

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF PURDUE UNIVERSITY]

The Photochlorination of 2-Methylpropane-2-*d* and α -*d*₁-Toluene; the Question of Free Radical Rearrangement or Exchange in Substitution Reactions^{1,2}

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RECEIVED DECEMBER 14, 1951

The liquid phase photochlorination of 2-methylpropane-2-*d* at -15° produces equimolar amounts of *t*-butyl chloride and deuterium chloride. This result indicates that no significant rearrangement of free radicals or hydrogen exchange between radicals and hydrocarbon occurred during chlorination. Similarly, within a somewhat larger limit of experimental error, no exchange was observed in the liquid phase competitive chlorination of cyclohexane and α -*d*₁-toluene at 80° . In the photochlorination reaction the relative reactivities of the deuterium atom of 2-methylpropane-2-*d* and the tertiary hydrogen of isobutane are 1.0:1.8 at -15° , while the relative reactivities of the deuterium and hydrogen atoms of α -*d*₁-toluene are 1.0:2.0 at 80° .

Introduction

An understanding of the factors controlling directive effects in aliphatic substitution is of considerable importance for both the theory and the practice of organic chemistry. For some time we have been engaged in the study of the free radical chlorination of various aliphatic derivatives in an attempt to attain generalizations which would be of value in this little-explored field.³ In the course of this work the question arose as to whether the chlorine substituent present in the final product was located at the position from which the hydrogen atom had originally been removed.

The nature of the problem may be understood by considering the divergent results obtained in the attack of a chlorine atom and a methyl free radical on isobutyric acid. In the peroxide-catalyzed chlorination of isobutyric acid⁴ the product is predominantly β -chloroisobutyric acid. On the other hand, decomposition of acetyl peroxide in isobutyric acid⁵ yields exclusively tetramethylsuccinic acid.

In free radical reactions it has been generally considered that the relative ease of attack upon a given atom in different positions in a molecule should correspond to the relative strength of the bonds involved. It is therefore disconcerting that a chlorine atom apparently attacks the β -hydrogen of isobutyric acid preferentially, whereas the free methyl radical apparently attacks the α -hydrogen exclusively. The rapid rearrangement or exchange of the free radicals first formed offers a possible explanation of this apparent anomaly.^{3b} In that event one could not conclude from the isolation of predominantly β -chloroisobutyric acid and exclusively tetramethylsuccinic acid that the primary attack had been in the β -position in the first case and in the α -position in the second.⁶

(1) Directive Effects in Aliphatic Substitutions. I.

(2) This paper is abstracted from a thesis submitted by Glen A. Russell in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

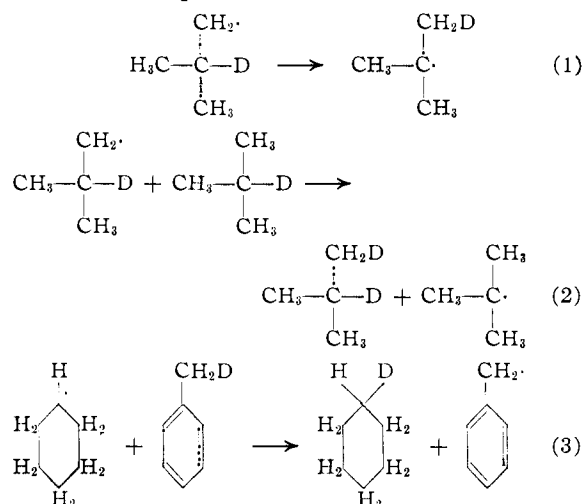
(3) (a) Arthur B. Ash, Ph.D. Thesis, Wayne University, 1948; (b) A. B. Ash and H. C. Brown, *Record of Chemical Progress*, **9**, 81 (1948).

(4) M. S. Kharasch and H. C. Brown, *THIS JOURNAL*, **62**, 925 (1940).

(5) M. S. Kharasch and M. T. Gladston, *ibid.*, **65**, 15 (1943).

(6) Alternate explanations involving effects other than relative bond strengths have been proposed as an explanation to this and similar phenomena. F. R. Mayo and C. Walling [*Chem. Revs.*, **46**, 269 (1950)] have suggested that polar effects between substrates and attacking radicals could explain certain anomalies in free radical reactions. Furthermore, S. D. Ross, M. Markarian and M. Nazzewski [*THIS JOURNAL*, **69**, 1914 (1947); **69**, 2468 (1947)] have proposed a steric effect to explain the unusual directive effects noted in the chlorination and bro-

In order to obtain evidence on the importance of free radical rearrangement or exchange in chlorination reactions, we undertook the photochlorination of compounds labeled with deuterium. 2-Methylpropane-2-*d* and a cyclohexane- α -*d*₁-toluene mixture were photochlorinated and the amount of deuterium chloride produced was compared with the products formed. If appreciable rearrangement (1) or exchange (2) and (3), were to occur, as illustrated in the equations



there would be no simple relationship between the quantity of deuterium chloride formed in the reaction and the amount of tertiary chloride or benzyl chloride found in the product.⁷

Results

Chlorination of 2-Methylpropane-2-*d*.—The 2-methylpropane-2-*d* was prepared by the action of deuterium chloride⁸ on *t*-butylmagnesium chloride. Mass spectrometric analysis of the product by the method of Stevenson and Wagner⁹ indicated the presence of the following impurities: 0.01% C₄H₈, 2.9 ± 0.3% C₄H₁₀ and 0.02 ± 0.02% C₄H₈D₂. The

mination of pentachloroethylbenzene. However, there seems to be insufficient evidence at the present time definitely to state that these effects are of general importance in free radical substitution reactions.

(7) It was originally planned to include deuterium labeled isobutyric acid in these studies in order to test the hypothesis advanced (ref. 3b). However, we learned that both Professor C. C. Price of Notre Dame University and Professor W. H. Urry of the University of Chicago were engaged in similar studies on this substance. For that reason it was not included in this investigation.

(8) H. C. Brown and C. Groot, *THIS JOURNAL*, **64**, 2223 (1942).

(9) D. P. Stevenson and C. D. Wagner, *J. Chem. Phys.*, **19**, 11 (1951).

deuterium and hydrogen chlorides produced during the 5–10 mole per cent. chlorinations at -15° were freed of hydrocarbon by distillation from a trap at -135° and converted to water by reaction with silver oxide at room temperature. The density of the water produced was determined by an Ostwald-type pycnometer of 0.5-ml. volume. The alkyl chlorides produced were freed of hydrocarbons by rectification and analyzed for tertiary chloride by hydrolysis in 80% ethanol. The difference between the total chlorine content of the chlorination product and the tertiary chloride concentration was assumed to be isobutyl chloride. The chlorinations of two samples of 2-methylpropane-2-*d* are summarized in Table I.

TABLE I
CHLORINATION OF 2-METHYLPROPANE-2-*d* AT -15° ^a

	EXPT. NO. 1	EXPT. NO. 2
Reactants:		
2-Methylpropane-2- <i>d</i> ^b	1.4	1.7
Chlorine	0.101 ± 0.005	0.108 ± 0.005
Products:		
<i>t</i> -Butyl chloride	.0227	.0247
Isobutyl chloride	.0783	.0817
Deuterium and hydrogen chlorides (from volume of gas)	.1014	.1078
Deuterium chloride (from water produced)	.0208	.0232
Hydrogen chloride (from water produced)	.0801	.0835
Water from deuterium and hydrogen chlorides, g.	.9301	.9853
Refractive index of water, n_D^{20}	1.3319	1.3319
Density of water at 20° (g./ml.)	1.0222	1.0235
Ratio of tertiary to primary chloride ^c	0.283	0.296
Ratio of deuterium to hydrogen chloride ^d	0.272	0.291
Reactivity of deuterium atom ^{e,f}		
Alkyl chloride ratio	2.55	2.66
Deuterium and hydrogen chloride ratio	2.45	2.62

^a All quantities in moles unless otherwise noted. ^b Containing 3% isobutane. ^c Corrected for isobutane impurity. ^d Reactivity of the primary hydrogen equal to 1.0.

In order to correct for the presence of 3% isobutane in the 2-methylpropane-2-*d*, the relative reactivity of primary to tertiary hydrogens of isobutane at -15° of 1.0:4.5¹⁰ was taken into account in the computation of the relative reactivities of Table I. The excellent agreement between the DCI/HCl and *t*-BuCl/*i*-BuCl ratios (Table I) clearly demonstrates the absence of any significant hydrogen exchange or free radical rearrangement during the chlorination of this substance. A sample of the hydrocarbon from Expt. 2 was observed mass spectrometrically after chlorination. This sample contained 0.01% C₄H₈, 3.0 ± 0.3% C₄H₈ and 0.24 ± 0.04% C₄H₈D₂. If the analysis for C₄H₈D₂ is accepted,¹¹ then an upper limit of 4% can be

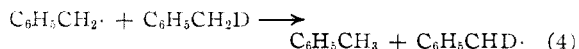
(10) Unpublished work

(11) Dr. D. P. Stevenson of the Shell Development Co., Emeryville, California, who generously made the mass spectrographic analyses, has expressed his confidence in the reliability of the analyses with regard to the 0.2% of C₄H₈D₂.

placed on the number of the isobutyl radicals which may have reacted with the excess hydrocarbon to produce *t*-butyl radicals (Eq. 2).

By comparison of the relative reactivity of deuterium and hydrogen atoms of 2-methylpropane-2-*d* (1.00:2.5₈) and of the tertiary and primary hydrogen atoms of isobutane (1.0:4.5), a tertiary deuterium and tertiary hydrogen atom of isobutane have a relative reactivity of 1.0:1.8 measured in the photochlorination reaction at -15° .

Photochlorination of α -*d*₁-Toluene.—The α -*d*₁-toluene was prepared from benzylmagnesium chloride and deuterium chloride and contained 1.57 ± 0.02% of toluene as estimated from the mass spectra. In order to test for exchange of the type



a sample of α -*d*₁-toluene was chlorinated at 80°, rectified from the benzyl chloride produced and rechlorinated at 80°. These chlorinations are summarized in Table II.

TABLE II
PHOTOCHEMICAL CHLORINATION OF α -*d*₁-TOLUENE AT 80°^a

	EXPT. NO. 1	EXPT. NO. 2
α - <i>d</i> ₁ -Toluene ^b	1.46	1.27
Chlorine	0.101 ± 0.005	0.0900 ± 0.005
Deuterium and hydrogen chlorides (from volume of gas)	.1056	.0944
Water from deuterium and hydrogen chlorides, g.	.9942	.8999
Density of water at 20° (g./ml.)	1.0211	1.0211
Deuterium chloride (from water produced)	0.0212	0.0192
Hydrogen chloride (from water produced)	.0868	.0785
Reactivity of deuterium atom ^{c,d}	.50	.50

^a All quantities in moles unless otherwise noted. ^b Containing 1.6% toluene. ^c Corrected for presence of 1.6% toluene. ^d Reactivity of the hydrogen atom equal to 1.0.

The excellent agreement of the two chlorinations given in Table II indicates the absence of any change in isotopic concentration during the chlorination of α -*d*₁-toluene.

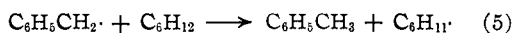
Competitive Chlorination of α -*d*₁-Toluene and Cyclohexane.—In order to obtain more information about the unusually high reactivity of cyclohexane observed in the competitive chlorination of cyclohexane and toluene at 80°¹⁰ and to examine the possibility of free radical exchange in this system, the competitive chlorination of α -*d*₁-toluene and cyclohexane was studied. The deuterium and hydrogen chlorides produced were distilled from a -80° bath to remove traces of hydrocarbons and converted to water by reaction with silver oxide. Benzyl chloride was determined in the chlorination product by the formation of ionic chlorine in a 50% solution of piperidine in ethanol. This procedure was thoroughly checked on prepared samples and under the conditions used chlorocyclohexane was found to be unreactive. Chlorocyclohexane was taken as the difference between the total alkyl chlorides and the benzyl chloride. The results of two chlorinations are given in Table III.

TABLE III
COMPETITIVE PHOTOCHEMICAL CHLORINATION OF α -*d*₁-TOLUENE AND
CYCLOHEXANE AT 80°^a

	Expt. No. 1	Expt. No. 2
Reactants:		
α - <i>d</i> ₁ -Toluene	0.948	0.959
Cyclohexane	.498	.481
Chlorine	.101 ± 0.005	.090 ± 0.005
Products:		
Benzyl chloride	.0176	.0158
Chlorocyclohexane	.0886	.0750
Deuterium and hydrogen chlorides (from volume of gas)	.1020	.0913
Deuterium chloride (from water produced)	.0039	.0040
Hydrogen chloride (from water produced)	.1024	.0880
Water from deuterium and hydrogen chlorides, g.	.9617	.8325
Density of water at 20° (g./ml.)	1.0026	1.0033
Attack on deuterium atom		
Observed	0.0039	0.0040
Calculated ^b	.0035	.0032
Hydrogen chloride from α - <i>d</i> ₁ -toluene ^c	.0156	.0160
Hydrogen chloride from cyclohexane	.0868	.0720

^a All quantities in moles unless otherwise noted. ^b From benzyl chloride concentration and data of Table II. ^c Deuterium chloride (2) (1.0/0.50).

The water produced during the analysis of the deuterium and hydrogen chloride for the chlorinations summarized in Table III contained 4.1 and 4.8% deuterium oxide. In the absence of exchange, deuterium oxide concentrations of 3.7 and 3.9% would be expected for complete agreement between the alkyl chlorides and the deuterium and hydrogen chlorides. The analytical procedure results in a possible absolute error in the deuterium oxide concentration of 0.5%. This could affect both the hydrogen-deuterium ratio in the chlorination of α -*d*₁-toluene (Table II) and the results of the competitive chlorination (Table III). On this basis the results obtained fall within the possible limits of error for no exchange. However, we cannot exclude the possibility of up to 10% exchange of benzyl radicals in accordance with the equation



It should be pointed out that exchange as represented by Eq. 5 would be proceeding in the opposite direction to that which is most probable from the point of view of the relative strengths of the carbon-hydrogen bonds involved (Eq. 3). On the basis of both theory and experiment it appears safe to conclude that exchange is not an important reaction in this system.

Discussion

The possible rearrangement or exchange of aliphatic free radicals has been a matter of concern for some time. It was shown that the alkyl radicals presumably formed in the decomposition of *n*- and isobutyryl peroxides in carbon tetrachloride do not undergo rearrangement in their reaction with the

solvent.¹² However, it has recently been suggested that acyl peroxide decompositions may not liberate significant quantities of free alkyl radicals.¹³ Moreover, the rearrangements of *n*- and isopropyl radicals have been reported in the (*n*, γ) reactions of bromine 81 in *n*- and isopropyl bromides.¹⁴

Rearrangements of the carbon skeleton appear to have been definitely proved for the neophyl and triphenylmethoxy radicals,^{15,16} but no rearrangements of this kind have ever been observed in photohalogenations.^{17,18}

The present study indicates that neither rearrangements involving hydrogen atoms (Eq. 1), nor hydrogen interchange between free radicals and the hydrocarbons present, represent an important reaction in photochlorination of aliphatic and alicyclic hydrocarbons. In the chlorination of 2-methylpropane-2-*d* there is no appreciable rearrangement of the isobutyl or *t*-butyl free radicals (Eq. 1) within the accuracy of the experimental method. Mass spectrometric analysis places an upper limit of 4% to the possible exchange between the isobutyl free radicals and the tertiary deuterium atom (Eq. 2). Within the lower limits of the competitive chlorination study of cyclohexane and α -*d*₁-toluene, there also does not appear to be any important exchange reaction (Eq. 3). It therefore appears that neither rearrangement of the carbon skeleton nor of the outer hydrogen sheath are significant reactions in free radical halogenations of hydrocarbons.

In photochlorinations the life time of the free radical is believed to be very short—the free radical reacts rapidly with the chlorine present in the reaction mixture. It is entirely possible that in other free radical reactions, in which the subsequent reactions of the free radical are slow,³ rearrangement or exchange reactions may become highly important. However, for the studies to be presently reported on directive effects in aliphatic chlorination, it appears safe to conclude that the chlorine substituent appears at the position in the molecule from which a chlorine atom had originally removed the hydrogen.

Experimental Details

Preparation of 2-Methylpropane-2-*d*.—Over a ten-hour period, 232.5 g. (2.5 moles) of freshly distilled *t*-butyl chloride dissolved in enough anhydrous ether to make 1500 ml., was added to 60 g. (2.5 g. atom) of magnesium turnings and 150 ml. of ether in a 2000-ml. three-necked flask equipped with a mercury sealed stirrer, pressure-equalized dropping funnel and Friedericks condenser fitted with soda-lime and calcium hydride drying tubes. The ethereal solution was concentrated to 1500 ml. and an aliquot analyzed for the concentration of Grignard reagent by hydrolysis in hydrochloric acid. Such analyses indicated a yield of *t*-

(12) M. S. Kharasch, S. S. Kane and H. C. Brown, *THIS JOURNAL*, **64**, 1621 (1942).

(13) F. G. Edwards and F. R. Mayo, *ibid.*, **72**, 1265 (1950).

(14) L. Friedman and W. F. Libby, *J. Chem. Phys.*, **17**, 647 (1949).

(15) W. H. Urry and M. S. Kharasch, *THIS JOURNAL*, **66**, 1438 (1944); S. Winstein and F. H. Seubold, Jr., *ibid.*, **69**, 2916 (1947).

(16) M. S. Kharasch, A. C. Poskus, A. Fono and W. Nudenberg, *J. Org. Chem.*, **16**, 1458 (1951).

(17) H. B. Hass, E. T. McBee and P. Weber, *Ind. Eng. Chem.*, **27**, 1193 (1935).

(18) The neophyl radicals produced in the peroxide-catalyzed chlorination of *t*-butylbenzene do not undergo significant rearrangement, since an excellent yield of neophyl chloride is produced; M. S. Kharasch and H. C. Brown, *THIS JOURNAL*, **61**, 2142 (1939).

butylmagnesium chloride of 2.20–2.24 moles (88–90%). The deuterium chloride, prepared from 20 g. (1 mole) of 99.8% deuterium oxide according to the method of Brown and Groot,⁸ was passed through an ice-trap and over the surface of the vigorously stirred Grignard solution. Water at 0° was circulated through the Friedericks condenser and the gas passing through this condenser was trapped by a Dry Ice-bath.

After the addition of the deuterium chloride, the ethereal solution was refluxed for one hour and approximately 300 ml. of 2-methylpropane-2-*d* and ether collected. To remove the excess ether this material was distilled using a reflux condenser at 0°. The 225 ml. of material collected was treated with 4 ml. of bromine which produced a reddish color that persisted after one-half hour of reflux in the dark. After distilling through a reflux condenser at 0°, the 2-methylpropane-2-*d* was carefully rectified in a 40-cm. vacuum jacketed column packed with glass helices and equipped with a low temperature head. A fraction of 104.5 g. (1.77 moles) boiling at –12.5 to –11.8° (743 mm.) was collected. Based on the deuterium oxide used, the yield of 2-methylpropane-2-*d* was 88.5%.

Preparation of α -*d*₁-Toluene.— α -*d*₁-Toluene was prepared by the reaction of excess deuterium chloride with benzylmagnesium chloride. Rectification of the ethereal solution of five preparations, wherein 679 g. (5.35 moles) of benzyl chloride was converted to the Grignard reagent and then treated with the deuterium chloride produced from 70 g. (3.50 moles) of 99.8% deuterium oxide, yielded 429 g. (4.62 moles) of α -*d*₁-toluene, b.p. 110.6° (cor. to 760 mm.), *n*_D²⁰ 1.4965–1.4966. The yield was 86.4% based on the benzyl chloride used.

Photochlorination Procedure.—Photochlorinations were performed in an apparatus in which accurate temperature control for the chlorinations was achieved by immersing the 200-ml. three-necked chlorination flask in a water-bath so that only the necks of the flasks protruded above the surface of the water. Illumination was provided by a 150-watt clear glass light bulb immersed in the water-bath 1 inch from the flask. For chlorinations at –15° the temperature was maintained by alcohol cooled with Dry Ice and illumination provided by a 150-watt bulb in a photo-flash reflector. A Dry Ice condenser was substituted for the condenser for the chlorination of 2-methylpropane-2-*d*.

Chlorinations were performed by the following procedure. After the water-bath had been brought to the desired temperature, the hydrocarbon was placed in the chlorination flask. Purified nitrogen was passed through the apparatus and the hydrocarbon to remove oxygen while chlorine was liquefied in a calibrated reservoir tube. This chlorine was then allowed to warm and was swept by the nitrogen into a 200-ml. mixing bulb and then into the hydrocarbon through a sintered glass disc with stirring and illumination.

The hydrogen and deuterium chlorides produced were trapped in a U-tube by liquid nitrogen and protected from moisture by a phosphorus pentoxide tube. After the desired amount of chlorine had been added, as determined by the volume of liquid chlorine in the reservoir tube, purified nitrogen was passed through the system for one to two hours to remove all hydrogen chloride.

Analysis of Deuterium and Hydrogen Chloride Mixtures.—The U tube was connected to a vacuum line and the deuterium and hydrogen chloride removed at a temperature low enough that the hydrocarbon impurities were non-volatile. The quantity of material collected was measured in a large bulb of known volume. Conversion to water was effected by allowing the gases to pass through a 16-mm. tube containing a 200% excess of tightly packed silver oxide. The reaction was highly exothermic and the silver oxide tube had to be cooled with ice water. The water collected was

transferred between a U-tube and a removable tube, and finally degassed by repeated freezings and evacuations. The amount of water collected was weighed and its density determined to $\pm 0.05\%$ at 20.0° with an Ostwald-type pycnometer (0.5 ml.). In all cases the water collected gave negative tests for chloride ion with silver nitrate. The percentage of deuterium oxide present was calculated using the value of 1.1053 g./ml. for the density of "heavy water" at 20°. By this method a sample of 0.0925 mole of hydrogen chloride, produced from the chlorination of isobutane, gave 0.833 g. of water (expected 0.831 g.) with a density at 20° of 0.9985 g./ml. (correct value 0.99823).

Deuterium oxide²⁰ (ca. 1.0 ml.) having a density of 1.1045 g./ml. at 20° (99.3%) was added to 150 ml. of freshly distilled benzoyl chloride at 140–150°. After the addition of the "heavy water," the benzoyl chloride was refluxed for 30 minutes. The deuterium chloride produced was passed through a trap at 0° to remove traces of benzoyl chloride and introduced into the vacuum line from a –80° bath. The gas collected had a volume corresponding to 0.1071 mole and yielded 1.0651 g. of water having a density of 1.1022 g./ml. at 20° (97.1% deuterium oxide).

Analysis of the Chlorination Product of 2-Methylpropane-2-*d*.—After chlorination was complete, the excess 2-methylpropane-2-*d* was removed by rectification at a 10:1 reflux ratio by means of a 40 cm. \times 12 mm. vacuum jacketed column packed with glass helices and equipped with a low temperature head. When reflux no longer occurred, 75 ml. of neutral, chlorine-free dioxane was added to the flask by washing the head and column. The contents of the flask were diluted to 100 ml. with dioxane and aliquots of the dioxane solution analyzed for total chlorine by the Rauscher method²¹ and for tertiary chloride by hydrolysis in 50% ethanol at room temperature. It was found advisable to use Dry Ice condensers for the total chlorine analyses with chlorides as volatile as the butyl chlorides. A prepared solution containing 0.0713 mole of *t*-butyl chloride and 0.1627 mole of isobutyl chloride was analyzed in this way and found to contain 0.0708 mole of *t*-butyl chloride and 0.1629 mole of isobutyl chloride.

Analysis of Product of Competitive Chlorination of Cyclohexane and α -*d*₁-Toluene.—Benzyl chloride was determined in the presence of chlorocyclohexane by reaction with a 50% solution of piperidine in ethanol. Chlorocyclohexane was obtained from the difference in total chlorine and ionic chlorine concentrations. After chlorination the product was carefully weighed and then weighed samples were taken for total chlorine and benzyl chloride analysis. For benzyl chloride, the samples were weighed into a 100-ml. volumetric flask and diluted to 100 ml. with the piperidine-ethanol solution. Reaction was complete within three to five hours as indicated from constant silver nitrate titers (potentiometric procedure). A prepared solution containing 5.21% benzyl chloride and 10% chlorocyclohexane in a 1:1 mixture of toluene and cyclohexane gave a constant silver nitrate titer after four hours and no increase in ionic chlorine was observed during the next 18 hours. This titer corresponded to 5.24% benzyl chloride.

Acknowledgment.—We are indebted to Mr. David P. Stevenson of the Shell Development Company for the mass spectrometric analyses reported in this paper.

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(19) L. Troustad and J. Brun, *Trans. Faraday Soc.*, **34**, 766 (1938).

(20) Obtained from the Stuart Oxygen Co., San Francisco, California.

(21) W. Rauscher, *Ind. Eng. Chem., Anal. Ed.*, **9**, 296 (1937).