

662. *Autoxidation. Part I. Liquid-phase Autoxidation of 5-Methylnonane.*

By R. R. ARNDT, J. B. BARBOUR (in part), (MISS) E. J. ENGELS,
D. H. S. HORN, and D. A. SUTTON.

Gas chromatography, in conjunction with a highly sensitive flame ionisation detector and infrared spectroscopy, has been used to analyse the mixture of reduced autoxidation products of 5-methylnonane, and so determine the relative susceptibilities of the various carbon atoms to attack. It is calculated that at minimum reaction a hydrogen atom of a tertiary carbon atom is removed nineteen times as fast as a hydrogen of a normal secondary one. The latter hydrogen atom is in turn removed four times as fast as one attached to a primary carbon atom. A large proportion of the product was composed of disubstituted derivatives produced by α -, β -, and γ -intra-molecular hydrogen transfer.

VALUABLE studies have been made recently by Twigg,¹ Benton and Wirth,² Pritzkow,³ and Wibaut and Strang⁴ of the position of radical attack on straight-chain hydrocarbons during autoxidation. The purpose of the present work has been to determine the effect, on the susceptibility of the various positions to attack, of the introduction of a methyl group into an otherwise straight-chain hydrocarbon. Hydrocarbons containing a single methyl branch or a limited number of branches, are present in considerable amounts

¹ Twigg, *Chem. Eng. Sci., Special Suppl.*, 1954, **3**, 5.

² Benton and Wirth, *Nature*, 1953, **171**, 269.

³ Pritzkow and Müller, *Annalen*, 1955, **597**, 167; Langenbeck and Pritzkow, *Fette u. Seifen*, 1953, **55**, 435.

⁴ Wibaut and Strang, *Proc. K. Ned. Akad. Wet.*, 1953, Series B, **56**, 340 and earlier references.

in the hydrocarbon mixture produced by the Fischer-Tropsch synthesis.⁵ A study has accordingly been made of the branched-chain hydrocarbon 5-methylnonane.

Pure 5-methylnonane was oxidised at 90° in oxygen. Samples were withdrawn at intervals for analysis and for reduction with lithium aluminium hydride to convert the products, assumed to be hydroperoxides, ketones, esters, and acids, into a mixture of the corresponding 5-methyl-nonanols and -nonanediols; short-chain alcohols derived from chain-fission products, and unchanged hydrocarbon were also present.

Attempts were first made to analyse this mixture, after preliminary fractionation, by infrared or mass spectroscopy, but the mono- and di-substituted products could not be isolated quantitatively. This difficulty was overcome by analysing the mixture directly by means of gas chromatography with the aid of a highly sensitive flame ionisation detector.⁶ This method had the advantage that partial analyses could be made at low oxidation levels, where the effect of secondary transformations involving fission were at a minimum, and that the more efficient column packings containing relatively small proportions of liquid phase⁷ could be used. A large number of possible reduced products was synthesised for identification of the chromatographic peaks.

On chromatography of the reduced mixture, any fission products were eluted first, followed, in order and with complete resolution, by the unchanged paraffin, 5-methylnonane-5-ol, a mixture of the 3- and the 4-alcohols, then the 2-, 1-, and side-chain alcohol, followed by a group of four diols corresponding to 5-methylnonane-4,5- and -3,5-diol, an unidentified diol or diol mixture (present in significant amounts only at higher levels of autoxidation), and the 2,5-diol.

Trial runs with a 5% solution of an artificial mixture of 5-methylnonanols in 5-methylnonane (see Table 1) indicate the accuracy of the method.

A similar accuracy was achieved by gas chromatography of an artificial mixture of 5-methylnonane-2,5-, 3,5-, and -4,5-diol and 5-methylnonane-1-ol.

The analyses of the reduced autoxidation mixtures are shown in Table 2. Some of these were obtained after preliminary separation of larger amounts of reduced products by distillation and partition chromatography into monol and diol groups for further characterisation. The mixture of 3- and 4-alcohols could not be resolved by gas chromatography, but it was possible, when sufficient material was available, to determine the proportion of the isomers present in the gas-chromatographic fraction by means of infrared absorption spectroscopy. One partial analysis was made at a level where peroxides only could be detected (Table 2, B1).

TABLE I. *Analyses of an artificial mixture of 5-methylnonanols.*

	5-ol	4- + 3-ol	2-ol	1-ol	Side-chain alcohol
Taken (%)	39	25	23	4	10
Found (%)	41	25	23	3	8
	40	25	23	3	7
	41	25	22	3	9

Whereas the susceptibility of the various carbon positions to attack was in the expected order, tertiary > secondary > primary, unexpected differences in the reactivity of the secondary carbon atoms were found. Position 2 was slightly more attacked than position 4, and both these were attacked 2–3 times as much as position 3. This could have been due to the ready removal, by a 3-peroxy-radical, of hydrogen from the active position 5 by β -intramolecular hydrogen-transfer,¹ so that a difunctional rather than a monofunctional 3-derivative was formed. This is unlikely, however, since 5-methylnonane-3,5-diol was present in relatively small proportions in the diol mixture. Alternatively, the most

⁵ Weitkamp, Seelig, Bowman, and Cady, *Ind. Eng. Chem.*, 1953, **45**, 343.

⁶ Harley, Nel, and Pretorius, *Nature*, 1958, **181**, 177.

⁷ Cheshire and Scott, *J. Inst. Petroleum*, 1958, **44**, 74.

TABLE 2. Analyses of reduced autoxidation products.

Expt. Wt. oxidised Sample	B 100 g.				A 140 g.*		C 25 g.		D 25 g.	
	B1	B2	B3	B4	A1	A2	C1	C2	D1	D2
O ₂ Absorption (mol. %)	0.3	1.1	2.4		2.3		8.5		13.8	
RO·OH (mol. %)	0.3	0.7	1.4		1.5		2.0		2.3	
Ketone (mol. %)	—	0.1	0.3		0.5		3.2		5.0	
Monols (%)	75	—	73		74		73		71	
Diols (%)	25	—	27		26		27		29	
Composition (%) of mono-alcohols										
5-ol	60	56	47	48 †	43	43 †	38	39 †	38	30 †
4-ol	20 ‡	21 ‡	27 ‡	18	27 ‡	20	29 ‡	17	31 ‡	21
3-ol	—	—	—	7	—	9	—	12	—	13
2-ol	13	15	19	19	21	21	23	23	22	26
1-ol	5	5	5	5	6	5	7	6	6	7
Side-chain alcohol	2	3	2	3	3	2	3	3	3	3
Composition (%) of di-alcohols										
2,5-diol	57	—	54	—	53	—	53	—	51	—
3,5-diol	26	—	25	—	25	—	26	—	25	—
4,5-diol	10	—	7	—	6	—	3	—	5	—
Unknown diols (?) (%)	7	—	14	—	16	—	18	—	19	—

* In ultraviolet light. † Monol concentrate. ‡ Too little for determination of 3:4-monol ratio.

stable conformations are expected to be those in which the position 3 is less accessible to attack by bulky alkoxy-radicals than the other secondary positions.

As would be expected, the three primary positions are equally attacked. The relative rates of attack of the unhindered positions at the lowest levels of reaction are calculated to be as follows: hydrogen is removed nineteen times more readily from a primary than a secondary (Twigg¹ has reported a value of about 20) and from a secondary four times as fast as from a primary carbon atom.

The apparent decrease in the amount of 5-alcohol and attack at position 5 with increasing oxygen absorption (see Table 2) is undoubtedly due to the increasing decomposition of the 5-peroxides to ketonic fragments, the amount of ketone increasing rapidly at higher oxidation levels. Reduction products of these substances, eluted before the methylnonanols, were found in increasing amounts as the reaction proceeded. Ethanol, butan-1-ol, and hexan-2-ol were the major substances detected and are clearly derived from chain-fission products of the most abundant product, 5-hydroperoxy-5-methylnonane: $\text{Bu}_2\text{CMe}\cdot\text{O}\cdot\text{OH} \longrightarrow \text{BuCOme} + \text{HOBu}$. Removal of the methyl group, to yield nonan-5-one, is not favoured as no nonan-5-ol could be detected. This is in conformity with George and Walsh's rule⁸ that cleavage of a tertiary peroxide occurs in such a way that the longer alkyl group bound to the oxygen-carrying carbon is separated.

A relatively large proportion of disubstituted autoxidation products was found, indicating that the chain reaction step, $\text{RO}\cdot\text{O}\cdot + \text{HR} \longrightarrow \text{RO}\cdot\text{OH} + \cdot\text{R}$, is propagated to a considerable extent by intramolecular elimination of hydrogen, as suggested by Twigg.¹ The ingenious work of Rust⁹ leads to the conclusion that hydrogen is most easily removed from the β -, and next most easily from the γ -carbon atom. However, Twigg concluded that little α - or β -attack takes place when n-decane is autoxidised. On the other hand, 5-methylnonane has been found to undergo more γ - than β -intramolecular attack, 2—3 times more 2,5- than 3,5-diol being formed. These differences are most likely to be due to differences in conformation, produced by increasing chain-branching, the presence of two close methyl branches, as in Rust's hydrocarbons,⁹ being most effective in producing β -attack.

The amount of 5-methylnonane-4,5-diol formed was relatively small, indicating that

⁸ George and Walsh, *Trans. Faraday Soc.*, 1946, **42**, 94, 264.

⁹ Rust, *J. Amer. Chem. Soc.*, 1957, **79**, 4000.

α -intramolecular attack is also possible but not favoured. At higher levels of oxidation, other diol peaks appeared in the gas chromatograms. These were not identified but are doubtless due to the formation of diols by intermolecular double attack.

An attempt was made to determine partially the composition of the diols by converting the diols having a 5-hydroxy-group, first into the 5-chloro-alcohols by concentrated hydrochloric acid, then into the monols by hydrogenation. The 3,5- and 4,5-diols were quantitatively converted in this way into the 3- and 4-monols respectively but the 2,5-diol was probably converted into a pentane-insoluble tetrahydrofuran oxonium salt, which on neutralisation reverted to the original diol.¹⁰

EXPERIMENTAL

Precise distillations were carried out in column "A" (a Heli-grid column, 13 mm. i.d., 3 ft. in length,¹¹ supplied by Messrs. Podbielniak Inc., Chicago, U.S.A.), and column "B" (a micro spinning-band column¹²).

Pure 5-methylnonane, prepared as described below, was autoxidised in an electrically heated silica flask fitted with a thermometer and a side-arm holding a fine capillary for withdrawal of samples without interruption of the reaction. The flask was connected to a gas burette, and the contents were stirred magnetically and kept at 90° by means of an electrically heated jacket.

Preparation of the Products for Analysis.—Samples (ca. 1 c.c.), withdrawn at different stages, were analysed for peroxides iodometrically¹³ and for ketones by comparing the intensity of the infrared absorption in the 5.85 μ region with that of 5-methylnonane-3-one dissolved in 5-methylnonane. Acids and esters were determined by acid and saponification values: at low levels of oxidation negligible amounts were present.

For gas chromatography the samples were diluted with dry ether and reduced with lithium aluminium hydride. The products were recovered by addition of dilute sulphuric acid. The ether extract was dried (Na_2SO_4), and the ether distilled off through a short column. The residue was analysed directly. Where larger samples were available at the end of the reaction, the reduced product was fractionated in column "B" into unchanged hydrocarbon, mono-alcohols (b. p. 71—104°/10.5 mm., n_D^{30} 1.4236—1.4317) and dialcohol residue. The alcohol fractions were further purified by chromatography in 80% ethanol on a reversed-phase partition column prepared from non-wetting Supercel¹⁴ (12 g.) and isoheptane (12 g.). The alcohols were located in the eluate (collected in 2 ml. fractions) by refractive-index measurements and spot tests with the Komarowski reagent.¹⁵ The combined alcohol fractions were diluted with an equal volume of water and extracted several times with pentane. Evaporation of the pentane yielded either the monol mixture (0.5—1 g.), n_D^{30} 1.4330 (Found: C, 75.5; H, 13.9; active H, 0.68. Calc. for $\text{C}_{10}\text{H}_{22}\text{O}$: C, 75.9; H, 14.0; active H, 0.63%), or the diol mixture (0.35 g.), n_D^{30} 1.4387. The latter was found by gas chromatography still to contain about 10% of monols (Found: C, 69.7; H, 12.8; active H, 1.17. Calc. for $\text{C}_{10}\text{H}_{22}\text{O}_2$: C, 68.9; H, 12.7; active H, 1.16. Calc. for a 1:9 monol-diol mixture: C, 69.6; H, 12.9; active H, 1.11%).

Gas-chromatographic Apparatus.—An apparatus, shown in the Figure, was constructed, incorporating a modified form of the flame ionisation detector of Harley *et al.*⁶ For high-boiling substances it was necessary to place the flame and electrodes well inside the heating jacket. The electrodes were made of platinum wire (0.5 mm. diam.), set in the opposite sides of the glass chimney 1.0—1.5 mm. apart and 1.0—1.5 * mm. above the flame jet. To avoid electrical interference from the heating jacket the electrodes were housed in thin glass tubes covered with woven-wire screening to the point of union with the chimney. The flow of hydrogen and of nitrogen were controlled with "Precision Regulator Valves" supplied by Negretti and Zambra Ltd., London. The air-flow was controlled with a pinch-cock. All three gas flows were measured by rotameters supplied by Emil Greiner and Co., New York, U.S.A. The voltage

* *Added in proof:* Owing to an error in drawing, this distance is shown too large in the Figure.

¹⁰ Froebe and Hochstetter, *Monatsh.*, 1902, **23**, 1088.

¹¹ Podbielniak, *Ind. Eng. Chem., Analyt.*, 1941, **13**, 639.

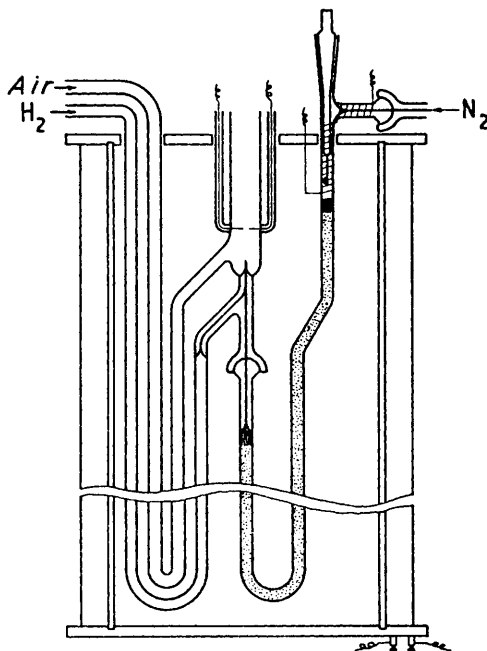
¹² Horn and Hougen, *J.*, 1953, **3535**.

¹³ Sully, *Analyst*, 1954, **79**, 86.

¹⁴ Howard and Martin, *Biochem. J.*, 1950, **46**, 532.

¹⁵ Rosenthaler and Vegezzi, *Branntweinwirtschaft*, 1953, **75**, 68; cf. *Chem. Abs.*, 1953, **47**, 7373.

to the detector circuit was stabilised with a "Stabiline" automatic voltage regulator, supplied by Superior Electric Co., Bristol, Conn., U.S.A. The nitrogen used was freed from oxygen by passing it over copper turnings at 400°.



The substance to be chromatographed was put on the column by stopping the nitrogen flow and replacing the B7 stopper by one fitted with a platinum loop filled with the liquid (0.2 mg.) to be chromatographed. For the detection of the monols, present as a 5% solution in 5-methylnonane, a larger loop of flattened wire holding 1–2 mg. was used. The tube surrounding the loop was heated with a wire coil to about 20–50° above the temperature of the jacket. This system was the most satisfactory for the introduction and rapid vaporisation of small amounts of liquids, essential with a detector of high sensitivity. Immediately the stopper was replaced, the nitrogen flow was restarted. The optimum flow rates of 28, 25, and 700 ml./min., for nitrogen, hydrogen, and air respectively, were used. The flame was simply ignited from the top of the chimney. The zero detector signal (base line) was normally independent of the column temperature or small variations in gas flows. However, it became sensitive to nitrogen flow rate if "bleeding" of the liquid phase took place. The columns, easily interchangeable by releasing the ball joints, were made of U tubes (50 cm. long, 4 mm. int. diam.). Coiled columns gave poorer resolution. The columns were packed under a vacuum with vibration. For the analysis of the monols a packing of polyethylene glycol 400 (manufactured by Olin Mathieson Chem. Corp., U.S.A.), 7% on "Embacel" (a purified kieselguhr, 60–100 mesh, supplied by May and Baker Ltd., England), was used with a column temperature of 80°. For the analysis of the diols a packing of polyethylene glycol 400, 5% on "Embacel," was used with a column temperature of 115°. For the analysis of the short-chain alcohol fragments a 5% 3-m. polyethylene glycol column at 80° was used.

Infrared Analysis of the 3-4-Monol Mixture.—A "Vapour Fractometer" Model 154B, supplied by Perkin-Elmer Corp., Norwalk, Conn., U.S.A., was modified so that the outlet from the detector cell was connected directly to a collection trap, by means of a short, electrically heated (to prevent condensation of the monols) pipe ($\frac{3}{8}$ " diam.). The monol mixture (40–50 mg.) in heptane (200 mg.) was chromatographed at 130° on a column (4 mm. diam., 3 m. long), packed with 1:5-polyethylene glycol 400—"Celite" (100 mesh) and a nitrogen flow rate of 20 ml./min. A high proportion of liquid phase was used to avoid overloading. When the 3-4-monol peak was detected, the exit gases were bubbled through 5-methylnonane (25 mg.). The solution so obtained was transferred to a sodium chloride microcell (0.133 mm.), and the

thickness of a variable space cell filled with 5-methylnonane and adjusted to eliminate the 13.7 μ band due to the hydrocarbon. The optical densities of the mixtures at 12.9 and 13.46 μ were measured with a Perkin-Elmer Model 21 infrared spectrometer fitted with a sodium chloride prism, and were used to determine the 4- and 3-alcohol concentrations by differential analysis. The extinction coefficients of the two pure alcohols at these wavelengths were determined at various concentrations in 5-methylnonane. Results with artificial mixtures were:

Isomer	Mixture I		Mixture II		Mixture III	
	Calc. (%)	Found (%)	Calc. (%)	Found (%)	Calc. (%)	Found (%)
3-ol	42	40	48	46	35	34
4-ol	58	60	52	54	65	66

Conversion of the Diols into Monols.—The diol mixture (20 mg.) obtained by distillation and partition chromatography was shaken with concentrated hydrochloric acid for 20 min., then extracted with purified pentane. Evaporation of the dried (Na_2SO_4) extract yielded the chloro-alcohols, the infrared spectrum of which, compared with that of the diols, showed a decrease in the hydroxyl absorption at 3.0 μ and a new absorption at 13.3 μ due to the C-Cl stretching vibration.

Hydrogenation of the chloro-alcohols with 2% palladium-calcium carbonate (0.2 g.) in methanol (5 ml.) yielded monols, which did not show an absorption at 13.3 μ . On chromatography no diols were detected, but the 2,5-diol was lost when this procedure was used.

5-Methylnonane-5-ol.—This alcohol, prepared as described by Whitmore and Woodburn,¹⁶ had b. p. 103–104°/24 mm., n_D^{25} 1.4328 (Found: active H, 0.61. Calc. for $\text{C}_{10}\text{H}_{21}\text{OH}$: active H, 0.63%).

5-Methylnonane.—5-Methylnonane-5-ol (500 g.) was slowly distilled from iodine (0.1 g.) at atmospheric pressure. The distillate was dried (CaCl_2) and redistilled to yield 5-methylnonane, b. p. 155–156°/655 mm. (380 g.) (Found: I val., 180. Calc. for $\text{C}_{10}\text{H}_{20}$: I val., 180). Hydrogenation of 5-methylnonane, at 100°/150 lb./in.² in the presence of 2% palladium-calcium carbonate, and fractionation of the product (column "A"), yielded pure 5-methylnonane,¹⁷ b. p. 160°/655 mm., n_D^{21} 1.4122 [Found: C, 84.6; H, 15.5. Calc. for $\text{C}_{10}\text{H}_{22}$: C, 84.4; H, 15.6%; I val. (Wijs 1 hr.), <1]. The 5-methylnonane in oxidation experiments gave no reaction with ferrous thiocyanate, when tested qualitatively for peroxides.

5-Methylnonane-4-ol.—5-Methylnonane-4-ol, prepared from 2-methylhexanoyl chloride¹⁸ and propyl bromide by the modified Grignard reaction of Percival *et al.*,¹⁹ was reduced with lithium aluminium hydride. The product, after distillation (column "B") and chromatography on alumina from pentane, yielded pure 5-methylnonane-4-ol,²⁰ b. p. 197.8–198.0°/654 mm., n_D^{25} 1.4340, n_D^{30} 1.4320 (Found: C, 75.8; H, 13.9. Calc. for $\text{C}_{10}\text{H}_{22}\text{O}$: C, 75.9; H, 14.0%).

5-Methylnonane-3-ol.—5-Methylnonane-3-ol (b. p. 194–196°/655 mm.), prepared from 3-methylheptanoyl chloride²¹ and ethyl bromide, gave as above 5-methylnonane-3-ol, b. p. 197.5–197.6°/655 mm., n_D^{26} 1.4326, n_D^{30} 1.4312 (Found: C, 75.9; H, 13.7. $\text{C}_{10}\text{H}_{22}\text{O}$ requires C, 75.9; H, 14.0%).

5-Methylnonane-2-ol.—5-Methylnonane-2-ol, prepared similarly from 1-bromo-3-methylheptane²² and acetyl chloride, yielded similarly 5-methylnonane-2-ol, b. p. 202.0–202.1°/655 mm., n_D^{25} 1.4320, n_D^{30} 1.4312 (Found: C, 76.0; H, 14.5. $\text{C}_{10}\text{H}_{22}\text{O}$ requires C, 75.9; H, 14.0%).

5-Methylnonane-1-ol.—Methyl hydrogen succinate (66 g.; m. p. 58°), 3-methylheptanoic acid (21 g.), and sodium (0.35 g.), in methanol (300 c.c.), were electrolysed as described by Linstead *et al.*²¹ The product was distilled and the mixture, b. p. 132–142°/60 mm. (28.5 g.), of methyl 5-methylnonanoate and dimethyl adipate was reduced with lithium aluminium hydride. The ether layer, after addition of dilute acid, was washed with water to extract most of the hexane-1,6-diol. The ether extract was distilled and the fraction of b. p. 213.6–216°/654 mm. (2.2 g.) was chromatographed on alumina to yield 5,8-dimethyldodecane (0.9 g.,

¹⁶ Whitmore and Woodburn, *J. Amer. Chem. Soc.*, 1933, **55**, 361.

¹⁷ Calingaert and Soroos, *ibid.*, 1936, **58**, 636.

¹⁸ Levene and Mikeska, *J. Biol. Chem.*, 1929, **84**, 571.

¹⁹ Percival, Wagner, and Cook, *J. Amer. Chem. Soc.*, 1953, **75**, 3731.

²⁰ Powell and Nielsen, *ibid.*, 1948, **70**, 3627.

²¹ Linstead, Shepard, Weedon, and Lunt, *J.*, 1953, 1538.

²² Levene and Marker, *J. Biol. Chem.*, 1931, **91**, 93.

eluted with pentane) and 5-methylnonan-1-ol, n_D^{30} 1.4340 (0.6 g., eluted with ether) (Found: C, 76.1; H, 14.5. $C_{10}H_{22}O$ requires C, 75.9; H, 14.0%).

2-Butylhexan-1-ol.—2-Butylhexanoic acid, b. p. 160—162°/35 mm., n_D^{30} 1.4396, prepared as described by Levene and Cretcher,²³ was reduced with lithium aluminium hydride, and the product distilled (column "B") and chromatographed on alumina from pentane, to yield 2-butylhexan-1-ol, b. p. 209.4°/655 mm., n_D^{30} 1.4328 (Found: C, 75.7; H, 14.3. $C_{10}H_{22}O$ requires C, 75.9; H, 14.0%).

5-Methylnonane-2,5-diol.—5-Oxohexan-2-ol²⁴ (12 g.) was treated with the Grignard derivative of n-butyl bromide (25 g.); the crude diol (10 g.), after distillation and recrystallisation from hexane, afforded 5-methylnonane-2,5-diol, b. p. 93°/0.25 mm., m. p. 70° (Found: C, 69.0; H, 12.7. $C_{10}H_{22}O_2$ requires C, 68.9; H, 12.7%).

5-Methylnonane-3,5-diol.—5-Oxohexan-2-ol²⁵ (22 g.) with the Grignard derivative of n-butyl bromide (60 g.) gave a crude diol (18 g.) which on distillation and chromatography on alumina from pentane, afforded 5-methylnonane-3,5-diol, b. p. 77.5°/0.1 mm., n_D^{30} 1.4407 (Found: C, 68.7; H, 12.9. $C_{10}H_{22}O_2$ requires C, 68.9; H, 12.7%).

5-Methylnonane-4,5-diol.—5-Methylnonan-4-ene (7 g.) was hydroxylated, following the procedure of Swern *et al.*,²⁶ with hydrogen peroxide (4 g., 130-vol.) and 98—100% formic acid (51 c.c.) for 20 hr. at 40°. The product, distilled and chromatographed on alumina from pentane, afforded 5-methylnonane-4,5-diol, b. p. 86°/0.5 mm., n_D^{30} 1.4463 (Found: C, 68.7; H, 12.4%).

The authors are grateful to Dr. J. R. Nunn and Professor F. L. Warren for their interest, and Dr. V. Pretorius for assistance with the development of the flame detector.

NATIONAL CHEMICAL RESEARCH LABORATORY,
SOUTH AFRICAN COUNCIL FOR SCIENTIFIC AND INDUSTRIAL RESEARCH,
PRETORIA, S. AFRICA.

[Received, April 20th, 1959.]

²³ Levene and Cretcher, *ibid.*, 1918, **33**, 508.

²⁴ Adams and Vander Werf, *J. Amer. Chem. Soc.*, 1950, **72**, 4368.

²⁵ Bergman and Resnik, *J. Org. Chem.*, 1952, **71**, 1292.

²⁶ Swern, Billen, and Scanlan, *J. Amer. Chem. Soc.*, 1946, **68**, 1504.