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ACETOXYMERCURATION OF 1-ARYL-1-PROPYNES

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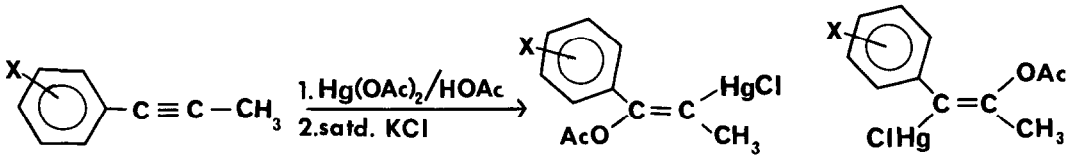
Whereas a large volume of experimental data has been accumulated on the acetoxymercuration of olefins[1], the corresponding reaction of acetylenes has been reported in only a few cases[1-4]. This reaction represents a potentially valuable synthetic means for functionalisation of acetylenes, since the mercury atom can subsequently be replaced by a variety of electrophilic reagents[2,5]. At present, however, our understanding of the stereochemistry of the addition process, of the regiospecificity of addition to unsymmetrical acetylenes, and indeed of the mechanism of the reaction itself, are hindered by the limited volume of data currently available.

We have chosen to investigate the mechanism of the acetoxymercuration reaction using a series of 1-aryl-1-propynes (1) substituted in the aromatic ring. In a typical experiment, 1 (8 mmol) in acetic acid (5 ml.) was added to $Hg(OAc)_2$ (6.5 mmol) in acetic acid (20 ml.), the reaction mixture shaken overnight at room temperature then poured into satd. aqueous KCl (50 ml.). The crude salts were isolated by filtration, washed with pentane, dissolved in chloroform, filtered to remove inorganic mercuric salts and the chloroform removed in vacuo. Individual components were isolated by fractional crystallisation from anhydrous ethanol (See Table I)[6].



1 X = p-OMe, p-CH_3, H, p-F, p-Cl, p-Br, m-Cl

2

3

In all cases, except 1-p-OMe which forms 2-p-OMe exclusively, both isomers 2 and 3 are formed with the ratio decreasing (Table I) with the expected ability of the aromatic substituent to stabilise the transition state from an electrophilic addition process. Similarly, the yields show a gradual decline, then a marked falloff to 1-m-Cl, although the yield in this latter case could be increased by increasing the reaction time. Isomer ratios are not dependent upon reaction time, and isomerically

Table I. Yields, isomer ratios and physical properties for individual components from acetoxymercuration of 1-X.

1-X	Ratio 2:3[a]	Crude yield (%) 2 + 3	m.p. 2-X (°C)	m.p. 3-X (°C)
p-OMe	100:0	93	155.5-156.5	b
p-CH_3	14.0:1	89	122.5-124	c
p-F	8.7:1	85	130-131	c
H	2.85:1	84	112-114	154-155
p-Cl	2.9:1	80	167-168	c
p-Br	1.95:1	83	175-177	190-192
m-Cl	1.1:1	50	116-117	c

a. Determined from the relative intensities of the AcO and CH_3 signals of the two isomers in the PMR spectrum.

b. Not formed.

c. This isomer could not be separated in pure form.

Table II. NMR Data for 2-X and 3-X[a]

Compound	$CH_3[J_{Hg-H}]$[b]	CH_3OCO	Aromatics $[J_{H-H}]$	X
2-p-OMe	1.99[188.5]	2.17	6.84, 7.39 [8.5]	3.77
2-p-Me	1.99[187.8]	2.16	7.12, 7.36 [8.25]	2.31
2-p-F	2.00[187.0]	2.16	7.00(J_{H-F}=8.5), 7.45(J_{H-F}=5.2)[8.5]	110.0[c]
2-H	2.03[186.5]	2.19	7.3-7.6 (complex mult.)	
2-p-Cl	2.01[186.2]	2.17	7.38, 7.50 [8.5]	
2-p-Br	2.00[185.4]	2.16	7.33, 7.45 [8.5]	
2-m-Cl	2.00[184.5]	2.16	7.0-7.4 (complex mult.)	
3-p-Me[d]	2.22 e	1.92	e	2.31
3-p-F[d]	2.25 e	1.91	e	115.4[c]
3-H	2.26[26.0]	1.90	7.05-7.4 (complex mult.)	
3-p-Cl[d]	2.24[25.4]	1.91	7.05, 7.3 [8.5]	
3-p-Br	2.22[25.5]	1.91	6.95, 7.39 [8.5]	
3-m-Cl[d]	2.21[25.4]	1.90	7.0-7.5 (complex mult.)	

a. Approximately 10% w/v solutions in $CDCl_3$, shifts from internal T.M.S.

b. From Hg satellites in ^1H NMR spectrum

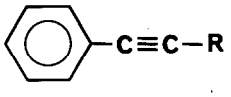
c. ^{19}F relative to $CFCl_3$.

d. Not isolated. Data from ^1H NMR spectrum of crude mixture.

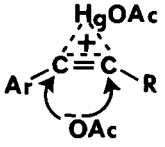
e. Signals obscured by major isomer.

pure samples of 2 and 3, isolated by fractional crystallisation, do not interconvert when redissolved in aecetic acid at room temperature, hence the ratios of 2:3 represent the kinetically controlled product distributions.

The trans configuration for 2 follows from their almost identical methyl and acetoxyl chemical shifts, and associated ^{199}Hg-^{1}H coupling constants (Table II), and the fact that 2-H had previously been shown to be trans by chemical transformation[2]. Similarly, 3 were also assigned as trans (Table II) since 3-H had also been shown to be trans[2]. In contrast, acetoxymercuration of 2-butyne affords the trans isomer at room temperature but some cis isomer as well at higher temperatures[3], while diphenylethyne affords the cis isomer exclusively[4].



4 R = Et, n-Pr, n-Bu



5

We can conclude that acetoxymercuration of acetylenes, as is the case for olefins[1], usually occurs with trans stereospecificity. The exclusive trans addition for 1 and 4[2] implies either the intermediacy of a mercurinium ion (5) which subsequently undergoes rearside attack, or a termolecular Ad_E3 transition state[1]. The preference for attack by acetate at the benzilic position, with the preference decreasing with the decreasing ability of the substituted aromatic ring to stabilise an adjacent incipient cation, is also observed for addition of sulfenyl halides to acetylenes[1,7-9]. This latter process is known to involve an intermediate bridged episulfonium ion[7,8] and thus strongly suggests the intermediacy of 5 in the acetoxymercuration process. The marked variation of the 2:3 ratio with the aromatic substituent (Table I) indicates that 5 cannot be symmetrically bridged, but not as unsymmetrical as the corresponding episulfonium ions which give a much higher proportion of attack at the benzilic position[7,8]. The steric effects on this reaction observed previously by Uemura and co-workers[2], where the ratio for benzilic to β-carbon attack (cf. 2 and 3) changed from 3.0:1 (1-H) to 16.5:1 (4-n-Bu), was also interpreted as due to the intermediacy of 5, with the steric dependence being due to the aryl and R groups bent out of the plane. It is difficult to see how an Ad_E3 mechanism[1] could accommodate either the electronic or steric effects observed for the acetoxymercuration of 1 and 4.

Any attempt at a more quantitative rationale of the reaction mechanism, and particularly the structure and charge distribution of the reaction intermediates, must await detailed kinetic studies on these, and other, acetylenic substrates.

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