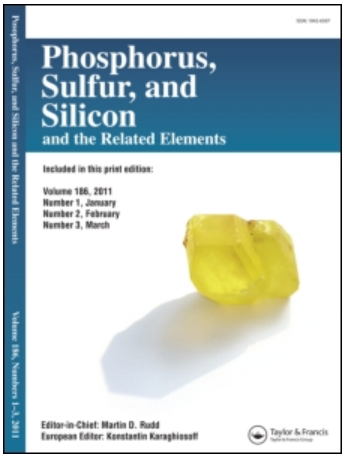

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PREPARATION OF BICYCLIC SECONDARY AND TERTIARY PHOSPHINES FROM RADICAL ADDITION OF PHOSPHINE AND PRIMARY PHOSPHINES TO LIMONENE

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In the presence of a free radical initiator, limonene combines with a primary phosphine to yield a 1:1 adduct (I). Initially the addition takes place at the isopropenyl moiety. The resulting secondary phosphine subsequently undergoes an intramolecular addition to produce two isomeric 2-alkyl-4,8-dimethyl-3-phosphabicyclo [3.3.1]nonanes (II, III) in >85% yield. Analogous bicyclic secondary phosphines are formed by free radical addition of phosphine to limonene. Yields are slightly lower due to the addition of the reactive secondary phosphines to a second mole of limonene.

A proton coupled ^{31}P NMR spectrum of II/III where R=isobutyl, contained two singlets (-50.34 and -56.62 ppm) and verified that II and III are tertiary phosphines. The relative areas are 1:1.17. The ^{31}P NMR spectrum of II/III derived from limonene and phosphine contained two doublets centered at -73.31 and -97.69 ppm. The H/P coupling constants are 2.419 and 2.367 ppm. The relative areas are 1.:0.84. The corresponding ^{13}C NMR spectrum for the secondary phosphine mixture contained twenty signals (8 CH_2 and 12 CH_3/CH) which are consistent with the twenty distinct carbons expected from a mixture of II and III.

The tertiary phosphines derived from optically pure limonene may have potential utility as chiral catalyst ligands. The bridgehead carbon configuration at position 5 will be fixed at R and S respectively when starting with R(+) and S(-) limonene. Fixing the configuration at position 5 will predetermine the configurations at 2 and 8.