SYNTHESIS OF N^6-ALKOXY-1,3-DIALKYLADENINIUM SALTS AND AN ATTEMPT TO SYNTHESIZE 1,3-DIMETHYLADENINE

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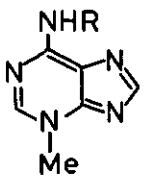
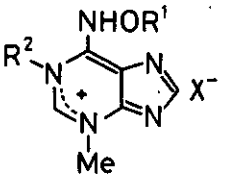
Methylation of N^6-methoxy-3-methyladenine (1) with MeI in $AcNMe_2$ gave the 1-methylated product 4 (X = I) (40% yield) and the N^6-methylated product 7 (X = ClO_4) (36%). The N^6-benzyloxy analogue 2 was similarly methylated to produce 6 (X = Cl) (34%) as well as 9 (X = Cl) (35%). An analogous ethylation of 1 with EtI furnished 5 (X = I) (21%) and 8 (X = ClO_4) (33%). Reduction of 4 (X = I) with $NaBH_4$ afforded the 1,2-dihydro derivative 10 (92% yield), which reverted to 4 (X = I) by dehydrogenation with iodine in EtOH. On hydrogenation with Raney nickel and hydrogen, 4 (X = I) gave 10 (26% yield) and the N^6-demethoxy derivative 11·HI (17%), and 10 furnished 11 on a similar reduction. Dehydrogenation of 11 with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) in chloroform yielded a crude solid presumed to be 1,3-dimethyladeninium salt (12), which was easily rearranged into N^6,3-dimethyladenine (3) through the monocycle 13. It has been found that hydrolysis of 4 (X = ClO_4) to give the imidazole 14 in water at pH 7.72 and 25°C proceeds *ca.* 270 times as fast as that of the 3,9-dimethyl analogue 15 to give the monocycle 16.

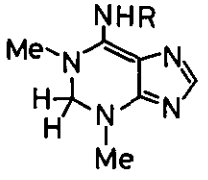


1: R = MeO
2: R = $PhCH_2O$
3: R = Me

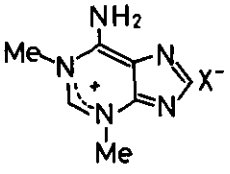


4: R^1 = Me; R^2 = Me
5: R^1 = Me; R^2 = Et
6: R^1 = $PhCH_2$; R^2 = Me

7: R^1 = Me; R^2 = Me
8: R^1 = Me; R^2 = Et
9: R^1 = $PhCH_2$; R^2 = Me



10: R = MeO
11: R = H



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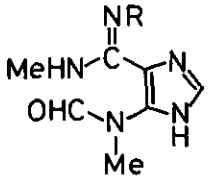
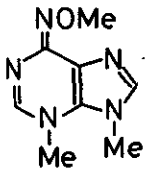


13: R = H
14: R = MeO



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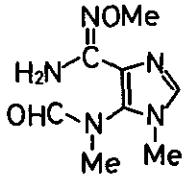

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