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REACTION OF BIS(*SYM*-COLLIDINE)-BROMINE(I) HEXAFLUOROPHOSPHATE WITH α-DIAZO ESTERS

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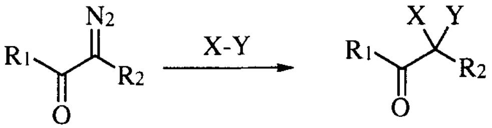
Abstract: Reaction of α-diazo esters with bis(*sym*-collidine)bromine(I) hexafluorophosphate in methylene chloride at -40°C led to α-bromo-α,β-unsaturated esters.

α-Diazocarbonyl compounds undergo α,α-substitution reactions when they were placed in the presence of electrophiles.[1]



In the particular case of phenylselenyl halides, subsequent oxidation of the selenium atom allowed the preparation of α-halo-α,β-unsaturated carbonyl compounds.[2]

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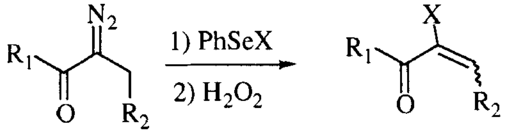
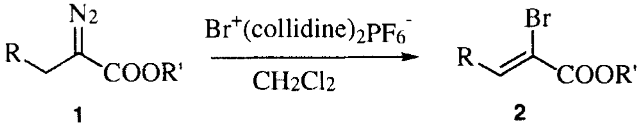
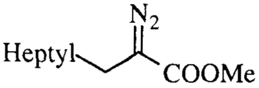
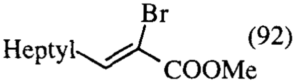
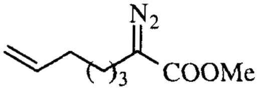
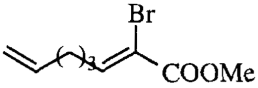
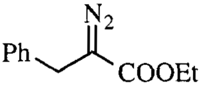
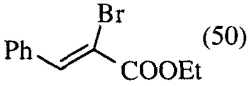
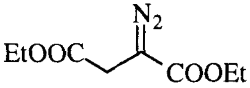
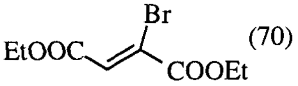
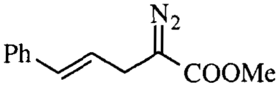
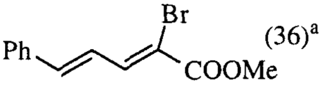


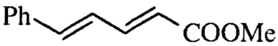
During our work concerning the reactivity of bis(*sym*-collidine)iodine(I) and bromine(I) hexafluorophosphate, we reported that these reagents were interesting for example for the halogenation of phenols,[3a] pyridinols,[3b] and acetylenic derivatives.[3c] These results were attributed to the particular electrophilic character of these reagents. We decided to examine their reactivity with α-diazo esters, since the absence of reactive counter anion should lead to specific reactions. The desired α-diazo esters were prepared by a reported procedure by reaction of α-substituted β-ketoesters with methanesulfonyl azide.[4] The diazo esters in methylene chloride solution, were then added slowly to bis(*sym*-collidine)bromine(I) hexafluorophosphate maintained at low temperature. Our results are reported in the Table.



Formation of α-bromo-α,β-unsaturated esters was observed. Their structures were determined from their NMR spectra. In particular their stereochemistries were deduced from the chemical shift of their vinylic hydrogens, and compared with the literature data. When an alkyl chain was present in the structure of the diazo esters **1**, a stereospecific reaction was observed at low temperature (entries a,b). This is not the case for the diazo esters **1c**, **1d**, for which the selectivity was low. The moderate yield observed with ester **1e** was due

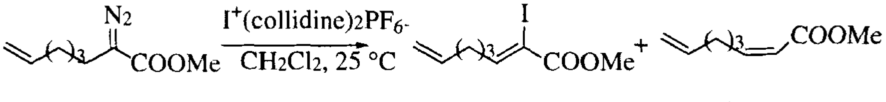
Table : Reaction of α-diazo esters with $Br^+(collidine)_2\ PF_6^-$

entry	α-diazo ester **1**	Reaction temperature	α-bromo ester **2** (Yield, %)
a		-40 °C	 *E*-*Z*: 0-100
b			
		-40 °C	*E*-*Z*: 0-100 (70)
		25 °C	*E*-*Z*: 7-93 (65)
c		-40 °C	 *E*-*Z*: 40-60
d		-20 °C	 *E*-*Z*: 44-56
e		-40 °C	 *E*-*Z*: 0-100

[a] 10 % of  was also isolated

to the degradation of the product during the reaction. α-Diazo ketones in the same conditions led only to a complex reaction mixture.

We examined also the reactivity of bis(collidine)iodine(I) hexafluorophosphate with the diazo ester **1b**. Addition at -40°C or 25°C of the diazo ester to the iodo reagent led to a mixture of (*Z*)-α-iodo-α,β-unsaturated ester **3** and (*Z*)-α,β-unsaturated ester **4**. We were unable to find conditions to avoid the formation of this ester **4**, due to the decomposition induced by the collidine of the diazo group.



3 (28%) **4** (52%)

Besides, methyl 2,7-octadienoate **4** was formed in excellent yield as a *E-Z* mixture, if the diazo ester was added at room temperature to a methylene chloride solution of bis(collidine)-silver(I) hexafluorophosphate (88% yield, *Z/E* : 57/43).

In conclusion the reaction of α-diazo esters with bis(collidine)bromine(I) hexafluorophosphate allows the preparation of α-bromo-α,β-unsaturated esters in moderate to good yields. The preparation of these bromo esters has previously reported mainly by Wittig reaction,[5] Peterson olefination [6] or bromination-dehydrobromination of α,β-unsaturated esters.[7] Some of these methods allowed the specific obtention of the *Z*-isomers.[8]

Experimental part

α-Diazo esters have been prepared by reaction of α-substituted β-ketoesters with methanesulfonyl azide.[4] The β-keto esters were either commercially available (entries c, d) or prepared by alkylation of methyl acetoacetate (entries a, b, e). α-Diazo esters **1b**,[9] **1c**,[10] **1d**,[11] **1e** [4] have been already described.

Methyl 2-diazodecanoate 1a: ^{1}H NMR (250 MHz, $CDCl_3$): δ 3.77 (s, 3H); 2.30 (t, J = 8 Hz, 2H); 1.50 (m, 2H); 1.30 (m, 12H); 0.91 (t, J = 6 Hz, 3H).

General procedure for the reaction of α-diazo esters 1 with bis(collidine)bromine(I) hexafluorophosphate. To bis(collidine)-bromine(I) hexafluorophosphate (0.75 g, 1.6 mmol) in methylene chloride (10 mL) cooled at -40°C was added a solution of the α-diazo ester (1.6 mmol) in methylene chloride (10 mL) by a push syringe over a period of 6 h. Subsequently, silica gel (1 g) was added to the warmed reaction mixture and the solvent was removed. The product was purified by flash chromatography (ether-hexane). The results are reported in the Table. The bromo esters **2c**,[12] **2d** [13] and **2e** [14] have been already reported.

Methyl (Z)-2-bromo-2-decenoate 2a: ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.28 (t, *J* = 7.3 Hz, 1H); 3.82 (s, 3H); 2.33 (t, *J* = 7 Hz, 2H); 1.30 (m, 10H); 0.88 (m, 3H). EI MS: *m/z* (%): 262-264 (M^+, 0.5); 183 (48); 165 (53); 167 (52); 123 (36); 81 (48); 55 (45); 41 (88); 43 (100); 39 (45). Anal. Calcd for $C_{11}H_{19}O_2Br$: C, 50.20; H, 7.28. Found: C, 50.42; H, 7.32.

Methyl (Z)-2-bromo-2,7-octadienoate 2b: ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.27 (t, *J* = 7 Hz, 1H); 5.81 (m, 1H); 5.03 (m, 2H); 3.84 (s, 3H); 2.36 (q, *J* = 7.6 Hz, 2H), 2.11 (q, *J* = 8 Hz, 2H); 1.60 (quin, *J* = 7.6 Hz, 2H). ^{13}C NMR: δ 162.9, 146.1, 137.6, 115.9, 115.2, 53.1, 33.1, 31.4, 26.6. EI MS: *m/z* (%): 234 (1.7); 232 (1); 93 (48); 67 (52); 59 (36); 55 (100); 41 (40); 39 (79). Anal. Calcd for $C_9H_{13}O_2Br$: C, 46.37; H, 5.62. Found: C, 46.43; H, 5.84.

Methyl (Z)-2-iodo-2,7-octadienoate 3: ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.24 (t, *J* = 7.6 Hz, 1H); 5.81 (m, 1H); 5.03 (m, 2H); 3.83 (s, 3H); 2.34 (q, *J* = 7.6 Hz, 2H), 2.11 (q, *J* = 8 Hz, 2H); 1.52 (quin, *J* = 7.6 Hz, 2H). Anal. Calcd for $C_9H_{13}O_2I$: C, 38.59; H, 4.68. Found: C, 38.42; H, 4.86.

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