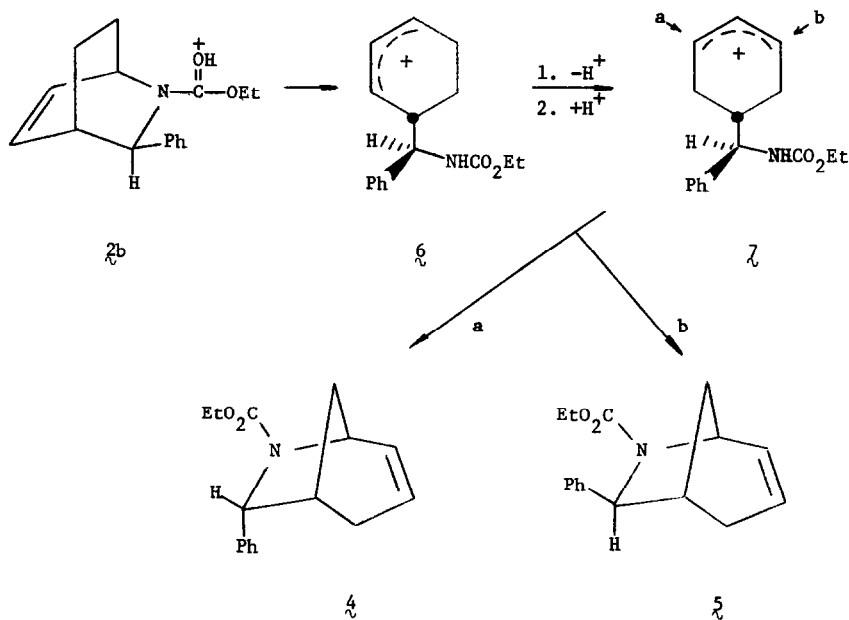


Similarly, separate solutions of either 83:17 or 90:10 exo-endo mixtures of 3-phenyl-N-carbethoxy-2-azabicyclo[2.2.2]oct-5-ene $\overset{2}{\lambda}$ afforded diphenylmethane (10%), small amounts of urethane and benzylurethane, and 18-25% yields of an oil, bp 130° (0.3 mm), which was separated by vpc (vide supra, 190°) into $\overset{3}{\lambda}$ (10-15%, RT 15 min), and a mixture of stereoisomers $\overset{4}{\lambda}$ (25-30%), RT 17 min) and $\overset{5}{\lambda}$ (55-65%, RT 20 min). Chemical shifts and major coupling constants for the endo-phenyl isomer $\overset{4}{\lambda}$ (δ , acetone-d₆) are: 7.20-7.24 (Ph), 6.08 (H₂), 5.40 (H₃, J_{2,3} = 9.0 Hz), 5.06 (H_{6x}, doublet, J_{5,6} = 5.7 Hz), 4.44 (H₁, J_{1,2} = 6.0 Hz), 3.92 (OCH₂), 2.72 (H₅), 2.5-1.9 (H_{4,4'}), 2.06 (H₈, J_{1,8} = 4.0 Hz), 1.88 (H₇, J_{7,8} = 11 Hz), 0.88 or 1.2 (CH₃). For the exo-phenyl isomer $\overset{5}{\lambda}$ the shift parameters are: 7.20-7.24 (Ph), 6.24 (H₂), 5.52 (H₃, J_{2,3} = 9.0 Hz) 4.68 (H_{6n}, singlet), 4.30 (H₁, J_{1,2} = 5.5 Hz), 3.92 (OCH₂), 2.48 (H₅), 2.50-1.90 (H_{4,4'}), 2.18 (H₈, J_{1,8} = 4.5 Hz), 1.60 (H₇, J_{7,8} = 11 Hz), 0.88 or 1.2 (CH₃).

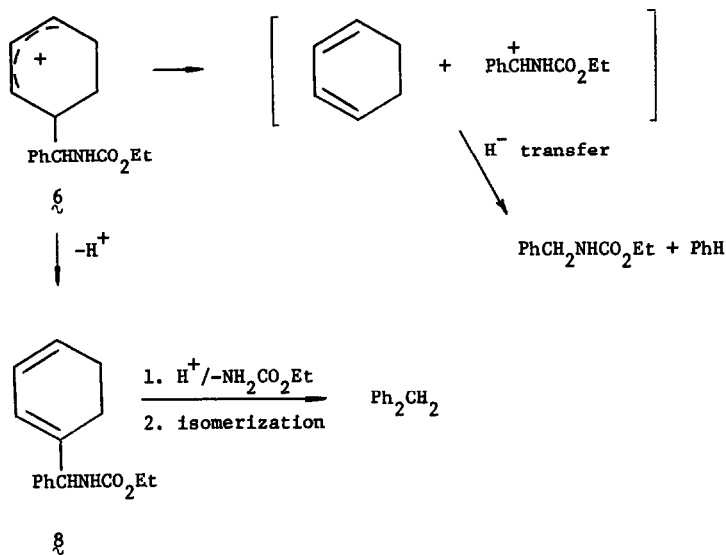
The stereochemical assignment and determination of isomer ratios follow from the resonance for H_{6n} of the exo-phenyl isomer $\overset{5}{\lambda}$, which because of the 90° dihedral angle with the adjacent bridgehead hydrogen appears only as a singlet, whereas in the exo-phenyl isomer $\overset{4}{\lambda}$, H_{6x} couples to the bridgehead hydrogen and appears as a doublet, (J_{6n,5} = 5.7 Hz). Reactions were generally terminated when most of the starting olefin $\overset{2}{\lambda}$ had rearranged. Longer reaction times led to decreasing amounts of $\overset{2}{\lambda}$, but also to disappearance of $\overset{4}{\lambda}$ and $\overset{5}{\lambda}$ via degradation to urethane, diphenylmethane, and unidentified polymeric material. When reaction was 50% complete, recovered $\overset{2}{\lambda}$ was not epimerized, indicating epimerization of phenyl does not precede isomerization. Variations in the relative amounts of $\overset{4}{\lambda}$ and $\overset{5}{\lambda}$ are an apparent result of moderate sensitivity to minor differences in reagent concentrations and reaction times.

The observed reaction products are consistent with a mechanism for rearrangement of ζ^b (exo-Ph) shown in Scheme I. Initial protonation of the urethane results in ring-opening to cyclohexenyl cation ξ . In the presence of water, the cyclohexenyl cation ξ can isomerize to ζ by a path involving proton loss and reprotonation.⁷ Allylic cation intermediate ζ can be attacked by urethane nitrogen at either of two positions to give endo-phenyl adduct ζ^a (path a) or exo-phenyl adduct ζ^b (path b). Since the same intermediate ζ will derive from the endo-phenyl isomer of ζ , this mechanism accounts for the observation that product stereochemistry shows no apparent relationship to the stereochemistry of starting olefin ζ . In addition, it can be readily shown that cyclohexenyl cation ξ is a rational precursor for the formation of benzylurethane, urethane, and diphenylmethane (Scheme II).

Scheme I



Scheme II



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