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Selective Conversion of α-Tetralones to Dihydronaphthalenes#

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Abstract: A simple procedure for selective conversion of α-tetralones to dihydronaphthalenes is described. A novel protic acid catalyzed hydride migration mechanism is proposed.

There are several methods for the conversion of carbonyl compounds to olefins, most of which are two or three step processes. In general, these procedures show little selectivity in preferentially converting one carbonyl group to an olefin over another. In a typical multistep procedure, a carbonyl functionality is first reduced to a hydroxyl,[1] which is then converted into a better leaving group (e.g. a tosylate or a halide)[2] and finally the leaving group is eliminated to give the olefin. Alternatively, the hydroxy compound is treated with a strong acid to eliminate water and afford the olefin. Another method of converting carbonyls to olefins is via the Bamford - Stevens reaction.[3] In all of the above procedures, the selective conversion of one carbonyl to an olefin would require laborious selective protection - deprotection of the unreacted carbonyl. In this communication, we report the one - step conversion of α-tetralones to dihydronaphthalenes in the presence of other carbonyls. A novel acid mediated hydride migration mechanism is proposed for this new reaction and supported by deuterium labelling experiments.

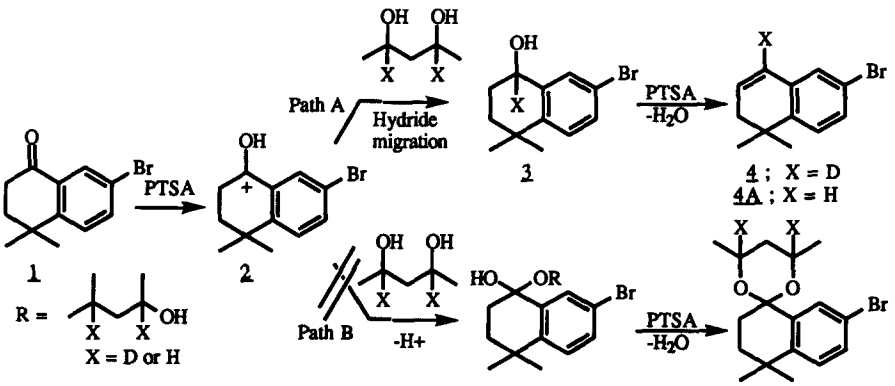
In the presence of acid catalyst, 2,4-pentane diol (PD) protects carbonyl functionalities e.g. aldehydes in the form of cyclic acetals. The mechanism involves nucleophilic attack of the oxygen of PD on the carbonyl carbon followed by elimination of water to give rise to the cyclic acetal. We have found that under similar conditions α-tetralones are converted selectively to the corresponding dihydronaphthalenes (Table I). The reaction is quite general and proceeds in moderate to good yields. In a typical reaction, ketone (1 mmol), PD (4 mmols) and p-TSA (5 mgs) in toluene (20 ml) was refluxed in a Dean-Stark apparatus until the reaction went to completion (TLC).[4] The product was obtained after quenching the reaction with aqueous sodium bicarbonate followed by extraction with ethyl acetate. The selectivity and differential reactivity of PD towards different carbonyls of similar redox-potential is illustrated in entries 2 and 5. As illustrated in entry 5, acetophenone can be effectively converted to the corresponding ketal. In entry 3, the α-tetralone carbonyl is selectively converted to the olefin while the acetophenone carbonyl is protected as its ketal and subsequently hydrolyzed to the ketone under the acidic (10% aqueous HCl)[5] work up conditions. Entries 6

#Dedicated to the memory of Prof. William S. Johnson

and 7 show the general utility of this reaction, in that, unsubstituted α-tetralone and 7-methoxy-1-tetralone are converted to the corresponding dihydronaphthalenes[6,7] in good yield.

The proposed mechanism for this conversion is illustrated in Scheme I. Protonation of the carbonyl of α-tetralone **1** leads to the formation of the oxonium ion, which is in resonance with the benzylic cation **2**. Hydride (deuteride) from C-2/C-4 of PD migrates to the benzylic cation to give the benzyl alcohol dervative **3**. Compound **3** eliminates water to give dihydronaphthalene derivative **4** under the acidic reaction conditions.

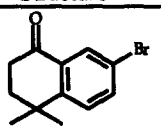
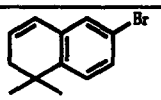
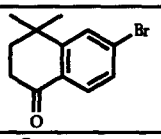
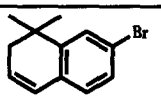
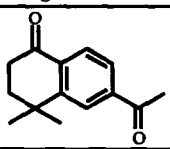
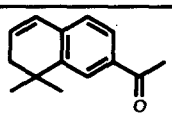
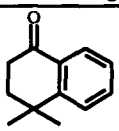
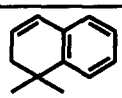
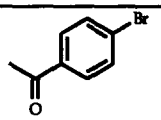
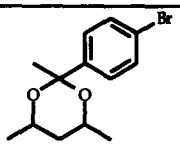
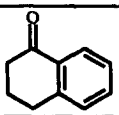
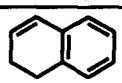
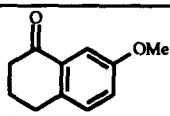
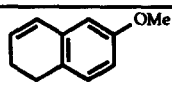
Scheme I



We did not attempt to detect the fate of the hydride donor PD; it is postulated that it would give rise to 4-hydroxy-2-pentanone, which under the reaction conditions would dehydrate to give pent-3-en-2-one. We demonstrated that the source of the hydride are the C-2/C-4 atoms of PD by employing 2,4-dideutero-pentane-2,4-diol.[8] The product **4** isolated exhibited the expected spectral pattern of a single deuterium atom at the benzylic carbon.[9] The nucleophilic attack of the hydride (Scheme I, path A) from PD, rather than the sterically hindered oxygen atom of secondary hydroxyl (scheme I, path B) of PD, on to the benzylic cation **2** suggests steric hindrance is playing a key role in this selective transformation. In the case of methyl ketones the oxygen of PD is accepted as a nucleophile, due to lower steric requirements, leading to the formation of the cyclic ketal. The proposed mechanism is similar to that of the Meerwein-Ponderff-Verley (MPV) reduction,[10] except that the MPV procedure employs aluminum alkoxide as reductant to generate the hydride required for reduction. In the present procedure a protic acid is used as catalyst. To the best of our knowledge this is the first example of a hydride migration in a protic acid catalyzed reaction.[11,12]

The procedure described here employs mild conditions and inexpensive, commercial reagents to effect the selective, one-step conversion of α-tetralones to dihydronaphthalenes in reasonable yields. The mild reaction conditions employed should be compatible with the presence of a wide variety of other functional groups in addition to other carbonyl groups. A novel protic acid catalyzed hydride migration mechanism is proposed for this conversion.

Table I

Entry	Structure[a,b]	Reaction time (h)	Product	Yield%
1		16		70
2		36		65
3		16		70
4		16		65
5		36		75
6		36		65
7		36		65

a) Synthesis of substrates **1** and **3** will be published elsewhere.

b) For synthesis of substrates **2** and **4** see : Mathur, N.C.; Snow, M.S.; Young, K.M. and Pincock, J.A.*Tetrahedron* **1985**, *41*, 1509

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References:

1. Larock, R.C. *Comprehensive Organic Transformations*, VHC Publisher, **1989**, 528.

2. Larock, R.C. *Comprehensive Organic Transformations*, VHC Publisher, **1989**, 151.

3. Shapiro, R.H., *Organic Reactions*; **1984**, *23*, 405.

4. Freshly distilled PD, a mixture of meso and racemic diols, was used. We have found freshly distilled PD

gave better yields.

5. The ketal obtained is a diastereomeric meso and racemic mixture, which on stirring with 10% aqueous hydrochloric acid for 5 min gave the ketone.

6. We thank one of the reviewers for suggesting these reactions to emphasize the general utility of this reaction.

7. These two reactions were conducted under argon atmosphere and with deoxygenated solvents.

8. Synthesis of 2,4-dideuteropentan-2,4-diol: 2,4-pentanedione in methanol and water was reduced with sodium borodeuteride according to the procedure of Pritchard, J.G. and Vollmer, R.L. *J. Org. Chem.* **1963**, *28*, 1545.

9. All new compounds are fully characterized. The relevant spectral data for selected compounds:

Compound **4a**:
^{1}HNMR (300MHz,$CDCl_3$, TMS): δ 1.24 (6H, s), 2.24 (dd, J=1.8, 4.4Hz, 2H), 5.98 (td, J=4.4, 9.6Hz, 1H), 6.37 (td, J=1.8, 9.6Hz, 1H), 7.14 (d, J=8.6, 1H), 7.16 (brs, 1H), 7.28 (dd, J=2.2, 8.6Hz, 1H). ^{13}CNMR (75MHz, $CDCl_3$): ppm 28.29, 33.31, 38.65, 119.75, 125.62, 126.54, 128.80, 129.07, 130.06, 134.98, 142.94.
LRMS (EI) calculated for $C_{12}H_{13}Br$ 236 and 238; found 236 and 238.

Compound **4**: ^{1}HNMR (300MHz, $CDCl_3$, TMS): δ 1.25 (s, 6H), 2.24 (d, J=4.1Hz, 2H), 5.98 (t, J=4.1Hz, 1H), 7.15 (d, J=8.5Hz, 1H), 7.16 (brs, 1H), 7.28 (dd, J=2.3, 8.5Hz, 1H). ^{13}CNMR (75MHz, $CDCl_3$): ppm 28.29, 33.31, 38.65, 119.75, 125.63, 126.25 (triplet, J(^{13}C-D)=24.6Hz), 128.65, 129.04, 130.70, 134.94, 142.96.
LRMS (EI) calculated for $C_{12}H_{12}BrD$ 237 and 239; found 237 and 239.
The ^{13}C NMR further confirmed the presence of single deuterium (in compound 4) on the benzylic (olefinic) carbon by the observed isotope shift at 126.25ppm.

10. March, J. *Advanced Organic Chemistry - Reactions, Mechanisms and Structure*, Wiley-InterScience Publication, third edition, **1985**, p 811-814.

11. Protic acid mediated triethylsilane reductions are also hydride migration processes. a) Kraus, G.A. Molina, M.T. and Walling, J.A. *J. Chem. Soc. Chem. Commun.*, **1986**, 1568; b) West, C.T. Donnelly, S.J. Kooistra, D.A. and Doyle, M.P. *J. Org. Chem.* **1973**, *38*, 2675 and references cited therein.

12. For hydrogen transfer reactions under pyrolytic conditions to reduce a carbonyl/olefin moiety, see a) Wuest, J.D. and Zacharie, B. *J. Org. Chem.* **1984**, *49*, 163 and 166; b) Wuest, J.D. *J. Org. Chem.* **1980**, *45*, 3120.

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