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Bicyclophosphites of Terminal-Substituted Glycerols

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For the first time a systematic study was performed for the phosphorylation of 1.2.3triols with total amides of phosphorous acid. The initial-matrix-structure dependence of phospholane-phospholane bicyclophosphites was found and investigated. The introducing of terminal substituents into a triol molecule was shown to essentially increase their stability.

$$1 R = R' = CH_2OCPh_3$$
; $2 R = Ph, R' = H$; $3 R = Et, R' = H$

The reactions of the obtained phosphites were studied that operated with retention of phosphobicyclic moiety or disruption of a ring. Rhodium(I) bicyclic complexes were synthesized. It was shown that the bicyclic esters reacted vigorously and regioselectively with chlorine and hydrogen peroxide to form monocyclophosphates of various cyclicity.

$$L + AcacRh(CO)_2 \qquad L-Rh$$

$$L = 1, 3$$

$$Ph$$

$$CHCl$$

$$Ph$$

$$CHCl$$

$$Ph$$

$$HO$$

$$O$$

$$Ph$$

$$HO$$

$$O$$

$$Ph$$

$$HO$$

$$O$$

$$Ph$$

$$HO$$

$$O$$

$$Ph$$

A correlation was made between structural parameters and chemical features of obtained phospholane-phospholane systems and previously known analogues. The structure of the compounds was proved by means of H, C, and P NMR spectroscopy, for isolated derivatives by means of X-ray analysis.