

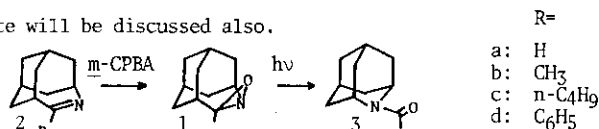
RING-TRANSFORMATION REACTIONS OF AZAHETEROMODIFIED ADAMANTANES AND RELATED DERIVATIVES

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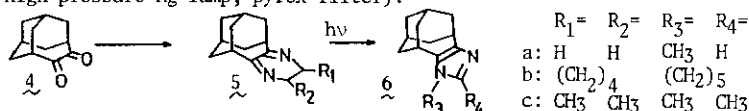
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We have been exploring new synthetic routes to heteromodified polycyclic skeletons as one of novel new-typed heterocycles. We have now developed the following routes to 2-azaadamantyl system, 4-azahomoadamantano-imidazoles and -isoquinolinones.

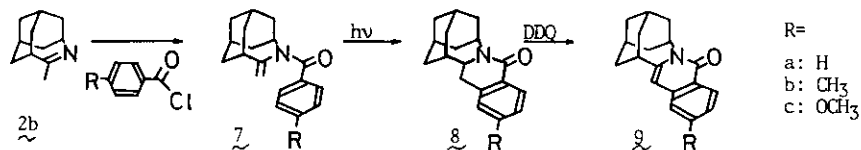
(i) Oxaziranes **2** were prepared by *m*-CPBA oxidation of 4-azahomoadamant-4-enes **1**. Compound **2** in cyclohexane was irradiated with a low pressure Hg lamp through a quartz filter under argon. The initial product in each cases was isolated by chromatography to afford N-acyl-2-azaadamantane **3** (44-67%). This ring-expansion and ring-contraction sequence of the adamantane skeleton thus provides a novel and convenient route to 2-azaadamantyl system.² Thermal reaction of **2** with IMAD and methyl propiolate will be discussed also.



(ii) Dihydropyrazines **5** prepared from 4,5-dione **4** rearranged to homoadamantanoimidazoles **6** in high yields on photolysis (a high pressure Hg lamp, pyrex filter).



(iii) The enamide derivatives **7** were readily obtainable from **2b** by acylation in high yields. Irradiation of **7** in ether through a quartz filter with a low pressure Hg lamp afforded photocyclization products **8** in 66-83% yields after chromatography.³ Dehydrogenation of **8** with DDQ gave the corresponding 4-azahomoadamantano[4,5-b]l(2H)isoquinolinones **9** in good yields.



References

- (1) Sasaki, T.; Eguchi, S.; Toi, N. *J. Org. Chem.* **1978**, *43*, 3810 and references cited therein.
- (2) Eguchi, S.; Asai, K.; Sasaki, T. *J. Chem. Soc., Chem. Commun.* **1984**, 0000.
- (3) Ninomiya, I.; Naito, T. *J. Synth. Org. Chem. Japan* **1984**, *42*, 224.