

contributions from C with X which are two bonds apart namely $C_1 \dots X_7$, $C_3 \dots X_7$, $C_2 \dots X_8$ and $C_4 \dots X_8$. There are four contributions from C with C which are two bonds apart, namely $C_1 \dots C_3$, $C_2 \dots C_4$, $C_3 \dots C_5$ and $C_4 \dots C_6$. There are three contributions from C with C which are three bonds apart, namely $C_1 \dots C_4$, $C_2 \dots C_5$ and $C_3 \dots C_6$.

TABLE I

THE BOILING POINTS OF THE ALKANE DIOLS CALCULATED WITH $A = 252$, $p_{cx_2} = 19$, $p_{cx_1} = -1$, $p_{cc_2} = 5$, $p_{cc_1} = 6$ and $p_{xx_2} = -16$

| Diols | Coefficients of the interactions | | | | | B.p., °C. | |
|-------------------------|----------------------------------|--------|--------|--------|--------|-----------|------------------|
| | cx_2 | cx_1 | cc_2 | cc_1 | xx_1 | 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 ^a |
| 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. Clendenning, 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.

There are three contributions from C with X which are three bonds apart, namely $C_2 \dots X_8$, $C_4 \dots X_7$, and $C_5 \dots X_8$; and there is one contribution from X with X which are three bonds apart, namely $X_7 \dots X_8$.

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

$$P_{2,3\text{-hexanediol}} = A + 4p_{cx_2} + 3p_{cx_1} + 4p_{cc_1} + 3p_{cc_2} + p_{xx_1}$$

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 $\pm 4^\circ$ 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 Nitroacetate¹

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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-

(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.

less oil; b.p. 135° (4 mm.), n_D^{20} 1.4514. *Anal.* Calcd. for $C_7H_{10}O_4N_2$: C, 45.16; H, 5.43; N, 15.05. Found: C, 45.21; H, 5.65; N, 15.31 (by the Micro-Chemical Laboratory of New York University).

Ethyl α -Nitroglutarate.—A solution of 1.15 g. (0.05 g. atom) of sodium in 75 ml. of *t*-butyl alcohol was added to a solution of 6.6 g. (0.05 mole) of ethyl nitroacetate and 5.5 g. (0.055 mole) of ethyl acrylate in 40 ml. of *t*-butyl alcohol. The mixture was refluxed for 90 minutes with stirring, and then was stirred overnight at room temperature, after which it was made acid to congo red with hydrochloric acid and most of the solvent was removed with the aid of an aspirator. The remaining solution was poured into four volumes of water and extracted by ether. The ether extract was washed twice with water, dried over anhydrous $MgSO_4$, and distilled. After a considerable amount of unreacted ethyl nitroacetate was distilled at 67° (3 mm.), ethyl α -nitroglutarate was obtained as a colorless oil, b.p. 128–129° (4 mm.), n_D^{20} 1.4410, yield 1.3 g. (11% based on starting material). *Anal.* Calcd. for $C_9H_{16}O_6N_2$: C, 46.35; H, 6.48; N, 6.01. Found: C, 46.47; H, 5.94; N, 6.09 (by the Micro-Chemical Laboratory of New York University).

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2,3-Dimethoxytriphenylmethane and Some of its Derivatives

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During the investigation of the structure of the lactone resulting from the addition of diphenylketene to *o*-benzoquinone there were prepared 2,3-dimethoxytriphenylcarbinol and the new 2,3-dimethoxytriphenylchloromethane.¹ We now wish to report the preparation of 2,3-dimethoxytriphenylmethane and several other compounds of this series, none of which have been previously described.

The synthesis of 2,3-dimethoxytriphenylmethane was accomplished by formic acid reduction of the corresponding carbinol. Methyl 2,3-dimethoxytriphenylmethyl ether was obtained by treating the same carbinol with methanolic sulfuric acid. 2,3-Dimethoxytriphenylacetone nitrile was prepared by heating 2,3-dimethoxytriphenylchloromethane with mercuric cyanide. Hydrolysis of the nitrile did not yield the corresponding 2,3-dimethoxytriphenylacetic acid,¹ a product obtained previously by the carbonation of 2,3-dimethoxytriphenylmethylsodium. Instead, it gave 2,3-dihydroxytriphenylacetic acid lactone.¹ Conventional methods used for the hydrolysis of nitriles had no effect, and when more vigorous methods were used, cleavage of the methoxyl groups as well as hydrolysis of the nitrile occurred to yield the lactone.

Experimental²

2,3-Dimethoxytriphenylmethane.—One gram of 2,3-dimethoxytriphenylcarbinol was boiled for 3.5 hours with 10 ml. of 88% formic acid.³ After standing several days, the oily product solidified; it was then pulverized, washed thoroughly with water and dried to give 0.88 g. of crude material, which, when crystallized three times from alcohol, yielded glistening white rhombs, m.p. 84.5–85°.

Anal. Calcd. for $C_{21}H_{20}O_2$: C, 82.86; H, 6.62. Found: C, 82.68; H, 6.76.

Methyl 2,3-Dimethoxytriphenylmethyl Ether.—One gram of 2,3-dimethoxytriphenylcarbinol was dissolved in 10 ml.

of boiling methanol; the solution was cooled, three drops of concentrated sulfuric acid was added, and the mixture warmed on the steam-bath for 20–30 minutes. When the solvent was removed by evaporation and the oily product was cooled, 0.96 g. of crude methyl ether separated. After three crystallizations from methanol, there were obtained glistening white hexagonal tablets, m.p. 119.5–120°.

Anal. Calcd. for $C_{22}H_{22}O_3$: C, 79.01; H, 6.63. Found: C, 79.00; H, 6.72.

2,3-Dimethoxytriphenylacetone nitrile.—Into a 500-ml. round-bottomed flask, fitted with an air condenser and calcium chloride drying tube, were placed 20.0 g. (0.059 mole) of 2,3-dimethoxytriphenylchloromethane¹ and 18.8 g. (0.073 mole) of mercuric cyanide.⁴ The mixture was heated at 150–170° for 1.5 hours in an oil-bath, then cooled, and the solid melt powdered and extracted with boiling benzene. The benzene solution was filtered, treated with low-boiling petroleum ether to precipitate oily impurities, and the filtered solution cooled. Upon standing, 4.5 g. (23%) of the crude nitrile crystallized. Recrystallization of the material from a small amount of glacial acetic acid (charcoal) yielded 2.3 g. of colorless leaflets, m.p. 157.5–158°.

Anal. Calcd. for $C_{22}H_{19}O_2N$: C, 80.21; H, 5.81; N, 4.25. Found: C, 79.51; H, 5.79; N, 4.13.

Simultaneous hydrolysis and demethylation of the nitrile was accomplished by boiling 120 mg. of the compound for 34 hours in a solution composed of 2 ml. of hydriodic acid (sp. gr. 1.70) and 5 ml. of glacial acetic acid. The cooled solution was treated with sufficient saturated sodium bisulfite solution to remove free iodine, and the fine white precipitate was collected, washed with a little water, and dried. There was thus obtained 110 mg. of 2,3-dihydroxytriphenylacetic acid lactone, m.p. 192.5–193°. After two crystallizations from a mixture of benzene and petroleum ether, the melting point was raised to 192.5–193.5°.

(4) E. Fischer and O. Fischer, *Ann.*, **194**, 260 (1878).

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5-Nitro-2-thenaldehyde

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In previous reports from this Laboratory we have enumerated several variously substituted 2-thenaldehydes which have been prepared by means of the one-step *N*-methylformanilide synthesis.¹ However, due to the failure of 2-nitrothiophene to form its corresponding aldehyde under the conditions of the reaction, it has been missing from our listing. With the advent of the synthesis of chloromycetin and its various aromatic and heterocyclic analogs,² the absence of this aldehyde has become more noticeable. With this in mind, we have attempted to prepare 5-nitro-2-thenaldehyde by another series of reactions.

Starting with 2-methyl-5-nitrothiophene³ we have converted it to 5-nitro-2-thenyl bromide using *N*-bromosuccinimide in the presence of benzoyl peroxide. Since the 2-methyl-5-nitrothiophene is relatively inactive toward this reagent, at least two to three hours of reflux were necessary before there was a noticeable reaction. A maximum of 24 hours was required for the completion of the reaction. The 5-nitro-2-thenyl bromide was characterized by

(1) W. J. King and F. F. Nord, *J. Org. Chem.*, **13**, 635 (1948).

(2) L. M. Long and H. D. Troutman, *THIS JOURNAL*, **71**, 2469 (1949); **71**, 2473 (1949); H. Keskin, C. D. Mason and F. F. Nord, *J. Org. Chem.*, **16**, 1333 (1951).

(3) I. J. Riukes, *Rec. trav. chim.*, **51**, 1134 (1932).

(1) J. L. E. Erickson and J. M. Dechary, *THIS JOURNAL*, **74**, 2644 (1952).

(2) All melting points are uncorrected.

(3) H. Kauffmann and P. Pannwitz, *Ber.*, **45**, 766 (1912).