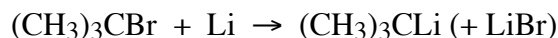
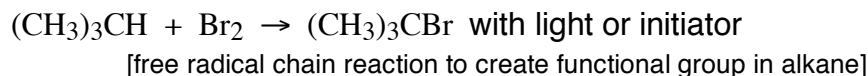
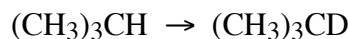


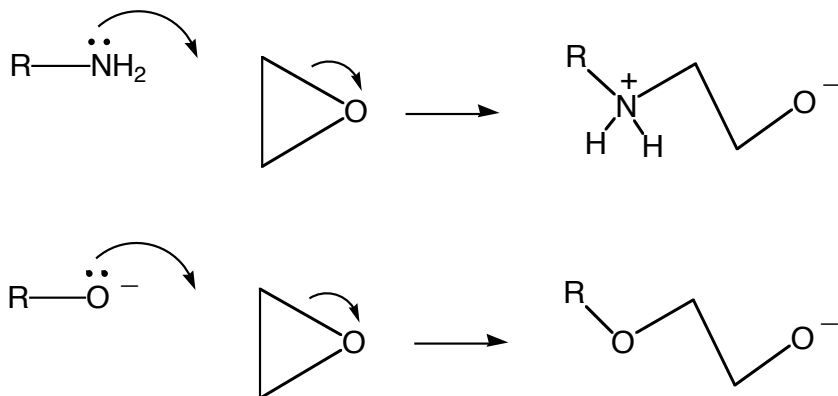
From 2004

6. (5 min) Show **reagents** for accomplishing the following conversion in a practical manner.
(No mechanisms are necessary, but do show the **isolable product from each reaction** in the required sequence).



10. (3 min) Show the product of the first step in the reaction of an amine with an epoxide and the product of the first step in the reaction of a phenoxide with an epoxide. ALSO add curved arrows to show electron flow in each reaction

[Curved arrows should be drawn carefully to show where the electron pair of the nucleophile begins and where it ends (between N or O and carbon), and to show where electrons in the bond to the leaving group begin and end. Remember that ring strain in "oxirane" makes O^- a competent leaving group.]



11. (3 min) Explain how you would expect a change in solvent from ethanol to hexane to influence the relative rates of the two reactions in Question 10. For the sake of argument, suppose that they have the same rate in ethanol.

The first reaction has neutral starting materials and is generating charges in the transition state, a transition that is favored by solvent polarity. The second reaction is dispersing the charge of the alkoxide in the transition state, and should be retarded by increased solvent polarity. Thus the first reaction should be slowed relative to the second by decreasing the solvent polarity. Loss of H-bonding stabilization of the alkoxide in the ethanol solution has the same effect.

[Few answers noted that it might be difficult to conduct the second reaction in hexane, because the alkoxide salt might not be soluble in this nonpolar solvent.]

- 12.** (7 min) Describe a real, convincing experimental proof that the normal course of an S_N2 substitution at carbon is stereochemical inversion, not retention or racemization. Try to give structures of the compounds and reagents actually used in the experimental proof.

Obviously this question asked for as detailed a description as you could summon up of the Kenyon and Philips experiment. More than half the class got a perfect score on this question (Congratulations!). Most of the others lost a few points because of lack of specificity on the nature of the compounds used or on the optical rotations that were measured.

[No one picked up on the word “normal”, which was designed to elicit mention that homogeneous solution reactions were considered normal, whereas early workers had suspected that Walden’s inversion must occur in the heterogeneous reaction of chlorosuccinic acid with solid silver oxide. This was a fine point and no points were deducted for failure to mention it.]

From 2006

- 5.** (5 min) Explain how comparing the rate constants for nucleophilic substitution on R-L using a range of R groups and a single leaving group helps choose between Dissociation/Association and Concerted (or Association/Dissociation) mechanisms.

Making the R group bulkier (methyl to ethyl to isopropyl to neopentyl) successively slows the S_N2 reaction. This is consistent with steric hindrance to formation of the more crowded pentavalent transition state (or intermediate) of the concerted (or A/D) process, but greater bulk would have been expected to accelerate loss of the leaving group in the D/A process, both through steric hindrance and through stabilization of a more substituted carbocation intermediate.

[had the question asked for specifics, it would have been important to specify the rate ratios]