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Photolysis of Phenyltellurotrifluoroacetimidates; A New Approach to Generation of α-Trifluoroacetimidoyl Radicals Leading to the Synthesis of Indole Derivatives

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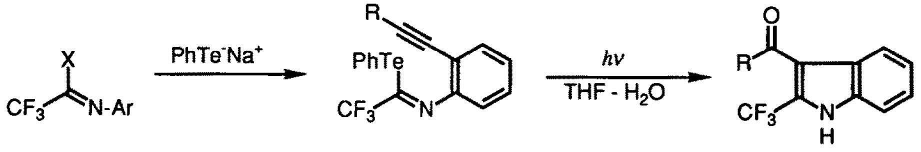
Summary; Photolysis of *N*-aryl phenyltellurotrifluoroacetimidates generates *N*-aryl trifluoroacetimidoyl radicals, which undergo an intramolecular exo-attack to carbon-carbon triple bond leading to indole derivatives.

The development of trifluoromethylated building blocks is of a current research interest, because trifluoromethylated organic compounds play an important role in medicinal and agricultural chemistries and material sciences.1,2) Recently, we have proposed *N*-aryl trifluoroacetimidoyl halides **1** are one of the promising building blocks for trifluoromethylated nitrogen heterocycles and usable as both the corresponding trifluoroacetimidoyl carbocations3) and carbanions.4) Here, we describe a first generation of the corresponding radical intermediates which undergo a novel 3-acylindole formation.



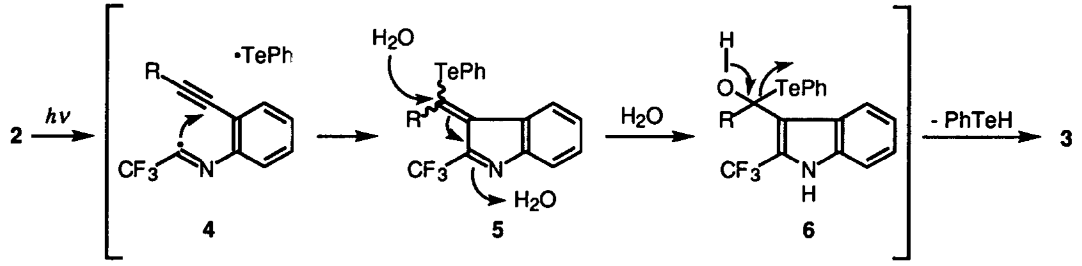
1; X = Cl
X = I

2a; R = n-Bu (95%)
2b; R = Ph (90%)
2c; R = $PhOCH_2$ (91%)
2d; R = $MEMOCH_2$ (93%)

3a; 68%
3b; 67%
3c; 54%
3d, 58%

The generations of nonfluorinated imidoyl radicals have been demonstrated by intermolecular radical reactions of isocyanides,5) isocyanates,6) isothiocyanates,6) imines,7) imidoyl chlorides,8) thioimidates,9) and selenoimidates.9) Meanwhile, the photochemical generation of acyl radicals from telluroesters,10) selenoesters,11) acylgermanes,12) acylcobalts,13) and acyl xanthates14) has been reported. On this basis, photolysis of the chalcogenoimidates [CF_3-C(MPh)=N-Ar, M; Se, Te] would be one of the potential methods for generation of the α-trifluoroacetimidoyl radicals.

Into a suspension of sodium phenyltellurolate prepared from $(PhTe)_2$ (0.3 mmol) and $NaBH_4$ (1.2 mmol) dissolved in dry EtOH (0.3 ml) and dry toluene (1.0 ml) at 0 °C for 20 min, the chloride **1** (0.6 mmol) dissolved in dry toluene (0.2 ml) was added quickly and the solution was stirred under N_2 at -80 °C for 10 min. The usual workup and chromatography (SiO_2, hexane-AcOEt) gave the telluroimidates **2** (90~95 %). Then, a solution of **2** (0.3 mmol) and a drop of water in dist. THF (3.0 ml) was irradiated with UV lamp (4 W x 2, 250~400 nm) at room temperature for 48~85 h to give 2-trifluoromethyl-3-acylindoles **3** (54~68%).



scheme 1

In contrast to the successful photolytic homolysis of C-Te bond of **2**, reaction of the corresponding selenoimidates required a longer time and gave a complicated mixture.

Solvent and an amount of water affected intensively the total reaction time and the yield of **3**, respectively. In benzene and hexane the reaction of **2a** was so slow that it took over 90 h to consume **2a** completely. On the other hand, substitution of phenyltelluro group (PhTe) with ethoxy group occurred exclusively in ethanol. Although water was essential for the acylindole transformation (scheme 1), use of an excess amount of water resulted in hydrolysis of the telluroimidates **2** to the corresponding trifluoroacetamides.

A possible reaction mechanism is shown in scheme 1. The telluroimidates **2** undergo homolytic cleavage of C-Te bond on photolysis10) to give the radicals **4**. The radicals **4** attack intramolecularly carbon-carbon triple bond to form the vinyl tellurides **5** as initial products, hydrolysis of which gives **3** via **6**.

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