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Functional Polymers and Sequential Copolymers by Phase Transfer Catalysis

4. A New and Convenient Synthesis of *p*- and *m*-Hydroxymethylphenylacetylene

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SUMMARY

p- And m-hydroxymethylphenylacetylenes were prepared by a two step sequence starting from a commercial mixture of p- and m-chloromethylstyrene, i.e., by the bromination of the vinylic monomer mixture followed by separation of m- and p- brominated derivatives by fractional crystallization, and simultaneous dehydrobromination and nucleophilic substitution of the -Cl with -OH.

INTRODUCTION

p- And m-hydroxymethylphenylacetylenes (HMPA) are important intermediates for the preparation of: functional polyacetylenes, functional initiators for cationic polymerization, telechelic polymers containing ethynylphenyl chain ends, as well as other acetylenic monomers. The currently used procedure for the synthesis of HMPA consists of the reduction of ethyl ethynylbenzoate with $LiAlH_4$(2). Ethyl p-ethynylbenzoate was initially prepared in eleven steps starting from p-bromotoluene (2). Recently, ethyl p-ethynylbenzoate was prepared by a three step method starting from p-bromobenzoic acid (3).

This paper describes a convenient two step procedure for the preparation of p- and m-HMPA starting from a commercial mixture of m- and p-chloromethylstyrene (CMS). The first step consists of the bromination of the m- and p-CMS mixture followed by separation of p-chloromethyldibromostyrene (CMBS) and m-CMBS by fractional crystallization. In the second step, both dehydrobromination and nucleophilic substitution of -Cl by -OH are accomplished simultaneously by treatment with a 50% aqueous NaOH solution in the presence of tetrabutylammonium hydrogen sulfate (TBAH) phase transfer catalyst (Scheme 1). Both the starting, intermediate, and final compounds were characterized by 200 MHz ^{1}H- and 50 MHz ^{13}C-NMR spectroscopy.

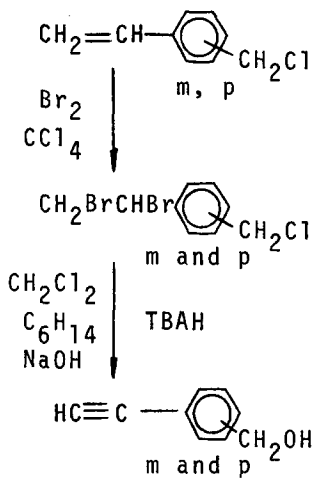
EXPERIMENTAL

A commercial sample of a mixture of m- and p-CMS (60% m, 40% p) kindly provided by Dow Chemical Co., was used as received. Tetrabutylammonium hydrogen sulfate (TBAH) (Aldrich) as well as other reagents were used as received. NMR spectra were recorded on Varian XL-200 and EM 360 instruments (200 and 60 MHz ^{1}H resonance frequencies, respectively and 50 MHz ^{13}C resonance frequency) in $CDCl_3$.

Synthesis of p- and m-CMBS

A solution of bromine (87.9 ml, 1.1 moles) in 150 ml of CCl_4 was added dropwise over a period of one hour to a stirred, ice-water cooled solution of CMS (76.3 g, 0.5 moles) in 200 ml of CCl_4. The reaction mixture

*For the previous paper in this series see reference (1)



Scheme 1.

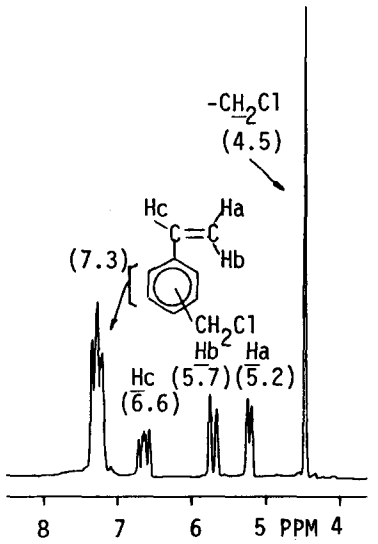


Figure 1. 200 MHz ^{1}H-NMR spectrum of m- and p-CMS mixture

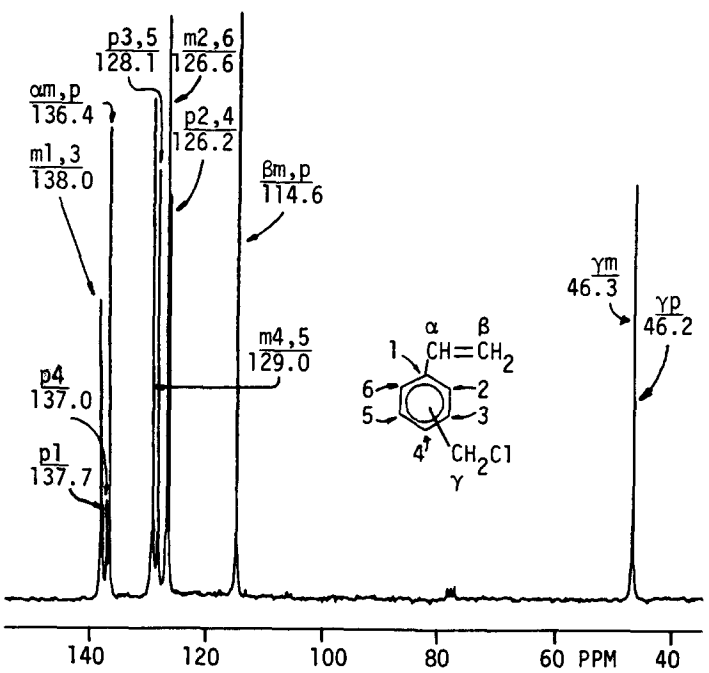


Figure 2. ^{13}C-NMR spectrum of m- and p-CMS mixture

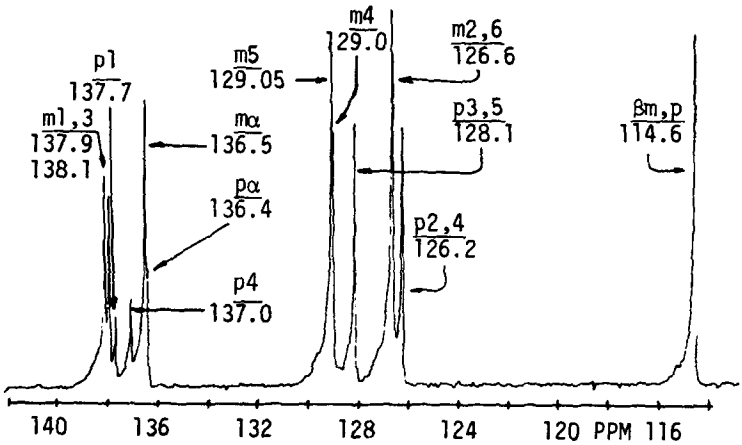


Figure 3. ^{13}C-NMR spectrum of m- and p-CMS: an expansion of the aromatic region

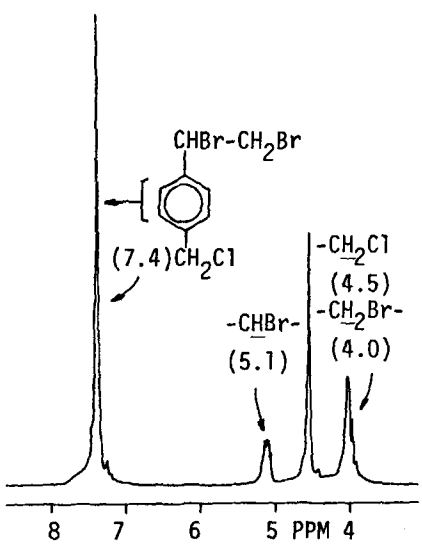


Figure 4. 200 MHz ^{1}H-NMR spectrum of p-CMBS

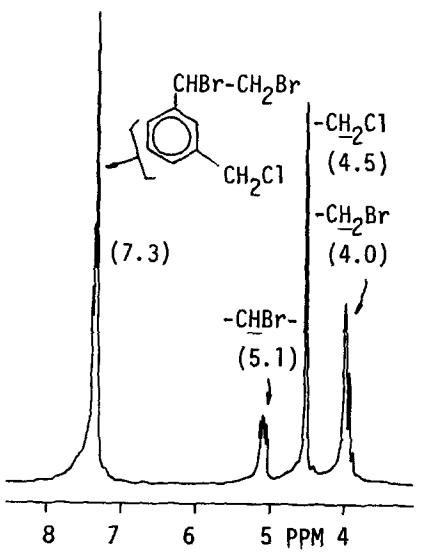


Figure 5. 200 MHz ^{1}H-NMR spectrum of m-CMBS

was stirred for one more hr at room temperature. The solvent and the excess bromine were removed on a rotary evaporator at room temperature. The oil obtained was mixed with 200 ml of hexane and left in a freezer for 24 hr. During this time p-CMBS crystallized. The solid was separated by filtration, and recrystallized twice from CCl_4 to afford 39 g (25%) of white crystals, mp 79-80°C. This material was identified as p-isomer (> 99%) by ^{13}C-NMR. The mother liquors (hexane fraction) were concentrated on a rotary evaporator to yield 109 g (70%) of an oil which contains 85% m-CMBS and 15% p-CMBS. No other attempts to increase the purity of this product were made.

Synthesis of p- and m-HMPA

p-CMBS (9.3 g, 0.03 moles) was dissolved in 50 ml CH_2Cl_2 and 50 ml of hexane was added followed by 30.6 g (0.09 moles) of TBAH. After a clear so-solution was obtained, 30 ml of NaOH (50% solution) was added with vigorous stirring. An exothermic reaction occured which brought the mixture to reflux. The exothermic reaction was over after 30 min. The reaction mixture was then stirred for 10 hr at room temperature; then the organic phase was washed several times with water, with a mixture of dilute H_2SO_4 and HBr,and again with water. The organic layer was dried over $MgSO_4$, and finally the solvent was removed on a rotary evaporator at room temperature. The white solid obtained was demonstrated by ^{1}H-NMR to contain 98% p-HMPA and 2% p-hydroxymethyl-α-bromostyrene. Two recrystallizations from petroleum ether afforded 3.86 g (85%) of white crystalline solid (mp 65 - 66°C). m-HMPA (liquid) was prepared in the same manner with about 100% conversion and 90% yield.

RESULTS AND DISCUSSION

The 200 MHz ^{1}H-NMR spectrum of the commercial mixture of m- and p-CMS is presented in Figure 1 together with the proton assignments. As can be seen, it is not possible to analyze the composition of this mixture at this field. This confirms the findings of previous authors who could not analyze this mixture at 100 MHz (4). In spite of the general interest in this monomer (4-11), assignment of the ^{13}C-NMR resonances is not available in the literature. Figure 2 presents the ^{13}C-NMR spectrum of the commercial CMS, and Figure 3 presents an expansion of the aromatic region. The composition of this mixture calculated from the intensities of the signals γp and γm or pα, mα is about 34% p and 66% m.

p-CMBS can easily be separated from the m- and p- mixture by fractional crystallization. While the purity of the p- isomer can be increased to 100% by recrystallization from CCl_4, no attempts to increase the purity of m-isomer to more than 85% were made. 200 MHz ^{1}H-NMR spectra of both products are presented in Figures 4 and 5. The only visible difference between these two spectra appears in the aromatic region. The spectrum of p-CMBS shows a sharp singlet at 7.4 ppm while the spectrum of m-CMBS shows a multiplet centered at 7.3 ppm. The quantitative analysis of these compounds was made by ^{13}C-NMR (Figures 6, 7). Figure 6 presents the spectrum of the pure p-CMBS and Figure 7 the spectrum of the m-CMBS together with the expansions of the aliphatic and aromatic regions. Resonance assignments were made by comparison with shifts calculated using ^{13}C chemical shift additivity rules for substituted benzenes (12). The last spectrum corresponds to m-CMBS obtained by the combination of both the CCl_4 and hexane mother liquors obtained after the recrystallization of the p- compound. Its composition can be calculated from the intensity of the signals α, β and γ for m- and p- products as well as from the intensity of the signals 3,5p or 2,6m and 2,5m. According to these calculations, the m-/p- ratio of this mixture is 80/20.

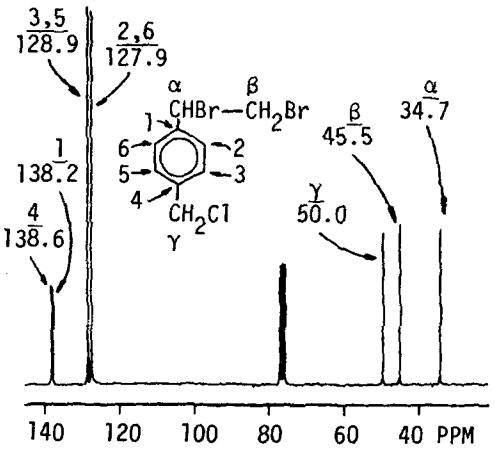
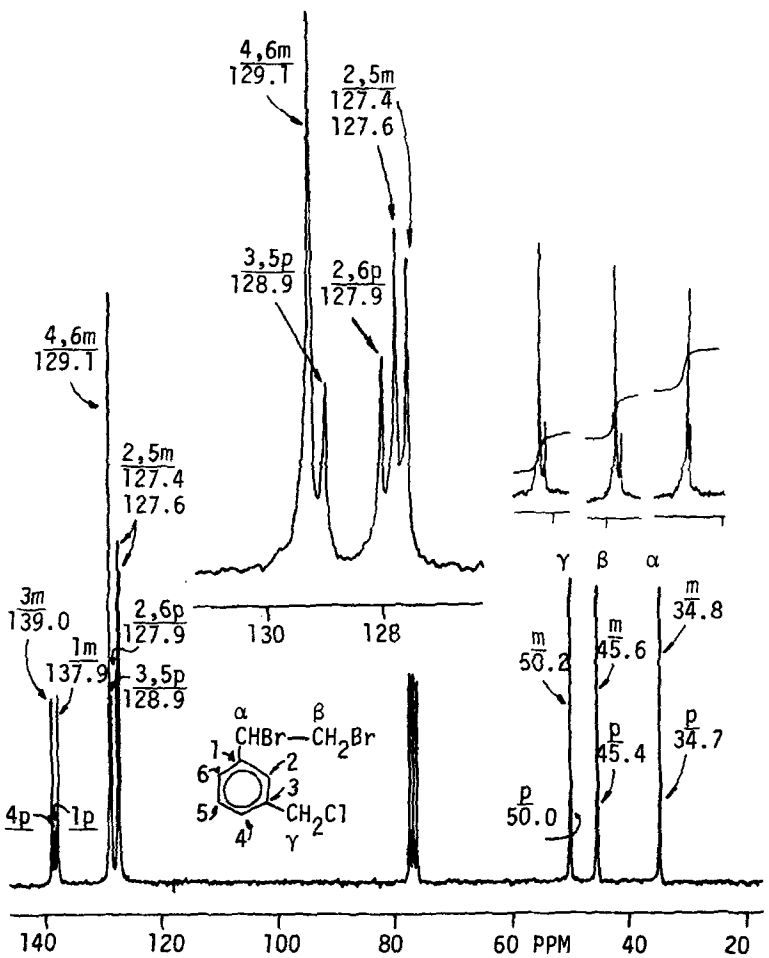


Figure 6. ^{13}C-NMR spectrum of p-CMBS

Figure 7. ^{13}C-NMR spectrum of m-CMBS



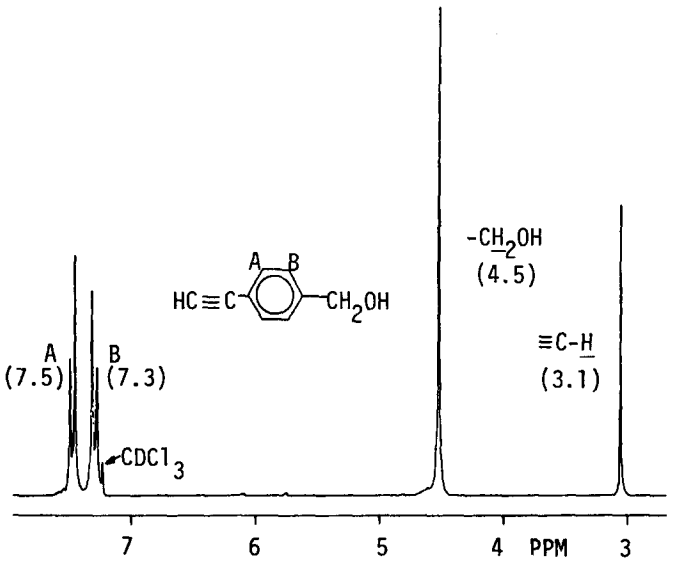


Figure 8. 200 MHz ^{1}H-NMR spectrum of p-HMPA

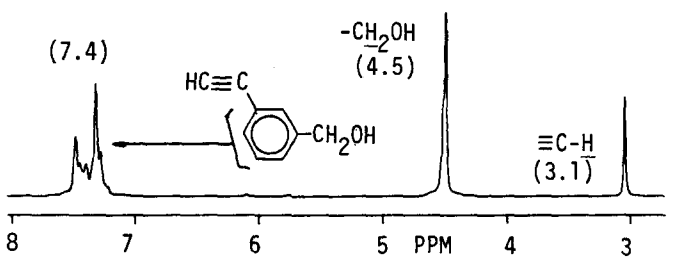


Figure 9. 200 MHz ^{1}H-NMR spectrum of m-HMPA

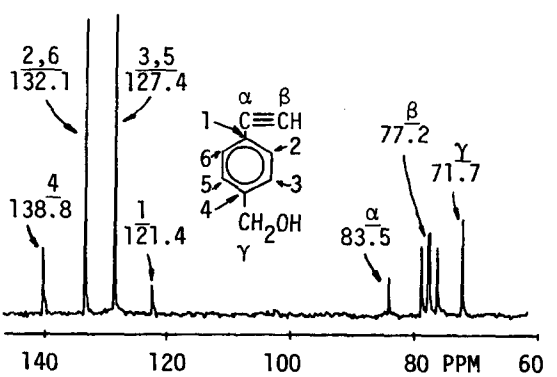


Figure 10. ^{13}C-NMR spectrum of p-HMPA

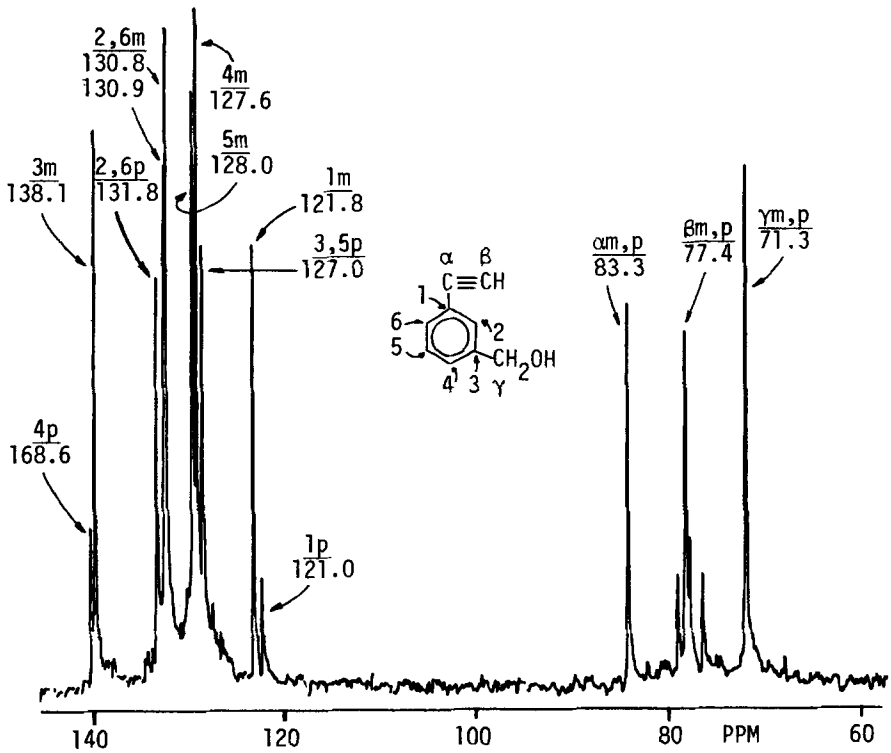


Figure 11. ^{13}C-NMR spectrum of m-HMPA

When the product was separated from the hexane fraction only, it contains 85% m-CMBS.

A first set of dehydrobromination experiments of m- and p-CMBS was carried out with potassium tert-butoxide both in ethyl ether and in tetrahydrofuran. Potassium tert-butoxide is known as a very strong base and a weak nucleophile (13) and consequently it was succesfully used for the dehydrobromination of p-(2-bromoethyl)benzyl chloride to give p-chloromethylstyrene (4-6, 9, 10). In our case some SN2 side reaction accompanied the dehydrobromination reaction of m- and p-CMBS. Distillation of the crude mixture did not provide the desired product in high yield.

The second dehydrobromination reaction was carried out with concentrated NaOH in the presence of TBAH as phase transfer catalyst. This procedure was succesfully applied to the preparation of acetylenic compounds (14) and in our hands it gave 100% conversions with 30-45 min reaction times (15). The dehydrobromination of m- and p-CMBS was followed by withdrawing samples from time to time and analysing their composition by 60-MHz ^1H-NMR. After one hr of reaction, the mixture still contained 50% chloromethyl-α-bromostyrene (=CH_2 signals at 5.7 and 6.05 ppm). After 10 hr of reaction, the conversion was always higher than 95%.

The 200 MHz ^1H-NMR spectra of p- and m-HMPA are shown in Figures 8 and 9. The chemical shift of -CH_2OH is identical with that of -CH_2Cl (Figures 1, 4, 5). No differences between the spectra of m- and p- compounds can be observed except for the aromatic regions which show an AA'BB' for p-com-

pound (Figure 8) and a supperposition of an AA'BB' with a complex pattern for the m-compound (Figure 9). ^{13}C-NMR spectra of p- and m-HMPA (Figures 10, 11) exhibit a resonance from the -$\underline{C}H_2OH$ (denoted as carbon γ) at 71.7 ppm, while the resonance of -$\underline{C}H_2Cl$ appears at 46.3 ppm in CMS (Figure 2) and 50.0, 50.2 ppm in m- and p-CMBS (Figures 6, 7). From the ^{13}C-NMR spectrum of p-HMPA it is free of the m-isomer (Figure 10). The composition of m-HMPA calculated from the intensity of the 1m and 1p signals, is 85% m- and 15% p-HMPA (Figure 11).

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