Addition of Phosphorus Reagents to Conjugated Double Bonds of Terpenic Compounds

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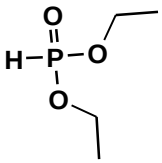
We have investigated the addition of diethylphosphite **1** to terpenic unsaturated ketones **2**, **3**, **4** and dibensylphosphinic acid **5** to unsaturated nitriles with terpenic (**6**, **7**) and modified-terpenic (**8**, **9**) structures.



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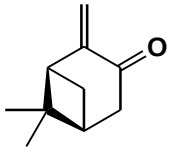

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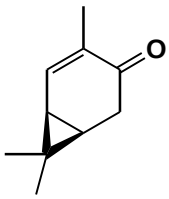

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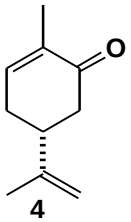

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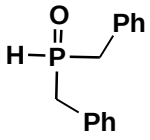

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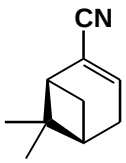

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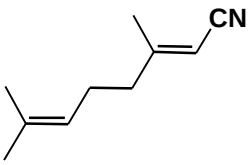

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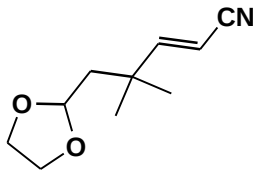

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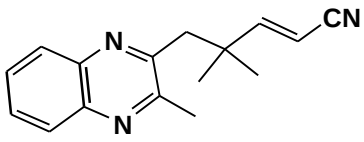

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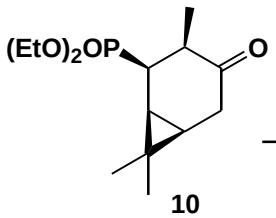
The interaction of diethylphosphite **1** with unsaturated ketones led to ketophosphonates **10, 11** and **12**. The reaction of carvone **4** resulted in formation of significant amounts of diphosphonate **12** (major product). The reaction proceeded stereoselectively, but the primary formed ketones **10 - 12** were transformed to equilibrium mixture of epimers on prolonged reaction time.

The treatment of unsaturated nitriles **6 - 9** with dibensylphosphinic acid **5** in aprotonic conditions led to aminophospholene oxides with general structure **14**. We have found that reaction occurred with high stereoselectivity in most cases. The majority of reaction products were obtained as a single isomer. The major product of reaction of nitrile **9** was phosphorylated enamine **15**. In this case the aminophospholene oxide was the minor product.



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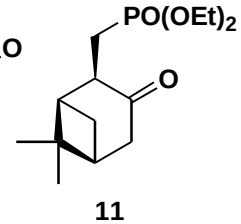

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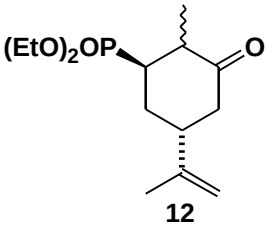

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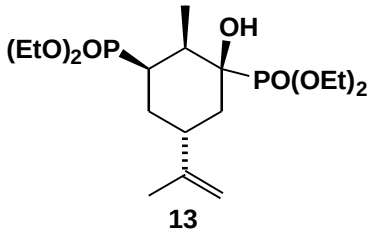

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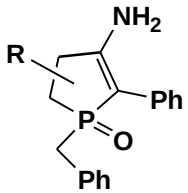

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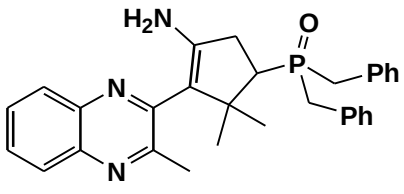

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