

This assignment agrees with the relative retention time of the isomer (A), as the *trans* isomers usually have longer retention time than *cis* isomers. The structural relationship of the *cis-trans* pair and related isomers of seven-membered ring phosphonates, are investigated further.

Experimental. 2-Ethoxy-6-methyl-2-oxo-1,2-oxaphospha-cycloheptane (I), and 4-methyl-4-pentene-diethoxy phosphonate (II). Triethylphosphite (50 g) and 2-methyl-1,5-dibromopentane (20 g) were kept with stirring for 7 h at 200°C. The ethyl bromide was continuously distilled off, and the remaining reaction mixture fractionated *in vacuo* in a heated jacket column to give 6.0 g (39 %) of I and 2.8 g (20 %) of II. The esters have the following specifications:

I: b.p.₁₀ 134°, n_D^{20} : 1.4590 (Found: C 49.89; H 8.85; Calc. for C₈H₁₇O₃P: C 50.02; H 8.86.)
 II: b.p.₁₀ 130°, n_D^{20} : 1.4425 (Found: C 54.28; H 9.47. Calc. for C₁₀H₂₁O₃P: C 54.55; H 9.54.)

The isomers (A) and (B) were separated by means of an Aerograph Autoprep A-700 gas chromatograph. GLC purity of the isomers was above 99 %.

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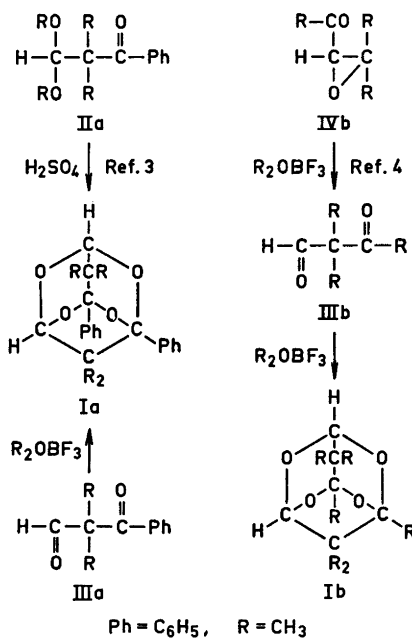
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Some 2,4,6,8-Tetraoxadamantanes

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Unlike their phospho¹ and thia analogues (IS),² 2,4,6,8-tetraoxadamantanes (I) seem to be unknown, except for the compound Ia, obtained from the acetal IIa by treatment with 80 % sulphuric acid.³



The (co)dimerization of several β -dicarbonyl compounds to I in the presence of boron fluoride-dimethyl ether (BD) or zinc chloride-acetic acid was discovered during the synthesis of IS. The structures of I were proved like those of IS. The observed GLC * retentions, PMR chemical shifts and fragmentation on electron impact accorded perfectly with those extrapolated from the corresponding data for IS, although the high oxygen contents

* Unless stated otherwise, the abbreviations and symbols in Ref. 2 are used.

strongly reduced the intensity of the parent peak in the mass spectra. Owing to the extremely low yields, most I obtained from β -diketones have so far been characterized only by GLC-mass spectrometry. By contrast, the dimerizations of the aldehydes IIIa and IIIb were apparently quantitative, invalidating the assumption that IIa but not IIIa may yield Ia.³ As expected from the reported rearrangement of the oxirane IVb to IIIb in the presence of boron fluoride-diethyl ether,⁴ Ib could also be prepared from IVb in one step.

Experimental details are given below for representative I. A full paper on the synthesis of I and the comparison between the physical properties of I and IS is planned in *Arkiv Kemi*.

Instrumental. The melting points were determined in sealed tubes and are corrected. The PMR spectra were recorded on a Varian HA-60 I spectrometer at 56.444 MHz and the mass spectra on an LKB 9000 gas chromatograph-mass spectrometer at 15 eV.⁵ If the GLC inlet system was not used (3% "SE-30" at 100–130° and 60 ml He/min), the ion source was kept at 130°. For each significant peak, assignment, *m/e*, and relative intensity are given in that order.

DL-9,9,10,10-Tetramethyl-1,3-diphenyl-2,4,6,8-tetraoxaadamanthane (Ia). Two drops of BD were added to 1.00 g of IIIa.⁶ The solution warmed to 40–50°, then cooled slowly and crystallized. After 30 min, the yellowish product was recrystallized from methanol. Yield 750 mg (75%), m.p. 157–158° (lit.³ 158.5°). The PMR and mass spectral data accorded well with those reported.³

DL-1,3,9,9,10,10-Hexamethyl-2,4,6,8-tetraoxaadamanthane (Ib) was prepared as Ia but from IIIb⁷ or IVb.⁸ In the latter case, the BD was highly diluted with ether and added gradually to keep the temperature below 40°. Yield from IIIb 80%, m.p. 78–79°. PMR spectrum in CCl₄: 9,9,10,10-R₄ 1.04s and 1.07s (broadened by mutual long range coupling),⁹ 1,3-R₂ 1.17s, 5,7-H₂ 4.58s. Mass spectrum: RCO⁺, 43, 13; $\frac{1}{2}$ M—CH₂CO, 72, 76; $\frac{1}{2}$ M—CO, 86, 48; $\frac{1}{2}$ M, 114, 100; P, 157, 1; M, 228, 1. (Found: C 63.0; H 8.8. Calc. for C₁₂H₂₀O₄: C 63.1; H 8.8).

1,3,5,7-Tetramethyl-2,4,6,8-tetraoxaadamanthane (Ic). 10 g of anhydrous zinc chloride, then

20 g of 2,4-pentanedione (IIIc) were dissolved in 50 ml of glacial acetic acid. After 48 h, 200 ml of water was added and the mixture extracted with 200 ml of cyclohexane. The extract was washed thoroughly with aqueous sodium carbonate, then with water, and the solvent removed by rotary evaporation below 40°. The residue was recrystallized from a few ml of petroleum ether (b.p. 40–60°; cooling to –20°). Yield 100 mg (0.5%), m.p. 152–153°. A similar result was obtained with BD as catalyst. PMR spectrum in CCl₄: 1,3,5,7-R₄ 1.36s, 9,9,10,10-H₄ 1.72 s. Mass spectrum: RCO⁺, 43, 45; $\frac{1}{2}$ M + H, 101, 100; P, 143, 70; M, 200, 5. (Found: C 59.7; H 8.1. Calc. for C₁₂H₂₀O₄: C 60.0; H 8.1).

1,3,5,7,9-Pentamethyl-2,4,6,8-tetraoxaadamanthane was obtained as Ic but from equimolar amounts of IIIc and 3-methyl-2,4-pentanedione.¹⁰ It was analyzed by GLC-mass spectrometry without isolation: RCO⁺, 43, 52; $\frac{1}{2}$ M—CH₂CO, 72, 75; $\frac{1}{2}$ M + H, 101 and 115, 33 and 100; P, 143 and 157, 6 and 36; M, 214, 3.

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