was added dropwise over one-half hour at a temperature under 5°. The yellow ether layer was carefully separated and washed with dilute sodium carbonate solution and finally with water. The aqueous solution was extracted with two 100-ml. ether portions which were washed with sodium carbonate solution and water. The combined ether extracts were allowed to stand at 7° over anhydrous sodium sulfate for one hour with occasional shaking, then over fresh sodium sulfate for three hours at 0–5°. A second drying with Drierite did not appreciably increase the final yield while lengthening of the drying time decreased the yield. A small amount of the ether solution was evaporated on a watch glass leaving the triazide (XVII) as a clear oil which could not be crystallized. This oil exploded violently when touched to a hot-plate (300°) and decomposed rapidly without explosion at 90–100°. The dried ether solution of XVII was added to 200 ml. of freshly prepared absolute ethanol and the ether was removed on the steam-bath. The ethanol solution was refluxed until all nitrogen evolution ceased (6 hours). After decolorizing with Norit, and reducing the volume of the ethanol solution to 100 ml., an equal amount of water was added and the solution was allowed to stand overnight at 0–5°. Lower temperatures caused oiling of the product. The yield was 4.1 g., m.p. 150–153°. Further evaporation and cooling of the mother liquor gave an additional 2.0 g. Approximately 6.0 g. of a thick, clear sirup was recovered from the mother liquor from which additional small amounts of carbamate crystallized over a long period. The yield of crude, sirupy material was 34% (17.5% of carbamate melting at 150–153°). Recrystallization of the latter from ethanol–water gave white needles melting at 160–162°. This material did not decolorize bromine in carbon tetrachloride or potassium permanganate solution.

Anal. Calcd. for $C_{12}H_{21}N_3O_6$: C, 47.52; H, 6.98; N, 13.98. Found: C, 47.45; H, 6.98; N, 13.86.

trans-**1,2,3-Tribenzamidocyclopropane (XX)**.—Ethyl *trans*-1,2,3-cyclopropanetricarbamate (1.0 g., 0.0033 mole) was hydrolyzed with concentrated hydrochloric acid for 8 hours. After decolorizing, the aqueous solution was extracted with ether, then evaporated to dryness. Approximately 0.3 g. (40–50%) of the crude triamine hydrochloride (XIX) melting at 185–195° with considerable decomposition, was obtained. This material could be recrystallized from ethyl acetate and ethereal hydrogen chloride (m.p. 190–195° (dec.)) but analyses were unsatisfactory. To a sample of the material (0.2 g.) in 2.0 ml. of 20% sodium hydroxide solution was added excess benzoyl chloride. The white flocculent solid (0.3 g., 75%) was recrystallized five times from 95% ethanol. The melting point was 288–290°.

Anal. Calcd. for $C_{24}H_{21}N_3O_3$: C, 72.13; H, 5.30; N, 10.52. Found: C, 71.85; H, 5.25; N, 10.59, 10.51.

CHARLOTTESVILLE, VA.

[CONTRIBUTION FROM THE PIONEERING RESEARCH LABORATORIES, U. S. ARMY QUARTERMASTER CORPS]

Physical Constants and Infrared Spectra of a Homologous Series of Dialkyl Sebacates

BY WILLIAM H. STAHL AND HELMUT PESSEN

RECEIVED MAY 5, 1952

The 18 diesters of sebacic acid with normal alcohols from methyl to octadecyl were prepared. Melting points, densities and refractive indices are given and the characteristics of the infrared absorption spectra are briefly discussed.

The compounds representing the homologous series of di-*n*-alkyl sebacates (dialkyl decanedioates) were synthesized primarily for use as substrates for the growth of certain bacteria and fungi as part of a study of the microbiological degradation of plasticizers.[1] Available data on these esters are scant; with the exception of di-*n*-octyl sebacate,[2] no physical constants for the esters above di-*n*-propyl sebacate appear in the literature. Although the first three members of the series have been described before, they are included here for the sake of completeness.

Experimental

Tridecyl, pentadecyl, hexadecyl, heptadecyl and octadecyl alcohols[3] were generously donated by Dr. E. Emmett Reid of Johns Hopkins University; nonyl alcohol was furnished by Dodge and Olcott, New York, with a specification of 98% purity, $n^{20}\text{D}$ 1.4340; tetradecanol was donated by Armour and Co., with a specification of 99% purity, m.p. 37.7°; hexyl alcohol was redistilled Eastman Kodak Co. technical grade, using the fraction boiling between 155–156°; all other alcohols were Eastman "white label" grade; methyl, ethyl and propyl were redistilled and all others used without further purification.

The sebacates were prepared by esterification of sebacic acid (Eastman "white label," recrystallized three times, m.p. 133.5°), with the appropriate alcohol in the presence of *p*-toluenesulfonic acid as catalyst. The crude product was dissolved in ether and thoroughly washed with 10% sodium bicarbonate. Those esters up to di-*n*-nonyl inclusive were distilled *in vacuo*, while the higher ones were further purified by repeated crystallization from acetone until successive crops showed constant melting point. A further purification of all products was achieved by chromatographing them as ether solutions through a column packed with freshly activated adsorbents. For adsorption of acidic impurities, anhydrous alumina was used; for alcohols, silica gel; and for color and odor, fuller's earth. The liquid esters were finally subjected to a high vacuum for several hours to remove any remaining traces of solvent. All resulting products showed an acid number < 0.05.

Melting points of the esters up to di-*n*-nonyl inclusive were taken by freezing in a test-tube containing a narrow range thermometer, stirring constantly upon partial melting, and noting the melting point at the disappearance of the last crystal. Melting points of the esters above di-*n*-nonyl were taken by means of a calibrated Kofler micro hot-stage melting-point apparatus.

Results and Discussion

The esters up to and including di-*n*-nonyl sebacate at room temperature were colorless liquids of relatively low viscosity and with boiling points above 290°. The higher esters were white waxy crystalline solids.

Melting points and carbon–hydrogen analyses for the eighteen sebacates are listed in Table I. It is pertinent to point out that if these melting points are plotted as a function of carbon atoms in the alkyl radical, the curve is comparable to one obtained for the corresponding adipates (hexanedioates) by Feagan and Copenhaver,[4] which exhibited a definite alternation in melting point values between odd and even alkyls. In the present case the same general phenomenon is noticeable, particularly above C_{11}. A curve of the values for odd-

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[1] W. H. Stahl and H. Pessen, *Applied Microbiology*, in press.

[2] J. T. Davies, *Trans. Faraday Soc.*, **44**, 909 (1948).

[3] J. D. Meyer and E. E. Reid, THIS JOURNAL, **55**, 1574 (1933).

[4] R. A. Feagan and J. E. Copenhaver, *ibid.*, **62**, 869 (1940).

Table I

Melting Points and Analyses of the Dialkyl Sebacates

Diester	M.p. (cor.), °C.	Carbon, % Theor.	Carbon, % Found	Hydrogen, % Theor.	Hydrogen, % Found
Methyl	23.8	62.65	...	9.64	...
Ethyl	+1.5	65.08	...	10.15	...
Propyl	0.0	67.09	...	10.56	...
Butyl	−9.2	68.75	68.84	10.90	11.22
Pentyl	−3.0	70.18	69.86	11.19	11.18
Hexyl	+1.2	71.30	71.17	11.42	11.60
Heptyl	18.4	72.31	72.29	11.63	11.56
Octyl	18.6	73.19	73.06	11.81	11.86
Nonyl	26.2	73.96	74.08	11.97	11.91
Decyl	31.5	74.63	74.74	12.11	12.40
Undecyl	45.2	75.24	75.50	12.23	12.31
Dodecyl	49.1	75.78	75.70	12.34	12.55
Tridecyl	53.2	76.27	76.50	12.44	12.34
Tetradecyl	53.5	76.71	76.97	12.53	12.75
Pentadecyl	59.1	77.11	77.43	12.62	12.89
Hexadecyl	60.0	77.48	77.42	12.69	12.71
Heptadecyl	65.0	77.81	77.89	12.76	12.93
Octadecyl	66.3	78.12	78.21	12.82	12.97

carbon alkyls is slightly above that for even ones; this behavior is analogous to that of esters of monocarboxylic acids[5] but is opposite to that of alcohols[3] and free monocarboxylic and dicarboxylic acids.[6]

Densities, refractive indices and molar refractions for those esters which are liquid near room temperature (*i.e.*, up to nonyl) are listed in Table II.

Table II

Density and Refractive Index of Certain Dialkyl Sebacates

Diester	d^{25}_4 [a]	n^{25}_D (Abbe) [b]	Mol. refr.[c] Theor.	Mol. refr.[c] Found
Methyl	0.9883	1.4368	60.92	61.02
Ethyl	.9590	1.4348	70.15	70.27
Propyl	.9451	1.4374	79.39	79.45
Butyl	.9321	1.4397	88.63	88.91
Pentyl	.9266	1.4426	97.86	97.92
Hexyl	.9183	1.4445	107.10	107.29
Heptyl	.9126	1.4460	116.33	116.48
Octyl	.9074	1.4480	125.57	125.87
Nonyl	.9040	1.4492	134.81	134.92

[a] Δd^{25}_4 per degree = −0.0004. [b] Δn_D per degree = −0.0004. [c] "Physical Methods of Organic Chemistry," A. Weissberger, ed., Interscience Publishers, Inc., New York, N. Y., 1945, p. 673.

Infrared spectrograms for the eighteen esters were obtained; those for C_1, C_5 and C_{18} alkyl esters are reproduced in Fig. 1. Except for some differences among the initial members of the series, the spectra appear conspicuously similar, all having absorption bands of nearly equal intensity at the same wave lengths. Among the most outstanding of these are the following, with indicated assignments based on published frequency charts[7-10]: a strong, narrow doublet at 3.44 and 3.52 μ (methylene stretching), another strong, narrow band at 5.77 (aliphatic ester carbonyl stretching), bands at 6.94 and 7.31 μ (methylene and methyl bending), a group of bands or inflections at 7.60, 8.00, 8.50, 8.90 and 9.12 μ (methylene twisting; ether linkage), and a weaker but distinctive band at 13.82 μ (apparently indicative of continuous chains of four or more carbon atoms due to methylene wagging[11,12] observed in particular for dicarboxylic acids above C_7[13]).

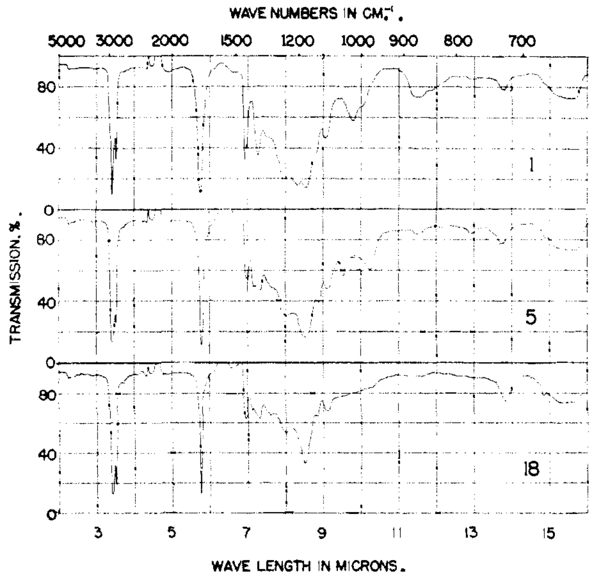

Fig. 1.—Infrared spectra of dimethyl, di-(*n*-pentyl) and di-(*n*-octadecyl) sebacates. Baird spectrograph with NaCl prism; 10.10% (C_1), 10.34% (C_5), 8.80% (C_{18}) in carbon disulfide solution; cell thickness, 0.1 mm.

It is of interest to note that when the total number of alkyl carbons begins to exceed the number in the acid chain (*i.e.*, beyond the dipentyl ester) the bands in the 9 to 12 μ region begin to become similar and remain so for all the higher homologs. The reason for this may be that the shorter alkyl chains are subject to special coupling effects which at first differ in character from one member of the series to the next, as evidenced by markedly different additional vibrations. Once the alkyl chains have reached a certain length these effects might be expected to remain constant and any further changes in the spectrum to be due solely to the effect of subsequent methylene groups attached to the chain at a point relatively far removed from the ester linkage.

By way of comparison with esters of monocarboxylic acids it may be pointed out that, although the molecules here dealt with are all symmetric, no special symmetry effects[7] should be expected since the acid carbon chain separating the two alkyl portions of the molecule is so long (C_{10}) that the alkyl chains vibrate virtually independently of each other.

The homologous series exhibits a small but defi-

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(5) J. H. Hoback, *et al.*, This Journal, **65**, 1606 (1943).

(6) L. F. Fieser and M. Fieser, "Organic Chemistry," D. C. Heath and Co., Boston, Mass., 1950, pp. 302, 409

(7) H. M. Randall, R. G. Fowler, N. Fuson and J. R. Dangl, "Infrared Determination of Organic Structures," D. Van Nostrand Co., Inc., New York, N. Y., 1949, pp. 17, 20 ff., 40 ff., 46 ff.

(8) W. H. Thompson and P. Tarkington, *J. Chem. Soc.*, 640 (1945).

(9) R. B. Barnes, R. C. Gore, R. W. Stafford and V. Z. Williams, *Anal. Chem.*, **20**, 402 (1948).

(10) H. W. Thompson, *J. Chem. Soc.*, 328 (1948).

(11) C. Schaefer and F. Matossi, "Das Ultrarote Spektrum," Julius Springer, Berlin, 1930, p. 268.

(12) O. D. Shreve, M. R. Heether, H. B. Knight and Daniel Swern, *Anal. Chem.*, **22**, 1948 (1950).

(13) J. Lecomte, *Compt. rend.*, **211**, 776 (1940).

nite progression in intensities of certain bands. As the alkyl chain length increases from 1 to 18 carbons, the intensity of the entire group of bands from 6.94 to 9.12 μ decreases from, *e.g.*, 46% transmission at 9.12 μ to 68%. This suggests a possible aid in the identification of the alkyl radical of an unknown sebacate by comparison of its % transmission under specified conditions at selected wave lengths with values taken from prepared plots of % transmission *vs.* number of skeletal carbon atoms at corresponding wave lengths.

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Philadelphia, Penna.

[Contribution from the Basic Sciences Research Department, U. S. Naval Civil Engineering Research and Evaluation Laboratory]

The Mechanism of the Reaction of Aniline with Furfural in the Presence of Acid[1]

By William M. Foley, Jr., Guy E. Sanford and Herbert McKennis, Jr.

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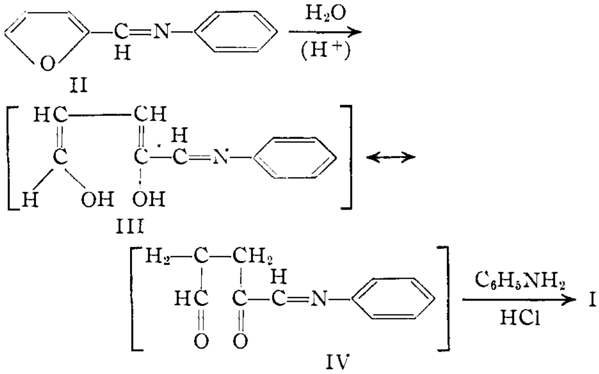
A study has been made of the Stenhouse reaction in which aniline and furfural react in the presence of acid to form a deep purple compound, the corresponding acid salt of 1-phenylimino-5-phenylamino-2-hydroxypenta-2,4-diene. Evidence is presented to show that the intermediation of water is not necessary for the reaction. A mechanism involving a 1,6-addition of the acid component to an anil followed by attack of aniline to give the resultant diene is proposed.

Stenhouse[2] observed that aniline, aniline hydrochloride and furfural react in alcohol to form a deep purple compound. Zincke and Mulhausen[3] found that the latter can be converted to 3-hydroxy-N-phenylpyridinium salts and suggested structure I[4] for the original condensation compound.

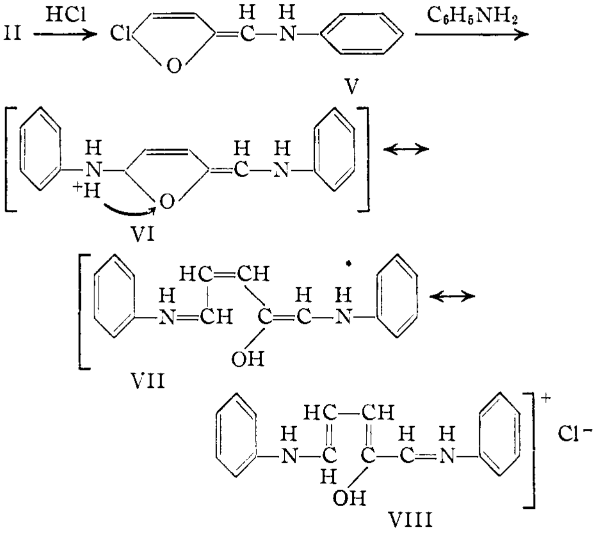
Ar·NH·CH:CH·CH:C(OH)·CH:N·Ar.HCl
I

An examination of structure I and the work of Pummerer and co-workers[5] on cleavages of furfuryl alcohol suggests in a general sense a mechanism which involves the intermediation of water:



Aniline and furfural react to form the furfural anil, II, which could then be hydrolytically cleaved to yield a 1,4-diol, III, which is tautomeric with the 1,4-dial, IV. Reaction of the hypothetical intermediate IV with aniline hydrochloride could then lead to the condensation compound, I.

Since no previous workers had reported success or failure in preparing I under anhydrous conditions, an alternate mechanism in which the anil II reacts directly with hydrogen chloride and then with aniline could not be excluded from consideration. In the reactions shown below, hydrogen chloride adds 1,6 to the anil II. The intermediate V, which bears an allylic chloride, is represented as reacting with aniline to form an intermediate salt VI. A subsequent proton transfer to the ring oxygen and ring cleavage results in the formation of the resonance structures, VII and VIII. The final product as represented by VII and VIII affords a more convenient picture of some of the resonance possibilities than does the classical formula employed by Zincke and others. The hypothetical intermediate V, in addition, offers a possible explanation for the decomposition observed when the anil of furfural is treated with a catalytic amount of hydrogen chloride.



To test the possibility of the mechanism II–VIII, both aniline hydrochloride and the anil of furfural were prepared in anhydrous condition and mixed in the presence of anhydrous solvent. The immedi-

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[1] Presented before the Division of Organic Chemistry, American Chemical Society, 121st Meeting, Buffalo, N. Y., March, 1952.

[2] J. Stenhouse, *Ann.*, **156**, 197 (1870).

[3] T. H. Zincke and G. Mulhausen, *Ber.*, **38**, 3824 (1905).

[4] A previous paper, R. W. Drisko and H. McKennis, Jr., This Journal, **74**, 2626 (1952), cites other references.

[5] R. Pummerer and W. Gump, *Ber.*, **56**, 999 (1923); R. Pummerer, O. Guyot and L. Birkofer, *ibid.*, **68**, 480 (1935).