bundles, themselves 400 Å.; and the swelling pressure from a chiefly mechanical origin being 10^5 dynes/sq. cm. for 0.05 N sodium palmitate curd. Glycerol softens the curd whereas sodium chloride makes it more rigid.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF SOUTH CAROLINA]

Dialkyl Adipates

BY ROBERT A. FEAGAN, JR., AND J. E. COPENHAVER[1]

This work was carried out because of the growing commercial importance of the higher alcohols and adipic acid, as well as to study the type of melting point curve exhibited by the esters of this dibasic acid. This investigation covers the normal alkyl esters from pentyl to eicosyl. Since the first four have been described previously, they were not prepared in this series but for completeness they are included in the curve.

TABLE I

MELTING POINTS AND ANALYSES OF THE DIALKYL ADIPATES

Diester	M. p. (cor.), °C.	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
Methyl	8[a]	...	...	...	...
Ethyl	−21[b]	...	...	...	...
Propyl	−20.25[c]	...	...	...	...
Butyl	−37.5[c]	...	...	...	...
Pentyl	−14	67.10	66.07	10.56	10.08
Hexyl	−9 to −7	68.75	68.78	10.90	11.08
Heptyl	3.8–4.5	...	...	...	...
Octyl	9.5–9.8	71.31	70.77	11.43	11.56
Nonyl	21.6[d]	72.31	72.50	11.63	11.37
Decyl	27.4	73.19	74.22	11.88	12.02
Undecyl	34.7	73.96	74.57	11.97	11.56
Dodecyl	39.3	74.63	75.17	12.11	12.04
Tridecyl	45.9	75.24	75.33	12.24	12.14
Tetradecyl	49.4	75.78	75.52	12.35	12.55
Pentadecyl	55.0	76.27	76.36	12.45	12.27
Hexadecyl	57.3[e]	76.71	76.63	12.54	12.31
Heptadecyl	61.8	77.11	76.53	12.62	12.27
Octadecyl	63.4	77.48	76.49	12.69	12.08
Nonadecyl	66.7	...	...	...	...
Eicosyl	65.2	...	...	...	...

[a] Bouveault, *Bull. soc. chim.*, **29**, 1042 (1920); M. van Rysselberge, *Bull. soc. acad. roy. Belg.*, [5] 11, 171–192 (1926).

[b] Timmermans, *Bull. soc. chim. Belg.*, **36**, 502–518 (1927), gave m. p. −21°, while H. Serwy, *Bull. soc. chim.*, **42**, 482–501 (1933), gave −19.9°.

[c] Timmermans, *Bull. soc. chim. Belg.*, **36**, 502 (1927).

[d] Staudinger and Schwalenstöcker, *Ber.*, **68**, 745 (1935), gave m. p. 17–18.5°.

[e] Staudinger and Schwalenstöcker, *ibid.*, gave the m. p. of 53°.

The esters up to and including dinonyl were colorless liquids at room temperature and above that compound they were white waxy solids. The melting points are given in Table I and plotted in Fig. 1. The alternation between the esters of the even and odd carbon alcohols was very slight, the odd esters exhibiting the unusual property of being a little above the mean curve. It will be noted that there is an even number of carbon atoms in all of these compounds.

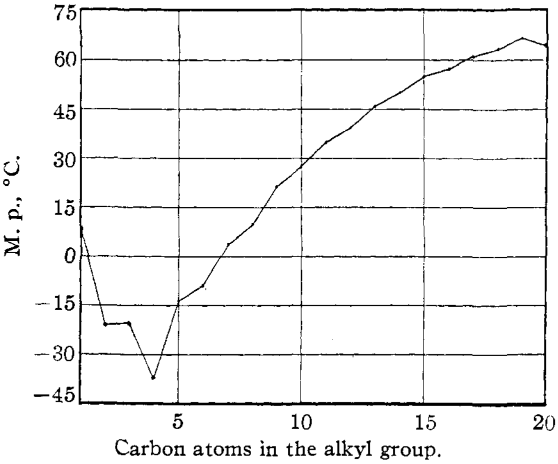

Fig. 1.—Melting points of the dialkyl adipates.

Experimental

Two methods were used for their preparation, *viz.*, the action of the alcohols on the acid or on adipyl chloride. In several cases, both methods were used and the products checked. A slight excess of the acid or the acid chloride was used above the theoretical quantity necessary for the formation of the diester. When adipic acid was used, the reaction mixture was heated at 150–155° for several hours, whereas with adipyl chloride, only slight warming was necessary.

The crude product from either method was dissolved in ether and thoroughly washed with 10% sodium carbonate. The recovered ester was recrystallized from

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[1] Presented in part before the Organic Division of the American Chemical Society at its 97th meeting, Baltimore, Maryland, April, 1939.

acetone, in which the higher derivatives were almost insoluble, while the corresponding alcohols were very soluble. Cooling with dry-ice was necessary to remove from solution the esters below tetradecyl.

The melting points were taken, with mechanical stirring, in a 200-cc. bulb, fitted with a side-arm for the thermometer and melting point tube. Standard Anschütz thermometers were used so the melting points may be regarded as corrected.

This problem was suggested by Dr. E. Emmet Reid, Research Adviser, University of South Carolina, and to him the authors wish to express their appreciation for his valuable help. The alcohols from decyl to octadecyl were furnished by Dr. Reid and were from those prepared by Meyer and Reid.[2] Thanks also are due E. I. du Pont de Nemours and Company for furnishing the adipic acid.

Summary

The diesters of adipic acid from *n*-pentyl to *n*-eicosyl alcohols were prepared and the melting points determined. The melting points show slight alternation, the esters of the odd carbon alcohols being slightly higher than the even on the mean curve.

(2) Meyer and Reid, THIS JOURNAL, **55**, 1574–84 (1933).

COLUMBIA, SOUTH CAROLINA RECEIVED FEBRUARY 7, 1940

[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY, YALE UNIVERSITY, AND THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

The Synthesis of 5-Methylchrysene and Related Compounds

BY MELVIN S. NEWMAN[1,2]

In a previous publication,[3] the author pointed out the desirability of synthesizing methyl derivatives of chrysene and described a new synthesis by which chrysene and 6-alkylchrysenes could be prepared readily. In order to explore the generality of this method for the preparation of various chrysene derivatives desired for biological testing in connection with the cancer problem, further work has been done. In this paper, the syntheses of 5-methylchrysene, 5-ethylchrysene and 5,6-dimethylchrysene are described, together with a new and more generally applicable procedure for the preparation of α,γ-diphenylbutyric acid, an important intermediate.

The α,γ-diphenylbutyric acid previously[3] used was prepared in five steps, of which the first was the condensation of benzaldehyde with acetophenone. The second step involved 1,4-addition of hydrogen cyanide to the chalcone thus produced. It was feared that in certain projected syntheses, the corresponding chalcones (bearing alkyl groups on the α-carbon) might prove difficult to prepare or purify and also that conditions for the addition of hydrogen cyanide might be difficult to find.[4] In the present work α,γ-diphenylbutyric acid was prepared by the alkylation of benzyl cyanide with phenethyl bromide using sodium amide.[5] The α,γ-diphenylbutyronitrile thus produced was hydrolyzed to the corresponding acid in excellent yield. Inasmuch as a variety of substituted phenethyl bromides and of substituted benzyl cyanides is easily prepared, the new approach is seen to be quite general.

The cyclization of the acid chloride of α,γ-diphenylbutyric acid by aluminum chloride was further improved (94% yield) by decreasing the time of reaction.[3] It was also determined that if the volatile phosphorus compounds formed when the acid was treated with phosphorus pentachloride were not removed prior to the treatment with aluminum chloride, the yield was decreased to 77%. The remaining steps in the synthesis are indicated in the chart.

The Reformatsky condensations of 1,2,3,4-tetrahydro-1-keto-2-phenylnaphthalene, I, with ethyl α-bromopropionate and ethyl α-bromobutyrate proceeded smoothly and the corresponding unsaturated acids, II (R = CH_3 and C_2H_5), were isolated in fair yields. The double bond is placed in the ring instead of the alternate position of conjugation with the carboxyl group as in the analogous case of 3,4-dihydro-2-phenyl-1-naphthaleneacetic acid.[3] It is interesting to note that from the neutral fraction of the reaction products (after dehydration and hydrolysis) con-

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(1) Part of the work herein reported was aided by a grant from the Jane Coffin Childs Memorial Fund for Medical Research, Yale University.

(2) Elizabeth Clay Howald Scholar at The Ohio State University, 1939–1940.

(3) Newman, THIS JOURNAL, **60**, 2947 (1938).

(4) Michael and Weiner, *ibid.*, **59**, 744 (1937), cite no instance of the addition of hydrogen cyanide to unsaturated ketones containing an alkyl group on the α-carbon.

(5) See Bergstrom and Fernelius, *Chem. Rev.*, **12** 138 (1933), and **20**, 455 (1937), for reviews of the use of sodium amide in alkylation studies.