

## LETTERS TO THE EDITOR

# Synthesis and Electrode Activity of 1,12-Bis[di(*p*-tolyl)phosphinoyl]- 2,11-dibutyl-2,11-diaza-5,8-dioxadodecane

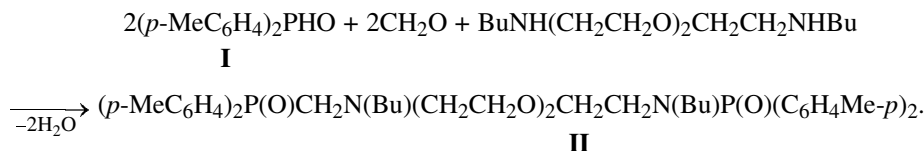
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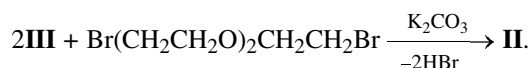
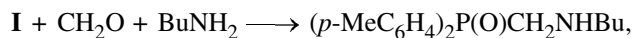
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Podands with phosphorus-containing terminal groups exhibit specific host–guest complex-forming properties and can be used as extractants, components of ion-selective electrodes, membrane carriers, etc. [1–3]. Here we report the synthesis of the first representatives of aza podands with  $\alpha$ -aminomethylphosphinoyl groups and the use of these compound as components

of ion-selective electrodes in determination of low concentrations of alkali metals. We found that the Kabachnik–Fields reaction in a ternary system containing di(*p*-tolyl)phosphinous acid (**I**), Paraform, and 1,10-dibutyl-1,10-diaza-4,7-dioxadecane provides a convenient synthetic route to 1,12-bis[di(*p*-tolyl)phosphinoyl]-2,11-dibutyl-2,11-diaza-5,8-dioxadodecane.



An alternative way to aza podand **II** is the reaction of (butylaminomethyl)phosphine oxide **III**, prepared from phosphine oxide **I**, Paraform, and butylamine by the Kabachnik–Fields reaction, with 1,8-dibromo-4,7-dioxaoctane (**IV**).



The electrode activity of phosphorylated aza podand **II** was studied by known procedures [4, 5] on an example of ion-selective electrodes with a liquid membrane made on the basis of this compound. It was found that the electrodes allow a highly selective determination of low concentrations of heavy alkali metal ions ( $\text{Rb}^+$ ,  $\text{Cs}^+$ ). The detection limit is  $10^{-5}$  M. Other alkali metals do not interfere with the determination.

The results of investigation of the ionophoric pro-

perties of phosphorylated aza podands will be described in more detail in further publications.

**1,12-Bis[di(*p*-tolyl)phosphinoyl]-2,11-dibutyl-2,11-diaza-5,8-dioxadodecane (**II**).** *a.* A mixture of 12 mmol of di(*p*-tolyl)phosphinous acid **I**, 12 mmol of Paraform, and 6 mmol of 1,10-dibutyl-1,10-diaza-4,7-dioxadecane was refluxed with 30 ml of benzene with a Dean–Stark trap for 40 min; therewith, ca. 95% of water evolved. The mixture was refluxed for an additional 40 min, the solvent was removed on a rotary evaporator and then in an oil-pump vacuum until constant weight. A viscous liquid was obtained, which was chromatographed on a column of Silica gel L 100/400, eluent chloroform–methanol (10:1), to obtain 3.3 g (74%) of a light yellow viscous tar-like liquid,  $\delta_p$  24.7 ppm (benzene). Found, %: C 73.84; H 8.76; P 6.96.  $\text{C}_{44}\text{H}_{62}\text{N}_2\text{O}_4\text{P}_2$ . Calculated, %: C 73.74; H 9.21; P 6.66.

*b.* Dibromide **IV**, 4.8 mmol, was added dropwise with stirring at  $50^\circ\text{C}$  to a solution of 9.62 mmol of amino-

phosphine oxide **III** in DMF containing 4.8 mmol of potassium carbonate. After the addition had been complete, the bath temperature was raised to 70°C, and the reaction mixture was stirred for 5 h, cooled, washed with water, extracted with chloroform, and dried over sodium sulfate. The chloroform was removed on a rotary evaporator and then in an oil-pump vacuum until constant weight. The crude product was purified by column chromatography as described above to obtain 2.43 g (68%) of compound **II**.

The  $^{31}\text{P}$  NMR spectra were obtained on a Varian Unity300 spectrometer against external 85% phosphoric acid.

## REFERENCES

1. Kron, T.E. and Tsvetkov, E.N., *Usp. Khim.*, 1990, vol. 59, no. 3, pp. 483–508.
2. Khramov, A.N., Garifzyanov, A.R., and Toropova, V.F., *Zh. Anal. Khim.*, 1994, vol. 49, no. 10, pp. 1124–1126.
3. Zabiroy, N.G., Brus'ko, V.V., Kashevarov, S.V., Sokolov, F.D., Shcherbakova, V.A., Verat, A.Yu., and Cherkasov, R.A., *Zh. Obshch. Khim.*, 2000, vol. 70, no. 8, pp. 1294–1302.
4. Cammann, K., *Das Arbeiten mit ionenselektiven Elektroden*, Heidelberg: Springer, 1977. Translated under the title *Rabota s ion-selektivnymi elektrodami*, Moscow: Mir, 1985, pp. 109–121.
5. Morf, W., *The Principles of Ion-Selective Electrodes and of Membrane Transport*, Budapest: Akad. Kiado, 1981. Translated under the title *Printsipy raboty ion-selektivnykh elektrodov i membrannyi transport*, Moscow: Mir, 1985, pp. 171–218.