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NEIGHBORING TERT-AMINE GROUP PARTICIPATION WITH REARRANGEMENT IN THE PRÉVOST REACTION

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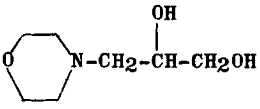
Silver halide dicarboxylates $(RCOO)_2AgX$ are known to effect hydroxylation of alkenes, supposedly via the acylated halogenohydrin (1). The role played by the acyloxy group of such intermediates in the second stage of the reaction was first studied by Winstein and Buckles (2).

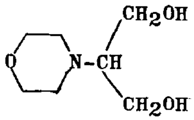
Although it has been reported (3) that amines destroy silver iodide dibenzoate (SID), very little is known about the possible interaction between a neighboring amine group and the Simonini complexes in the Prévost reaction. To our knowledge the "wet" Prévost hydroxylation has been attempted in only one case with an amino alkene (4), namely the anhydromethyltetrahydroberberine-A. This hydroxylation was unsuccessful because of neighboring group participation by the tertiary nitrogen.

The present work describes the first two reported cases of the Prévost reaction on amino alkenes occurring with rearrangement. The results indicate that participation of the nitrogen atom is the rule rather than the exception, at least when the nitrogen atom itself is located in a favorable position.

Thus, when N-allylmorpholine (III) was allowed to react with SID according to standard procedure (1), an unusually vigorous reaction ensued which was brought to completion by refluxing for four hours. The crude dibenzoate was saponified with alcoholic potassium hydroxide to give only one glycol, b.p. 117°/ 0.125 mm., n_D^{20} 1.4964. The yield was 30% based on the amount of olefin used. (Calcd. for $C_7H_{15}O_3N$: C, 52.15; H, 9.38; O, 29.78; N, 8.69. Found: C, 52.21; H, 9.13; O, 30.01; N, 8.79). The NMR spectrum of this diol proved that it was 2-morpholino-1,3-propanediol (II) instead of the product of "normal" hydroxylation, 3-morpholino-1,2-propanediol (I).



I



II

In structure II there are 8 methylene protons associated with oxygen and 5 (4 methylene and one methine) protons associated with nitrogen; in structure I the distribution is 7 to 6, respectively. The NMR spectrum* of our diol in D_2O (3-trimethylsilyl-1-propane sulfonic acid sodium salt as internal reference) shows a multiplet at $\delta = 3.4-3.9$ (relative area 8) and a multiplet at $\delta = 2.4-2.9$ (relative area 5). The signals from the protons associated with oxygen are usually located in the low field side of the spectrum from protons coupled with nitrogen.**

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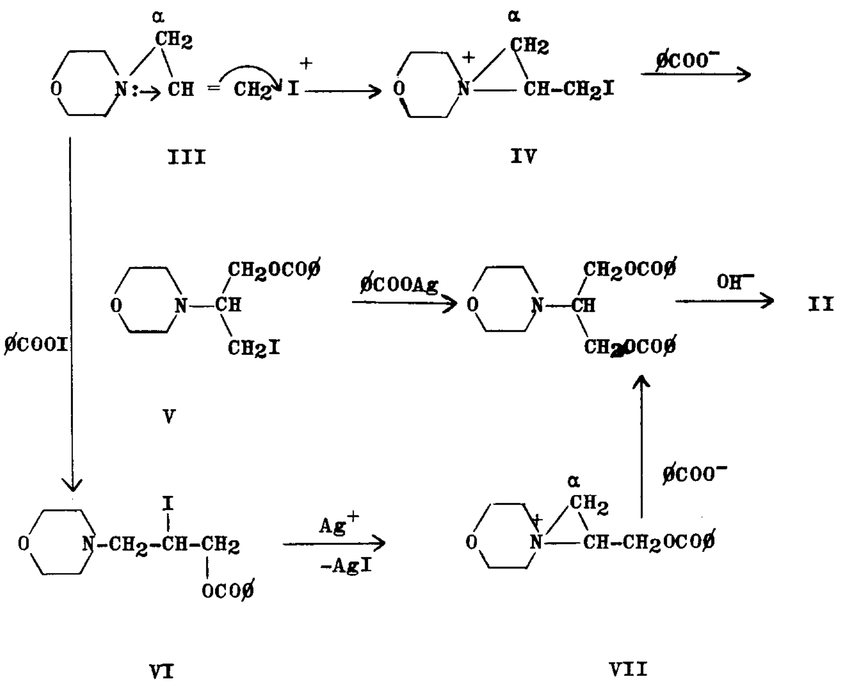
* A Varian A60 spectrometer was used.

** Compare, for instance, the spectrum of morpholine, *Varian NMR Spectra Catalog* (1962), spectrum No. 83.

We suggest, as outlined in Figure I, that the rearrangement is the result of the concerted attack III with formation of the ethylene-immonium ion IV, followed by attack of øCOO$^-$ on the α-carbon and formation of the rearranged iodohydrin benzoate V. Alternatively the ion VII could arise from the participation of the neighboring <u>tert</u>.-amino nitrogen in the replacement process of the I$^-$ in the "normal" intermediate iodohydrin VI; in the latter case attack of øCOO$^-$ on the α-carbon would thus occur in the second stage of the hydroxylation.

FIG. I



N-(β-vinyloxyethyl)piperidine by reaction with silver iodide dibenzoate gave two main products (yield ca 40%): a solid, m.p. 73-74°, and a liquid, b.p. 43°/0.10 mm. The IR spectrum of the solid product indicated a benzoate ester structure; the empirical formula $C_{16}H_{14}O_4$ was calculated from the elemental analysis (found: C, 71.01; H, 4.99; no N) and from the saponification equivalent (found 135.5); the NMR spectrum (CCl_4) showed complex multiplets at $\delta = 7.95$ (4 protons) and $\delta = 7.35$ (6 protons), and a singlet at $\delta = 4.55$ (4 protons). The above data permitted identification of this product as 1,2-ethanediol dibenzoate (calcd.: C, 71.10; H, 5.22). Further evidence was provided by mixed melting point and spectroscopic (IR) comparison with authentic material. The IR spectrum (liquid film) of the liquid product showed absorptions at 1640 cm^{-1} (s) (C=O) and 1360 cm^{-1} (w) (acetyl CH_3). The NMR spectrum showed the signals of piperidine ring protons at $\delta = 1.61$ (6 protons) and $\delta = 3.45$ (4 protons), plus a singlet at $\delta = 2.05$ (3 protons). On the basis of these data this product was identified as N-acetylpiperidine. Anal. calcd. for $C_7H_{13}ON$: C, 66.10; H, 10.30; N, 11.01. Found: C, 66.20; H, 10.50; N, 10.84. Its identity was confirmed by comparison with authentic material (IR).

Although a mechanistic interpretation of the fragmentation reaction of N-(β-vinyloxyethyl)piperidine seems less obvious, there is no doubt that this is another case of neighboring tert.-amine group participation. We are presently engaged in obtaining more data which would enable us to discuss both reactions in more detail.

Acknowledgement

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