Benzylation for recovery of structure directing agent (Di-n-propylamine) from process effluent of aluminophosphate synthesis

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\textit{Receipt/Acceptance Data} [DO NOT ALTER/DELETE THIS TEXT]
\textit{Publication data} [DO NOT ALTER/DELETE THIS TEXT]
DOI: 10.1039/b000000x [DO NOT ALTER/DELETE THIS TEXT]
The $^1$H NMR spectrum displayed resonances attributable to DPBA ($\delta$ (ppm, aromatic, 5H), 7.40-7.42, 7.34-7.36; $\delta$(-N-CH$_2$, 4H), 3.42 & 3.19; $\delta$(-CH$_2$, 4H), 1.64 & 1.54; $\delta$(-CH$_3$, 6H), 0.92-0.95 & 0.7-0.81. It appears that both the propyl groups experience ‘dissimilar environment’, probably arising from ‘allylic strain’ and rotation about amide bond. In addition, impurities are also identifiable; benzoyl chloride ($\delta$ 8.03-8.5, 7.52-7.55 ppm); dipropylamine ($\delta$ 2.92-2.89, 2.04, 1.76-1.87, 1.20 ppm) and solvent peak at $\delta$ 2.08 ppm.
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(Assignment of $^{13}$C-NMR spectrum of product, DPBA)

$^{13}$C NMR in Acetone-d6

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Explanation for $^{13}$C-NMR

Generally, 8 different carbons are predicted represented by eight different peaks in the $^{13}$C-NMR spectrum of DPBA. The dipropyl groups should have given rise to 3 different peaks; however, surprisingly we observed 6 different peaks indicating that these groups experience ‘dissimilar environment’. The methylene carbons immediately next to N-atom appeared at 50.36 & 47.58, and the ones next to this carbon showed up at 22.14 & 20.73 ppm. The end methyl groups appear to be nearly in the same ‘environment’ and show up at 12.28 & 11.86 (shoulder). In the published literature also similar observations were reported (http://sdb.sriodb.aist.go.jp/sdb/cgi-bin/cre_index.cgi, see spectra for diethylbenzamide and dimethylbenzamide (next page); www.rsc.org/suppdata/cc/c1c11635e/c1cc11635e.pdf, Electronic Supplementary Material (ESI) for Chemical Communications, the Royal Society of Chemistry 2011). It is also reported in the case of diethylbenzamide that this could be due to strong steric squeezing of the ethyl groups (allylic strain) leading to the amide group turn and attenuated $\pi$-electronic coupling between of aromatic group and amide moieties [P. Majewskaa, J. Paja ka, M. Rospenka and A. Filarowski, J. Phys. Org. Chem. 2009, 22 130–137. (www.interscience.wiley.com) DOI 10.1002/poc. 1437; P. Kawski, A. Kochel, M. G. Perevozkina, A. Filarowski, J. Mol. Struct. 2006, 790, 65]. In view of this, we are convinced that our assignment of $^{13}$C-NMR is correct.
Major IR absorption peaks observed at 3056-2876, 1631-1460, 1378-1300, 1101, 785, 759 & 709 cm\(^{-1}\) may be attributed to \(v_{\text{CH}}\) (sp\(^2\) & sp\(^3\)), \(v_{\text{C=O}}, v_{\text{C=C}}\) (aromatic), \(v_{\text{CH}}, v_{\text{C=H}}\) (bend), \(v_{\text{C-C}}\) (stretch) of the compound, DPBA. The \(v_{\text{CH}}\) (bends) were observed at 785-709 cm\(^{-1}\). The absorption at 1713 and 652 cm\(^{-1}\) may be due to \(v_{\text{C=O}}\) and \(v_{\text{C-Cl}}\) of benzoyl chloride impurities.
The broad absorption band in the range 230-290 nm may be attributed to \( \pi-\pi^* \) transition due to aromatic and –C=O groups in the compound.
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($^{27}$Al-NMR Spectrum for the recovered AlPO$_4$, 8 kHz)

The MAS $^{27}$Al NMR spectrum displayed three resonance signals at δ 47.69, 8.77 and -9.16 ppm. They can be attributed Al in tetrahedral, pentagonal and octagonal geometries made up of AlO$_x$ polyhedra. The most intense peak -9.16 ppm is characteristic of hydrated AlPO$_4$ [J. Mol. Str. 470 (1-2), 1998, 221-228; Bleam et al., Phy. Chem. Minerals (1989), 16: 809-816].
* Spinning side bands

The $^{31}\text{P}$ MAS NMR spectra showed two resonance at δ 2.97 and -7.67 ppm, apart from spinning side bands on either side. These signals can be attributed to PO$_4^{3-}$ polyhedra; the former appears to be due to protonated PO$_4^{3-}$ [Bleam et al., Phy. Chem. Minerals (1989), 16: 809-816].
The powder XRD indicated crystalline powder which displayed diffractions at 2θ = 8.06, 9.76, 14.04, 17.08, 18.98, 21.38, 22.66, 24.3, 28.48 and 33.32 deg. Several of these diffractions match with reported XRD of AlPO₄ [Li and Davis, J. Chem. Soc. Faraday Trans. 1933, 89, pp. 957-964].