Lambert [10] and Buys.[11] The calculated torsional angles are approx. 44° and 48° for I and II, respectively. Similar values have been found for 2-chloro-, 2-phenyl-, and 2-phenoxy-1,3,2-oxathiaphospholanes[1].

*Experimental.* *2-Methoxy-1,3,2-oxathiaphospholane* (I) was prepared from 2-chloro-1,3,2-oxathiaphospholane[1] and methanol in ether solution using triethylamin as base, $b.p._{0.1}$ 34°.

*2-Methylthio-1,3,2-oxathiaphospholane* (II) was prepared from 2-chloro-1,3,2-oxathiaphospholane and methanethiol in ether solution using triethylamin as base, $b.p._{0.1}$ 62°.

The PMR spectra were measured at 28°C in 50 % solution of I and II in $CDCl_3$ and were recorded on a 60 MHz, JEOL, C-60H instruments. The line positions were taken as an average of several spectra. The computation was carried out using an IBM 360/50 computer. The magnitudes of the chemical shifts and coupling constants involved have been determined by the iterative computer program LAOCN3.[12] The final RMS error observed was 0.05, when all parameters were allowed to vary.


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# Electrophilic Bromination of 2-Methyl-4-carbethoxy-1,3,6,7-tetraazacycl[3.3.3]azine


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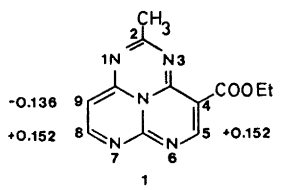
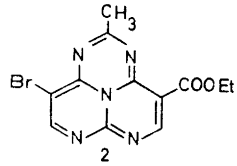
The preparation of 2-methyl-4-carbethoxy-1,3,6,7-tetraazacycl[3.3.3]azine, *1*, has recently been described.[1] Simple HMO calculations suggested[1] that *1* should be electrophilically substituted at C-9. (*cf.* Fig. 1).



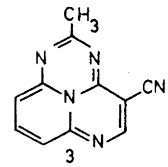

1

*Fig. 1.* Charge densities at C-5, C-8, and C-9 in 2-methyl-4-carbethoxy-1,3,6,7-tetraazacycl[3.3.3]azine.

In order to verify the theoretical predictions, *1* was treated with *N*-bromosuccinimide in chloroform at room temperature.[2,3] A 60 % yield of 9-bromo-4-carbethoxy-2-methyl-1,3,6,7-tetraazacycl[3.3.3]azine, *2*, was isolated. The mass spectrum shows molecular ion peaks at $m/e = 335$ and 337 m.u. (intensity 1:1) in agreement with the formula $C_{12}H_{10}N_5O_2Br$. The fragmentation pattern of *2* is entirely analogous with that of the 9-bromo derivative of *3*.[3] In the NMR spectrum of *1*[4] the H-8 and H-9 signals appear as two doublets centered at 7.75 and 5.75 ppm, respectively. In the spectrum of *2*, the signal at higher field has vanished and the lower-field signal remains as a singlet at 8.00 ppm. Therefore, substitution has occurred at C-9. The H-5 singlet is found at 8.30 ppm.




2



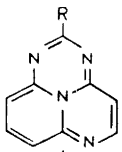

3

On a TLC plate and in the dry state, *2* is destroyed when not protected from air and light. In chloroform solution at −20°, *2* seems to be stable.

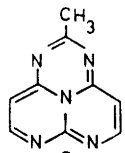
The conditions necessary to monobrominate *1* were somewhat more vigorous than those needed to produce the 9- or 7-bromo derivatives of the 1,3,6-triazacycl-[3.3.3]azine *3*.[3]

Efforts to prepare *2*, by treating *1* with bromine in glacial acetic acid were unsuccessful since *1* is unstable in this medium.

Attempts to decarboxylate *1* by the method used to prepare *4* [5,6] from its 4-carbethoxy derivative (diphenyl ether, traces of *p*-toluenesulphonic acid,[6] 100–258°) in order to obtain the symmetrical system *5* failed, since *1* was unstable under these conditions.



4



5

R = $CH_3$ and H

The observations reported above thus indicate that the 1,3,6,7-tetraazacycl[3.3.3]-azine system *1* is less susceptible to electrophilic substitution and, at least in some respects, chemically more unstable than the corresponding 1,3,6-analog *3*.

*Experimental. General.* Nuclear magnetic resonance (NMR) spectra were determined in $CDCl_3$ with a Varian Model A-60 spectrometer, using tetramethylsilane as internal reference. Mass spectra were recorded with a GEC-AEI MS 902 instrument at the Department of Medical Biochemistry, University of Göteborg. Thin-layer chromatography (TLC) was performed on Silica Gel $GF_{254}$ (Merck) according to Stahl and the spots were visualized by means of short-wave ultraviolet light. For column chromatography, silica gel, 0.05–0.2 mm (Merck), was used.

*Bromination of 1 with NBS.* A mixture of 45 mg of *1* and 135 mg of *N*-bromosuccinimide in 9 ml of chloroform was stirred at *ca.* 25°. The formation of *2* was followed by TLC (EtOAc). After 6 h the starting material had vanished and red-violet *2* was present ($R_F$ = 0.68). The volume of the reaction solution was reduced to *ca.* 5 ml and succinimide and unreacted NBS, which then precipitated, were removed by filtration. The filtrate was poured on to a column of silica gel (25 × 2.5 cm) and the red-violet band was eluted with chloroform–ethylacetate (1:1). After careful evaporation under reduced pressure at *ca.* 30° 36 mg (60 %) of *2* was obtained. It was immediately dissolved in chloroform and kept in the dark in a Dewar vessel together with dry ice.

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# The Structure of 3,4-Dimethyl-6a-selenathiophthene

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So far X-ray structure determinations of two 6a-selenathiophthenes have been reported.[1,2] The Se–S bonds in 6a-selenathiophthene (I) [1] were found to be 2.446(5) Å, and the Se–S bonds in 2,5-diphenyl-6a-selenathiophthene (II) [2] were found to be 2.433(3) Å and 2.419(3) Å, respectively.

A structure investigation of 3,4-dimethyl-6a-selenathiophthene (III) has been carried out in order to obtain further information about the bonding in the 6a-