CONCLUSIONS

The feasibility of obtaining organometallic titanium compounds based on the recombination of the triphenylmethyl radical with Ti^{2+} and Ti^{3+} compounds was demonstrated.

LITERATURE CITED

1. I. Sh. Guzman, O. K. Sharaev, E. I. Tinyakova, and B. A. Dolgoplosk, Dokl. Akad. Nauk SSSR, 202, 1329 (1972).
2. S. I. Beilin, G. N. Bondarenko, V. M. Vdovin, B. A. Dolgoplosk, I. N. Markevich, N. S. Nametkin, V. A. Poletaev, V. I. Svergun, and M. B. Sergeeva, Dokl. Akad. Nauk SSSR, 218, 1347 (1974).
3. N. N. Lichtin and N. P. Leftin, J. Am. Chem. Soc., 79, 2475 (1957).
4. F. X. Werber, C. J. Benning, W. R. Wszolek, and G. E. Ashby, J. Polymer. Sci., 6, 743 (1968).
5. O. N. Yakovleva, O. K. Sharaev, K. G. Miesserov, T. K. Vydrina, G. N. Bondarenko, E. N. Tinyakova, and B. A. Dolgoplosk, Dokl. Akad. Nauk SSSR, 218, 593 (1974).
6. R. Prshibil, Complexons in Chemical Analysis [Russian translation, Inostr. Lit. (1960).
7. F. S. D'yachkovskii, N. E. Khrushch, and A. E. Shilov, Kinet. Katal., 9, 1006 (1968).
8. O. S. Poshchupkina, N. E. Khrushch, F. S. D'yachkovskii, and Yu. G. Borod'ko, Zh. Fiz. Khim., 6, 1329 (1971).

THE REACTION OF 2,5-BIS(DIETHYLAMINOMETHYL)-HYDROQUINONE WITH DI- AND TRIALKYL PHOSPHITES

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It was previously shown [1, 2] that the reaction between trialkyl phosphites (TAPh) and various different phenolic Mannich bases (PMB) leads to the formation of esters of alkoxybenzylphosphonic acids via alkoxyphosphorane intermediates. In a number of cases these alkoxyphosphoranes have been isolated and characterized [2].

In order to prepare phosphorylated dihydric phenols which are of practical interest, we have studied the reaction between 2,5-bis(diethylaminomethyl)hydroquinone (I) and trialkyl phosphites (TAPh) [3].

The reaction between (I) and triethyl phosphite was carried out in xylene at 145 to 150°C and was accompanied by the evolution of a low-boiling-point fraction which, according to gas–liquid chromatographic data, consisted of diethylamine and a small amount of ethanol impurity. A signal with $\delta = 30$ ppm was recorded on the ^{31}P NMR spectrum of the reaction mixture while the absorption band due to the P=O group was absent from the corresponding IR spectrum. On the basis of this data and data which had previously been obtained [2], the structure 2,2,2,6,6,6-hexaethoxy-2,3,6,7-tetrahydro-2,6-diphosphafuro[2,3-d]benzo[1,2-b]furan (II) with two pentacoordinated phosphorus atoms was ascribed to the product.

The crystalline product (II) was stable at about 20°C and upon recrystallization from nonabsolute solvents was completely transformed into the tetraethyl ester of 3,6-dihydroxy-1,4-xylylenediphosphonic acid (III). An intense absorption band is visible in the ~1250 cm^{-1} region of the IR spectrum of (III) which is characteristic of the P=O group as well as bands due to the phenolic hydroxyl groups in the 3280-3250 cm^{-1} region.

If the reaction between (I) and TAPh is carried out at about 180°C and over a longer period of time, then (II) isomerizes into the tetraethyl ester of 3,6-diethoxy-1,4-xylylenediphosphonic acid (IV)

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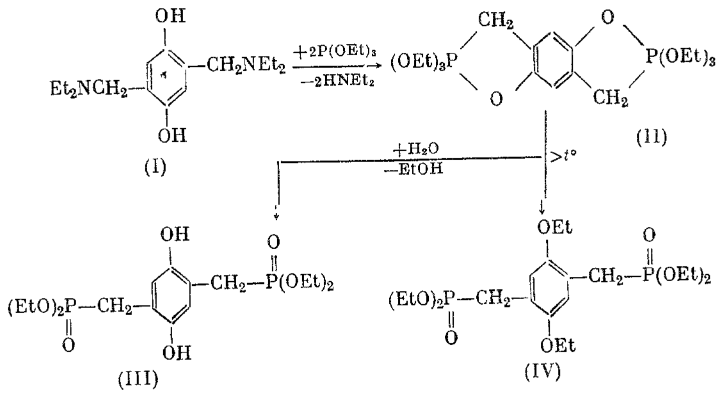
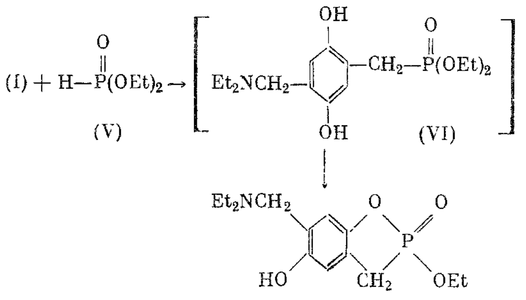

(I) (II) (III) (IV)

The reaction between (I) and diethylphosphorous acid (V) in xylene only takes place with great difficulty (150-155°C, 6 h) and is accompanied by significant resin formation and the evolution of a low-boiling-point fraction. The latter, according to the data obtained using gas−liquid chromatography, consists of ethanol, diethylamine, and a small amount of triethylamine impurity. After the solvent and the other low-boiling-point products had been removed under high vacuum, a resin-like product was obtained which contained nitrogen and phosphorus and which had $\delta_{^{31}P} = 42$ ppm.

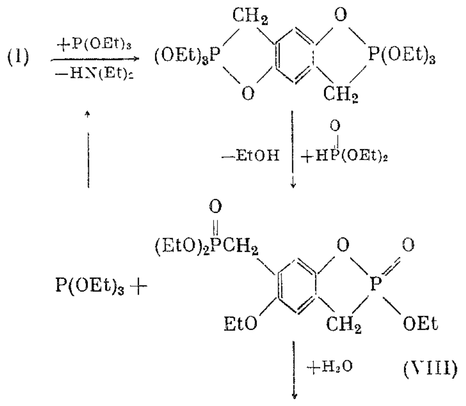
This data enables us to suggest that the reaction mainly takes place on one aminomethyl group and, in the final count, yielded the product 2-oxo-2-ethoxy-5-hydroxy-6-diethylaminomethyl-1-oxa-2-phosphoindane (VII)

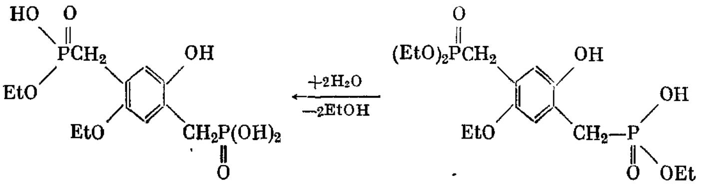

(V) (VI) (VII)

It was previously noted that [4] the addition of triethyl phosphite to the reaction mixture when other phenolic Mannich bases were reacted with diethylphosphorus acid significantly facilitated the reaction and enabled the yield of the main product to be increased. In accordance with this, various different amounts of triethyl phosphite were added to a mixture of (I) and (V): 0.17 to 0.20 mole of triethyl phosphite per aminomethyl group in (I) was found to be the optimal amount which enabled us to separate the reaction product in an individual form.

The reaction between (I) and triethyl phosphite leads, as was considered above, to the formation of compound (II). Compounds of this type react with (V) giving a product with an oxaphosphaindane structure and triethyl phosphite [5].

In the case which is being considered (V), apparently, reacts with only one phosphorane ring and this reaction is accompanied by the isomerization of the second which leads to (VIII) while the triethyl phosphite is again returned to the reaction according to the scheme:


(VIII)



(X) (IX)

There are two signals with $\delta = 45$ ppm and $\delta = 25$ ppm in the ^{31}P NMR spectrum of the reaction mixture which may be assigned to structure (VIII). The compound (VIII) is unstable and rapidly hydrolyzes even when washed with nonabsolute ether and is converted into the triethyl ester of 3-ethoxy-6-hydroxy-1,4-xylylenediphosphonic acid (IX).

Hence, when a Mannich base made out of hydroquinone is reacted with diethylphosphorous acid in the presence of triethyl phosphite, the compound (IX) is obtained with a yield of 90%. This compound is susceptible to further hydrolysis upon its recrystallization from aqueous alcohol with the formation of the ethyl ester of 3-ethoxy-6-hydroxy-1,4-xylylenediphosphonic acid (X).

EXPERIMENTAL

The ^{31}P NMR spectra were recorded on a KGU-4 (10.2 MHz) instrument with respect to 85% H_3PO_4 (external standard). The low-boiling-point fractions which distilled off during the course of the reaction were studied using gas–liquid chromatography on a "Chrom-3" instrument with a flame-ionization detector (80°C, helium carrier gas, polymethylsiloxane phase).

2,5-Bis(diethylaminomethyl)hydroquinone was synthesized according to the method given in [6].

Reaction between 2,5-Bis(diethylaminomethyl)hydroquinone (I) and Triethyl Phosphite. a) A quantity (14 g, 0.05 mole) of (I) and 16.6 g (0.1 mole) of triethyl phosphite were heated for 4 h in a flask with a rod-and-disk type fractionating column at 145-150°C in 20 ml of absolute xylene. The low-boiling-point fraction (gas–liquid chromatography) consisted of diethylamine and a small ethanol impurity. After the solvent had been removed and 50 ml of absolute ethanol had been added, the reaction mixture was crystallized: 14.3 g (61.5%) of (II) was obtained. mp 125-126°C (from absolute acetone). Found: C 51.26; H 7.72; P 13.44%. $C_{20}H_{36}O_8P_2$. Calculated: C 51.50; H 7.72; P 13.30%.

b) A quantity (22 g, 0.08 mole) of (I) and 26.56 g (0.16 mole) of triethyl phosphite in 30 ml of n-nonane were heated for 12 h at 155-170°C. 22 g (59%) of (IV) was obtained. mp 93-95°C (from n-hexane). Found: C 51.70; H 8.12; P 13.65%. $C_{20}H_{36}O_8P_2$. Calculated: C 51.50; H 7.72; P 13.30%.

c) A quantity (14 g, 0.05 mole) of (I) and 16.6 g (0.1 mole) of triethyl phosphite were heated at 145-150°C for 4 h in 25 ml of absolute o-xylene. After removal of the solvent from the reaction mixture and the addition of aqueous ethanol, 15 g (73.1%) of (III) was obtained, mp 178-180°C (from ethanol). Found: C 47.00; H 7.03; P 15.13%. $C_{16}H_{28}O_8P_2$. Calculated: C 46.82; H 6.82; P 15.12%.

Reaction of (I) with Tripropyl Phosphite. A quantity (7 g) of (I) and 15.9 g (excess) of tripropyl phosphite were heated for 3 h at 155°C in 15 ml of absolute o-xylene. After removing the solvent, the excess of tripropyl phosphite, and other low-boiling-point products under vacuum, 7.5 g (64.3%) of the tetrapropyl ester of 3,6-dihydroxy-1,4-xylyenediphosphonic acid was isolated. mp 126-127°C. Found: C 51.40; H 7.74; P 13.06%. $C_{20}H_{36}O_8P_2$. Calculated: C 51.50; H 7.72; P 13.30%.

A 72.3% yield of the tetrabutyl ester of 3,6-dihydroxy-1,4-xylyenephosphonic acid with mp 117-118°C was obtained from (I) and tributyl phosphite in an analogous manner. Found: C 55.30; H 8.56; P 12.05%. $C_{24}H_{44}O_8P_2$. Calculated: C 55.17; H 8.43; P 11.8%.

Reaction of (I) with (V) in the Presence of Triethyl Phosphite. a) A quantity (14 g, 0.05 mole) of (I), 13.8 g (0.1 mole) of (V), and 1 ml (0.006 mole) of triethyl phosphite in 25 ml of absolute xylene were heated for 3-4 h at 155°C. After removing the solvent and the other volatile products under vacuum, 14.9 g (99.6%) of (VII) (a solid resin-like product) was obtained. mp 108-113°C. Found: N 4.62; P 9.83%. $C_{14}H_{22}NO_4P$. Calculated: N 4.68; P 10.30%.

b) A quantity (14 g) of (I), 13.8 g of (V), and 2.9 g triethyl phosphite in 25 ml of absolute xylene were heated for 6.5 h at 151-153°C. The low-boiling-point fraction, according to the gas–liquid chromatographic data, consisted of ethanol and diethylamine. The solvent and other low-boiling-point products were removed under vacuum. There were crystals in the residue which "float" on air. After washing them with ether, 18.5 g (90%) of (IX) was obtained. mp 165-167°C. Found: C 46.71; H 6.70; P 14.95%. $C_{16}H_{28}O_8P_2$. Calculated: C 46.82; N 6.82; P 15.12%. By recrystallizing them from aqueous ethanol crystals of (X) were obtained, mp 190-192°C. Found: C 40.87; H 5.73; P 17.29%. $C_{12}H_{20}O_8P_2$. Calculated: C 40.67; H 5.65; P 17.51%.

CONCLUSIONS

1. An intermediate alkoxyphosphorane with two pentacoordinated phosphorus atoms was isolated and characterized during the reaction of 2,5-bis(diethylaminomethyl)hydroquinone with trialkyl phosphites.

2. A method has been developed for the synthesis of phosphorylated dihydric phenols.

3. The triethylether of 3-ethoxy-6-hydroxy-1,4-xylyenediphosphonic acid was prepared by the interaction of 2,5-bis(diethylaminomethyl)hydroquinone with diethylphosphorous acid in the presence of triethyl phosphite.

LITERATURE CITED

1. B. E. Ivanov and L. A. Valitova, Izv. Akad. Nauk SSSR, Ser. Khim., 1087 (1967).
2. B. E. Ivanov, L. A. Valitova, L. A. Kudryavtseva, T. G. Bykova, K. A. Derstuganova, and E. I. Gol'dfarb, Izv. Akad. Nauk SSSR, Ser. Khim., 672 (1974).
3. B. E. Ivanov, L. A. Valitova, V. I. Gaidai, T. G. Bykova, and N. I. Kuchma, Author's Certificate No. 431,170, November 18 (1972); Byul. Izobr., No. 21 (1974).
4. L. A. Khismatullina, L. A. Valitova, and B. E. Ivanov, Author's Certificate No. 362,844, March 22 (1971); Byul. Izobret., No. 3 (1972).
5. B. E. Ivanov, L. A. Valitova, T. G. Bykova, K. Kh. Khairullin, and L. A. Khismatullina, Symposium on Several Problems of Organic and Physical Chemistry, Kazan', Inst. Org. Fiz. Khim., Kaz. Fil. Akad. Nauk SSSR (1972), p. 61.
6. Benno Reichert, Die Mannich Reaktion, Berlin (1959), p. 150.