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Oxidative Rearrangement of Alkynes to Carboxylic Acid Esters by [Hydroxy(tosyloxy)iodo]benzene in Methanol

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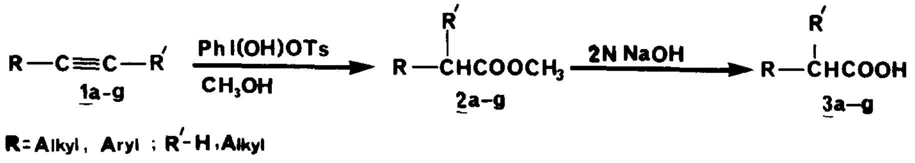
Summary A direct synthesis of methyl aryl alkanoate via oxidative rearrangement of alkynes using [hydroxy(tosyloxy)iodo]benzene in methanol is described.

Recently attention has been directed towards the synthesis of arylalkanoic acids as anti-inflammatory agents[1,2]. As part of our studies on synthetic uses of hypervalent iodine,[3] we became interested in the synthesis of arylalkanoic acids using this method. Hypervalent iodine reagents react with alkynes to give various products depending upon the reaction conditions, e.g., i) terminal alkynes react with [hydroxy(tosyloxy)iodo]benzene to yield alkynyl iodonium tosylates,[4] which are important intermediates for the syntheses of alkynyl carboxylates,[5] phosphates,[5] and triflates,[6] ii) reaction of (perfluoroalkyl)phenyl iodonium salts with terminal alkynes yields a mixture of substitution and addition products,[7] iii) non-terminal alkynes are converted to α-diketones by oxidation with iodosobenzene in the presence of ruthenium, while terminal alkynes afford carboxylic acids.[8] Oxidation of alkynyl ethers and alkynyl amines with C_6H_5IO in the presence of Ru(II) catalysts yields α-ketoesters and α-ketoamides[9] respectively, iv) bis-trifluoroacetoxyiodobenzene (PIFA) reacts with non-terminal alkynes to give α-diketones,[10] while terminal alkynes yield α-hydroxyketones.[10,11] Recently the cleavage of alkynes to carboxylic acids has been accomplished using PIFA/C_6H_6/H_2O under reflux conditions.[12]

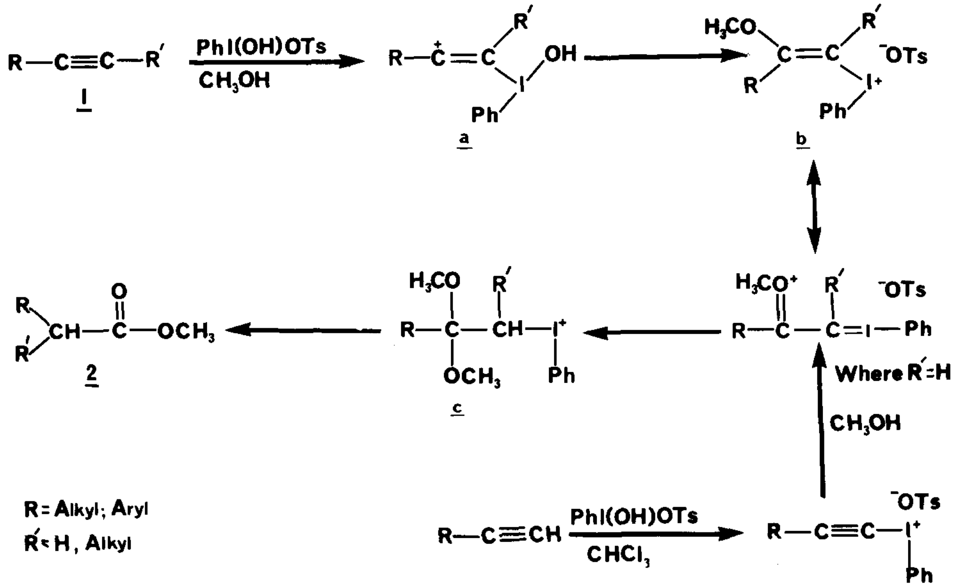
We now report the oxidative rearrangement of alkynes to esters using [hydroxy(tosyloxy)iodo]benzene in methanol for the synthesis of arylalkanoic acids as illustrated in Scheme I.



Scheme I

In a typical procedure phenyl-1-propyne (1d) (0.01mol) was added to a solution of [hydroxy(tosyloxy)iodo]benzene (0.013 mol) in methanol (60 ml). The solution was refluxed for 96 hrs, cooled to room temperature and then treated with a saturated solution of $NaHCO_3$. Extraction with CH_2Cl_2 (3x50 ml) followed by drying ($MgSO_4$) and concentration *in vacuo* gave a mixture of methyl α-methylphenylacetate (2d) and iodobenzene. The ester (2d) was purified by column chromatography on silica gel using hexane: ether (5:1). Hydrolysis in 2N NaOH solution yielded α-methylphenylacetic acid (3d) in 66% yield. All known products were identified by their IR and ^{1}H-NMR spectral data and are listed in Table 1.

The oxidative rearrangement of terminal alkynes may proceed via the formation of alkynyl iodonium tosylates as shown by the fact that phenylethnyl iodonium tosylate (4) affords under refluxing methanol, methyl phenylacetate (2b). A possible mechanistic pathway is presented in Scheme II for both terminal and non-terminal alkynes. Initial electrophilic addition of $C_6H_5\overset{+}{I}OH$ yields vinyl cation a. Coordination of a with methanol and loss of a molecule of water yields vinyl iodonium ion b. Addition of a second molecule of methanol yields c which in analogy with the known instability of alkyliodonium species,[13] would be expected to undergo rapid dissociative reductive elimination of C_6H_5I and concomitant 1,2 migration yielding eventually 2 after acid hydrolysis of the initially formed orthoester.



Scheme II

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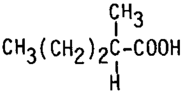
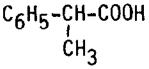
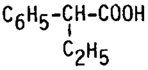
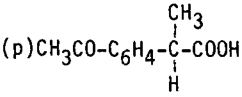
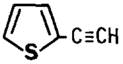
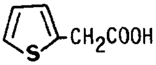
Table 1. Oxidative Rearrangement of Acetylenes with [Hydroxy(tosyloxy)iodo]benzene in Methanol

Starting Materials	Conditions	Product	% Yield	m.p. or B.P. °C
$CH_3(CH_2)_3C{\equiv}CH$ 1a	a) reflux,72h b) 2N NaOH	$CH_3(CH_2)_4COOH$	58	b.p. 202° Lit.[a] b.p. 202-203°
$C_6H_5C{\equiv}CH$ 1b	a) reflux,72h b) 2N NaOH	$C_6H_5CH_2COOH$	65	m.p. 77° Lit.[a] m.p. 77-78°
$CH_3(CH_2)_2C{\equiv}C\text{-}CH_3$ 1c	a) reflux,78h b) 2N NaOH	 $CH_3(CH_2)_2\overset{CH_3}{\underset{H}{C}}\text{-}COOH$	64	b.p. 186° Lit.[a] b.p. 186°
$C_6H_5C{\equiv}C\text{-}CH_3$ 1d	a) reflux,96h b) 2N NaOH	 $C_6H_5\text{-}\underset{CH_3}{CH}\text{-}COOH$	66	b.p 262° Lit.[a] b.p. 260-262°
$C_6H_5C{\equiv}C\text{-}C_2H_5$ 1e	a) reflux,96h b) 2N NaOH	 $C_6H_5\text{-}\underset{C_2H_5}{CH}\text{-}COOH$	57	m.p. 43° Lit.[a] m.p. 42-44°
$(p)CH_3CO\text{-}C_6H_4\text{-}C{\equiv}C\text{-}CH_3$ 1f	a) reflux,96h b) 2N NaOH	 $(p)CH_3CO\text{-}C_6H_4\text{-}\overset{CH_3}{\underset{H}{C}}\text{-}COOH$	62	m.p. 57 Lit.[14] m.p. 57°
 1g	a) reflux,110h b) 2N NaOH		54	m.p. 64° Lit.[a] m.p. 63-67°

[a] Aldrich catalog, 1986.

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