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α-Tosyloxylation of Enolizable Ketones using Thallium(III)p-tolylsulphonate (TTS).

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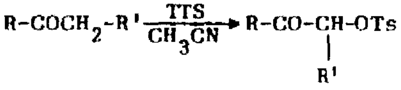
Key words : Thallium(III)p-tolylsulphonate; Enolizable Ketones; α-Tosyloxylation.

Abstract: Thallium(III)p-tolylsulphonate(TTS) in refluxing acetonitrile provides a new useful one step conversion of enolizable ketones to α-tosyloxy ketones.

The synthetic utility of thallium(III) salts for the oxidation of a wide variety of organic compounds has been extensively reviewed[1]. In continuation of our systematic study of the utility of thallium(III) salts as oxidants[2-5], we have been able to carry out smooth conversion of various enolizable ketones into the corresponding α-tosyloxy ketones, using thallium(III)-p-tolylsulphonate (TTS)[6] in acetonitrile (Scheme 1).



$$\text{R-COCH}_2\text{-R'} \xrightarrow[\text{CH}_3\text{CN}]{\text{TTS}} \text{R-CO-}\underset{\displaystyle \text{R'}}{\underset{|}{\text{CH}}}\text{-OTs}$$

1 2

Scheme I

In a typical procedure thallium(III)p-tolylsulphonate (TTS; 0.011 mole) was added to a solution of enolizable ketone (0.01 mole) in acetonitrile (15-20 ml) and the reaction mixture after refluxing for 15-20 minutes (the progress of the reaction was monitored by T.l.c.), was cooled to room temperature and poured into ice cold water. The residue so obtained was extracted with CH_2Cl_2 (3x50 ml) and washed with saturated aq $NaHCO_3$ followed by water (3x50 ml) and dried ($MgSO_4$). The solvent was distilled off under reduced pressure, the residual mass upon trituration with hexane yielded **2** in almost quantitative yield. The generality of this transformation was established by treating several substituted enolizable ketones (1b-i) with TTS under similar conditions. All the known compounds were identified by m.mp and comparison of IR and ^{1}H-NMR spectral data with those of authentic samples (Table 1).

The most probable mechanistic course (Scheme II) may involve the electrophilic attack of thallium(III)p-tolylsulphonate upon enol form

Table 1 : Oxidation of Enolizable ketones to α-Tosyloxy ketones using TTS[a].

Compounds 1	Products 2	Yields[b] %	mp (lit. mp) °C
a; R = C_6H_5 R' = H	a; R = C_6H_5 R' = H	92	97-98 (98-99)[7]
b; R = 4-BrC_6H_4 R' = H	b; R = 4-BrC_6H_4[c] R' = H	90	132-33
c; R = 4-$CH_3C_6H_4$ R' = H	c; R = 4-$CH_3C_6H_4$[c] R' = H	94	82-83
d; R = 4-$CH_3OC_6H_4$ R' = H	d; R = 4-$CH_3OC_6H_4$[c] R' = H	94	115-16
e; R = 4-$NO_2C_6H_4$ R' = H	e; R = 4-$NO_2C_6H_4$[c] R' = H	96	130-31
f; R = C_6H_5 R' = CH_3	f; R = C_6H_5[c,d] R' = CH_3	92	68-69
g; R = 4-$CH_3OC_6H_4$ R' = CH_3	g; R = 4-$CH_3OC_6H_4$[c,d] R' = CH_3	90	64-65
h; R = C_6H_5 R' = C_6H_5	h; R = C_6H_5 R' = C_6H_5	90	105(105.5-6)[8]
i; R = CH_3 R' = CH_3	i; R = CH_3 R' = CH_3	90	35 (35)[8]

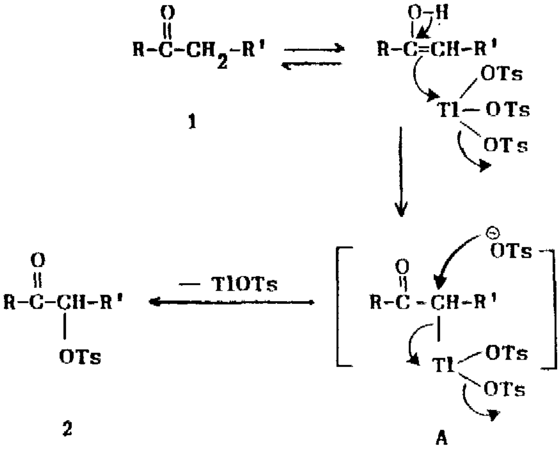
a; Same results (as given for 1a-i) were obtained by the <u>in situ</u> formation of TTS using thallium(III)acetate (1 equivalent) and p-toluene sulphonic acid (3.3 equivalents) in refluxing acetonitrile.

b; The yields are based upon the isolated solid products.

c; Satisfactory spectral data and C & H analysis were obtained.

d; *The reaction mixture was refluxed for 30-40 minutes.*

1 to give an intermediate A. Intermolecular nucleophilic displacement of the weak C-Tl bond by tosylate leads to the formation of 2.



Scheme II

The α-tosyloxy ketones have earlier been obtained using a wide variety of reaction conditions, such as treatment of enolizable ketones with [hydroxy(tosyloxy)iodo]benzene[8-9], silver tosylate[10]; base catalyzed rearrangement of deoxybenzoin oxime tosylate[11]; treatment of α-diazoacetophenone with p-toluenesulphonic acid (p-TSA)[7] and the condensation of α-hydroxyacetophenone with sulphonyl chloride[12,13]. The yields in these cases were not very good (16-80%) due to the involvement of multiple steps or the formation of iodobenzene as byproduct[8,9].

The ease and generality of the synthesis reported herein provides convenient, quick one step access to α-tosyloxy ketone in almost quantitative yields and the present communication should facilitate further investigations of their chemistry. Studies on the effect of various thallium(III) sulphonates on the course of oxidation of enolizable ketones are under way and the results will be published elsewhere.

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