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SYNTHESIS OF SOME NOVEL HOMOADAMANTANO[4,5]FUSED AZAHETEROCYCLES

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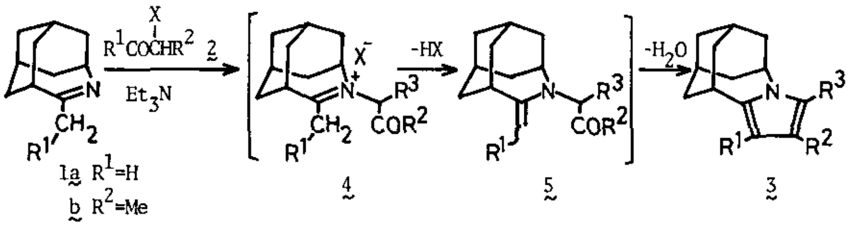
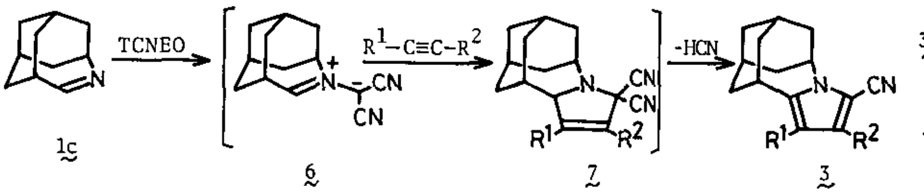
As a part of continuing efforts in our laboratories to synthesize adamantaneheterocycles and in conjunction with our interest in their biological properties, we have been currently concerned with synthetic study of heterocycles fused to homoadamantane ring system. We describe here synthesis of some novel homoadamantano[4,5]fused type azaheterocycles by utilizing heterocyclization and cycloaddition of 4-azahomoadamant-4-enes readily obtainable from adamantanone.

Treatment of 5-alkyl 4-azahomoadamant-4-ene (1a,b) with α-haloketones (2) in the presence of Et_3N afforded directly 4-azahomoadamantano[4,5-a]pyrrole derivatives (3a-f) in 13-77% yields (Scheme 1). The formation of 3 is explained most reasonably by an initial formation of the corresponding N-alkyl immonium salt 4, followed by its conversion to eanmine 5 by Et_3N and an intramolecular cyclization of 5 under aromatization via dehydration.



	R^1	R^2	R^3	Yield
3a	H	Ph	H	77%
b	H	Me	H	56%
c	H	Ph	Me	67%
d	Me	Ph	H	64%
e	Me	Me	H	37%
f	Me	Ph	Me	13%

As a second route to 3, generation and 1,3-dipolar cycloadditions of an azomethine ylide 6 have been examined. Treatment of 4-azahomoadamant-4-ene (1c) with tetracyanoethylene oxide in the presence of acetylenic dipolarophiles gave also 3 (Scheme 2). Thus, reactions with DMAD and methyl propiolate gave 3g and 3h respectively. Synthesis of some other related azaheterocycles like 4-azahomoadamantanopyridone will also be discussed.



3g R^1=R^2=COOMe (34%)
h R^1=COOMe R^2=H (14%)