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## The High Temperature Oxidations of 2,2,4-Trimethylpentane and 2,2-Dimethylbutane

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"Isooctane"—2,2,4-trimethylpentane—and neohexane—2,2-dimethylbutane—have been treated with oxygen in the vapor phase at *ca.* 450°. The principal transformations involve degradation of the hydrocarbon molecule to olefins. 2,2,4,4-Tetramethyltetrahydrofuran and 1-*t*-butyl-2-methyltrimethylene oxide from "isooctane" and 1,2,2-trimethyltrimethylene oxide from neohexane are significant oxidation products. Evidence for a possible free radical rearrangement is presented and the pertinent details of the mechanism are discussed.

Although "isooctane"—2,2,4-trimethylpentane—has for years been a primary reference for measuring gasoline anti-knock ratings and both it and neohexane are valuable as synthetic components of gasoline, almost nothing is definitely known concerning either their actual mechanism of oxidation or the products which are intermediates of their combustion.

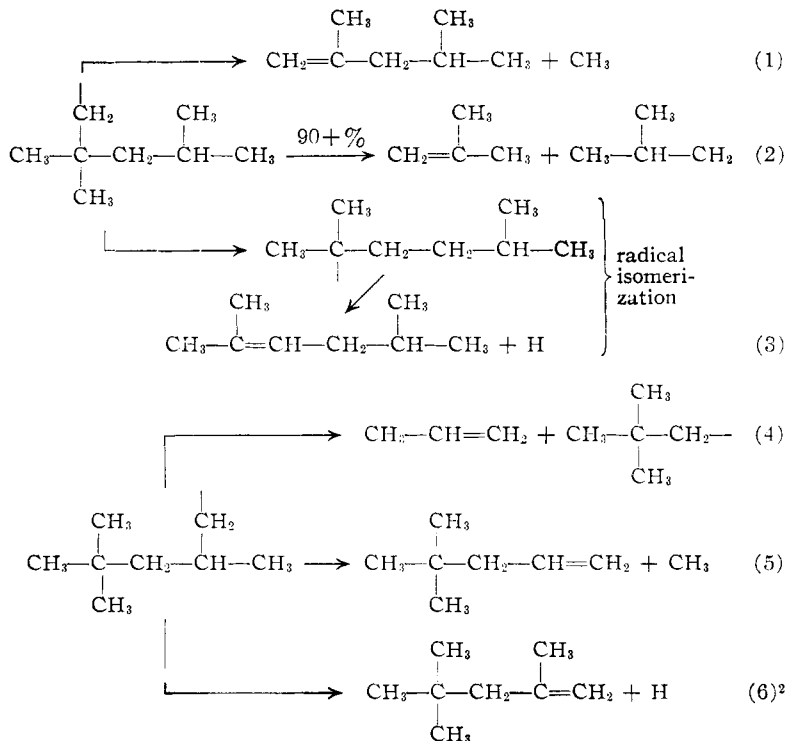
Although these hydrocarbons are resistant to the low temperature, liquid phase conditions which are suitable for oxidizing the normal or less branched paraffins, recent and often cited comment on the mechanism suggests a course drawn by analogy from low temperature studies.<sup>1</sup> This path, in the case of "isooctane," supposes that preferential attack at the tertiary hydrogen is followed by hydroperoxide formation and oxygen-oxygen bond scission. The resultant alkoxy radicals would then undergo  $\beta$ -scission with the formation of acetone and a smaller alkyl radical which would in turn associate with oxygen and follow the same reaction sequence.

The present studies indicate the previously proposed steps to be an oversimplification at the high temperature (*ca.* 450°) required for the oxidation of "isooctane" and neohexane. Some of the oxidation products are explainable only on the basis of initial attack on the primary hydrogen atoms of the methyl groups and in no case need any identified product be necessarily attributed to the initial removal of a tertiary or secondary hydrogen atom. This is not to deny that tertiary, secondary and primary hydrogen atoms in that order will in most cases show decreasing susceptibilities toward oxidation, but to suggest rather that in a "bunched" hydrocarbon where the potentially more reactive atoms are shielded, and at temperatures sufficiently high to reduce selectivity, initial reaction may be largely confined to the more strongly bonded hydrogen atoms of the exposed methyl groups.

Following an initial breach in the hydrogen "shell" about the "isooctane" molecule there is formed one of four possible alkyl radicals.

The two most probable radicals, undergoing  $\beta$ -scission, degrade as

(1) A. D. Walsh, *Trans. Faraday Soc.*, **42**, 268 (1946).

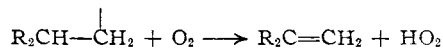


The resultants of these reactions, isobutylene and propylene, have been identified as major products of the reaction. The other olefins—or their isomers—have been hydrogenated with platinum oxide catalyst and the resulting paraffin hydrocarbon identified. Heptene formation as a consequence of  $\text{C}_8$  radical-oxygen interaction is discussed below.

The radical fragments from the above decompositions can abstract hydrogen atoms from other molecules to give hydrogen, methane, isobutane and neopentane or, in the case of isobutyl or neopentyl, lose methyl to yield further amounts of propylene or isobutylene.

It is to be emphasized that this fragmentation of the molecule in the presence of oxygen is taking place well below the range of appreciable thermal cracking for these relatively small paraffins, although the mechanism by which oxygen brings about initiation of this decomposition is not clear.

(2) It is anticipated that olefin formation may just as well follow a course giving rise to  $\text{HO}_2$  as to expulsion of a hydrogen atom

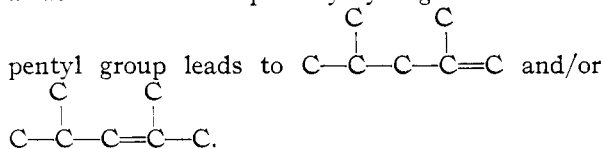


The importance of the competitive paths would be determined by reactant concentrations, temperature, etc.<sup>3</sup>

(3) J. A. Gray, *J. Chem. Soc.*, 741 (1953).

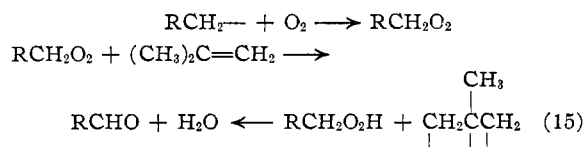


The same sequence of events following initial attack on one of the primary hydrogens of the neo-



The fractions containing these olefins were hydrogenated and the resulting hydrocarbons identified by their infrared spectra.

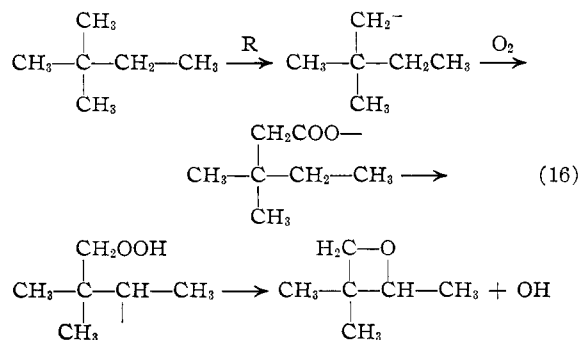
Isobutyraldehyde, methacrolein and trimethylacetaldehyde are derivable from the isobutyl, methallyl and neopentyl fragments, respectively. Their probable course of formation is



Earlier work<sup>4</sup> has shown that aldehydes are derived from alkoxy radicals by disproportionation particularly in the absence of an adequate hydrogen donor. The appearance of large amounts of isobutylene in the reaction mixture should, however, favor the formation of intermediate hydroperoxides.

There are a number of possible paths by which water, carbon monoxide, carbon dioxide, formaldehyde and methane can be formed, but the present work contributes little new toward the resolution of these transformations.

Neohexane oxidation follows the courses which would be predicted from the results of "isooctane" oxidation.  $\beta$ -Scission reactions following the removal of hydrogen atom lead to isobutylene and tertiary amylene; association of the  $\text{C}_6$  hydrocarbon radical with oxygen leads to the production of 1,2,2-trimethylene oxide, as well as a number of oxygenated degradation products. No hexenes indicative of radical rearrangement were isolated.



Knowledge of substituted trimethylene oxides is extremely sketchy. In a recent paper,<sup>5</sup> the isolation of substituted furans from high temperature hexane oxidation is reported plus certain other unknown products whose properties, we believe, can be ascribed to trimethylene oxides formed by a sequence of steps analogous to that given above.

(4) F. F. Rust, F. H. Seubold, Jr., and W. E. Vaughan, *THIS JOURNAL*, **72**, 338 (1950).

(5) H. C. Bailey and R. G. W. Norrish, *Proc. Roy. Soc. (London)*, **212**, 311 (1952).

Some closely related dimethyltrimethylene oxides have been prepared and the infrared spectra presented by Barrow and Searles.<sup>6</sup> Attention is directed to the characteristic 10.2–10.3  $\mu$  absorption of the trimethylene oxide ring which is apparent in the derivative of neohexane (and isooctane); see Fig. 2. The other oxidation products isolated are derived from the olefins. In this category are tiglaldehyde ( $\text{CH}_3-\text{CH}=\text{C}(\text{CH}_3)\text{CHO}$ ) and probably methyl isopropenyl ketone ( $\text{CH}_3\text{COC}(\text{CH}_3)=\text{CH}_2$ ) from tertiary amylenes, and isobutylene glycol and  $\alpha$ -methacrolein from isobutylene.

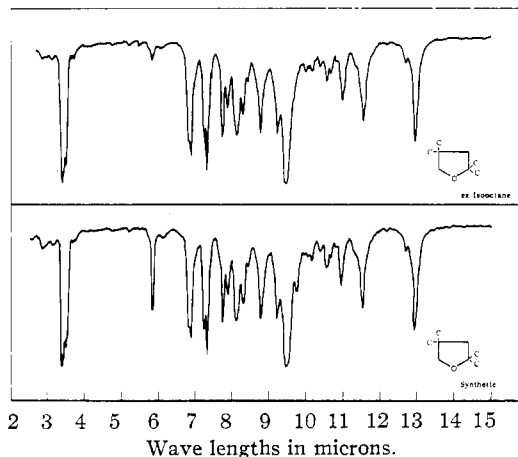


Fig. 2.—Infrared spectra of 2,2,4,4-tetramethyltetrahydrofuran synthetic (bottom); from isooctane oxidation (top).

### Experimental

**Materials.**—The isooctane—2,2,4-trimethylpentane—was obtained from the Shell Oil Company. The infrared absorption agreed in all details with that of spectroscopically pure 2,2,4-trimethylpentane. The neohexane was Phillips pure grade (99+%) and was used without further treatment.

Isooctane and oxygen were metered through rotameters, mixed and the mixture reacted at ca. 450° in a 2.5 × 88 cm. Pyrex tube 60 cm. of which was heated by a well controlled electric furnace. The product mixture passed through a water-cooled condenser and a 500-cc. liquid condensate collector. Uncondensed material passed into a Dry Ice-cooled trap and the remaining gaseous product was sampled by an aspirator bottle. The condensate from the 500-cc. collector was chilled to Dry Ice temperature and combined

TABLE I			
PRODUCTS FROM THE OXIDATION OF ISOCTANE			
50 cc./min. $\text{O}_2$ —0.5 cc./min. $\text{C}_8\text{H}_{18}$ (liq.)—450–475°			
Total throughput: 6.75 moles $\text{C}_8\text{H}_{18}$ ; 3.39 moles $\text{O}_2$			
Products	Moles	Products	Moles
Water	3.26	1-4-Butyl-2-methyl-	
Carbon monoxide	1.50	trimethylene oxide	0.047
Isobutylene	1.49	Isobutane	.047
Methane	0.58	Propane	.034
Propylene	.41	2-Methyl-1-butene	0.035
Acetone	.18	2-Methyl-2-butene	.021
Formaldehyde	.14	2,4,4-Trimethyl-1-pentene	.023
Carbon dioxide	.12	Isobutylene glycol	.018
Acetaldehyde	.12	2,5-Dimethylhexene	.007
Ethylene	.11	2,4,4-Trimethyl-2-pentene	< .003
Isobutylene oxide	.10	1-Butene	< .01
Hydrogen	.10	Ethane	< .01
Methacrolein	.09	$\alpha,\beta$ -Diketone	< .01
Isobutyraldehyde	.08	Neopentane	< .01
2,2,4,4-Tetramethyl-		Trimethylacetaldehyde	< .01
tetrahydrofuran	.05	2,4-Dimethylpentene	< .01
		5,5-Dimethylpentene	< .01

(6) G. M. Barrow and S. Searles, *THIS JOURNAL*, **75**, 1175 (1953).

TABLE II

PRODUCTS FROM THE OXIDATION OF NEOHEXANE			
63 cc./min. O <sub>2</sub> —0.5 cc./min. C <sub>6</sub> H <sub>14</sub> (liq.)—420–450°			
Total throughput: 7.5 moles C <sub>6</sub> H <sub>14</sub> ; 5.2 moles O <sub>2</sub>			
Products	Moles	Products	Moles
Water	4–5	Ethane	0.094
Carbon monoxide	2.84	1,2,2-Trimethyltri-	
Methane	0.915	methylene oxide	.072
Ethylene	.7	Propylene	.019
Acetone	.44	Butanes	< .01
Isobutylene	.39	Tiglaldehyde	< .01
Carbon dioxide	.25	Methyl isopropenyl	
2-Methyl-2-butene	.22	ketone	< .01
Hydrogen	.17	Methacrolein	< .01
3,3-Dimethyl-1-butene	.126	Alcohol	(0.547 eq.)
2-Methyl-1-butene	.108	$\alpha$ -Glycol	(0.083 eq.)
Formaldehyde	.12		

with the contents of the Dry Ice trap. The upper organic layer was then decanted from the solid aqueous phase and fractionated on a still with a Dry Ice-acetone-chilled head. The C<sub>3</sub> and C<sub>4</sub> fractions were analyzed by standard Orsat procedures and by mass spectrometry. The remaining fractions to isoöctane were separated on a helices-packed column and then refractionated on a Piros-Glover microstill. Isoöctane was then separated from the higher boiling products and the latter again fractionated on the microstill. Derivatives were prepared from some fractions and in other instances identification was obtained by functional group analysis or infrared spectrum comparison. Essentially the same procedure was followed for neohehexane.

**Identification of Products.**—The following compounds from isoöctane were separated from the fractions containing them as the 2,4-dinitrophenylhydrazones derivatives

Acetone	m.p. 125.0–125.5°	Mixed m.p. 125.5°
$\alpha$ -Methacrolein	m.p. 205°	Mixed m.p. 205°
Isobutyraldehyde	m.p. 183° { m.p. 149° % Carbon 43.0 % Hydrogen 3.9	Mixed m.p. 183° Lit. 147° 42.85 3.6
Trimethylacetaldehyde	m.p. 203.5–204°	Mixed m.p. 205.5–206°
From neohehexane:		
Tiglaldehyde	m.p. 215°+	Mixed m.p. 218°

The permanent gases passing through the Dry Ice traps were determined by standard Orsat procedure and checked by mass spectra; these were carbon monoxide, carbon dioxide, ethylene, hydrogen, methane and ethane.

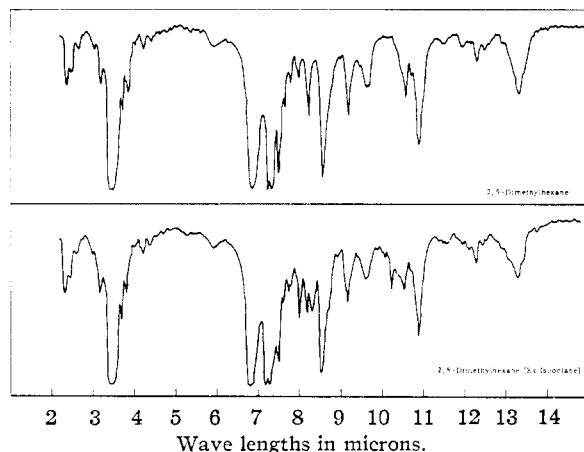


Fig. 3.—Infrared spectra of 2,5-dimethylhexane (top) and 2,5-dimethylhexane derived from isoöctane (bottom).

Low temperature distillation fractions were checked by their mass spectra. In this way analyses for propane, pro-

pylene, isobutane, isobutylene, 1-butene, neopentane, 2-methyl-1-butene and 2-methyl-2-butene were obtained.

The isobutylene oxide was identified from its infrared spectrum and its presence confirmed by an epoxide determination using hydrogen chloride in dioxane.<sup>7</sup>

The trimethylpentenes (diisobutylenes) were present in the isoöctane fraction as minor components. Concentration was effected by first washing the isoöctane fraction three times with 50% sulfuric acid, then with water and finally drying with potassium carbonate. The hydrocarbon was then run through a silica gel column and the adsorbed olefins eluted with ether. After the ether was removed by distillation, a concentrate of 10–12% olefin content in octane was obtained which was analyzed by infrared spectroscopy for the isomeric diisobutylenes.

The fractions containing 2,5-dimethylhexene, and 2,4- and 4,4-dimethylpentenes were hydrogenated in a bottle shaker at room temperature over platinum oxide. The resultant product was washed with sulfuric acid and refractionated on a Piros-Glover microstill. The hydrocarbons were then identified by their infrared spectra. The spectra of a known sample of 2,5-dimethylhexane and of the isoöctane-derived product are included for comparison (Fig. 3). There is some isoöctane as an impurity in the latter sample. 2,2,4,4-Tetramethyltetrahydrofuran was synthesized by dehydration of the C<sub>8</sub>-glycol, (CH<sub>3</sub>)<sub>2</sub>C(CH<sub>2</sub>OH)CHOHCH(CH<sub>3</sub>)<sub>2</sub>, with cold concentrated sulfuric acid. (The glycol was prepared by a potassium hydroxide catalyzed condensation of isobutyraldehyde.<sup>8</sup>) This compound (b.p. 120°,  $n_D^{20}$  1.4061) was found by its infrared spectrum to be identical with the product boiling between 117.5–119° which was isolated from the isoöctane oxidation (Fig. 3). In further confirmation the isoöctane derivative showed neither a qualitative carbonyl nor an alcohol test. *Anal.* Calcd. for C<sub>8</sub>H<sub>16</sub>O: C, 75.0; H, 12.5. Found: C, 75.6; H, 13.0.

The trimethylene oxide derivatives—1,2,2-trimethyltrimethylene oxide from neohehexane and 1-*t*-butyl-2-methyltrimethylene oxide from isoöctane—were obtained as discrete fractions boiling at 99–100° and 136.5–138° with  $n_D^{20}$  1.4050 and 1.4136, respectively.

The assignment of the cyclic ether structure to the C<sub>8</sub> derivative is further supported by the negative qualitative tests for carbonyl, hydroxyl and unsaturation.<sup>9</sup> Elemental analysis gave carbon 72.0%; hydrogen 12.3%; theory: carbon 72.0%; hydrogen 12.0%. The fraction containing the C<sub>8</sub> derivative was treated with lithium aluminum hydride to reduce carbonylic impurities<sup>9</sup> and then recovered by fractionation in a Piros-Glover microstill. The resultant product gave a negative test for alcohol and the carbon-hydrogen analysis was close to theory. *Anal.* Calcd. for C<sub>8</sub>H<sub>16</sub>O: C, 75.0; H, 12.5. Found: C, 74.8; H, 12.3.

The strong 10.2 to 10.3  $\mu$  bands shown in the infrared spectra of these compounds characterize the three carbon ether ring in the methyl substituted trimethylene oxides studied by Barrow and Searles. Further, the characteristic aspect of the 7.18 to 7.35  $\mu$  bands in Fig. 2 support the conclusion that a *t*-butyl group is attached to the ring.

The  $\alpha,\beta$ -dicarbonyl was isolated as the nickel glyoxime, but was not identified. Carbon-hydrogen analysis indicated a probable four carbon compound.

Isobutylene glycol was isolated from the high boiling product residues by vacuum distillation (68° at 10 mm.). Its identification was completed by a positive periodate test for  $\alpha,\beta$ -glycol and by a carbon-hydrogen analysis. *Anal.* Calcd.: C, 53.3; H, 11.1;  $n_D^{20}$  1.4350. Found: C, 53.0; H, 11.3;  $n_D^{20}$  1.4339.

Formaldehyde was determined colorimetrically with chromotropic acid. Water was determined by the Fischer-HCN procedure.

**Acknowledgment.**—The authors are indebted to Dr. F. S. Mortimer for running and interpreting the infrared spectrograms.

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(7) J. Mitchell, Editor, "Organic Analysis," Vol. I, Interscience Publishers, Inc., New York, N. Y., 1953, p. 135.

(8) A. Franke, *Monatsh.*, **71**, 85 (1896).

(9) Some indications of carbonyl and hydroxyl can still be discerned on the spectrograms.