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IODOTRIMETHYLSILANE DEOXYGENATION OF CARBONYL CONJUGATED ALLYLIC ETHERS

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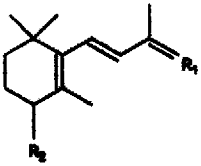
Summary: The attempted demethylation of 4-methoxy-β-ionone[1] (1) with iodotrimethylsilane gave the unexpected product, β-ionone (2). This reagent may prove useful in the cleavage of allylic ethers conjugated to ketones.

Iodotrimethylsilane (TMSI) has proven to be a useful reagent for the cleavage of methyl ethers to alcohols.[2] In the course of our studies in the area of retinoid synthesis, we had occasion to effect this transformation. However, when 1 was treated with TMSI to prepare 4-hydroxy-β-ionone (3), only the cleavage product 2 rapidly resulted (-78°C, 2.5 eq., CH_2Cl_2, 5 min; 60%).[3]



1 R_1 = O, R_2 = OCH_3

2 R_1 = O, R_2 = H

3 R_1 = O, R_2 = OH

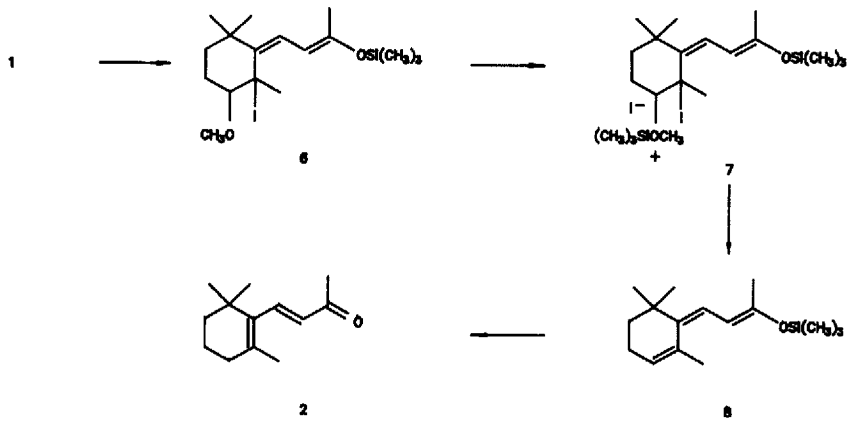
4 R_1 = CH_2, R_2 = OCH_3

5 R_1 = CH_2, R_2 = OH

The formation of 2 was observed whether TMSI was employed or made in situ ($(CH_3)_3SiCl$/NaI 0°C, 2 eq., CH_3CN, 5 min.) That the conjugated ketone was responsible for this result was suggested by the need for 2-2.5 eq. of reagent to achieve this transformation. As a test of this hypothesis, the related triene 4 was synthesized.[4] This compound, when treated with TMSI, afforded the expected corresponding alcohol 5.[5]

We propose the following mechanism for the conversion of 1 to 2. Initial 1,6 conjugate addition of TMSI to the dienone produces intermediate 6.[6] Reaction of a second eq. of TMSI with the ether oxygen gives iodide salt 7. The silyltrienol ether 8 is formed via β-elimination initiated by iodide ion. The cleaved product 2 is formed from 8 upon aqueous workup.[7]

Deoxygenation of simple allylic ethers has been previously reported[8] but under harsher conditions incompatible with carbonyls. Although TMSI has been previously employed for cleavage of ethers to alkanes, reduction with Zn/HOAC is required to complete the reaction.[9] The proposed mechanism may also provide an explanation for the unexplained result seen by



Cherbas *et al.*[10] The technique reported here is a mild one-pot method which should prove applicable to various systems for the deoxygenation of carbonyl conjugated allylic ethers.

References and Notes

1. This compound was made by allylic bromination followed by alkaline methanolysis. MS, m/e (relative intensity) (M+) 222 (81), 123 (100); NMR ($CDCl_3$) δ 1.00, 1.03 (2s,6,$C(CH_3)_2$), 1.3-1.7 (m,4,CH_2), 1.77 (s,3,5CH_3), 2.27 (s,3H,9CH_3) 3.36 (s,3,OCH_3), 3.48 (m,1,4H), 6.10 (d,1,8H, J=16.5Hz), 7.16 (d,1,7H, J=16.5Hz).
2. a) Jung, M.E.; Lyster, M.A. J. Org. Chem. 1977, 42, 968. b) Olah, G.A.; Narang, S.C.; Gupta, B.G.B.; Malhotra, R. J. Org. Chem. **1979**, 44, 1247.
3. This **2** was identical in all respects to an authentic sample.
4. The triene **4** was synthesized via Wittig reaction using the appropriate phosphonium salt. MS, m/e (relative intensity) (M+) 220 (100); NMR ($CDCl_3$) δ 0.97, 1.00 (2s,6, $C(CH_3)_2$), 1.3-1.7 (m,4,CH_2), 1.75 (s,3,5CH_3), 1.87 (s,3,9CH_3), 3.36 (s,3,OCH_3), 3.48 (m,1,4H), 4.92 (d,2,10H, J=6Hz), 6.02 (d,1,8H, J=16Hz), 6.13 (d,1,7H, J=16Hz).
5. Alcohol **5** exhibited the following spectral properties: MS, m/e (relative intensity) (M+) 206 (100); NMR ($CDCl_3$) δ 0.98, 1.01 (2s,6,$C(CH_3)_2$), 1.3-1.7 (m,4,CH_2), 1.80 (s,3,5CH_3), 1.88 (s,3,9CH_3), 3.98 (m,1,4H), 4.94 (d,2,10H, J=6Hz), 6.01 (d,1,8H, J=16Hz), 6.12 (d,1,7H J=16Hz).
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9. Morita, T.; Okamoto, Y.; Sakurai, H. Synthesis **1981**, 32.
10. Cherbas, P.; Trainor, D.A.; Stonard, R.J.; Nakanishi, K. J. Chem. Soc., Chem. Commun. **1982**, 1307.
11. Partially supported by a grant from the National Cancer Institute (CA40967).

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