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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.

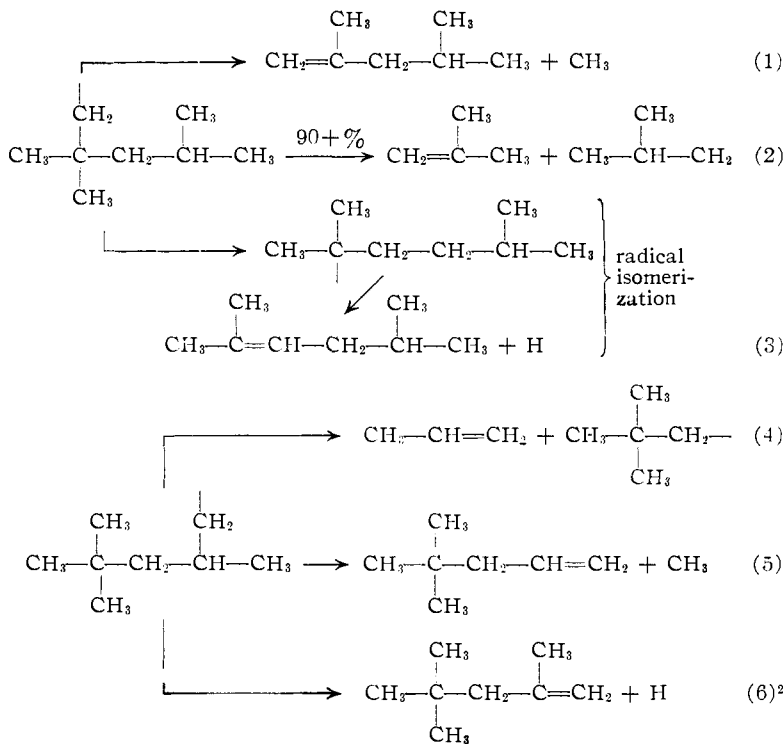
Although "isooctane"—2,2,4-trimethylpentane—has for years been a primary reference for measuring gasoline anti-knock ratings and both it and neohexane are valuable as synthetic components of gasoline, almost nothing is definitely known concerning either their actual mechanism of oxidation or the products 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.¹ 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 β -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 β -scission, degrade as

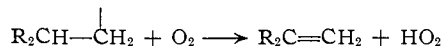


The resultants of these reactions, isobutylene and propylene, have been identified as major products of the reaction. The other olefins—or their isomers—have been hydrogenated with platinum oxide catalyst and the resulting paraffin hydrocarbon identified. Heptene formation as a consequence of C₃ radical-oxygen 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 HO₂ as to expulsion of a hydrogen atom

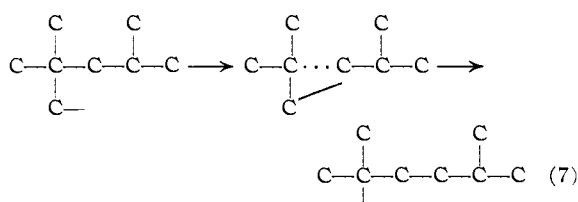


The importance of the competitive paths would be determined by reactant concentrations, temperature, etc.³

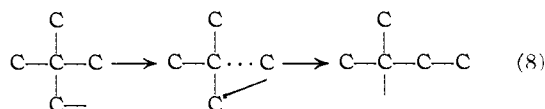
(3) J. A. Gray, *J. Chem. Soc.*, 741 (1953).

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

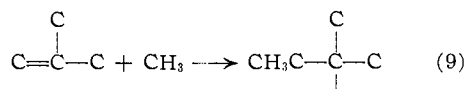
Special attention is called to the evidence for radical rearrangement as exemplified by the formation of *t*-amylenes and 2,5-dimethylhexene inasmuch as such rearrangements of alkyl radicals are currently unknown. The transformations may be pictured as



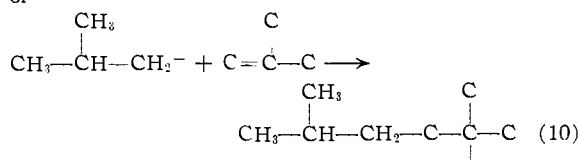
or



On the basis of the present data the formation of these carbon structures by rearrangement cannot be conclusively distinguished from their possible formation by the addition of radicals to olefins



or



The principal reasons for favoring the rearrangement process are the 450–470° temperature where radical-olefin *additions* are usually subordinated to hydrogen abstractions plus the fact that the radical-oxygen combination is a far more rapid process than the competitive radical-olefin association. Thus the probability of a radical-olefin addition mechanism seems remote.

Although the principal feature of the high temperature oxidation of a large molecule such as iso-

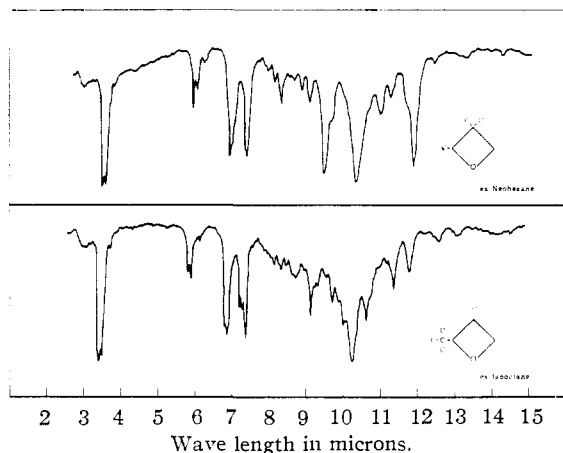
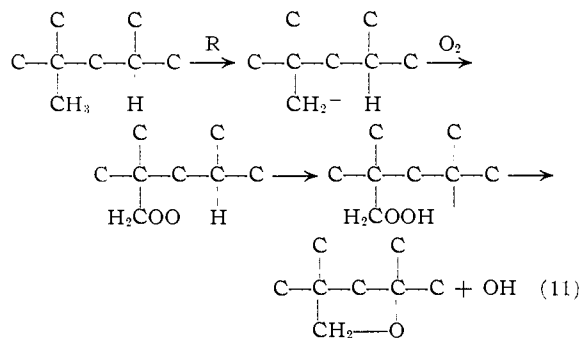
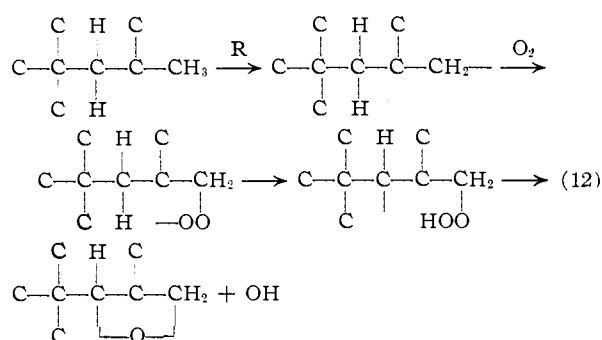


Fig. 1.—Infrared spectra of substituted trimethylene oxides: 1,2,2-trimethyltrimethylene oxide from neohexane; 1-*t*-butyl-2-methyltrimethylene oxide from iso-octane.

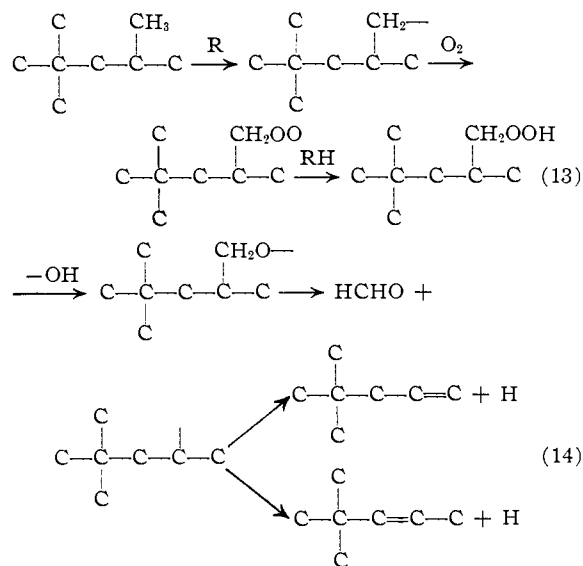
octane is the fragmentation of the initial radical, the association of oxygen with the C₈ radical is a competitive process and some of the products of such reactions have been isolated. Of particular interest is the appearance of the cyclic ethers 2,2,4,4-tetramethyltetrahydrofuran and, presumably, 1-*t*-butyl-2-methyltrimethylene oxide (see Fig. 1 for spectral identification). An intramolecular oxidation process is suggested



and

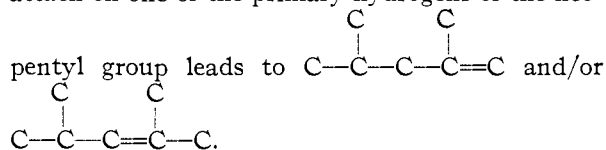


Cyclic ether formation is one, but not necessarily the only consequence of oxygen addition to the C₈ radicals. The loss of a methyl group to give eventually either of two C₇ olefins by oxidation is illustrated as



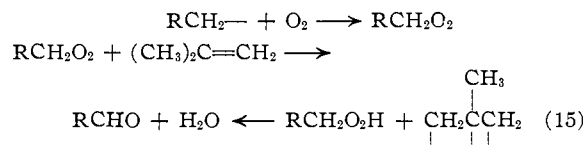
(Of course the C₇ radical will preferably degrade to propylene and a *t*-butyl radical.)

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.

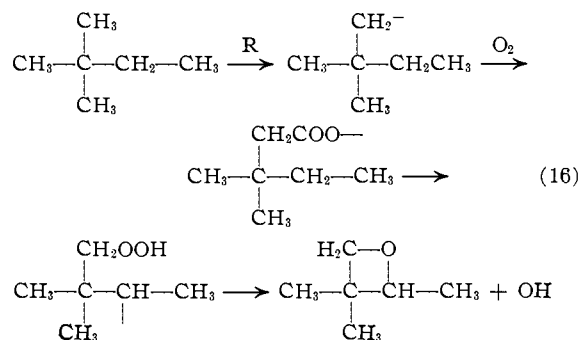
Isobutyraldehyde, methacrolein and trimethylacetaldehyde are derivable from the isobutyl, methallyl and neopentyl fragments, respectively. Their probable course of formation is



Earlier work⁴ 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 "isoöctane" oxidation. β -Scission reactions following the removal of hydrogen atom lead to isobutylene and tertiary amylene; association of the 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,⁵ 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. Seibold, 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.⁶ Attention is directed to the characteristic 10.2–10.3 μ absorption of the trimethylene oxide ring which is apparent in the derivative of neohexane (and isoöctane); 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 α -methacrolein from isobutylene.

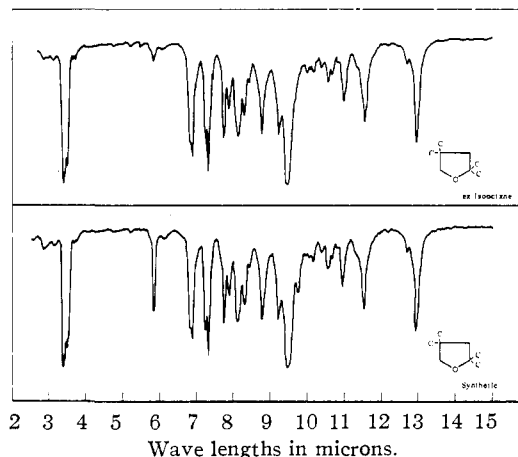


Fig. 2.—Infrared spectra of 2,2,4,4-tetramethyltetrahydrofuran synthetic (bottom); from isoöctane oxidation (top).

Experimental

Materials.—The isoöctane—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.

Isoöctane 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 ISOÖCTANE
50 cc./min. O_2 —0.5 cc./min. C_8H_{18} (liq.)—450–475°
Total throughput: 6.75 moles C_8H_{18} ; 3.39 moles O_2

Products	Moles	Products	Moles
Water	3.26	1-Butyl-2-methyl-trimethylene oxide	0.047
Carbon monoxide	1.50	Isobutane	.047
Isobutylene	1.49	Propane	.034
Methane	0.58	2-Methyl-1-butene	0.035
Propylene	.41	2-Methyl-2-butene	.021
Acetone	.18	2,4,4-Trimethyl-1-pentene	.023
Formaldehyde	.14	Isobutylene glycol	.018
Carbon dioxide	.12	2,5-Dimethylhexene	.007
Acetaldehyde	.12	2,4,4-Trimethyl-2-pentene	< .003
Ethylene	.11	1-Butene	< .01
Isobutylene oxide	.10	Ethane	< .01
Hydrogen	.10	α,β -Diketone	< .01
Methacrolein	.09	Neopentane	< .01
Isobutyraldehyde	.08	Trimethylacetaldehyde	< .01
2,2,4,4-Tetramethyl-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 ₂ —0.5 cc./min. C ₆ H ₁₄ (liq.)—420–450°			
Total throughput: 7.5 moles C ₆ H ₁₄ ; 5.2 moles O ₂			
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	α -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 C₃ and C₄ 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 Piro-Glover micro-still. Isoöctane was then separated from the higher boiling products and the latter again fractionated on the micro-still. 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-dinitrophenylhydrazone derivatives

Acetone	m.p. 125.0–125.5°	Mixed m.p. 125.5°
α -Methacrolein	m.p. 205°	Mixed m.p. 205°
Isobutyraldehyde	m.p. 183°	Mixed m.p. 183°
	m.p. 149°	Lit. 147°
Acetaldehyde	% Carbon 43.0	42.85
	% Hydrogen 3.9	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.

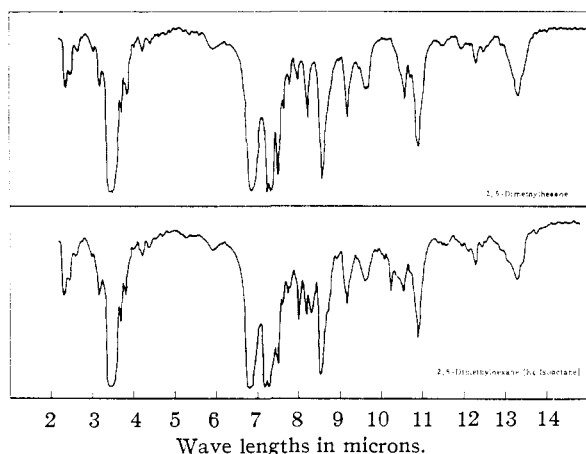


Fig. 3.—Infrared spectra of 2,5-dimethylhexane (top) and 2,5-dimethylhexane derived from isoöctane (bottom).

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.⁷

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 Piro-Glover micro-still. 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 C₈-glycol, (CH₃)₂C(CH₂OH)CHOHCH(CH₃)₂, with cold concentrated sulfuric acid. (The glycol was prepared by a potassium hydroxide catalyzed condensation of isobutyraldehyde.⁸) This compound (b.p. 120°, *n*_D²⁰ 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 C₈H₁₆O: 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*_D²⁰ 1.4050 and 1.4136, respectively.

The assignment of the cyclic ether structure to the C₈ derivative is further supported by the negative qualitative tests for carbonyl, hydroxyl and unsaturation.⁹ Elemental analysis gave carbon 72.0%; hydrogen 12.3%; theory: carbon 72.0%; hydrogen 12.0%. The fraction containing the C₈ derivative was treated with lithium aluminum hydride to reduce carbonylic impurities⁹ and then recovered by fractionation in a Piro-Glover micro-still. The resultant product gave a negative test for alcohol and the carbon-hydrogen analysis was close to theory. *Anal.* Calcd. for C₈H₁₆O: C, 75.0; H, 12.5. Found: C, 74.8; H, 12.3.

The strong 10.2 to 10.3 μ 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 μ bands in Fig. 2 support the conclusion that a *t*-butyl group is attached to the ring.

The α,β -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 α,β -glycol and by a carbon-hydrogen analysis. *Anal.* Calcd.: C, 53.3; H, 11.1; *n*_D²⁰ 1.4330. Found: C, 53.0; H, 11.3; *n*_D²⁰ 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.