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HYDROGENOLYSIS OF ENOL TRIFLATES; A NEW METHOD FOR THE REDUCTION OF KETONES TO METHYLENE COMPOUNDS

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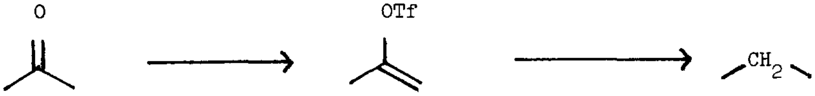
Summary: Hydrogenolysis of enol trifluoromethanesulphonates (enol triflates) gives the hydrocarbon in high yield; ketones can thus be converted to the corresponding methylene compounds in a two-step process under mild conditions.

The paramount importance of the carbonyl group in organic synthesis makes methods for its efficient removal of considerable relevance. Classical procedures for reduction of ketones to methylene compounds involve strong acids or bases, which preclude their application to sensitive compounds. Recently, attention has been given to milder procedures, and methods developed include the reduction of tosylhydrazones with sodium cyanoborohydride[1] or catecholborane[2], and the reduction of selenoacetals in various ways[3].

Enol trifluoromethanesulphonates (enol triflates) have been known for some time, and widely used as precursors for vinyl cations[4] and, for primary systems, alkylidene carbenes[5]. Only recently, however, has a good general method become available for the preparation of these potentially-useful synthetic intermediates from carbonyl compounds[6], involving the use of the sterically-hindered base 2,6-di-*t*-butyl-4-methyl pyridine[7]. Since then, McMurry has reported that enol triflates couple efficiently with cuprates[8], a reaction in which the enol triflates behave similarly to, but better than, enol phosphates[9]. We now report that enol triflates, again with similarity to the behaviour of enol phosphates[10], undergo rapid hydrogenolysis in very high yield to the saturated hydrocarbon, thus giving a mild, two-step procedure for the deoxygenation of ketones. Some of our findings are summarised in the Table; all the



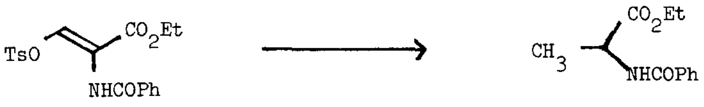
hydrogenolyses were carried out at room temperature using 1 atm. of hydrogen gas with platinum oxide as catalyst, although for Entry 2, palladium-on-charcoal catalyst was equally effective. The solvent used was ethanol, except for entry 6, where dichloromethane was used.

A typical procedure was as follows:

Androstane (Entry 4) - To a solution of androstan-3,17-dione (0.42 g, 1.5 mmol) in CH_2Cl_2(25 ml) was added triflic anhydride (0.90 g, 3.2 mmol) and 2,6-di-*t*-butyl-4-methylpyridine (0.71 g, 3.44 mmol). The mixture was heated under reflux overnight, and evaporated to dryness. Dry pentane was added and the solid pyridinium triflate filtered off (the free base can be recovered[6a]) and washed with pentane. The washed (cold 1 M HCl, then NaCl solution), dried (K_2CO_3) pentane solution was evaporated and the residue chromatographed over silica eluting with toluene to yield the ditriflate (0.58 g). A recrystallised sample had m.p. 83-85°; δ 5.5-5.7, 2H,m.

A portion of this material (184 mg, 0.33 mmol) in EtOH (10 ml) was hydrogenated at 1 atm. over PtO_2 (20 mg). Uptake of H_2 was 30 ml. Filtration and a standard workup have a solid, recrystallised from MeOH-H_2O to give androstane (83 mg, 70% overall) m.p. 46-48° (lit.[11] 50-50.5°).

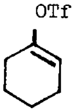
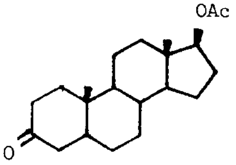
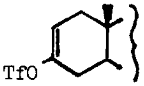
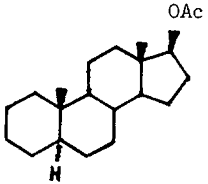
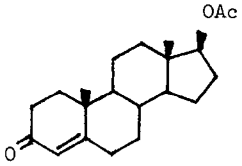
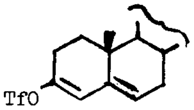
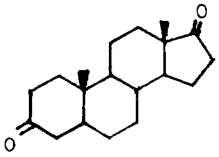
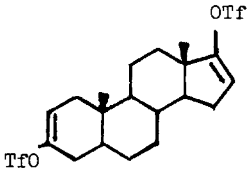
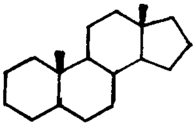
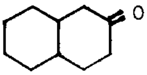
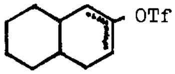
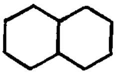
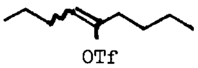
Other types of enol sulphonates, such as enol tosylates, are not easily prepared from carbonyl compounds[12] except in cases where the carbonyl compound is highly enolised[13]. Such systems, however, also appear to be easily hydrogenolysed; when enol tosylate (1) in ethanol was stirred under hydrogen at 1 atm. with Pd/C, N-benzoyl-D,L-serine ethyl ester (2) was produced in near quantitative yield.



(1) (2)

We thank S.E.R.C. for financial support.

TABLE

Entry	Starting Material	Triflate[a,b]	Hydrogenolysis[b] Product	Overall Yield %[c]
1			Cyclohexane	90
2		 d)	 m.p. 74-76° (Lit[14] 72-75°)	64
3		 e)		70
4				70
5				80
6	5-nonanone		*n*-nonane	80

a) Satisfactory microanalytical results were obtained for new compounds;
b) Spectroscopic data in agreement with structures; c) Yields of pure isolated material, except Entry 1 (by g.c.); d) m.p. 123-124°, δ4.6(t,1H), 5.7(m,1H);
e) m.p. 110-112°, δ4.6(t,1H), 5.6(m,1H), 6.0(bs,1H).

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