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Discussion

Comments on "Methyl phenylacetate enolate generated with the P4-*t*Bu Schwesinger base: 'naked' or not?"☆

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A recent report by some of us[1] indicated that addition of P4-*t*Bu base (1 M in hexane) to methyl phenylacetate in THF-d_8 led to ^{1}H and ^{13}C NMR spectra that depended dramatically on the final ratio of THF to hexane present in the dissolving media. These observations were interpreted by proposing that a 'naked' enolate was present in THF/hexane 9/1 by volume, leading to the spectra illustrated in Fig. 1a of the original paper, while in THF/hexane 7.8/2.2 by volume, an 'aggregated enolate' was proposed to be present, giving the data shown in Fig. 1c of the original paper.

We now report observations from both of our laboratories which establish that the results summarized in Ref. 1 are not reproducible as described. Spectra consistent with those shown in Fig. 1a of Ref. 1 were observed in solutions having THF/hexane ratios as low as 6/4 by volume. However, upon standing for 3–4 days in the NMR tube, monitoring of the NMR spectra over time indicated that the spectra slowly changed from the species shown in Fig. 1a to that shown in Fig. 1c, regardless of the relative THF and hexane concentrations that are present. These new findings, establishing the irreproducibility of the original results, are unlikely to be caused by a 'naked' to 'tight ion pair' transition occurring as a result of a modest change in solvent composition. Rather, a more complicated, and irreversible, decomposition process is probably operative.

The original authors regret this misinterpretation. Further studies will be necessary to fully understand these results.

References

1. Fruchart, J.-S.; Gras-Masse, H.; Melnyk, O. *Tetrahedron Lett.* **2001**, *42*, 9153.

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