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Synthesis of Ethynyl-Substituted Benzoyl Chlorides and of Related α,ω-Ethynyl Oligomers

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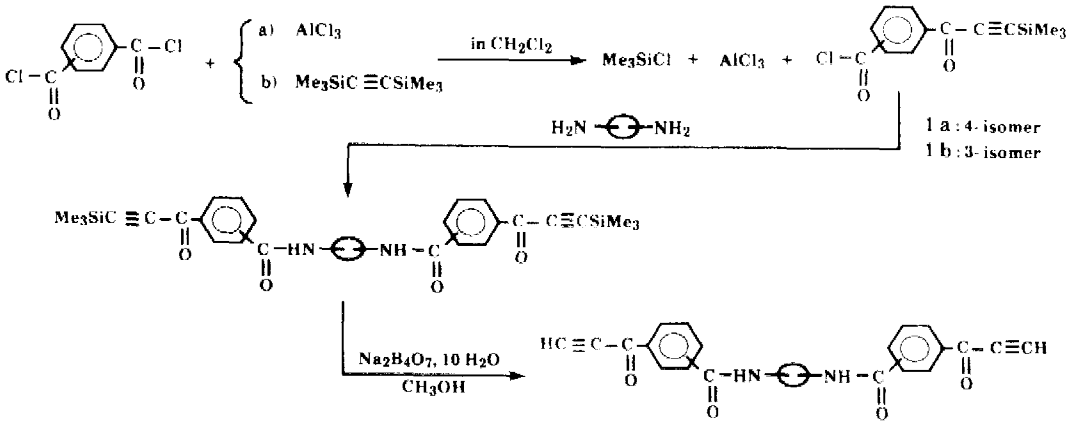
Abstract : *Isophthaloyl and terephthaloyl chlorides can react with half an equivalent of bis-trimethylsilyl acetylene (BTMSA) to afford 3- and 4-ethynyl substituted benzoyl chlorides, key intermediates in the synthesis of various mono- and di-ethynyl oligomers.*

For some years, a growing interest has been developed about telechelic diethynyl oligomers, that prove themselves suitable precursors of thermostable polymeric networks[1]. As the introduction of ethynyl groups into aromatic rings is very often the key pathway of the synthesis of such functional compounds, various preparative methods have been proposed. They involve either the transformation of aryl-methyl ketones into acetylenic derivatives according to Vilsmeier's reaction[2,3] or the substitution of aryl halides by trimethylsilylacetylene, in the presence of Pd-complex based catalysts[4].



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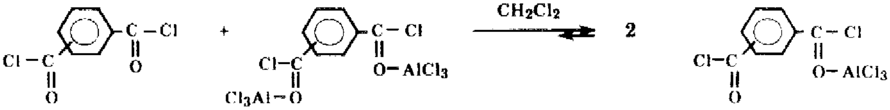
This paper deals with a new three step method consisting, first in the preparation of trimethylsilyl group capped acetylenic precursors, further in the use of the precursors in various condensation reactions with oligomeric amines, and last in the unblocking of the terminal ethynyl functions. It is mainly concerned with the direct preparation of the capped ethynyl precursors **1a** and **1b**, whose synthesis is achieved by reacting terephthaloyl or isophthaloyl dichloride with half an equivalent of bis-trimethylsilyl acetylene (BTMSA), in the presence of half an equivalent of aluminium trichloride.

The selective formation of the mono-acetylenic derivative should be linked with a stability of the mono-adduct -C(O)Cl-$AlCl_3$ better than that of the di-adduct, in the conditions of the first reaction step. Moreover, even if bis-ketoacetylenic compounds were obtained in some instances[5], the dropwise addition of BTMSA to the solution may favor the formation of the mono-adduct.



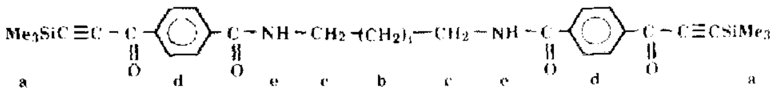
The main characteristics of the precursors **1a** and **1b** are reported in table 1.

Table 1 - Main characteristics of precursors 1a and 1b

	m.p. (°C)	$\nu_{cm^{-1}}$ (IR)	δ_{ppm} (^1H NMR)	mass spectom.
1a[a]	86 ± 1	2170 -C≡C- 1740, 1770 -C(O)Cl 1650 -C(O)-	0.35 s 9 H $SiMe_3$ 8.15 s 4 H aromatic	very weak molar peak (0.9%) m/z = 229 (100%) (M-Cl$^{\cdot}$) m/z = 249 (77%) (M-$CH_3^{\cdot}$) m/z = 201 (23%) (M-COCl$^{\cdot}$)
1b[a]	46 ± 1	2150 -C≡C- 1750 -C(O)Cl 1640 -C(O)-	0.35 s 9 H $SiMe_3$ aromatic 7.6 t 1 H, 8.3 d 1 H, 8.4 d 1 H (J = 9 Hz) 8.8 s 1 H	very weak molar peak m/z = 249 (100%) (M-$CH_3^{\cdot}$) m/z = 229 (58%) (M-Cl$^{\cdot}$)

[a] The analysis of C and H has given satisfactory results : example, C : found 59.3 ; calc. 58.9 and H : found 4.6 ; calc. 4.9, for 1a

As for the second step of the process, the precursor **1a** has been reacted with hexamethylene diamine (HMDA), 1,4-phenylene diamine (PDA) and 4,4'-diamino diphenylsulfone (DDPS) to afford the corresponding difunctional diamides **2**,**3** and **4**. The main characteristics of these compounds are given in table 2.



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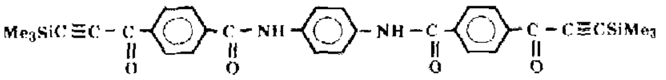

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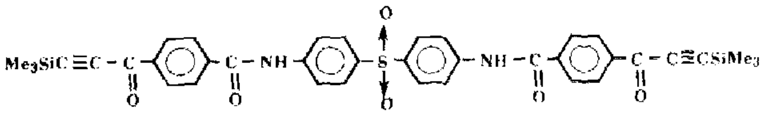

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Table 2 - Main characteristics of the α,ω-substituted diamides **2** (from HMDA), **3** (from PDA) and **4** (from DDPS)

compound	m.p. (°C)	$\nu_{cm^{-1}}$ (IR)[a]	δ_{ppm} (^{1}H NMR)[b]
2	144 ± 2	2180 -C≡CSiMe$_3$ 1650 ⎤ ⎥ amide 1540 ⎦	0.3 s 18 H : a 1.4 m 8 H : b 3.3 m 4 H : c 8.0 m 8 H : d 6.9 m 2 H : e
3	> 300	3380 -NH 2160 -C≡CSiMe$_3$ 1650 ⎤ ⎥ amide 1540 ⎦ 1250 -C-Si	insoluble in common solvents
4	softens about 150°C	3350 -NH 2160 -C≡CSiMe$_3$ 1650 ⎤ 1590 ⎥ amide 1540 ⎦	0.4 s 18 H (SiMe$_3$) 7.8-8.1 m 16H (aromatic)

[a] CHCl$_3$ solutions for **2** and **4**, KBr dispersions for **3** ; [b] CDCl$_3$ solutions

From the difunctional diamides, the unblocking of the ethynyl end groups has been achieved by reaction with sodium tetraborate, according to a previously described method[5]. The α,ω-ethynyl oligomers thus obtained are potential intermediaries in the synthesis of thermostable materials. Indeed their thermal polymerization may afford polymeric networks with rigid links and stable junctions.

Experimental Part

*Synthesisof the 4-substituted and 3-substituted benzoyl chloride **1a** and **1b***

Terephthaloyl dichloride (0.03 mol : 6g) and freshly grinded aluminium trichloride (0.03 mol : 4g) were dissolved in 120ml CH_2Cl_2. The solution was stirred for 20 minutes. Then, BTMSA (0.03 mol : 7 ml in 20 ml CH_2Cl_2) was dropwise added into the solution (15 to 20 minutes for the whole addition), before the reaction mixture was stirred (at room temperature) for 3 hours.

The mixture was hydrolyzed in 100 ml cold 0.1N HCl and the organic layer was extracted (several times) with CH_2Cl_2 or with ethyl ether and dried (Na_2SO_4). After the solvent was removed, the raw product was purified on a silica gel column (elution with 5% ethyl ether/pentane solvent). The yield in purified products was about 75%, related to BTMSA.

For compound 1b, the whole preparative process was the same (from isophthaloyl chloride) except for the reaction time (5 h instead of 3 h) and the elution solvent (pure pentane). The yield was about 65%

*Preparation of the bis-trimethylsilyl keto-ethynyl derivatives **2**, **3** and **4** from **1a***

A solution of **1a** (1 g : 4 10^{-3} mol) in 5 ml $CHCl_3$ was mixed with a HMDA aqueous solution (0.22 g in 40ml H_2O). After addition of 8 ml 10% aqueous NaOH and 5 minutes of vigourous stirring (at room temperature), the organic layer was quickly extracted with $CHCl_3$ and dried (Na_2SO_4). After the solvent was removed, the biamide **2** was obtained as a yellow solid (yield about 85%).

As for the diamide **3**, PDA (0.27 g : 2.5 10^{-3} mol) was dissolved in 20 ml warm THF. Triethylamine NEt_3 (0,7ml) and a THF solution of **1a** (1.3 g : 5 10^{-3} mol) were added and the mixture was stirred (at room temperature) for 1 hour. After filtration of Et_3NH^+,Cl^- and distillation of the solvent, **3** was obtained as a brown solid, insoluble in common solvents (yield about 85%). The same process allowed to obtain **4** as a yellow powder, slightly soluble in THF and $CHCl_3$ (yield about 90%).

*Removing of trimethylsilyl groups in diamides **2**, **3**and **4***

Each diamide (0.3 to 0.5 g) was dissolved (or dispersed) in 20 to 30 ml methanol (2 to 5 ml THF added), in the presence of 2.5 to 4 ml $Na_2B_4O_7$, 10 H_2O aqueous solution (0.01 M). The mixture was allowed to stand for 10 minutes at room temperature, before 10 ml 0.1 N HCl were added. The precipitate immediately formed was filtered off and washed with methanol and ethyl ether. In its IR spectrum (KBr dispersions), the C≡CSiMe3 band (2160 cm^{-1}) was replaced by a band at 2090-2100 cm^{-1}, which is characteristic of the C≡CH group. The yields of the trimethylsilyl group removing were fairly good (about 70 to 80%).

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