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THE AROMATIC OXY-COPE REARRANGEMENT

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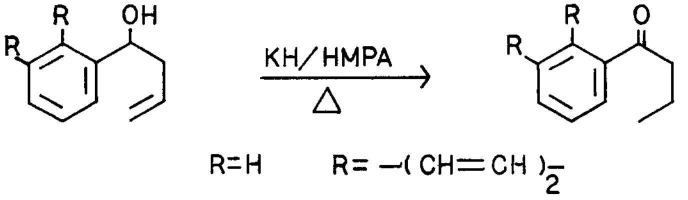
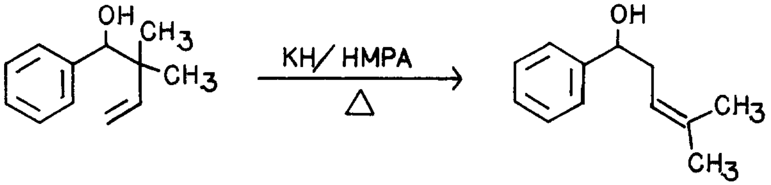
An aromatic oxy-Cope rearrangement can be achieved under anionic conditions (KH + HMPA) in low yield with a naphthalene ring but not a phenyl.

We have recently measured the activation parameters for an aromatic Cope rearrangement,[1] and these suggest that rearrangement of 4-phenyl-1-butene would require $\Delta H^{\neq} \simeq 42$ kcal/mol. Searching for ways to reduce this barrier, we were quite obviously attracted by the large reduction in activation energy associated with the anionic oxy-Cope rearrangement.[2] Thus, we initiated a study of the aromatic oxy-Cope rearrangement, and we are now prompted to report our progress by the recent report of the elegant and related work of Jung.[3]

Our initial attempts to realize an anionic aromatic oxy-Cope rearrangement were abortive. Heating 1-phenyl-3-buten-1-ol or 1-α-naphthyl-3-buten-1-ol with a slight excess of potassium hydride in HMPA overnight gave butyrophenone (48%) and butyro-α-naphthone (85%) as the only products. Attributing this reaction to a base catalyzed double bond migration, we rearranged 1-phenyl-2,2-dimethyl-3-buten-1-ol under the same conditions (75° overnight). Once again, the



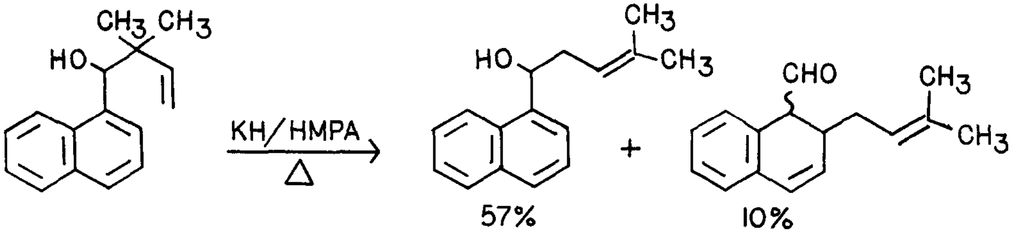
(1)



(2)

reactant evaded the desired rearrangement, undergoing solely a 1,3-shift (85%). The 1,3-shift can be suppressed by using sodium hydride in DME, but no reaction is observed in 16 hours at 85°.[4] Neither potassium nor sodium salts of the butenols react at 85° in DME. To date, we have found no conditions under which a phenyl ring will participate in the anionic oxy-Cope rearrangement. This is in total agreement with Jung's findings.

The reluctant anionic aromatic Cope rearrangement was finally realized, albeit in low yield, when 1-α-naphthyl-2,2-dimethyl-3-buten-1-ol was heated four hours at 65° in the presence of



(3)

potassium hydride and HMPA. The major product was the result of a formal 1,3-sigmatropic shift, but a low yield of 2-(γ,γ-dimethylallyl)-1,2-dihydroaphthalene-1-carboxaldehyde was obtained. This aldehyde was relatively unstable toward rearomatization and proved difficult to separate from the reaction mixture in pure form. It was identified by its spectral properties, ir (neat) 1705 cm^{-1}; nmr (CCl_4)δ, 9.44 (1H, d, J=2 Hz), 7.02-7.23 (4H, m), 6.34 (1H, d, J=9.5 Hz), 5.92 (1H, d of d, J=6, 9.5 Hz), 5.08 (1H, t, J=5.3 Hz), 3.28 (1H, m), 1.92-2.18 (3H, m), 1.69 (3H, s), 1.48 (3H, s).

The anionic oxy-Cope rearrangement does occur, but the high barrier for the aromatic Cope rearrangement leaves too much freedom for competitive processes to intervene, and the anionic oxy-Cope does not appear to provide a general answer to the problem of facilitating the aromatic [3,3] sigmatropic reaction for all-carbon systems.

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References

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4. We are indebted to Prof. D. A. Evans for the suggestion to study the reaction under these conditions.[5]
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