, %	$n^{25}D$	Composition
60–80	0.7	1.3860	......
80–81	86.4	1.3874	2,2,3-Trimethylbutane
89–90	12.3	1.3894	2,3-Dimethylpentane (major) 2-Methylhexane (major)
Above 90	0.6	1.3940	2,2,3-Trimethylbutane (trace)

were obtained using a Perkin–Elmer single beam spectrometer equipped with sodium chloride optics. The samples were run in the liquid phase using a cell of 0.103 mm. length. The catalog of infrared spectral data (API Project 44) was used as a reference. The liquid reaction products were water-white, sulfur- and olefin-free. The gaseous product was pure isobutane. The acid layer acquired a brown coloration and in the case of 98% sulfuric acid has an odor of sulfur dioxide. The results are presented in Tables I and II and infrared spectra in Figs. 1 and 2.

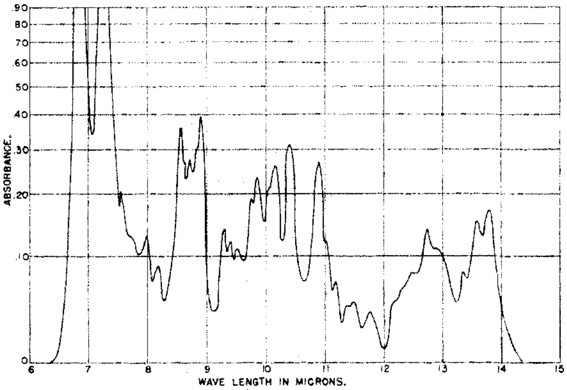

Fig. 1.—Spectrum of products from 2,4-dimethylpentane and 98% sulfuric acid, fraction 89–90.5°: Wave lengths in μ of the absorption bands used in the qualitative identification of the hydrocarbons present are listed below as observed (superscripts denote absorption bands characteristic of: (1) 2,4-dimethylpentane, (2) 2,3-dimethylpentane, (3) 2-methylhexane, (4) 3-methylhexane.)

$7.53^{1,2}$
7.65^{2}
7.98^{1}
8.18^{3}
8.55^{1}
8.72^{2}
8.90^{2}
9.30^{1}
9.40^{2}
9.50^{2}
9.75^{2}
9.85^{2}
10.07^{2}
10.15^{1}
10.40^{2}
10.90^{1}
11.02^{2}
11.18^{3}
11.36^{4}
11.48^{1}
11.74^{2}
12.17^{3}
12.48^{2}
12.75^{2}
12.92^{4}
13.34^{2}
13.56^{4}
13.78^{3}

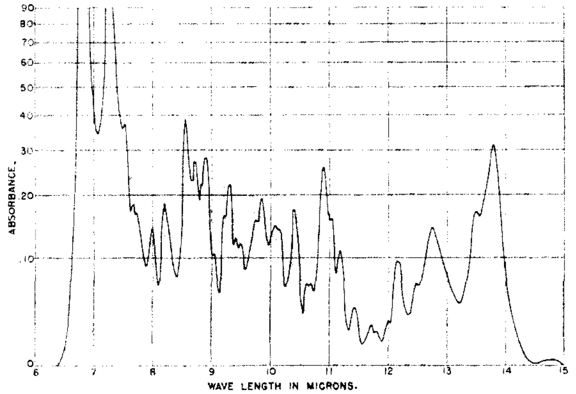

Fig. 2.—Spectrum of products from 2,2,3-trimethylbutane and 98% sulfuric acid. Fraction 89–90°: the wave lengths in μ used for the qualitative identification of the hydrocarbons present are listed below as observed (superscripts denote absorption bands characteristic of: (1) 2,4-dimethylpentane, (2) 2,3-dimethylpentane, (3) 2-methylhexane, (4) 3-methylhexane. The remaining twelve bands are common to two or three of the compounds listed.)

7.67^{2}
7.72^{1}
7.98
8.18^{1}
8.57
8.60^{3}
8.72
8.90^{2}
9.03^{3}
9.22^{3}
9.30
9.40^{2}
9.50
9.75^{2}
9.85
10.07^{2}
10.40^{2}
10.63^{1}
10.70
10.90
11.02^{1}
11.18^{1}
11.41
11.71^{2}
11.77
12.17^{1}
12.48^{2}
12.75
13.56
13.78^{1}

Discussion of Results

It is clear from an examination of the experimental results that two different reactions took place. Isomerization is the only reaction at the milder experimental conditions. Some destructive alkylation takes place with 98% sulfuric acid and higher temperatures, as indicated by the production of low and high boiling compounds.

The reaction with sulfuric acid differs from the action of aluminum chloride in two major respects. Only traces of the paraffin are lost to the sulfuric acid layer while as much as 20% may combine with the aluminum chloride.[7] Dealkylation to isobutane is the main reaction in the case of aluminum chloride while the main products with sulfuric acid are compounds boiling near the original boiling point of the paraffin.

In the experiments with *n*-octane and neohexane there is no reaction even at the boiling point of respective hydrocarbon and 98% sulfuric acid concentration. 2,4-Dimethylpentane isom-

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(7) V. I. Komarewsky and S. C. Ulick, This Journal, **69**, 492 (1947).

erizes mostly to 2,3-dimethylpentane, with minor amounts of 2-methylhexane and 3-methylhexane. The main products of triptane isomerization were 2-methylhexane and 2,3-dimethylpentane. These results substantiate the observations of previous investigators that sulfuric acid is a specific catalyst for shifting the methyl group along the hydrocarbon chain and that only such paraffin hydrocarbons which contain tertiary carbon atoms are susceptible to isomerization with this catalyst.

Acknowledgment.—The authors wish to express their appreciation to the Standard Oil Company (Indiana) for the fellowship grant, to the Ethyl Corporation for the sample of triptane used, and to Mr. D. V. Kniebes for the infrared analyses.

Summary

The action of concentrated sulfuric acid on various paraffin hydrocarbons indicates that this acid is a satisfactory isomerization catalyst for liquid paraffins containing at least one tertiary carbon atom. In contrast with the action of aluminum chloride, there is only a very small loss of paraffin to the acid layer. Conditions may be chosen so that the major portions of the product are isomers.

CHICAGO 16, ILLINOIS RECEIVED AUGUST 4, 1949

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF DE PAUL UNIVERSITY]

The Pyrolysis of Methyl Phthalate[1]

BY ROBERT P. ZELINSKI, JEROME T. SIEDLECKI[2] AND ALFORD L. ANDERSEN, JR.

This study of the pyrolysis of methyl phthalate was undertaken as part of a program to determine the nature of the materials produced at various temperatures by the thermal decomposition of some common plasticizers. The literature on the subject seems to be meager and, in particular, does not report data concerning the effect of increasing temperature on the nature of the degradation products.

That methyl phthalate is stable at its boiling point is known,[3] but apparently only one attempt has been made to study the products formed when it is heated to the point of decomposition. Meyer and Hofmann[4] pyrolyzed it at a "glowing heat," reported that the products were methyl benzoate (a trace), formaldehyde, methyl biphenyltricarboxylate and methyl biphenyldicarboxylate.

In the present investigations methyl phthalate was pyrolyzed in Sillimanite tubes at temperatures of 400 to 1000° at atmospheric pressure, and without diluents. The amount of decomposition at 405° was small, but at similar rates of delivery (*ca.* 0.4 g./min.) it increased to 36% at 608°. 97% at 805° and was complete at 1000°.

Analysis of the condensable degradation products formed at 405° showed that they consisted of formaldehyde, water (4.6%), phthalic anhydride (28.2%) and unidentified neutral fraction (51.0%).[5] However, at 608° new products appeared and the condensable fraction contained phthalic anhydride (3.4%), benzene (2.7%), toluene (5.6%), xylene (3.7%), methyl benzoate (37.3%) and a neutral, unsaponifiable fraction (5.8%). Increasing the temperature of pyrolysis to 805° produced condensable materials which consisted of only benzene (16.3%), toluene (1.4%) and the unsaponifiable portion (12.1%). At 1000° the condensable fraction (8.7%) was too small to be analyzed by the methods employed. At all temperatures except 1000° formaldehyde was qualitatively identified among the products but quantitative analyses were unsuccessful.

The non-condensable products proved to be a mixture of carbon dioxide, carbon monoxide, hydrogen, methane, acetylene, ethylene and higher olefins. At low temperatures carbon dioxide constituted 93% of the mixture, but as the temperature of pyrolysis increased, this rapidly diminished. Thus, at 1000° carbon monoxide and hydrogen accounted for three-fourths of the gases. These and other data are presented in Tables I and II.

Attempts to separate the components of the high molecular weight unsaponifiable fractions were unfruitful. Only biphenyl could be isolated and identified.

At 405° methyl phthalate is decomposed to phthalic anhydride, probably by the elimination of methyl ether with subsequent decomposition of the latter[6] to formaldehyde and gaseous hydrocarbons in a manner analogous to that found for other ethers.[7,8] However, at 608° the methyl phthalate is decomposed along a different degradation path, probably through methyl *o*-toluate and from this to aromatic hydrocarbons and methyl benzoate.

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(1) This work was performed with the aid of U. S. Navy funds under Subcontract 2, Contract NOrd 9709, and Subcontract 1, Contract NOrd 10431, both prime contracts with the Hercules Powder Company, Allegany Ballistics Laboratory.

(2) Taken in part from a thesis presented by Jerome T. Siedlecki to the Graduate School of De Paul University in partial fulfillment of the requirements for the degree of Master of Science (1949).

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(5) Parenthesized values are percentages by weight of the methyl phthalate decomposed.

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