Addition of Phosphorus Reagents to Conjugated Double Bonds of Terpenic Compounds

Vasiliy D. Kolesnik, Alexey V. Tkachev
Novosibirsk Institute of Organic Chemistry, Ave. Lavrentiev 9, Novosibirsk, 630090, Russia, fax: +7(3832)344855, e-mail: kolesnik@nioch.nsc.ru.

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.

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.