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ALLYL AND BENZYL ETHYNYL ETHERS: UNUSUALLY FACILE CLAISEN-TYPE REARRANGEMENTS

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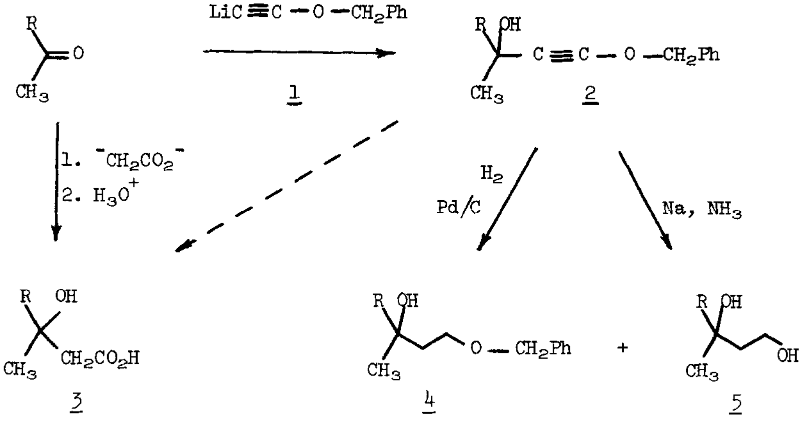
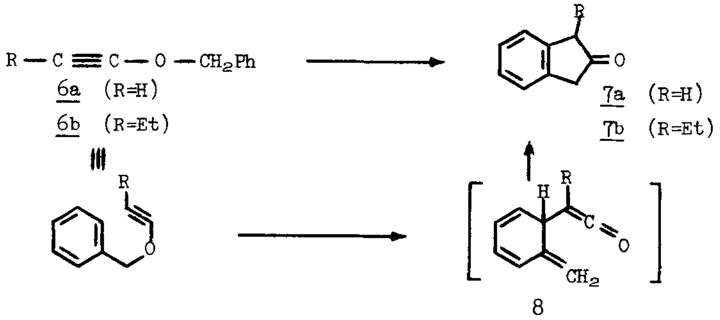
During the course of an investigation of methods for the preparation of β-hydroxyacids (3) that avoid the strongly basic acetate enolate, we prepared benzyl ethynyl ether (6a).[1,2] This compound appeared particularly attractive, as its acetylide derivative (1) should be a good nucleophile but only a weak base; further, the benzyloxyethynyl carbinol adducts (2) seemed potentially convertable to the desired system by selective hydrogenolytic debenzylation under neutral or basic conditions that should avoid the production of unsaturated esters that are normally formed from these systems under acid conditions.[2a]

The lithio derivative 1 added smoothly to 2-octanone to give 2; however, attempted cleavage with hydrogen over palladium gave only 4 (57%), and with sodium in liquid ammonia, only 5 (56%), revealing the particular sensitivity of the acetylene group to saturation.



(R = n-C_6H_{13}-)

During the preparation of 6a we were struck by the facility with which this ether underwent a thermal rearrangement. White crystals, which collected in the condenser during the distillation of 6a at ca. 90°, were found to be 2-indanone (7a). The conversion to 7a could be effected in ca. 75% yield, by warming 6a neat or in carbon tetrachloride solution, to 90° for 0.5 hr.



6a (R=H)

6b (R=Et)

7a (R=H)

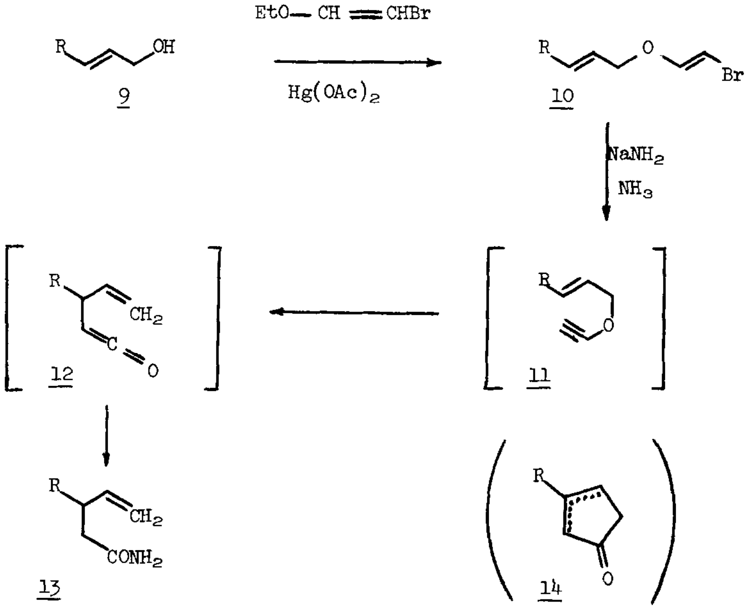
7b (R=Et)

8

This rearrangement, which has been reported for the corresponding ethyl analog (6b → 7b),[3] appears to proceed via a Claisen-type rearrangement, followed by a rapid cyclization of the dearomatized ketene 8. A similar series of intermediates were postulated by Trahanovsky to rationalize the formation of indanones in the thermolytic rearrangements of phenyl propargyl ethers.[4]

As this rearrangement provides a remarkably simple synthesis of benzocyclopentenones, we considered its extension to non-aromatic systems in the hopes of synthesizing cyclopentenones (14). Initial attempts to prepare allyl ethynyl ethers of type 11 by reaction of a copper (I) allyloxide with an iodoacetylene[5] gave only the acetylene dimer. Selective bromination of allyl vinyl ethers with pyridinium bromide perbromide or bromine also proved unsatisfactory. However, a bromovinyl exchange between (E)-2-hexen-1-ol (9) and 2-bromovinyl ethyl ether produced 2-bromovinyl (E)-2-hexenyl ether (10) in 30% yield. Treatment of 10 with sodium amide in liquid ammonia gave the unsaturated amide 13 in 40% yield after crystallizatio with no evidence of ketonic material (14).

As the formation of 13 is consistent with the trapping of 12,[6] formed via 11, we attempted to achieve the final dehydrobromination under non-nucleophilic conditions. Treatment of 10 with butyllithium gave only debrominated starting material and 9, while reaction with lithium diisopropylamide or 1,5-diazobicyclo[5.4.0]5-undecene gave only polymeric product. Attempts to prepare the ketene 12 by an alternate route - treatment of the acid chloride derived from 13 (by hydrolysis and reaction with thionyl chloride) with triethylamine - gave only high molecular weight material, which was shown by ir to be free from carbonyl compounds.



(R=n-C_3H_7-)

Our observation that the β,γ-unsaturated ketene 12, generated by the remarkably facile Claisen-type rearrangement of 11, fails to cyclize to a cyclopentenone, is consistent with two recent reports:[7] the same species, generated by a copper-catalyzed thermolytic rearrangement of β,γ-unsaturated diazoketones, gives ester in the presence of methanol, but only polymer in hydrocarbon solvents. The fact that the aromatic ketene 8 undergoes exclusive recyclization is most likely related to the exothermicity that attends the rearomatization.

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1. The preparation of this compound has been reported in a patent by D. Ginsburg and J. Hescheles (Chem. Abs. 52 (1958), p 14683f), who also noted its thermal instability.
2. For reviews describing the preparation and reactions of alkyl ethynyl ethers, see: (a) J. F. Arens, Advan. Org. Chem., 2, 163 (1960); (b) L. Brandsma, H. J. T. Bos, and J. F. Arens, "Chemistry of Acetylenes," H. G. Viehe, Ed., Mercel Dekker, New York, N. Y., 1969, p 776.
3. H. Olsman, A. Graveland, and J. F. Arens, Recueil, 83, 301 (1964).
4. W. S. Trahanovsky and P. W. Mullen, J. Amer. Chem. Soc., 94, 5911 (1972).
5. G. M. Whitesides, J. S. Sadowski, and J. Lilburn, J. Amer. Chem. Soc., 96, 2829 (1974).
6. We have tried to trap the ketene intermediate in the aromatic series (8). Rearrangement of 6a was carried out in the presence of excess butylamine or butanethiol in carbon tetrachloride. 2-Indanone was produced in undiminished yield in the presence of butanethiol, but in the presence of butylamine, a tarry, black product was obtained. Chromatographic analysis of this material showed that it contained no 2-indanone. We have been unable to isolate butyl o-tolylacetamide, the expected trapping product, from this material.
7. (a) A. B. Smith, J. Chem. Soc. Chem. Commun. 695 (1974); (b) J. P. Lokensgard, J. O'Dea and E. A. Hill, J. Org. Chem., 23, 3355 (1974). See also, A. B. Smith, J. Chem. Soc. Chem. Commun. 274 (1975).