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Addition of Benzodioxahalogenophosphoranes to the Carbonyl Group: New Phosphoranes and their Reactivity

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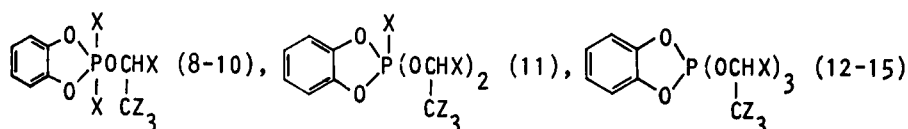
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ADDITION OF BENZODIOXAHALOGENOPHOSPHORANES TO THE CARBONYL GROUP: NEW PHOSPHORANES AND THEIR REACTIVITY

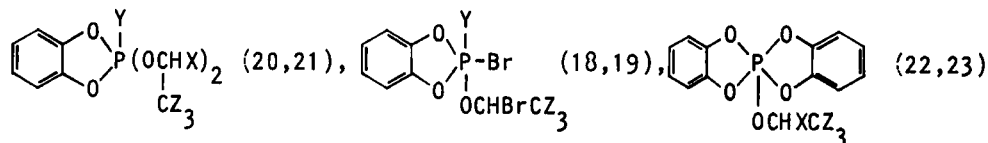
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Halogenophosphoranes catPX_3 ($X = \text{Cl}, \text{Br}$) (1, 2), cat_2PBr (3), catPBr_2Y [$\text{Y} = \text{CHF}_2\text{CF}_2\text{CH}_2$ (4), F (5), $\text{OCH}=\text{CBr}_2$ (6), CN (7), $\text{cat} = \text{C}_6\text{H}_4\text{O}_2\text{-o}$] react with aldehydes containing electron-withdrawing groups (CZ_3CHO , $\text{Z} = \text{Cl}, \text{Br}$) in solvent to form the products of insertion in P-X bond. The structure of compounds (12-15) and their diastereomeric composition were determined by the NMR ^1H , ^{13}C , and ^{31}P spectroscopy. Phosphoranes (8-11) disproportionate to PX_3 and $\text{cat}_2\text{POCHXCZ}_3$ ($X, \text{Z} = \text{Br}, \text{Br}; \text{Cl}, \text{Br}$) (16, 17). Dibromophosphoranes (4-7) and monobromophosphorane (3) are also added to the carbonyl group of CZ_3CHO to form unsymmetric P(V) derivatives $\text{catPBr}(\text{OCHBrCZ}_3)\text{Y}$ (18, 19) and (16, 17, 20-25). The thermal behaviour of compounds (18, 19) was investigated.



$X, \text{Z} = \text{Cl}, \text{Cl}$ (8, 12); Cl, Br (9, 13); Br, Cl (10, 11, 14); Br, Br (15)



$X, Y, \text{Z} = \text{Br}, \text{OCH}_2\text{CF}_2\text{CHF}_2, \text{Cl}$ (20); $\text{Br}, \text{OCH}_2\text{CF}_2\text{CHF}_2, \text{Br}$ (21)

$Y, \text{Z} = \text{Br}, \text{Cl}$ (18); Br, Br (19); Br, Cl (22); Br, Br (23)

