Synthesis and Characterization of Ylidic and Carbenic Polymers

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ABSTRACT

The synthesis of two bisylides obtained in pyridinium benzoylmethylide with terephthaloyl dichloride or 1,3-bis(p-chloroformylphenyl)parabanic acid is reported in this paper. By thermal decomposition or upon microwave irradiation, these two bisylides form the corresponding two polycarbenic derivatives. Also, the synthesis of an ylidic polymer, derived from 4,4'-dipyridylium diphenylmethylide and terephthaloyl dichloride, is announced for the first time. All obtained products have been controlled principally by $^1$H NMR spectra.

Key Words: bisylide, ylidic polymer, N,N'-dipyridylium diphenylmethylide, terephthaloyl dichloride, 1,3-bis(p-chloroformylphenyl)parabanic acid

INTRODUCTION

Polymer-ylide chemistry is a subject of growing interest by their applications as initiators for homo- and copolymerization of vinyl monomers [1-3]. The pyridinium dicyanomethylide [4, 5] and α-picolinium-p-chlorophenacylide [6] have been used as radical initiators for homopolymerization of styrene [7, 8] and methyl methacrylate as well as to obtain the alternating copolymers of these two monomers [9]. Earlier, by polycondensation in phase-transfer processes the ylide polymer derivatives in 4,4'-dipyridyl and 3,3-bis(chloromethyl)oxetane or 1,3-bis(p-chloroformylphenyl)parabanic acid have been reported [10].

In this paper we report the synthesis and characterization of some ylidic and carbenic polymer by two different methods both involving the ylidic derivatives as starting materials. The synthesis of polycarbenic derivatives by thermal and upon microwave decomposition's of bisylides is for the first time reported.

EXPERIMENTAL

Instruments

The IR spectra have been recorded with a Perkin-Elmer 1310 Spectrometer. The $^1$H NMR spectra have been performed using a Bruker AM-250MHZ in DMSO-d$_6$.

Synthesis

N-Phenacylpyridinium bromide (1) has been synthesized by the salt method [11].
Bisylide 4
Terephthaloyl dichloride (0.18 g, 0.9 mmol) was added with vigorous stirring to a solution of N-phenacylpyridinium bromide (0.5 g, 1.8 mmol), in chloroform (20 mL). The salt was only partially dissolved in chloroform. A solution of 1 mL of triethylamine in 5 mL chloroform was added gradually with a dropping funnel. The formed intermediate pyridinium ylide was completely dissolved. The reaction mixture was allowed to stand during 4 h with constantly shaking. The obtained solid product was filtered and washed with chloroform, yield = 80 %.

IR Spectra (KBr)(cm⁻¹): 3389 (w), 1658 (w), 1562 (w), 1484 (s), 1390 (m), 1339 (m), 1206 (w), 1093 (w), 894 (m), 769 (m), 733 (m). ¹H NMR Spectra, DMSO-d₆ δ (ppm): 8.75, 4 H ortho/N⁺; 8.39, 2 H para/N⁺; 7.96, 4 H meta/N⁺; 7.04, 4 H ortho/CO; 6.96, 2 H para/CO; 6.93, 4 H meta/CO; 6.87, 4 H remaining terephthaloyl.

Bisylide 6
N-phenacylpyridinium bromide (1 g, 3.6 mmol) was suspended in 20 mL chloroform in a 100 mL two necked flask fitted with a dropping funnel and a condenser. A solution of 0.7 g (1.8 mmol) of 1,3-bis(p-chloroformylphenyl)parabanic acid 3 in 5 mL nitrobenzene was added gradually. The addition was completed with 2 mL of triethylamine dissolved in 5 mL chloroform. The reaction mixture was left during 12 h at room temperature with stirring. The obtained crude solid was filtered and washed with ethyl ether. Yield: 54 %.

IR Spectra (KBr)(cm⁻¹): 3420 (w); 1703 (w); 1628 (w); 1580 (w); 1543 (m); 1490 (s); 1454 (s); 1419 (s); 1338 (s); 1280 (m); 1225 (w); 1087 (w); 1013 (w); 887 (m); 818 (m); 785 (w); 693 (m). ¹H NMR Spectra, DMSO-d₆ δ (ppm): 9.20, 4 H, ortho/N⁺; 8.92, 4 H, meta/N⁺; 7.34, 4 H, ortho/CO; 7.24, para/CO; 7.22, meta/CO; 6.93, 4 H meta/CO; 6.87, 4 H remaining terephthaloyl.

Polymer 9
A mixture of 0.55 g (1 mmol) of N,N'-diphenacyl-4,4'-dipyridylium dibromide in 20 mL chloroform was placed in a 250 mL round bottomed flask equipped with an additional funnel. A solution of 0.44 g (2 mmol) terephthaloyl dichloride dissolved in 10 mL chloroform was added. The addition was completed with 1 mL (8 mmol) triethylamine dissolved in 5 mL chloroform. The reaction mixture became of a violet colour. Stirring at room temperature was continued in absence of light, during 12 h. The crude solid was filtered and washed with ethyl ether. The product of 0.15 g was obtained after drying.

IR Spectra (KBr)(cm⁻¹): 3423 (w); 1703 (w); 1628 (w); 1580 (w); 1543 (m); 1490 (s); 1454 (s); 1419 (s); 1358 (s); 1280 (m); 1225 (w); 1087 (w); 1013 (w); 887 (m); 818 (m); 785 (w); 693 (m). ¹H NMR Spectra, DMSO-d₆ δ (ppm): 9.20, 4 H, ortho/N⁺; 8.73, 4 H, meta/N⁺; 7.24, 4 H, ortho/CO; 7.24, para/CO; 7.22, meta/CO; 6.93, 4 H, terephthaloyl fragment.

Thermal Decomposition of Bisylides 4 and 6
A mixture of 0.2 g bisylide 4 or 6 in 20 mL DMSO was placed in a flask fitted with a condenser. The resulting solution was warmed at 185 °C during 30 min. A change of colour from yellow to brown has been observed. The solvent was distilled at reduced pressure. The crude solid was washed with ethyl ether and dried at 60 °C. The reaction is quantitative:

IR Spectra (KBr)(cm⁻¹): * 10: 3449 (w); 2962 (m); 1718 (m); 1599 (m); 1495 (w); 1404 (w); 1260 (s); 1091 (s); 917 (s); 801 (w); 694 (w). * 11: 3311 (w); 2929 (m); 1695 (s); 1635 (m); 1602 (s); 1521 (m); 1409 (m); 1311 (m); 1122 (s); 968 (w); 856 (w); 696 (w). ¹H NMR Spectra, DMSO-d₆ δ (ppm): * 10: 12.65, H (COOH); 9.45 and 8.90, H (pyridine ring in starting polymer); 8.05—7.93 and 7.49—6.83, H (benzene ring and remaining terephthaloyl); 5.40, H (CH₂—OH). * 11: 12.60, H (COOH); 8.10—6.90, H (benzene ring and parabanic fragment), 5.35, H (CH₂—OH).

Decomposition of Bisylide 4 Upon Microwave
Bisylide 4 of 0.4 g was dissolved in 40 mL anhydrous DMSO and it was added in a Synthewave 402 monomode reactor fitted by a condenser and a mechanical stirring. The mixture was irradiated (2450 MHz) with stirring at a constant temperature of 175 °C during 40 min or 2 h. After cooling, the solvent DMSO was
distilled at reduced pressure. The residue was washed with ethylether and dried.

IR Spectra (KBr)(cm⁻¹): 3000 (w); 1652 (s); 1599 (s); 1495 (m); 1404 (m); 1216 (s); 1098 (m); 1010 (s); 896 (w); 692 (w). ¹H NMR Spectra, DMSO-d₆, δ (ppm): 6.80–8.40 ppm.

In the IR spectra, the weak IR bands at 3400–3300 may certainly correspond to OH groups of water because the intensity decreases after warming.

RESULTS AND DISCUSSION

In reaction between pyridinium phenacylide 2 formed "in situ" in corresponding salt 1 and terephthaloyl dichlorid 3, the bisylide 4 is obtained (Scheme I).

The same monosubstituted carbanion ylide 2, reacts with 1,3-bis(p-chloroformylphenyl)parabanic acid 5 giving the corresponding bisylide 6 (Scheme II).

Mainly, the ¹H NMR spectra of these two bisylides in DMSO-d₆ confirmed the proposed structures (Figures 1 and 2).

The protons of pyridine ring in compounds 4 and 6 are found, very well resolved in the range 8–9 ppm in the order meta, para and ortho in respect to positive charged nitrogen atom.

However, in the same two compounds the protons belonging to terephthaloyl and of 1,3 bis(p-chloroformylphenyl)parabanic acid rings are superposed on the phenyl cycles in benzoyl groups. The chemical shift assignments have been realized comparing the ¹H NMR spectra in Figures 1 and 2, with those of starting compounds; pyridinium phenacylide

Scheme I

Scheme II
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and 1,3 bis(p-chloroformylphenyl)parabanic acid. The aromatic protons at 8.28 ppm in terephthaloyl dichloride appear at 6.87 ppm in bisylide 4 and at 6.99 ppm in ylidic polymer 9.

Also, the same protons in benzene ring of 1,3 bis(p-chloroformylphenyl)parabanic acid at 7.60 and 8.10 ppm appear as a single large peak centered at 7.07 ppm in bisylide 6.

The protons assigned to pyridine ring of the dipyridylium salt 7 at 9.32 and 8.34 ppm are found at 9.20 and 8.73 ppm, respectively, in the polymer 9. In these ylidic compounds the ν C=O bands are always strongly displaced to lower wave function number (1600 cm⁻¹). Next, by a polycondensation between bisylide 8 and terephthaloyl dichloride could be obtained an ylidic polymer 9 (Scheme III).

The ¹H NMR spectra in DMSO-d₆ of ylide polymer 9 is presented in Figure 3. Between its spectra and those of bisylide 4 a clear difference could be observed.

In order to determine the degree of polymerization, the signals centred at 8.73 and 8.90 ppm and those of aromatic terephthaloyl ring have been taken in consideration on the polymer obtained with excess of dichloride. Thus a value of n≈4—5 may be calculated with a good reproducibility. The high molecular weight polymers are not soluble in DMSO-d₆.

In synthesis of ylide polymer 9, another new polymer 10 has been always observed (Scheme IV), which corresponds to a cleavage of N'-C' ylide bond with formation of an intermediate reactive carbene which provide a new type of polymerization on the level of carbenic atoms (Figure 4).

In the ¹H NMR spectra of the polymer 10 the
protons corresponding to bipyridyl vanish and two different signals at 5.40 and 12.65 ppm appear, indicating the hydrolysis of carbene CH—OH and chloride acyl group COOH.

Generally, in order to verify this thermal decomposition the bisylide 6 has been submitted at the same treatment and give a new polymer 11.
Figure 5. The $^1$H NMR spectrum of polycarbenic polymer 11.

(Scheme V). The $^1$H NMR spectra of corresponding polycarbenic polymer is given in Figure 5.

As in the previous decomposition the two signals due the presence of CH–OH and COOH groups at 5.40 and 12.65 respectively have been observed.

Figure 6. The $^1$H NMR spectrum of incomplete microwave decomposition of bisylide 4.

Figure 7. The $^1$H NMR spectrum of complete microwave decomposition of bisylide 4.

Comparing the integrals assigned to aromatic protons with those of terminal CH group at 12.65 ppm the degree of polymerization n=12 and n=16 for polymers 10 and 11, respectively have been determined.

Only the bisylide 4 dissolved in DMSO has been submitted to a decomposition upon microwave for 40 min and 2 h.

The $^1$H NMR spectra of two corresponding obtained polymers are given in Figures 6 and 7.

The two signals in the range 8–9 ppm show an incomplete decomposition of bisylide yet a more ordered formed polymer 10. After a warming for 2 h all quantity of bisylide 4 is decomposed but the obtained polymer is less arranged. In our further investigations we will deal with this controlled polymerization upon microwave.

All synthesized polymers reported in this paper are studied by DSC in order to find some specific
CONCLUSION

In this paper, we reported the synthesis of two bis-ylides 4 and 6 a ylide polymer 9 and two polycarbenic polymers 10 and 11. The latest polymers have been obtained by two different techniques by thermal and upon microwave decompositions.

Mainly, the $^1$H NMR spectra in DMSO-6 have been used in order to control the performed synthesis. The bisylide decomposition is the first example of synthesis of polycarbenic polymers, via ylides.

REFERENCES

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