Carbonyl Participation in Acid-catalyzed Cyclization Reactions Involving Olefinic Bonds[1]

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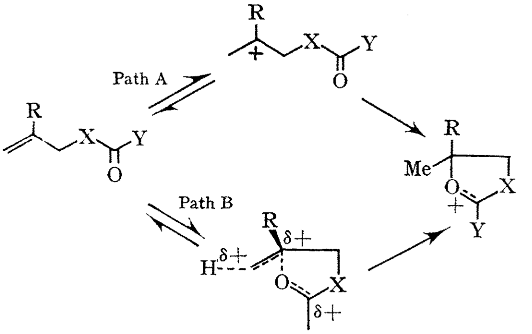
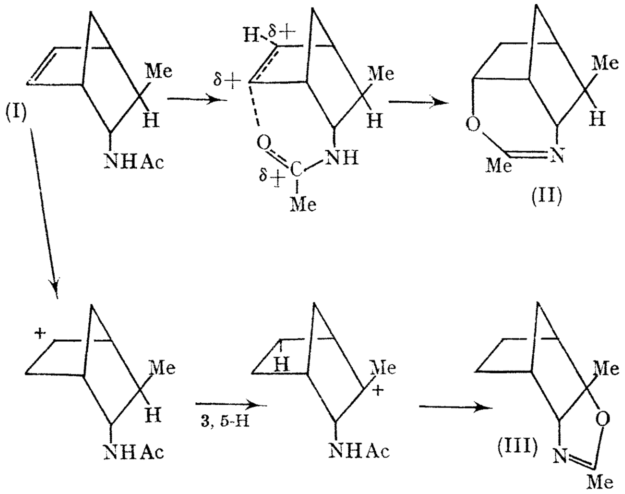
INTRAMOLECULAR participation by non-bonding and π-bonding electron pairs has received considerable attention. Examples include participation by halogen,[2] olefinic bonds,[3] and carbonyl oxygen[4] in solvolytic reactions of trialkyloxonium ions, halides, and sulphonates. Evidence for participation commonly includes kinetic data and in some cases isolation of intermediates.

Recent reports have described the observation of heterocyclic ions from the cyclization in strong acid media of various olefinic amides,[5] carbamates,[5] esters,[6] ketones,[7,8] and thiolesters.[6] All of these reactions may occur by initial carbonium-ion formation (Path A) and subsequent cyclization, or by a concerted process (Path B) which involves intramolecular carbonyl participation during protonation. Studies[5-7] with D_2SO_4 and H_2SO_4 in varying concentrations have not allowed a clear choice between Paths A and B.



We have studied *endo*-2-acetamido-*exo*-3-methylbicyclo[2,2,1]hept-5-ene (I), which may give alternative cyclic products. Since heterocyclic ions of the type described here are relatively stable once formed,[5] this system potentially allows one to demonstrate whether participation of the carbonyl oxygen as shown in Path B is important in these reactions. The two probable reaction paths are detailed below. Either protonation at C-5 with subsequent cyclization (Path A) or neighbouring carbonyl oxygen participation (Path B) would give (II). Protonation at C-6 followed by a 3,5-hydride shift[9] and then cyclization leads to the oxazoline (III).



When (I) is heated to 120—130° in polyphosphoric acid (10 min.), then poured over ice and neutralized, a liquid (70%, b.p. 52°/0·75 mm., picrate m.p. 207—208°), is produced. Its 100 MHz n.m.r. spectrum (CCl_4) supports structure (III) (2,4-dimethyl-3-oxa-5-aza-*endo*-tricyclo [5,2,1,$0^{2,6}$]dec-4-ene): τ 8·74 (s, 2-Me), 8·11 [d, 4-Me, J (CH–N) 1·2 Hz[10]], and 6·35 for (d, 6-H, J 4·6 Hz).

Any other structure possible by other rearrangement of the bicyclic nucleus[9] can likewise be excluded by the n.m.r. analysis.

While our results may not be completely general for cyclization reactions of non-cyclic carbonyl-containing olefins, it appears that intramolecular carbonyl-oxygen participation during protonation offers little lowering in transition state energy for cyclization.

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