

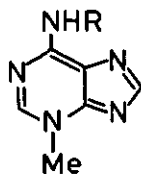
SYNTHESIS OF  $N^6$ -ALKOXY-1,3-DIALKYLADENINIUM SALTS AND  
AN ATTEMPT TO SYNTHESIZE 1,3-DIMETHYLADENINE

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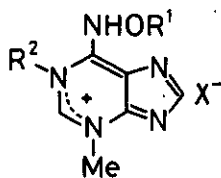
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Methylation of  $N^6$ -methoxy-3-methyladenine (**1**) with MeI in AcNMe<sub>2</sub> gave the 1-methylated product **4** (X = I) (40% yield) and the  $N^6$ -methylated product **7** (X = ClO<sub>4</sub>) (36%). The  $N^6$ -benzyloxy analogue **2** 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<sub>4</sub>) (33%). Reduction of **4** (X = I) with NaBH<sub>4</sub> 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<sub>4</sub>) 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**.



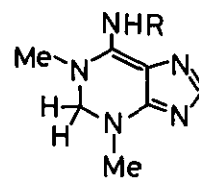
- 1**: R = MeO  
**2**: R = PhCH<sub>2</sub>O  
**3**: R = Me



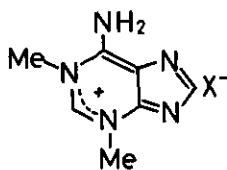
- 4**: R<sup>1</sup> = Me; R<sup>2</sup> = Me  
**5**: R<sup>1</sup> = Me; R<sup>2</sup> = Et  
**6**: R<sup>1</sup> = PhCH<sub>2</sub>; R<sup>2</sup> = Me



- 7**: R<sup>1</sup> = Me; R<sup>2</sup> = Me  
**8**: R<sup>1</sup> = Me; R<sup>2</sup> = Et  
**9**: R<sup>1</sup> = PhCH<sub>2</sub>; R<sup>2</sup> = Me



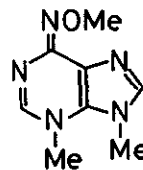
- 10**: R = MeO  
**11**: R = H



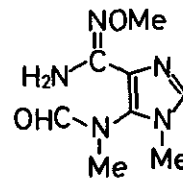
**12**



- 13**: R = H  
**14**: R = MeO



**15**



**16**