Nitration of Some 2,3-Dihydro-1,4-Diazepinium Perchlorates

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NUCLEOPHILIC, free-radical, and electrophilic attack on the 2,3-dihydro-1,4-diazepine nucleus by neutral and negatively charged species is known.[1] Attack by a positively charged species however, has not been reported. It has been clearly demonstrated[2] that the nitrating species in nitric acid–sulphuric acid mixtures is NO_2^+. I now report substitution of the 2,3-dihydro-1,4-diazepine nucleus by positively charged species.

2,3-Dihydro-5,7-dimethyl-1,4-diazepinium perchlorate (I) and 2,3-dihydro-1,4,5,7-tetramethyl-1,4-diazepinium perchlorate (II) undergo mononitration in nitric acid–sulphuric acid. The perchlorates (I) and (II) were heated at 70° for 2 hr. with nitric acid in 90% sulphuric acid. Yellow perchlorates (III) and (IV) were obtained on pouring the reaction mixture on to crushed ice, and had melting points (needles from water) 240—242° (III) and 231—232° (IV).

(II) has λ_{max} 318 mμ and ϵ_{max} 13,800 ± 50. (IV) has λ_{max} 328 mμ and ϵ_{max} 18,000 ± 50. The infrared spectra of (III) and (IV) are very similar to those of the parent compounds, but show intense absorptions at 1330 cm.$^{-1}$ which is generally associated with a nitro-group. The ^{1}H n.m.r. spectra of (III) and (IV) consist of three singlets, one less than (I) and (II) (Table).

The protons at τ 2·25 (I) and τ 2·8 (III) underwent deuterium exchange rapidly whilst those at τ 4·9 (I) and (II) underwent slow exchange [$k = 1{\cdot}02 \pm 0{\cdot}05 \times 10^{-6}$ sec.$^{-1}$ for the pseudo-first-order exchange of the C-6 proton in (I)].[3]

TABLE

Proton	Solvent	Chemical shift τ (I)	(II)	(III)	(IV)
N-*H*	MeCN	2·25	—	2·8	—
N-C*H*$_3$	Me$_2$SO	—	6·65	—	6·65
H-6	Me$_2$SO	4·9	4·9	—	—
2(3)-C*H*$_2$	Me$_2$SO	6·45	6·45	6·40	6·40
5(7)-C*H*$_3$	Me$_2$SO	7·7	7·7	7·55	7·50

From a comparison of the spectral data and analytical figures it is concluded that (III) and (IV) are respectively 2,3-dihydro-5,7-dimethyl-6-nitro-1,4-diazepinium perchlorate and 2,3-dihydro-6-nitro-1,4,5,7-tetramethyl-1,4-diazepinium perchlorate.

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