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THE FORMATION OF STABLE ADDUCTS BY REACTION OF DIPYRIDINE BROMINE(I) PERCHLORATE WITH OLEFINS AT LOW TEMPERATURES[1a]

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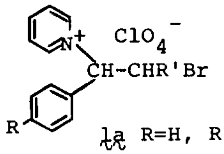
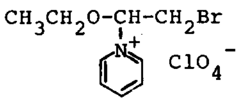
We have been investigating the use of dipyridine bromine(I) perchlorate as a mild, bromide-free source of electrophilic bromine.[2] We have found that, under suitable conditions, brominated pyridinium perchlorate salts of styrenes and vinyl ethers can be prepared in good yields with this reagent. The addition is, in all cases, regiospecific and, where possible, stereospecific. In the presence of nucleophilies stronger than pyridine, BrX addition is observed and the pyridinium adduct is not formed.

The adducts of styrene (1a), 4-methylstyrene (1b), trans-1-phenyl-1-propene (1c), anethole (1d), ethyl vinyl ether (2) and dihydropyran (3) have been prepared and their structures established by ir and nmr and by elemental analysis. 3- and 4-Nitrostyrenes failed to react. We assume that the formation of pyridinium derivative is dependent on the stability of the β-bromo-α-carbonium ion (4) or (5).



1a R=H, R'=H
1b R=CH_3, R'=H
1c R=H, R'=CH_3
1d R=OCH_3, R'=CH_3



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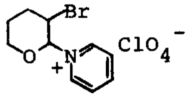

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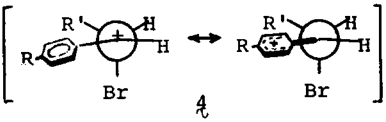

4

$$\left[CH_3CH_2\overset{+}{O}=CH-CH_2Br\right]$$

5

The regiospecifity observed leads us to believe that there is very little bridging in the intermediate, in agreement with the kinetic studies of Ralston and Yates[3] and the labelling experiments reported by Hassner, Boerwinkle and Levy[4]. No product of nucleophilic attack at the β-carbon was found, although this site is less sterically hindered than the α-carbon. Where the α-carbonium ion was blocked by the presence of a methyl group (α-methyl- and α,o,o,p-tetramethylstyrene), the adduct did not form; the reaction led instead to a mixture of bromostyrenes, similar to that found by Huyser and Kim for the bromination of the tetramethyl compound.[5]

The adducts were formed by the addition of an equimolar amount of the powdered dipyridine bromine(I) perchlorate salt to solutions (2-3% by weight) of the olefin methylene chloride at -70°. Low-temperature nmr observations of CD_2Cl_2 solutions showed clearly that addition accurred and differentiation of the pyridine moieties was apparent (Fig. 1). The adducts were isolated by warming the reaction mixture to room temperature, washing it with water to remove free pyridine and removing the methylene chloride with a rotary evaporator. (A cleaner product could be obtained by adding a three-fold excess of pyridinium chloride to the solution at ca. -40° and washing the oily product with both carbon tetrachloride and water at room

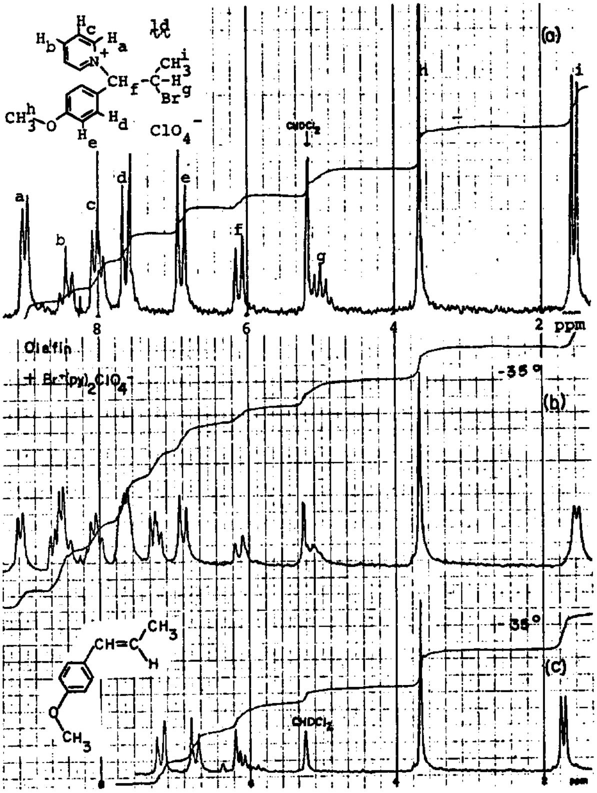

Figure 1 - 90 MHz spectra in CD_2Cl_2 of (a) isolated anethole adduct (1d) at room temperature, (b) anethole + $Br^+(py)ClO_4^-$ at -35°, (c) anethole at -35° (relative to TMS internal lock).

temperature.) Styrene and 4-methylstyrene gave oils; the other products were all white powders. The purified adducts were examined by nmr in CD_2Cl_2 solution. The downfield shifts of the pyridinium protons heterocyclic ring.[6] The simplicity of the alkyl region of the spectrum attested to the regiospecificity and stereospecificity of the reaction: only one isomer was observed. The assignment of its structure as the erythro-β-bromo-α-pyridinium adduct could be made by comparison with the reported spectra of the dibromides and methoxybromides.[7]

The infrared spectra clearly indicated the presence of perchlorate anion in the product (Fig. 2). The bands at 1150 and 625 cm^{-1} are characteristic for perchlorate[8] and were present in the spectra of all of the adducts, in addition to bands corresponding to the hydrocarbon substrates and pyridinium, whose presence had been deduced from the nmr spectra.

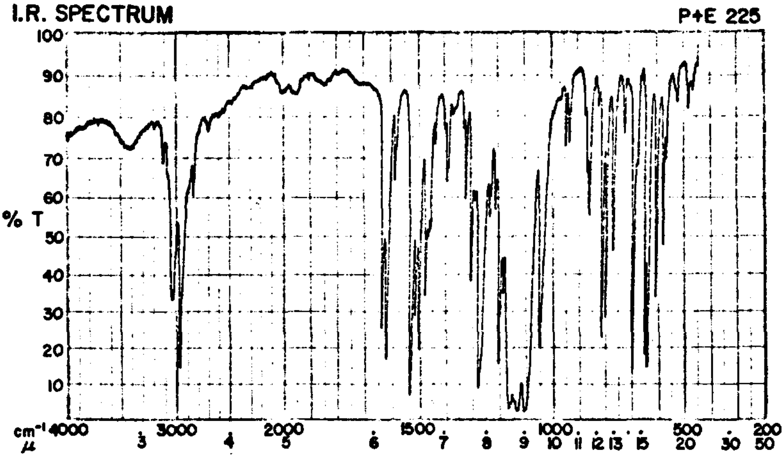

Figure 2 - IR spectrum (KBr disk) of anethole adduct (1d)

The adducts were shown to be fairly stable. The incorporated pyridine did not exchange with free pyridine-d_5. Even overnight refluxing in methanol saturated with sodium bicarbonate did not decompose the products, nor did the addition of HBr, HCN, LiBr or pyridinium chloride to methylene chloride solutions. (The styrene and 4-methylstyrene adducts did degrade somewhat after *ca.* one week at room temperature.)

These results indicate that dipyridine bromine(I) perchlorate may find significant application as a source of electrophilic bromine for theoretical studies and for the synthesis of usual compounds incorporating weak nucleophiles. The vinyl ether derivatives constitute a new type of compound, in which there is a carbon bound both to an oxygen and to a positively-charged nitrogen.

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