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Synthesis and Structure of B-Carboranylphosphonates

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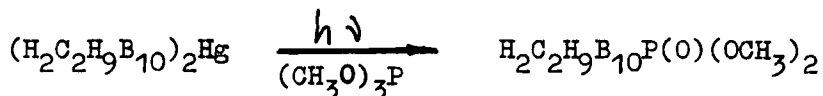
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Synthesis and Structure of B-Carboranylphosphonates

V.I.Bregadze*, V.Ts.Kampel, E.I.Matrosov, V.A.Antonovich, A.I.Yanovsky, Yu.T.Struchkov, N.N.Godovikov, M.I.Kabachnik. A.N.Nesmeyanov Institute of Organo-Element Compounds, USSR Academy of Sciences, Vavilov St. 28, Moscow, USSR.

Photolysis of bis(m-carboran-9-yl)mercury and bis(p-carboran-2-yl)mercury in trimethylphosphite leads to the formation of dimethyl ethers of (m-carboran-9-yl)- and (p-carboran-2-yl)-phosphonic acids:



The presence of phosphorus-boron bond in B-carboranylphosphonates prepared was confirmed by ^{11}B and ^{31}P NMR spectra. The structure of these compounds was confirmed by IR-spectra. The comparison of spectra of the solid samples with the ones in CCl_4 shows the high frequency shift of ν_{CH} ($\Delta \nu_{\text{CH}} = 15-75 \text{ cm}^{-1}$) and ν_{PO} ($\Delta \nu_{\text{PO}} = 20-35 \text{ cm}^{-1}$) bands. This may indicate the formation of hydrogen bond $\text{CH}\dots\text{OP}$ of one CH carborane bond and phosphoryl group in crystal. The existence of hydrogen bond $\text{CH}\dots\text{OP}$ in a crystal was confirmed by X-ray study of p-isomer. This hydrogen bond is responsible for the formation of centre symmetric dimeric associates. σ^{Φ} -Constants of B-carboranyl groups were estimated on the basis of $\Delta \nu_{\text{OH}}$ dependence on $\sum \sigma^{\Phi}$ of H-complexes of p-fluorophenols with phosphoryl compounds. σ^{Φ} -Constants of 2-p- $\text{H}_2\text{C}_2\text{H}_9\text{B}_{10}$ -group and of 9-m- $\text{H}_2\text{C}_2\text{H}_9\text{B}_{10}$ -group were found to be -1,68 and -1,81 respectively.