dilute solutions were involved, the usual drop in yield expected because of the dilution effect became apparent.

Effect of Variation of Alkyl Component of Ester.—This variable was studied by heating the methyl, ethyl, propyl, isopropyl, isobutyl and *t*-butyl esters of durenecarboxylic acid with amine in methanol. Blank experiments in which the amine was omitted were also carried out. The results are summarized in Table I. It can be seen that the esters fall in the order to be expected if the similarity to the Menschutkin reaction is recalled.[17] With the *t*-butyl and isobutyl esters pyrolysis (independent of amine influence) is the main reaction. In no case was the recovered ester contaminated with methyl ester.

Salt Effect.—Duplicate experiments at 140° for 5 hours, except for the addition to one of 0.002 g. and to the other of 0.2 g. (1.50×10^{-3} mole) of the hydrochloride of N-methylpiperidine to the usual charge of methyl ester (2.0×10^{-3} mole), amine (4.0×10^{-3} mole), and methanol (4 cc.) indicated that there was little if any effect on the yield of durenecarboxylic acid produced by the added salt and no noticeable trend.

TABLE I

REACTIONS OF ALKYL DURENECARBOXYLATES WITH N-METHYLPIPERIDINE IN METHANOL (2.0×10^{-3} MOLE, 4.0×10^{-3} MOLE AMINE, 4 CC. OF METHANOL)

$(CH_3)_4C_6HCOOR$ R =	Ester reacted in 25 hours, % At 140°	160°	180°
Methyl	81(0)[a]		
Ethyl	6	8(0)	14(0)
Propyl	1	3(0)	6(0)
Isopropyl	0	0	0(0)
Isobutyl	Trace	3(3)	6(6)
t-Butyl	59(59)	89(86)	

[a] The figures in parentheses represent % ester reacted when amine was omitted.

When experiments were conducted with added sodium methoxide, it was observed that the added methoxide ion produced durenecarboxylic acid in the absence of amine, undoubtedly with the formation of dimethyl ether, as

$$C_{10}H_{13}COOCH_3 + NaOCH_3 \longrightarrow C_{10}H_{13}COONa + CH_3OCH_3 \quad (4)$$

We made no attempt to confirm this in view of the fact that such a reaction has been well established.[18] When both amine and methoxide were added, the amount of acid produced was just about that to be expected from the independent reactions. No catalytic effect was noticed.

Equilibrium Studies.—The low conversions of methyl durenecarboxylate to acid by heating with *t*-amine in solvents such as benzene, dioxane, acetone and nitrobenzene might be a result of the effect of solvent on the position of equilibrium or on the rate of approach to equilibrium (5).

$$C_5H_{10}NCH_3 + C_{10}H_{13}COOCH_3 \rightleftarrows (C_{10}H_{13}COO^-)(C_5H_{10}N(CH_3)_2)^+ \quad (5)$$

Accordingly separate experiments involving the heating of equimolar amounts of reactants on the one hand and product on the other in methanol, dioxane and nitrobenzene at 140° for 280 hours were performed. In methanol, a true equilibrium was at hand in which the salt greatly predominated, the amounts of isolated materials in both cases being 4% of ester and 88% of salt (estimated by acidification and weighing of durenecarboxylic acid). In dioxane: when starting with amine and ester, 90% of ester was recovered and no acid at all; starting with quaternary salt 89% of ester and 6% of salt were isolated. Thus the point of equilibrium in dioxane is far on the ester side. In nitrobenzene: when starting with amine and ester, 70% of ester and no acid were obtained; starting with quaternary salt, 70% of ester and 11% of acid were obtained. Thus the point of equilibrium is far on the ester side in nitrobenzene. The material balance in this solvent was poor because of the formation of a fair amount of discolored decomposition products undoubtedly arising from interaction with the solvent.

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[17] E. D. Hughes and C. K. Ingold, *J. Chem. Soc.*, 250 (1935), found for the reactions of alkyl iodides and trimethylamine in alcohol the following relative rates: methyl, 100; ethyl, 8.8; propyl, 1.7; isopropyl, 0.2.

[18] J. F. Bunnett, M. M. Robinson and F. C. Pennington, THIS JOURNAL, **72**, 2378 (1950), and references therein.

NOTES

The Boiling Point of Alkane Diols as an Additive Property

BY H. J. BERNSTEIN

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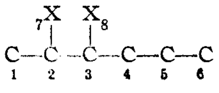
It has been shown[1-4] that the non-bonded interactions will account for the additive properties of the isomeric alkanes. It is of interest therefore to investigate whether non-bonded interactions will also account for the additive properties in the straight chain and branched alkane diols in which there is considerable hydrogen bonding.

A convenient way of taking non-bonded interactions into account so as to distinguish between the isomeric diols is to consider interactions which are two and three bonds apart only. Further, let us assume that the hydroxyl groups may be considered as single particles which we shall call X. We define the contribution to the additive property from interaction between a carbon atom and X which are two and three bonds apart as p_{cx_2} and p_{cx_3}, respectively; the contribution from interaction between two carbon atoms which are two and three bonds apart as p_{cc_2} and p_{cc_3}, respectively; and that due to X with X three bonds apart as p_{xx_3}.

The additive molecular property under consideration may be written as

$$P = A + a_{cx_2}p_{cx_2} + a_{cx_3}p_{cx_3} + a_{cc_2}p_{cc_2} + a_{cc_3}p_{cc_3} + a_{xx_3}p_{xx_3} \quad (1)$$

where *A* is a constant for all molecules and the coefficients *a* are determined for each molecule by inspection of its graphic formula. For example in 2,3-hexanediol shown in the figure there are four



$$\begin{array}{cccccc} & {}_7X & X_8 & & & \\ & | & | & & & \\ C- & C- & C- & C- & C- & C \\ 1 & 2 & 3 & 4 & 5 & 6 \end{array}$$

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[1] W. J. Taylor, J. M. Pignocco and F. D. Rossini, *J. Research Bur. Standards*, **34**, 413 (1945).

[2] H. Wiener, *J. Chem. Phys.*, **15**, 766 (1947); THIS JOURNAL, **69**, 17, 2636 (1947).

[3] J. R. Platt, *J. Chem. Phys.*, **15**, 419 (1947).

[4] H. J. Bernstein, *ibid.*, **19**, 140 (1951); **20**, 263 (1952).

contributions from C with X which are two bonds apart namely $C_1 \ldots X_7$, $C_3 \ldots X_7$, $C_2 \ldots X_8$ and $C_4 \ldots X_8$. There are four contributions from C with C which are two bonds apart, namely $C_1 \ldots C_3$, $C_2 \ldots C_4$, $C_3 \ldots C_5$ and $C_4 \ldots C_6$. There are three contributions from C with C which are three bonds apart, namely $C_1 \ldots C_4$, $C_2 \ldots C_5$ and $C_3 \ldots C_6$. There are three contributions from C with X which are three bonds apart, namely $C_2 \ldots X_8$, $C_4 \ldots X_7$, and $C_5 \ldots X_8$; and there is one contribution from X with X which are three bonds apart, namely $X_7 \ldots X_8$.

TABLE I

THE BOILING POINTS OF THE ALKANE DIOLS CALCULATED WITH $A = 252$, $p_{cx_2} = 19$, $p_{cx_3} = -1$, $p_{cc_2} = 5$, $p_{cc_3} = 6$ and $p_{xx_3} = -16$

Diols	Coefficients of the interactions cx₂	cx₃	cc₂	cc₃	xx₃	B.p., °C. Calcd.	Obsd.
1,2-Propane	3	1	1	0	1	183	186[a]
1,3-Propane	2	2	1	0	0	217	214[a]
1,2-Butane	3	2	2	1	1	193	191[a]
1,3-Butane	3	2	2	1	0	209	207[a]
1,4-Butane	2	2	2	1	0	228	228[a]
2,3-Butane	4	2	2	1	0	190	184[b]
2-Me-1,2-propane	4	3	3	0	1	172	
2-Me-1,3-propane	2	4	3	0	0	225	
1,2-Pentane	3	2	3	2	1	204	206[a]
1,3-Pentane	3	3	3	2	0	219	
1,4-Pentane	3	2	3	2	0	220	
1,5-Pentane	2	2	3	2	0	239	238[a]
2,3-Pentane	4	3	3	2	1	184	187[b]
2,4-Pentane	4	2	3	2	0	201	199[a]
2-Me-1,2-butane	3	3	4	2	1	208	206[b]
2-Me-1,3-butane	4	2	4	2	0	206	204[b]
2-Me-1,4-butane	2	3	4	2	0	243	
2-Me-2,3-butane	5	3	4	2	1	170	177[b]
1,2-Hexane	3	2	4	3	1	215	
1,3-Hexane	3	3	4	3	0	230	
1,4-Hexane	3	3	4	3	0	230	
1,5-Hexane	3	2	4	3	0	231	
1,6-Hexane	2	2	4	3	0	250	250[b]
2,3-Hexane	4	3	4	3	1	195	207[b]
2,4-Hexane	4	3	4	3	0	211	
2,5-Hexane	4	2	4	3	0	212	221[c]
3,4-Hexane	4	4	4	3	1	194	
2-Me-1,2-pentanediol	4	3	5	3	1	200	
2-Me-1,3-pentanediol	3	5	5	3	0	233	
2-Me-1,4-pentanediol	3	3	5	3	0	235	
2-Me-1,5-pentanediol	2	3	5	3	0	254	
2-Me-2,3-pentanediol	5	4	5	3	1	180	
2-Me-2,4-pentanediol	5	2	5	3	0	198	197[b]
2-Me-3,4-pentanediol	4	3	5	3	1	200	
3-Me-1,2-pentanediol	3	3	5	4	1	225	
3-Me-1,3-pentanediol	4	3	5	4	0	222	
3-Me-1,4-pentanediol	3	3	5	4	0	241	
3-Me-1,5-pentanediol	2	2	5	4	0	263	
3-Me-2,3-pentanediol	5	4	5	4	1	186	
3-Me-2,4-pentanediol	4	4	5	4	0	221	
2,3-diMe-1,2-butanediol	4	4	6	3	1	204	
2,3-diMe-1,3-butanediol	4	4	6	3	0	220	
2,3-diMe-1,4-butanediol	2	4	6	3	0	258	
2,3-diMe-2,3-butanediol	6	4	6	3	1	170	173[b]
Miscellaneous diols							
1,7-Heptanediol	2	2	5	4	0	261	259[b]
3-Et-1,3-hexanediol	4	4	7	7	0	249	244[b]
3,4-diEt-3,4-hexanediol	6	8	10	12	1	236	230[b]

[a] K. A. Clendening, F. J. Macdonald and D. E. Wright, *Can. J. Research*, B28, 608 (1950). [b] "Handbook of Chemistry and Physics," Chemical Rubber Publishing Co., Cleveland, Ohio. [c] "Higher Diols," Carbide and Carbon Chemicals, Ltd., N. Y., 1951.

In Table I, the properties of these diols are expressed in terms of *A* (according to equation (1)) and the coefficients of the interactions, thus

$$P_{2,3\text{-hexanediol}} = A + 4p_{cx_2} + 3p_{cx_3} + 4p_{cc_2} + 3p_{cc_3} + p_{xx_3}$$

The boiling points of these diols have been calculated from the coefficients and are given in column 7 of the table. The values of *A* and the *p*'s have been obtained by a best fit to all of the 21 observed boiling points and are listed in the caption to the table. The agreement between the calculated and observed boiling points is reasonably good and it seems that the boiling point may be calculated with an average deviation from the mean of ±4° and a maximum deviation of 12°.

The formulas of the table do not give satisfactory results when used to calculate the molecular volumes and refractivities (both at 20°). A simple additive scheme, however, in which only contributions from bonds or atoms are considered, can be used with fair accuracy for these properties. It is not surprising that these formulas do not yield calculated results in good agreement with the data for molar refraction and volume since the percentage error in the boiling point calculation (about 2%) is practically the whole extent of the isomeric effect for molar volume (about 2%) and greater than the whole isomeric effect for molar refraction (< 1%).

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Reactions of Aliphatic Nitro Compounds. Michael Condensations with Ethyl Nitroacetate[1]

BY ROBERT NEILSON BOYD AND RICHARD LESHIN

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In connection with other work, we had occasion to treat ethyl nitroacetate with acrylonitrile and with ethyl acrylate. Michael-type condensations took place, giving two new compounds, ethyl α-nitro-γ-cyanobutyrate and ethyl α-nitroglutarate. Both compounds gave the blue color characteristic of secondary nitro compounds in the Victor Meyer test.

Ethyl α-Nitro-γ-cyanobutyrate.—A solution of 6.6 g. (0.05 mole) of ethyl nitroacetate in 20 ml. of absolute alcohol was cooled to 10° and 5 ml. of 20% alcoholic KOH was added. With the temperature being kept below 10°, a solution of 2.7 g. (0.05 mole) of acrylonitrile in 10 ml. of absolute alcohol was added dropwise with stirring. The mixture was then allowed to come to room temperature and it was stirred for one hour. The reaction was stopped by cooling the mixture and adding concd. H_2SO_4 until the solution was acid to congo red. The precipitated K_2SO_4 was filtered off, and the filtrate was distilled under reduced pressure. Ethyl α-nitro-γ-cyanobutyrate distilled as an orange-yellow oil at 130° at 1 mm. pressure; yield 1.8 g. (19% based on starting material). This was redistilled and it gave a nearly color-

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[1] Based on a portion of the dissertation submitted by Richard Leshin to the Department of Chemistry, New York University, February, 1952, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.