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A REINVESTIGATION OF THE RESOLUTION OF METHYLETHYL-n-PROPYLTIN IODIDE

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SUMMARY

The reinvestigation of the only reported resolution[1] of an asymmetric organotin compound showed that the claim for the resolution was in all probability based on erroneous results. This finding is in agreement with the result of recent NMR studies which indicated that inversion is rapid at the tin center of asymmetric organotin halides.

In recent years there has been considerable interest in the optically active compounds of the Group IVA elements. While the literature about optically active organosilicon and organogermanium compounds has been accumulating steadily the only claim for the resolution of an asymmetric organotin compound dates back to 1900 when Pope and Peachey reported[1] the resolution of methylethyl-n-propyltin iodide (I).

Verbal reports of unsuccessful attempts of repeating this work have been circulating for some time, nevertheless the 'resolution' has continued to be quoted in the literature. For this reason we wish to report our results of reinvestigating the reported resolution of (I).

According to the original authors when the diastereomeric champhor-β-sulphonate was formed by agitating (I) with aqueous silver (+)- camphor-β-sulphonate only one of the diastereomers (m.p. 125–126°) crystallized from the solution Moreover, on evaporation of the solvent (water) all of the compound was obtained as this diastereomer. This of course is perfectly possible, and if genuine, it would be one of the very first examples of what we now describe as second order asymmetric transformation. Samples of (I) recovered from a freshly prepared cold aqueous solution of the isolated diastereomer by the addition of KI were reported to have specific rotations that varied between 0 and +23°.

Since by this method only the dextrorotatory enantiomer of (I) could be obtained Naumov and Manulkin[2] tried to isolate the levorotatory enantiomer by using silver (−)-camphor-β-sulphonate as the resolving agent. Although all they obtained were inactive samples of (I) they never questioned the work of Pope and Peachey. Instead they drew the rather curious conclusion that what is possible with (+)-camphor-β-sulphonate as resolving agent is not possible with (−)-camphor-β-sulphonate.

The only characterization given for (I) in the original paper was that it distilled at 270° without decomposition at atmospheric pressure. In contrast to this we found that the boiling point of (I) was 222°/757 mm with extensive decomposition. The diastereomeric camphor-β-sulphonate isolated by us had poorly defined melting point around 81° which is also at variance with the value (125-126°) reported by Pope and Peachey. These authors reported a molecular rotation of +95° for the diastereomer isolated by them and, on the basis of additivity of molecular rotations, assigned +45° to the activity of the asymmetric tin center.

We carried out a large number of fractional crystallizations of the diastereomeric compound. The conditions for the recrystallizations were varied from slow evaporation of a dilute solution at 25° or below to rapid cooling of a hot saturated solution. However, the melting points and molecular rotations of the various crops of crystals remained virtually unchanged. Although all of the work of the original authors was apparently restricted to aqueous solutions (no experimental details were given) we tried several recrystallizations from acetone, but the results were equally negative.

Recent NMR studies[3] demonstrated that the rate of inversion of methylphenylneophyltin chloride is far too rapid for a separation of the enantiomers to be possible. It was further shown that the rapid inversion was due to the presence of the tin–halogen bond. These results make it very unlikely that (I) could ever have been isolated in an optically active form. In view of this, and the discrepancies between the observed properties of (I) and those reported by Pope and Peachey we believe, that the resolution of (I) is not only unrepeatable but, that the claim for it was based on erroneous results.

EXPERIMENTAL

Methylethyl-n-propyltin iodide

This compound was synthesized by the stepwise replacement of methyl groups in tetramethyltin according to the procedure of Naumov and Manulkin[2]. B.p. 118–120°/25 mm, 222°/757 mm, n_D^{25} 1.5530 (lit.[2] b.p. 108–110°/11 mm, 226–230°/720 mm, n_D^{17} 1.5548.) (Found: C, 21.40; H. 4.84; Sn, 35.38. $C_6H_{15}ISn$ calcd.: C, 21.65; H, 4.54; Sn, 35.67%.)

Methylethyl-n-propyltin (+)-camphor-β-sulphonate

Silver (+)-camphor-β-sulphonate[2] (1.292 g, 0.00382 mole) dissolved in 50.0 ml H_2O ($[\alpha]_D^{20}+14.7°$; $[M]_D^{20}+49.8°$) was added to methylethyl-n-propyltin iodide (1.272 g, 0.00382 mole) and the heterogeneous mixture was agitated for 2 h on a steam bath. The precipitated silver iodide was filtered off and the filtrate evaporated to dryness. The colorless syrupy residue (1.80 g) solidified into transparent plate-like crystals, m.p. 80–83° (poorly defined), $[\alpha]_D^{20}+10.9°$, $[M]_D^{20}+47.9°$ (c=0.656 g/100 ml in H_2O). Repeated recrystallization from water left both melting point and optical activity unchanged. (Found: C, 43.63; H, 7.14; S, 7.53. $C_{16}H_{30}O_4SSn$ calcd.: C, 43.97; H, 6.92; S, 7.34%.)

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REFERENCES

1 W. J. Pope and S. J. Peachey, *Proc. Chem. Soc.*, 16 (1900) 42.
2 C. N. Naumov and Z. M. Manulkin, *Zh. obshch. Khim.*, 5 (1935) 281.
3 G. J. D. Peddle and G. Redl, *Chem. Commun.*, (1968) 627.