

# New Compounds: Symmetrically Substituted Tetraalkyl Methanes

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**Abstract** □ The syntheses of tetrakis(3-hydroxypropyl)methane, tetrakis(3-bromopropyl)methane, tetrakis(3-cyanopropyl)methane, and tetrakis(3-carboxypropyl)methane are described. An abnormal conversion of tetrakis(β-bromoethyl)methane to tris(β-iodoethyl)-β-bromoethylmethane is discussed.

**Keyphrases** □ Tetraalkyl methanes, symmetrically substituted—synthesis □ Tetrakis(3-hydroxypropyl)methane, tetrakis(3-bromopropyl)methane, tetrakis(3-cyanopropyl)methane, and tetrakis(3-carboxypropyl)methane—synthesis

During an investigation on polyquaternary salts, it was of interest to prepare and study the reactions of some symmetrically substituted tetraalkyl methanes. An examination of the literature (1) shows that there are only a few examples of these relatively simple compounds, mainly derivatives of pentaerythritol and compounds such as I. This series has been extended to the next higher homologs, II.

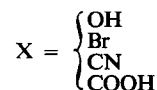
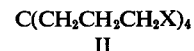
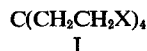
The synthetic route proceeded by the reduction of I (X = COOC<sub>2</sub>H<sub>5</sub>) to the corresponding tetraol (II, X = OH), which was then converted to the tetrabromide (II, X = Br). Exchange of the tetrabromide by tetranitrile (II, X = CN) followed by hydrolysis gave methane tetrabutyrac acid (II, X = COOH).

An interesting observation was made in the attempted preparation of the corresponding tetraiodo compound from I (X = Br). By refluxing the tetrabromide with an excess of sodium iodide for various periods of time, only three bromine atoms were replaced. This is in contrast with pentaerythritol tetrabromide, which readily gave the tetraiodo compound (2). Attempts to convert the pentaerythritol tetrabromide to the tetranitrile have been unsuccessful over several years. However, the conversion of I (X = Br) to the tetranitrile proceeds in almost quantitative yield. In addition, the exchange of bromide in I (X = Br) for triethylamine at 90° for 24 hr. yielded only starting bromide.

## EXPERIMENTAL<sup>1</sup>

**Tetrakis(3-hydroxypropyl)methane (II, X = OH)**—A solution of 10 g. (0.024 mole) of tetrakis(β-carboethoxyethyl)methane (1) in 100 ml. of ether was added dropwise to a solution of 10 g. of lithium aluminum hydride dissolved in 1 l. of ether, and the mixture was stirred for 24 hr. at room temperature. After decomposition of

<sup>1</sup> Microanalyses were performed by the Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. All melting points were obtained with a Thomas-Hoover capillary-type melting-point apparatus and are corrected. All compounds corresponded in structure to their IR spectra.



the reaction mixture with 40 ml. of water and filtering, the filter cake was extracted three times with boiling absolute alcohol. All filtrates were combined and evaporated. The solid, 4.2 g. (70.4%), when recrystallized from absolute alcohol and then from a methanol-ether mixture, gave m.p. 164–165°. An additional crystallization from water did not change the melting point.

*Anal.*—Calc. for C<sub>13</sub>H<sub>28</sub>O<sub>4</sub>: C, 62.87; H, 11.36. Found: C, 62.71; H, 11.35.

**Tetrakis(3-bromopropyl)methane (II, X = Br)**—To a mixture of the above polyol, 4.1 g. (0.0165 mole), and 100 ml. of 48% HBr was slowly added, with cooling, 50 ml. of sulfuric acid. The solution was heated on a steam bath overnight, diluted with water, and filtered, 8 g. (97%), m.p. 72–74°. The crude product was recrystallized from ethyl acetate-petroleum ether, m.p. 73–74°.

*Anal.*—Calc. for C<sub>13</sub>H<sub>24</sub>Br<sub>4</sub>: C, 31.23; H, 4.84; Br, 63.93. Found: C, 31.23; H, 4.72; Br, 63.75.

**Tetrakis(3-cyanopropyl)methane (II, X = CN)**—A mixture of 7 g. (0.014 mole) of the tetrabromide, 150 ml. of acetonitrile, 20 ml. of water, and 15 g. of potassium cyanide was refluxed for 8 hr. The reaction mixture was separated from a small amount of salt layer and stripped of solvent. The residue was recrystallized from ethanol-acetonitrile, 3.7 g. (93%), m.p. 169–170°.

*Anal.*—Calc. for C<sub>17</sub>H<sub>24</sub>N<sub>4</sub>: C, 71.79; H, 8.51; N, 19.70. Found: C, 72.02; H, 8.45; N, 19.58.

**Tetrakis(3-carboxypropyl)methane (II, X = COOH)**—The tetranitrile, 3.5 g. (0.0123 mole), was hydrolyzed with 130 ml. of concentrated HCl. As the reaction proceeded, the solution became clear; after continued refluxing, the product precipitated. After 8 hr. the solid was filtered, 3.5 g. (79%), and recrystallized from ethanol (500 ml.), m.p. 241–242°.

*Anal.*—Calc. for C<sub>17</sub>H<sub>28</sub>O<sub>8</sub>: C, 56.66; H, 7.83. Found: C, 56.82; H, 8.05.

**Tris(β-iodoethyl)-β-bromoethylmethane**—A solution of 6 g. (0.0132 mole) of tetrakis(β-bromoethyl)methane dissolved in 600 ml. of acetonitrile was treated at reflux with 12 g. of sodium iodide dissolved in a minimal amount of water. The mixture was refluxed for 4 hr., filtered hot, diluted with 200 ml. of water, and allowed to crystallize. The crude product, 6.4 g. (82.9%), was twice recrystallized from ethyl acetate, m.p. 214–216°.

*Anal.*—Calc. for C<sub>9</sub>H<sub>18</sub>BrI<sub>3</sub>: C, 18.05; H, 2.75; Br, 13.68; I, 65.09. Found: C, 18.35; H, 2.82; Br, 13.57; I, 65.41.

## REFERENCES

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