A NOVEL GENERATION OF BRIDGEHEAD IMINES VIA INTRAMOLECULAR AZA-WITTIG REACTIONS. SYNTHESIS AND REACTIONS OF 4-AZAHOMO-ADAMANT-3(4)-ENE AND 4-AZA-4-HOMOBREND-3(4)-ENES.

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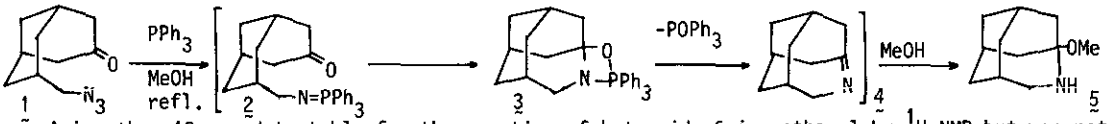
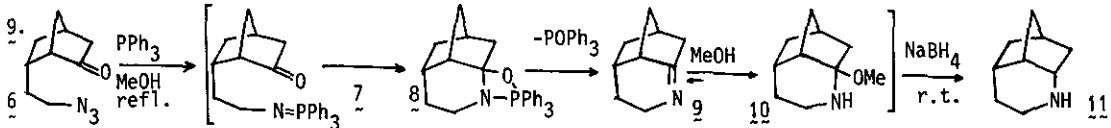
Bridgehead imines have been studied increasingly. However, the synthetic methods of these systems are quite limited yet. We report a novel method of synthesis of bridgehead imines via aza-Wittig reactions.

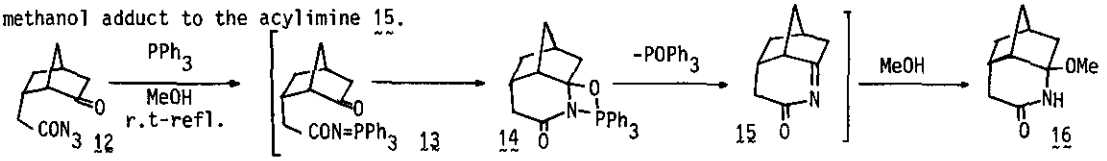
Bicyclic ketoazide 1 was treated with triphenylphosphine in refluxing methanol to give 5, a methanol adduct to 4-azahomoadamant-3(4)-ene (4). The reaction was followed by ^1H and ^{13}C NMR to reveal the intermediacy of oxazaphosphetane 3 which was formed by Staudinger reaction of azide 1 and phosphine followed by cycloaddition.



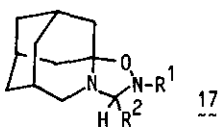
Aminoether 10 was detectable for the reaction of ketoazide 6 in methanol by ^1H NMR but was not isolable. Methanol addition to the imine 9 is, therefore, reversible due to the decreased strain of 9. Treatment of the reaction mixture with $NaBH_4$ afforded 4-aza-4-homobrendane (11). In this case, oxazaphosphetane 8 was not detectable by ^1H NMR because of the rapid conversion to the imine



Treatment of ketoacylazide 12 with triphenylphosphine in refluxing methanol gave 16, a stable methanol adduct to the acylimine 15.



1,3-Dipolar cycloaddition of bridgehead imines 4, 9, and 15 with nitrones proceeded successfully to afford oxadiazolidines 17, 18, and 19 regio- and stereoselectively.



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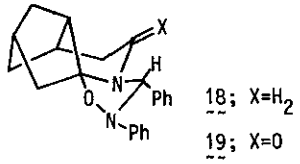

18; X=H_2
19; X=O