reaction; hence the unsubstituted conjugated system is the only one which reacts.

5. The structure of Willgerodt's 2,4,5-trimethylphenylacetic acid was proved by two independent syntheses.

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[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE ETHYL GASOLINE CORPORATION]

The Methyl Nonanes

BY GEORGE CALINGAERT AND HAROLD SOROOS

In the course of a study on the correlation of the physical properties of the alkanes[1] it was found that considerable uncertainty exists regarding the properties of the alkanes above C_8 with one methyl group in the side chain. In order partly to fill this lacuna and also to enlarge the scope of usefulness of the correlation plot described in the above reference the four isomeric methylnonanes have been prepared and purified, and some of their physical properties have been determined.

Preparations

The conventional Grignard method of synthesis was used as before.[2] In the present work the carbinols were dehydrated and hydrogenated simultaneously by treatment with hydrogen under 200 atmospheres pressure at 250° in the presence of 4% of Raney nickel catalyst[3] in accordance with the procedure outlined by Adkins and Wojcik,[4] using the autoclave previously described.[5] Under the conditions applied, this reaction was observed to stop before completion, due, apparently, to the separation of water. In the case of 2-methylnonane, the reaction was interrupted at that point, which accounts for the low yield. In the other three cases, when hydrogen absorption ceased, the autoclave was cooled, the contents removed, and after separation of the water the partially hydrogenated material was hydrogenated further over a fresh batch of catalyst. The materials used, the products obtained, and the yields are listed in Table I.

The crude alkanes were treated with 98% sulfuric acid, washed, dried, refluxed over sodium–potassium alloy and finally fractionated carefully through a column packed with crushed carborundum. The final yields and the physical properties of the purified compounds are given in Table II, where the physical properties of *n*-decane are included for comparison.

Discussion

The physical properties of the 2- and 3-methyl isomers align themselves in relation to those of *n*-decane in accordance with the predictions based on the lower homologs of the series.[6]

No reliable information is available from the literature to make possible an accurate prediction of the physical properties of the 4- and 5-methyl isomers.[1] On the other hand, the values reported above for the density of 4- and 5-methylnonane are shown on the plot of reference.[1] They indicate that the data reported in the literature for 4-methylheptane[7] and 4-methyloctane[8] are probably inaccurate, and that the true values must lie close to 0.705 for 4-methylheptane and 0.721 for 4-methyloctane.

The data in Table II indicate that a shift of the methyl group from the 3-position toward the center of the molecule: (a) progressively lowers the boiling point, but with a decreasing increment, (b) decreases the index of refraction slightly, the increment becoming almost imperceptible after the 4-isomer, (c) decreases the density, except that the 5-methyl isomer shows a slight increase in density, probably caused by the increased symmetry of the molecule.

It is evident that as the length of the chain increases, the effect of the shift of a methyl group becomes less and less perceptible. Only those properties, such as melting point, which are affected by symmetry, still show sharp differences. It seems probable, therefore, that above C_{10} the identification of branched chain alkanes can no longer be based on the measurement of the common physical properties.

(1) George Calingaert and J. W. Hladky, THIS JOURNAL, **58**, 153 (1936).

(2) Graham Edgar, George Calingaert and R. E. Marker, *ibid.*, **51**, 1483 (1929).

(3) U. S. Patent 1,628,190 (1927).

(4) H. Adkins and B. Wojcik, *ibid.*, **55**, 1293 (1933).

(5) George Calingaert and F. J. Dykstra, *Ind. Eng. Chem., Anal. Ed.*, **6**, 383 (1934).

(6) Graham Edgar and George Calingaert, THIS JOURNAL, **51**, 1540 (1929); also ref. 1.

(7) d^{20}_4 0.7169, L. Clarke, *ibid.*, **33**, 520 (1911).

(8) d^{15}_{15} 0.7320, or d^{20}_4 0.7274, L. Clarke, *ibid.*, **34**, 683 (1912).

TABLE I

MATERIALS USED, PRODUCTS AND YIELDS

Bromide		Isopropyl	Ethyl	*n*-Propyl	*n*-Butyl
Moles used		8.8	11.0	8.8	17.25
Material		*n*-Heptaldehyde	Me-*n*-Hex	Me-*n*-Am ketones	EtOAc
Moles used		8.0	9.4	6.2	8.3
Intermediate products	( )-Methylnonanol-( )	2,3	3,3	4,4	5,5
	Yield, %	66	77	76	79
	B. p. (10 mm.), °C.	90–95	87–88	86–87	83–86
	$n^{20}D$	1.435	1.436	1.434	1.434
Final products	( )-Methylnonane	2	3	4	5
	Yield, %	29	83	89	82

TABLE II

PHYSICAL PROPERTIES OF THE METHYLNONANES

	Total amounts	M. p., °C.[9]	B. p., °C. (760 mm.)	d^{20}_4	$n^{20}D$	C. T. S. aniline, °C.
2-Methylnonane	221	− 74.69 ± 0.05	166.8	0.72805	1.4099	80.3
3-Methylnonane	855	− 84.86 ± .03[a]	167.8	.73335	1.1425	78.25
4-Methylnonane	573	−101.62 ± .05[a]	165.7	.73234	1.4123	78.3
5-Methylnonane	698	− 86.80 ± .03	165.1	.73255	1.4122	77.9
n-Decane	...	− 30.1[10]	174.1[11]	.73014[11]	1.41203[11]	77.5[11]

[a] The nature of the freezing and melting curves indicates the presence of more than one allotrope, including one other form of the 4-methyl isomer melting at −99.0 ±0.1°.

Samples of these compounds will be loaned upon request to laboratories interested in determining some of their properties.

(9) The authors wish to express their appreciation to Dr. J. D. White, of the American Petroleum Institute Research Project 6 at the National Bureau of Standards, for the melting point determinations.

(10) I. Simon, *Bull. soc. chim. Belg.*, **38**, 47 (1929).

(11) A. L. Henne, A. F. Shepard and T. Midgley, THIS JOURNAL, **53**, 1951 (1931).

Summary

The four isomeric methyl nonanes have been prepared and purified, and some of their physical properties have been determined. The influence of structure upon their physical properties is discussed.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

The Chemistry of the Lipids of Tubercle Bacilli. XLIV. Comparative Study of the Lipids of the Human Tubercle Bacillus[1]

BY J. A. CROWDER,[2] F. H. STODOLA,[3] M. C. PANGBORN[4] AND R. J. ANDERSON

Previous work in this Laboratory on the lipids of the human tubercle bacillus[5] was carried out on only one type of bacillus, namely, the old strain H-37, a strain which has been cultivated for many years on artificial media. Since it is possible that the organism might have undergone changes in metabolic activity and in virulence during its artificial cultivation, it seemed of importance to determine whether recently isolated bacilli when grown on the Long[6] synthetic medium would produce lipids possessing chemical and biological properties identical with those previously isolated from H-37. Accordingly the present investigation was started with the object of securing further information on this subject. Four different cultures of bacilli, recently isolated from human cases of tuberculosis, have been studied, while for comparison a freshly grown lot of H-37 was also examined, identical procedures being used throughout.

In many past investigations it has been shown that the age of the culture, the type of bacilli and

(1) An abstract of this paper was presented before the Division of Biological Chemistry at the meeting of the American Chemical Society, New York, April, 1935. The present report is a part of a coöperative investigation on tuberculosis; it has been supported partly by funds provided by the Research Committee of the National Tuberculosis Association.

(2) Holder of a National Tuberculosis Association Fellowship, Yale University, 1934–35.

(3) Holder of a National Tuberculosis Association Fellowship, Yale University, 1934–36.

(4) Holder of a National Tuberculosis Association Fellowship, Yale University, 1933–34.

(5) R. J. Anderson, *J. Biol. Chem.*, **74**, 525 (1927).

(6) E. R. Long, *Am. Rev. Tuberc.*, **13**, 393 (1926).