Pergamon

Tetrahedron Letters 40 (1999) 1495–1498

TETRAHEDRON LETTERS

Halodecarboxylation of α,β-acetylenic and α,β-ethylenic acids

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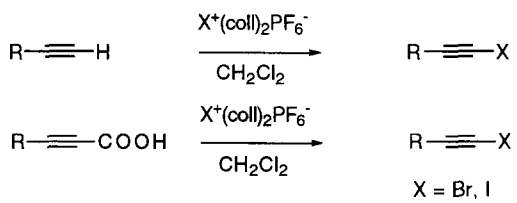
Received 18 November 1998; accepted 21 December 1998

Abstract : Reaction of bis(collidine)iodine(I) (or bromine (I)) hexafluorophosphate with acetylenic acids led to the corresponding iodo(or bromo)acetylenes in high yields. This halodecarboxylation reaction was also observed with acrylic acids substituted in position 3 by an aryl group or an heteroatom.

keywords: carboxylic acids, alkynyl halides, alkenyl halides, Hundsdiecker reaction.

During our research project on the preparation of medium ring lactones,[1] we decided to examine the cyclization of an ω-ethylenic-α,β-acetylenic acid using bis(*sym*-collidine)iodine(I) hexafluorophosphate (BIH). However, instead of the expected iodolactone we obtained the corresponding iodoacetylenic compound. Since such iododecarboxylation reactions are not well known,[2] we decided to study the scope of this interesting reaction. In addition, we have recently reported that acetylenic compounds reacted easily with BIH to give the corresponding iodoacetylenes,[3] so the results presented herein constitute an alternative way for their preparation (Scheme 1).



Scheme 1

The acetylenic acids studied were either commercially available or prepared by standard methods. In particular, 8-nonene-2-ynoic acid (Table 1, entry b) was obtained by carboxylation of oct-1-ene-7-yne,[1] and hexa-2,4-diyne-1,6-dioic acid (Table 1, entry f) was obtained from 1,4-*bis*(trimethylsilyl)buta-1,3-diyne.[4] These different acetylenic acids were reacted with BIH and bis(collidine)bromine(I) hexafluorophosphate (BBH); the results are reported in Table 1. The reactions were carried out at room temperature in methylene chloride (30 min). The solvent was then removed and the products purified by liquid chromatography.[5] The products were characterised from their ^{1}H and ^{13}C NMR spectra. Satisfactory results were obtained for all acids studied.

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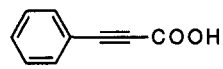
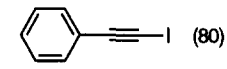
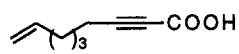
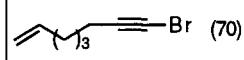
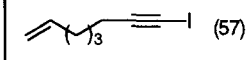
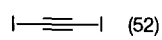
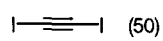
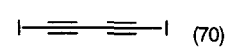
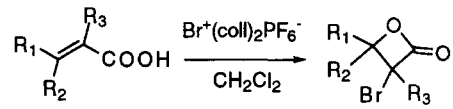
0040-4039/99/$ - see front matter
PII: S0040-4039(99)00021-0

Table 1. Reaction of acetylenic acids with bis(*sym*-collidine) iodine (I) and bromine(I) hexafluorophosphate

entry	acid	bromoacetylene (Yield, %)	iodoacetylene (Yield, %)
a		 (95)	 (80)
b		 (70)	 (57)
c	pentyl—≡—COOH	pentyl—≡—Br (65)	pentyl—≡—I (68)
d	HOOC—≡—COOH	–	 (52)
e	H—≡—COOH	–	 (50)
f	HOOC—≡—≡—COOH	–	 (70)

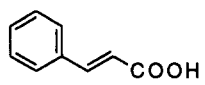
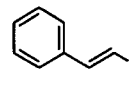
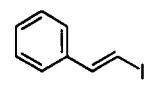
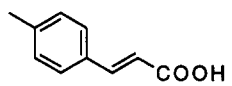
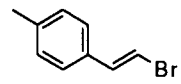
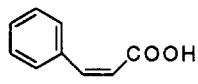
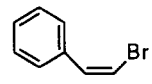
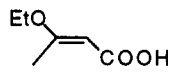
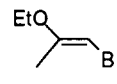
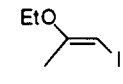
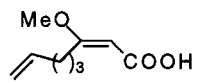
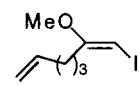
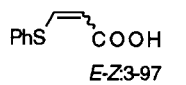
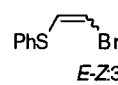
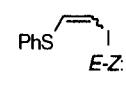
Subsequently we decided to examine several α,β-ethylenic acids. We have previously reported that the reaction of BBH with these acids led generally to the formation of β-lactones by a 4-*endo-trig* cyclization process[7] (Scheme 2).



Scheme 2

To observe an halodecarboxylation reaction we found that it was necessary to use α,β-ethylenic acids unsubstituted in α and substituted in β by a group able to strongly stabilise a carbocationic charge. The acids studied were commercially available except for Z-cinnamic acid (Table 2, entry c) which was obtained by catalytic hydrogenation (using Lindlar catalyst) of phenylpropiolic acid, and 3-methoxyocta-2,7-dienoic acid (Table 2, entry e) prepared in two steps from methyl 3-oxo-7-octenoate [8] by reaction with methyl orthoformate in ethanol (TsOH, 48h, 20 °C, 72%), followed by saponification of the ester function (65 %). The halodecarboxylation reactions were carried in the same conditions as for the acetylenic acids. Our results are reported in Table 2. The products were characterised from their ^{1}H and ^{13}C NMR spectra and by comparison with the data from the literature.[9]

Table 2. Reaction of ethylenic acids with bis(*sym*-collidine) iodine (I) and bromine(I) hexafluorophosphate

entry	acid	bromoalkene (Yield, %)	iodoalkene (Yield, %)
a	 *E*-*Z*: 100-0	 *E*-*Z*: 96-4 (88) *E*-*Z*: >99-<1 (70) [b]	 *E*-*Z*: 95-5 (28) [a]
b	 *E*-*Z*: 100-0	 *E*-*Z*: 96-4 (93)	–
c	 *E*-*Z*: 0-100	 *E*-*Z*: 13-87 (72)	–
d	 *E*-*Z*: 100-0	 *E*-*Z*: 80-20 (60)	 *E*-*Z*: 80-20 (69)
e	 *E*-*Z*: 100-0	–	 *E*-*Z*: 80-20 (58)
f	 *E*-*Z*:3-97	 *E*-*Z*:34-66 (72) *E*-*Z*:15-85 (82) [b]	 *E*-*Z*:12-88 (70)

[a] After 10h at reflux. [b] In toluene

With the cinnamic acids (entries a-c), only the bromine reagent gave satisfactory results. In addition these reactions are highly stereospecific. The slight isomerization observed in the case of the *E*-isomer was suppressed when the reactions were carried out in toluene.[10] With the acrylic acids bearing an heteroatom in β (entries d-f), the iodo and bromo reagents gave similar results. It is interesting to note that the acid studied in entry e did not lead to the formation of the 8-membered ring iodolactone but to the product of iododecarboxylation.

In conclusion, we have reported a mild and efficient preparation of iodo and bromo unsaturated compounds from their corresponding acids using bis(collidine)iodine(I) or bromine(I) hexafluorophosphate. Our method is complementary to the Hunsdiecker-Cristol reaction since it was established that the latter was not efficient in this case,[11] and required either a two step process [12] or the use of N-halosuccinimides in the presence of additives.[13]

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5. **Representative procedure**: to a solution of phenylpropionic acid (2 mmol) in methylene chloride (40 mL) was added bis(collidine)iodine(I) hexafluorophosphate [1] (1.13 g, 2.2 mmol). After stirring the reaction mixture 30 min at rt, the solvent was removed under vacuum and the residue purified by chromatography over silica gel (hexanes/ether: 95/5).
6. Selected data: **1-iodo-7-octen-1-yne**. ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.52 - 1.68 (qt, J = 6 Hz, 2H); 2.08 - 2.20 (m, 2H); 2.62 (t, J = 6.0 Hz, 2H); 4.92 - 5.10 (m, 2H); 5.68 - 5.88 (m, 1H). ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 3.8; 16.2; 24.2; 25.6; 28.5; 94.2; 116.3; 121.6. **1,4-iodobut-1,3-diyne**. ^{13}C NMR δ -3.2; 97.7. **1-iodohept-1-yne**. ^{1}H NMR δ 0.88 (t, J = 6.0 Hz, 3H); 1.25 - 1.45 (m, 4H); 1.45 - 1.60 (m, 2H); 2.35 (t, J = 7.5 Hz, 2H). ^{13}C NMR δ -6.2; 13.6; 21.6; 23.2; 29.0; 31.2; 94.6. **1-bromohept-1-yne**. ^{1}H NMR δ 0.87 (t, J = 6 Hz), 1.25 - 1.45 (m, 4H); 1.42 - 1.55 (m, 2H); 2.15 - 2.25 (t, J = 7.5 Hz, 2H). ^{13}C NMR δ 14.95; 20.6; 21.3; 29.5; 32.7; 38.6; 80.3.
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9. Selected data: **1-iodo-2-methoxyhepta-1,6-diene.** ^{1}H NMR. *E*-isomer: δ 1.55-1.70 (m, 2H), 2.00-2.10 (m, 2H), 2.38-2.47 (t, J = 7.5 Hz, 2H), 3.57 (s, 3H), 4.85 (s, 1H), 4.95-5.15 (m, 1H). *Z*-isomer: δ 1.65-1.80 (m, 2H), 2.00-2.15 (m, 2H), 2.70-2.75 (t, J = 7.5 Hz, 2H), 3.20 (s, 3H), 4.95-5.15 (m, 3H), 5.70-5.92 (m, 1H).
10. **Large scale preparation of (*E*)-β-bromostyrene**: A 250 mL three-necked round-bottomed flask containing a stirring bar is equipped with a nitrogen inlet, a thermometer and a condenser. The flask is charged with 10 g of *trans*-cinnamic acid (0.07 mol), 140 mL of toluene, 0.4 g of 2,6-di-*tert*-butyl-4-methylphenol and 40 g of bis(2,4,6-trimethylpyridine)bromine(I)hexafluorophosphate (0.086 mol). The solution is heated at 65°C for 1 h and formation of a white precipitate is observed. After cooling at 25°C, 100 mL of ether are added and the organic phase is washed with 4x100 mL of 1N HCl, 100 mL of saturated sodium chloride solution and dried over sodium sulphate. The organic phase is concentrated under vacuum and 1 g of 2,6-di-*tert*-butyl-4-methylphenol is added. The mixture is distilled under high vacuum to give (*E*)-bromostyrene (8.5 g - 9 g, 66-70%, *E-Z*: 99.5-0.5) as a light yellow liquid: bp 50°C under 0.1 mmHg.
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