

BRIEF COMMUNICATIONS

TRANSFORMATIONS OF DIETHYL PHOSPHITE IN THE PRESENCE OF

$Mn_2(CO)_{10}$

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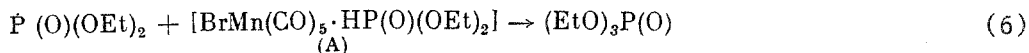
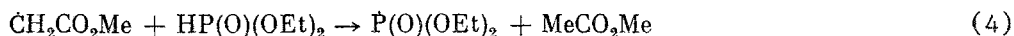
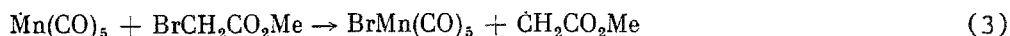
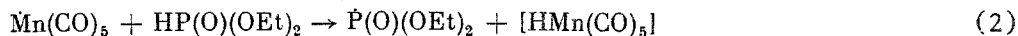
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Upon heating with $Mn_2(CO)_{10}$ -BrR systems, diethyl phosphite is partially converted to $(EtO)_3P(O)$. Evidence is given for a radical complex mechanism for these transformations.

In a study of the radical telomerization of hexene-1 by diethyl phosphite (DEP) initiated by $Mn_2(CO)_{10}$ a new pathway was revealed for the transformation of DEP, which holds independent interest and is the subject of the present work.

Heating DEP in the presence of $Mn_2(CO)_{10}$ gave slight amounts of $EtP(O)(OEt)_2$ and $(EtO)_3P(O)$ (Table 1, No. 2). Carrying out this reaction upon the addition of EtBr led to a greater yield of $(EtO)_3P(O)$ (Table 1, No. 4). This indicates a significant difference of this reaction from the Michaelis-Bekker reaction, which is carried out in the presence of alkali metals and leads to phosphonates [1, 2].

The addition of C_4H_9Br , $BrCH_2CO_2Me$ (MBA), and bromide enhance the yield of $(EtO)_3P(O)$ (Table 1, Nos. 5-9). Of the bromides studied, MBA proved most efficient (Table 1, Nos. 6-9). A study of the products of the transformation of MBA showed $MeCO_2Me$ and $(MeO_2CCH_2)_2$, which indicates the possibility of the intermediate formation of $\dot{C}H_2CO_2Me$ radicals. This reaction proceeds by a radical mechanism as follows [3-6]:



(A)
+ products

In accord with this scheme, the $Mn_2(CO)_{10}$ -BrR system should initiate the telomerization of 1-hexene by DEP by analogy to peroxides, that is, (in contrast to $Mn_2(CO)_{10}$ [5]) without an induction period or thermal aftereffect and with an identical telomer distribution in both cases. This proposal was supported experimentally (Nos. 11 and 12).

The role of the bromide in accelerating the formation of phosphate may be related, in particular, with the significant difference in the rates of reactions (2), (3), and (4). In other words, the rate of formation of $\dot{P}(O)(OEt)_2$ radicals in steps (3) and (4) may be greater than in step (2). The formation of phosphate in step (6) probably proceeds with the participation of complexes such as (A), analogous to those reported by Nifant'ev [7].

EXPERIMENTAL

The 1H and ^{13}C NMR spectra were taken on a Bruker WP-200 spectrometer with CCl_4 as the internal standard using the DEPT mode. The gas-liquid chromatographic analysis was carried out on an LKhM-80 chromatograph in a helium stream using a katharometer with temperature programming from 35 to 270°C (6°C/min) on 1) a 3000 × 3-mm column packed with 20% SKTFT-50 on Chromosorb (0.16-0.20 mm) and 2) a 2000 × 3-mm column packed with 15% Carbowax on Chromaton N-AW (0.16-0.20 mm). Preparative gas-liquid chromatographic analysis was carried out on a

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TABLE 1. Reaction of DEP (3.9 mmoles) with $Mn_2(CO)_{10}$ (4 mole % relative to DEP) in the Presence of Bromine Compounds at 140°C over 1 h

No.	Conversion of DEP, K, %	Bromine compound, mole % relative to DEP (conversion, %)	Identified reaction products			
			EtP(O)(OEt) ₂	(EtO) ₃ P(O)	MeCO ₂ Me	(CH ₂ CO ₂ Me) ₂
			% relative to DEP consumed	% relative to starting MBA		
1*	—	—	Traces	—	—	—
2**	—	—	Traces	—	—	—
3***	—	EtBr, 20	Traces	—	—	—
4	45	EtBr, 20	1	8	—	—
5	55	BuBr, 20	1	7	—	—
6	25	MBA, 1 (100)	1	5	70	1
7	50	MBA, 4 (100)	1	11	87	2
8	20	MBA, 10 (65)	2	23	65	3
9	50	MBA, 20 (60)	2	24	59	3
10	30	Br, 1	1	7	—	—

*3.9 mmoles DEP, 1 mole % TBP (relative to DEP), K = 1-2%.

**K = 1-2%.

***In the absence of $Mn_2(CO)_{10}$, K = 1-2%.

Tsvet chromatograph at 160°C on a 1700 × 9-mm column packed with 15% SKTFT-50 on Chromaton N-AW (0.20-0.25 mm). The weight content of the reaction products was calculated relative to the peak areas using methyl caproate and dimethyl malonate as standards and by internal normalization with the introduction of corrections. The products were identified by gas-liquid chromatography using authentic samples of EtP(O)(OEt)₂ [8], (EtO)₃P(O) [9], and C₆H₁₃P(O)(OEt)₂ [5].

Experimental Technique. The amounts of the starting reagents indicated in Table 1 were placed in ~3-cm³ glass ampuls. The reaction mixture was purified to remove traces of air by the freeze-thaw method. The ampuls were filled with argon, sealed, placed in metal casings, and heated with stirring at 140°C for 1 h by rotation in a silicon oil bath at about 8 rpm. Each experiment was carried out at least twice to monitor the reproducibility of the results.

Reaction of DEP with $Mn_2(CO)_{10}$. Experiments 1-10 were carried out as described above. The reagent charges, reaction conditions, and results are given in Table 1. The unreacted starting reagents were distilled off. The residue was separated into fractions, from which preparative gas-liquid chromatography gave EtP(O)(OEt)₂ and (EtO)₃P(O). PMR spectrum of EtP(O)(OEt)₂ (δ, ppm): 1.3 t (6H), 4.6 m (4H), 1.6 q (2H), 1.1 t (3H). PMR spectrum of (EtO)₃P(O) (δ, ppm): 1.9 q (9H), 4.5 m (6H). ¹³C NMR spectrum (δ, ppm): 16.1 (Me), 62.6 (CH₂) [10].

Telomerization of 1-Hexene by DEP in the Presence of $Mn_2(CO)_{10}$ and MBA. Experiments 11 and 12 were carried out by the above technique with the following reagent ratios: 4 mole % $Mn_2(CO)_{10}$, 10 mole % MBA, 1-hexene/DEP = 1 (experiment 11) and 5 (experiment 12). Gas-liquid chromatographic analysis data for telomer mixtures (EtO)₂P(O)(CH₂CHC₄H₉)_nH(T_n) (mole % relative to the sum of T_n, n = 1-3): experiment 11: T₁ = 81, T₂ = 17, T₃ = 2, ΣT_n = 40 wt. %; experiment 12: T₁ = 50, T₂ = 38, T₃ = 12, ΣT_n = 25 wt. %.

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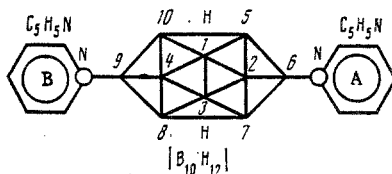
STRUCTURES OF TWO MODIFICATIONS OF 6,9-BIS-PYRIDINE-NIDO-DECABORANE(12)

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An x-ray diffraction structural analysis showed the molecular and crystal structures of two modifications of 6,9-bis-pyridine-nido-decaborane(12). The orientation of the pyridine rings relative to the $|B_{10}H_{12}|$ unit proposed by Graybill and Hawthorne [1] was not confirmed for the crystalline states of $B_{10}H_{12}(C_5H_5N)_2$.

In previous work [2], we studied the physicochemical properties of 6,9-bis-pyridine-nido-decaborane(12), $B_{10}H_{12}(C_5H_5N)_2$ and noted two crystalline modifications for this compound. Recrystallization from hot DMF gives mostly lemon-yellow crystals of the nonsolvated compound (modification (I)). Orange crystals were also obtained in 0.1% yield with the same composition but differing in IR spectral details and density (modification (II)). Structural data have not been published for $B_{10}H_{12}(C_5H_5N)_2$, but this molecule has been represented by the following topological scheme:



This compound is interesting because it combines aromatic pyridine rings with a borane nido cluster $|B_{10}H_{12}|$, which also has aromatic nature. On the basis of a qualitative MO examination in our previous work [1], we proposed a structure for $B_{10}H_{12}(C_5H_5N)_2$, in which the pyridine rings lie in a single plane passing through boron atoms 2, 4, 6, and 9 of the $|B_{10}H_{12}|$ cluster. The finding of two modifications of this compound suggested that this structure may not be realized in the crystal since rotation of the pyridine rings about the B-N bonds is possible.

In the present work, we established the structures of the $B_{10}H_{12}(C_5H_5N)_2$ molecules in crystalline modifications (I) and (II) by x-ray diffraction structural analysis.

The unit cell parameters for (I) are as follows: $a = 7.791(1)$, $b = 14.109(2)$, $c = 15.694(4)$ Å, $\beta = 107.20(2)^\circ$, $V = 1648.0(5)$ Å³, $M = 278.47$, space group $P2_1/n$, $Z = 4$, $d_{calc} = 1.122(1)$, $d_{exp} = 1.121(1)$ g/cm³. The unit cell parameters for (II) are as follows: $a = 15.694(2)$, $b = 13.840(2)$, $c = 15.234(2)$ Å, $\beta = 101.83(1)^\circ$, $V = 3238.4(8)$ Å³, $M = 278.47$, space group $A2_1/n$, $Z = 8$, $d_{calc} = 1.142(1)$, $d_{exp} = 1.139(1)$ g/cm³. The intensities of 2157 (modification (I)) and 4777 independent reflections (modification (II)) were measured on a Syntex $P2_1$ automatic diffractometer using $CuK\alpha$ radiation, a graphite monochromator, and $\theta/2\theta$ scanning with $0.27 \times 0.39 \times 0.40$ -mm and $0.37 \times 0.50 \times 0.60$ -mm crystals, respectively.

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