Tetrahedron Letters,Vol.27,No.28,pp 3303-3306,1986 0040-4039/86 $3.00 + .00
Printed in Great Britain Pergamon Journals Ltd.

A NEW ELECTROPHILIC ADDITION TO ACETYLENES. SYNTHESIS OF 1,2-IODOFUNCTIONALIZED OLEFINS

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Abstract: Acetylenes react with bis(pyridine)iodo(I) tetrafluoroborate (**1**) in the presence of a wide variety of nucleophiles (F,Cl,Br,I,SCN,pyridine,OAc,anisole,H) to give 1,2-iodofunctionalized olefins (**4**).

The synthesis of olefins 1,2-disubstituted by two electronegative groups can not be considered a simple target based on handly methods. This is particularly true when one of the substituents is an iodine. In fact, the additions of iodine[1,2] and pseudohalogens[1,3] to acetylenes is a relatively well documented process but it results quite often in mixtures of products which arise through different reaction mechanisms still not fully understood.[2] Thus there exists in the literature the lack of a general method to carry out the addition of I^+Nu^- species to acetylenes as a straightforward route to 1,2-functionalized iodoolefins. Although the reactivity of acetylenes and olefins towards electrophiles is far from being comparable,[4] these facts prompted us to study the reactions of bis(pyridine)iodo(I) tetrafluoroborate (**1**) with acetylenes based on that, as we reported earlier, it is highly versatily reagent in the electrophilic iodofunctionalization of olefins and dienes.[5]

Now, we have found that (**1**) reacts with acetylenes (**2**) in the presence of a wide variety of nucleophiles to afford in a clean 'one pot' single step process, the corresponding 1,2-iodofunctionalizated olefin (**4**) in good to aceptable yields (Scheme 1).

Reagent (**1**), after attack of the iodine to acetylene gives two equivalents of free pyridine which is able to act in the place of the nucleophile (**3**) if the

$$R^1C\equiv CR^2 \quad + \quad NuH(Nu^-) \quad \xrightarrow{I(C_5H_5N)_2.BF_4\ \mathbf{(1)}} \quad R^1C(Nu)=C(I)R^2$$

(**2**) (**3**) (**4**)

(**2a**) $R^1 = R^2 = C_2H_5$
(**2b**) $R^1 = C_6H_5$; $R^2 = CH_3$
(**2c**) $R^1 = C_6H_5$; $R^2 = H$

(**3A**) Nu= F
(**3B**) Nu= Cl
(**3C**) Nu= Br
(**3D**) Nu= I
(**3E**) Nu= SCN
(**3F**) Nu= NC_5H_5
(**3G**) Nu= OAc
(**3H**) Nu= $p\text{-}C_6H_4\text{-}OCH_3$
(**3I**) Nu= H

Scheme 1

latter shows insufficient reactivity. This restriction for the nucleophile is easily obviated by adding first the equivalent amount of an ethereal solution of tetrafluoroboric acid which leads to the fast formation of pyridinium tetrafluoroborate. Reactions are faster in all instances when (**1**) is treated with tetrafluoroboric acid prior to the iodination reaction.

Different combinations of acetylenes (**2**) and nucleophiles (**3**) successfully essayed are summarized in Table 1. All compounds reported show ^1H and ^{13}C N.M.R., IR, and mass spectra as expected for the given structures.

The reaction of acetylenes with iodine in methanol has been shown to afford 1,2-diiodoalkenes and a radical mechanism has been suggested.[2b] By contrast, the 1,2-iodofunctionalization of acetylenes now reported allows, in a nonexhaustive screening, the introduction of F^-, Cl^-, Br^-, I^-, SCN^-, pyridine, AcO^-, C^- (anisole), and H^- as anionic-counterparts of the I^+ in processes that appear to be best rationalized in most cases by an ionic mechanism. The functionalized iodoolefins (**4**) should be valuable synthetic intermediates since, on the one hand, iodoolefins can undergo many useful transformations through either ionic (vinyl cations[6]), or radical[7] paths and, on the other hand, they have in some cases the structure of analogous of enol ethers formally derived from α-iodocarbonylcompounds. Work is in progress to determine the scope of the synthesis of compounds (**4**) and their synthetic applications.

Acknowledgements: This research was partially supported by the Comisión Asesora de Investigación Científica y Técnica (CAICYT), two of us (M.A.R. and J.M.G.) thanks the Ministerio de Educación y Ciencia for a predoctoral scholarship.

TABLE 1. IODOFUNCTIONALIZATED OLEFINS

ACETYLENE **2**	NUCLEOPHILE **3**	METHOD (a)	SOLVENT	t (h)	PRODUCT **4**	YIELD (%) (b)
a	**A** F^- (c)	A	CH_2Cl_2	1.5	**Aa**	50 (d)
a	**B** Cl^- (c)	B	Dioxane/H_2O	0.5	**Ba**	56
a	**C** Br^- (c)	B	Dioxane/H_2O	0.5	**Ca**	60
a	**D** I^- (c)	B	Dioxane/H_2O	13	**Da**	70
b	**D** I^- (c)	B	Dioxane/H_2O	13	**Db**	50
c	**D** I^- (c)	B	Dioxane/H_2O	13	**Dc**	55
a	**E** NCS^- (e)	B	Dioxane/H_2O	13	**Ea**	53
a	**F** C_5H_5N (f)	A	CH_2Cl_2	4	**Fa**	57
a	**G** CH_3COOH	A	CH_3COOH/CH_2Cl_2 (1:1)	13	**Ga**	71
b	**H** Anisole	C	CH_2Cl_2	13	**Hb**	56
b	**I** $(C_2H_5)_3SiH$	C	CH_2Cl_2	1.5	**Ib**	70

(a) See note 8.

(b) Yield of isolated products, relative to starting $I(C_5H_5N)_2.BF_4$ and not optimized. The resulting crudes were the esentially pure (g.c. purity > 90%) regioisomers above indicated. Only the product **4Hb**, and **4Ib** were purified by column chromatography (silica, hexane-ether 98:2).

(c) As ammonium, lithium or sodium salt in a mole ratio **1**:**3**= 1:3.

(d) Compound **4Aa** partially decompose, the yield was obtained by NMR.

(e) As potassium salt in a mole ratio **1**:**3**= 1:10.

(f) From compound **1** and omitting the acid treatment.

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8.- The following represents the typical experimental procedures for iodofunctionalization of acetylenes.

Method A: To a solution of **1** (5 mmol, 1.86 g) in anhydrous CH_2Cl_2 (15 ml) at room temperature (-40°C for **4Aa**) HBF_4 (10 mmol, 1.40 ml of ether. 54% solution) and the nucleophile was added under argon atmosphere. After two minutes of stirring, the corresponding acetylene (5 mmol) dissolved in CH_2Cl_2 (5 ml) was introduced into the reaction flask. After stirring (see Table 1) the red solution was hydrolized, extracted with CH_2Cl_2, dried with anh. Na_2SO_4 and evaporated in vacuo.

Method B: In a mixture of dioxane (15 ml) and water (3 ml) the inorganic salt, HBF_4 (10 mmol, 1.40 ml of ether. 54% solution), and the corresponding acetylene (5 mmol) were dissolved, then **1** (5 mmol, 1.86 g) was added. After stirring at room temperature, the solution was extracted with CH_2Cl_2 and it treated by the procedure above described in A.

Method C: A mixture of anhydrous CH_2Cl_2 (15 ml) and HBF_4 (10 mmol, 1.40 ml of ether. 54% solution) was cooled at -50°C under inert atmosphere. **1** (5 mmol, 1.86 g) and the corresponding acetylene (5 mmol) was added. After twenty minutes of stirring at this temperature the nucleophile was introduced into the reaction flask and the red solution was allowed to arise at 0°C and treated by the procedure described in A.

(Received in UK 21 May 1986)