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Abnormal Reactivity of Arylaminomethylenebisphosphonates Aminomethylation on Benzene Ring in Base Medium

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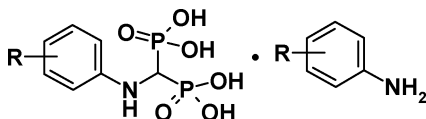
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Abnormal Reactivity of Arylaminomethylenebisphosphonates Aminomethylation on Benzene Ring in Base Medium

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It was new simple procedure offered in 2004 for synthesis of N-substituted aminomethylenebisphosphonic acids.¹ Our attempt to reproduce this method results in clear distinction between alkyl- and aryl-ones. While N-alkylsubstituted acids are well crystallizable and were obtained with high yields, the aryl-analogs are hard to be isolated. At the same time they give well crystallizable salts with anilines. We have isolated the synthesized products as such salts:

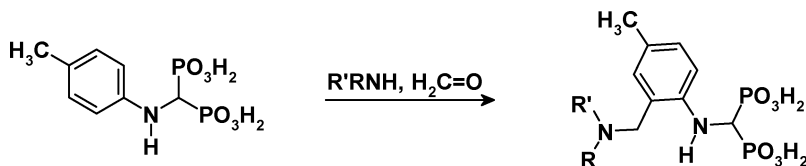


R = p-Me-, p-H₂N-, p-HO-, p-MeO-, p-Cl-, m-O₂N-.

SCHEME 1

As we have established, the reason of the properties distinction are the difference between ionic forms, in which aminobisphosphonates exist in solutions. While alkylamino-methylenebisphosphonic acids exist as internal salts, the aryl-analogs do not forms internal salts, that proved by chemical shift magnitude of their signals in NMR ³¹P spectra.

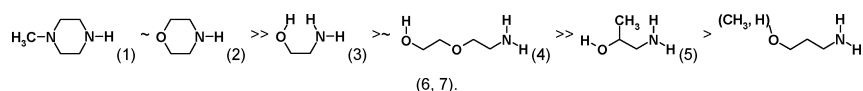
The aminomethylation reaction was investigated on the p-toluilaminomethylenebisphosphonic acid example:



SCHEME 2

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As we found, speed and result of this reaction strongly depends on amine applied. Reaction ability of applied amines decreased in next order:



SCHEME 3

While it was enough 24 h at 80°C for the reaction with amines 1 and 2, heating as long as 72 h at 95°C was needed with amines 3 and 4. Resulted mixture was consisted of 60–70% of the desired product, 10–25% of unchanged p-toluilaminomethylene-bisphosphonic acid and 5–10% of disubstituted product. Pure final products with amines 1–4 were allocated from mixtures by crystallization at individually selected conditions. The reaction with amines 5–7 was proved to be unsuccessful. Unknown by-reaction that was insignificant with more reactive amines, with amines 5–7 becomes major.

REFERENCE

- [1] M. S. Wu, R. Y. Chen, and Y. Huang, *Synth. Commun.*, 1393 (2004).