

XLVI.—*A Note on Phenyl dimethylallyl ammonium Compounds.*

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The work which forms the subject of this note was commenced some eight months ago, but its completion was unavoidably delayed, and in the meanwhile a paper was published on the subject by H. O. Jones (Trans., 1903, 83, 1400) which contained results differing in some respects from those obtained by the author.

In this investigation, an attempt has been made to prepare and resolve into their optically active components, substituted quaternary compounds containing two similar groups.

Phenyl dimethylallyl ammonium iodide was prepared by mixing molecular proportions of dimethylaniline (48 grams) and allyl iodide (67 grams). After a few days, the semi-solid product was finely ground and filtered, 67 grams of solid phenyl dimethylallyl ammonium iodide being obtained. The impure product, which rapidly deliquesced on exposure to air, was further purified by washing with acetone, the final purification being effected by solution in absolute alcohol and precipitation by the cautious addition of ether. Phenyl dimethylallyl ammonium iodide, when pure, melts at $86-88^{\circ}$, and when crystallised from acetone forms large, pink tables, which were never obtained colourless; the pure substance was not deliquescent.

Phenyl dimethylallyl ammonium *d*-camphorsulphonate was prepared by mixing molecular proportions of the iodide and silver *d*-camphorsulphonate; both constituents were finely powdered before mixing, and the mixture was boiled for one hour in a mixture of equal parts of ethyl acetate and acetone. The precipitated silver iodide was filtered off and the salt, which crystallised very readily, was obtained in six fractions by successive crystallisations. No alcohol was used in the preparation and the product was never gummy. The salt crystallised in fine, colourless needles melting at 156° .

The rotatory power, for sodium light, of each of these fractions, in a two per cent. solution, was found to be the same, and the calculated $[M]_D$ was identical, within the limits of experimental error, with that

of the activity due to the active acid ion, namely, $[M]_D + 51.7^\circ$. It was repeatedly observed that an alteration in the concentration of the solution caused a different value for the specific rotation to be obtained at the same temperature, thus, a 1 per cent. solution gave $[\alpha]_D + 11.9^\circ$, whilst a 2 per cent. solution had $[\alpha]_D + 13.3^\circ$.

As it was possible that a separation of the dextro- and lævo-isomerides might be effected by crystallisation at a higher temperature, search was made for a suitable solvent having a high boiling point. Pyridine was chosen, as phenyldimethylallylammonium *d*-camphorsulphonate is fairly soluble in this solvent in the cold and readily so at the boiling point. A crop of crystals was thus obtained at about the temperature of boiling water. This fraction was not, however, found to exhibit any optical activity due to the basic ion.

As this substance was found to be very sparingly soluble in ethyl acetate, and as Jones described it as readily soluble in ethyl acetate, its solubility in this solvent was determined and found to be less than 8 parts in 5000 parts of a boiling solution of the salt in ethyl acetate. Four separations of the *d*-camphorsulphonate were obtained by the successive addition of quantities of ethyl acetate to a cold solution of the salt in pyridine, and these four fractions also showed no activity due to the basic ion.

0.2006 gave 0.4697 CO_2 and 0.1423 H_2O . $\text{C} = 63.8$; $\text{H} = 7.8$.
 $\text{N}(\text{C}_6\text{H}_5)(\text{CH}_3)_2 \cdot \text{C}_3\text{H}_5 \cdot \text{C}_{10}\text{H}_{15} \cdot \text{O} \cdot \text{SO}_3$ requires $\text{C} = 64.1$; $\text{H} = 7.8$ per cent.

Phenyldimethylallylammonium platinichloride was obtained as a pale yellow crystalline precipitate on adding the requisite quantity of platinic chloride to an aqueous solution of the final fraction from ethyl acetate and acetone of phenyldimethylallylammonium *d*-camphorsulphonate, acidified with hydrogen chloride. The precipitated salt, which was collected and thoroughly washed with water, when dried in the air, melted at $162\text{--}165^\circ$ with decomposition.

0.5130 gave 0.1439 Pt. $\text{Pt} = 26.9$.

$[\text{N}(\text{C}_6\text{H}_5)(\text{CH}_3)_2 \cdot \text{C}_3\text{H}_5]_2\text{PtCl}_6$ requires $\text{Pt} = 26.6$ per cent.

A cold aqueous solution of the platinichloride, which is slightly soluble in water, was examined in the polarimeter, but was found to be quite inactive. A further examination was made by suspending about half a gram of the salt in water, slightly acidified with hydrogen chloride; the platinichloride was then decomposed by passing a current of hydrogen sulphide through the cold solution; the precipitated platinum sulphide was filtered off and the solution examined in the polarimeter. This solution, also, was found to be inactive.

As Jones has succeeded in obtaining *d*- and *l*-isomerides of phenylbenzylmethylethylammonium salts having optical rotations of similar

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arithmetical value (Trans., 1904, 85, 223), the author proposes to revise the work of Pope, Peachey, and himself, who failed to find such a close agreement in the case of the *d*- and *l*-phenylbenzylmethylallylammonium salts.

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