

NOTES.

Some Derivatives of Tri-p-tolylsilicane. By ALFRED RAYMOND STEELE and FREDERIC STANLEY KIPPING.

THE distillation of the crude product of the interaction of silicon tetrachloride and magnesium *p*-tolyl bromide (Pink and Kipping, J., 1923, **123**, 2832) gives a considerable fraction collected from about 250° to 300° which deposits crystals in the course of several weeks; when separated by filtration and recrystallised from hot light petroleum, this solid gives *tri-p-tolylsilicyl chloride*, $\text{Si}(\text{C}_7\text{H}_7)_3\text{Cl}$, in colourless rhomboidal prisms, m. p. 115—116° (Found: Cl, 10.8. $\text{C}_{21}\text{H}_{21}\text{ClSi}$ requires Cl, 10.5%). The chloride is readily soluble in most of the common solvents; it does not fume appreciably on exposure to moist air and is only slowly decomposed by cold water.

Tri-p-tolylsilicol, $\text{Si}(\text{C}_7\text{H}_7)_3\cdot\text{OH}$, was prepared by treating the chloride with a dilute solution of ammonium hydroxide in aqueous

acetone. It separates from light petroleum in compact lustrous crystals, apparently octahedra, m. p. 99—100° (Found: Si, 8·8. $C_{21}H_{22}OSi$ requires Si, 8·8%). It is very readily soluble in chloroform, benzene and acetone, but much less so in cold light petroleum or alcohol.

Tri-p-tolylsilicyl oxide, $[Si(C_7H_7)_3]_2O$, is obtained when an alcoholic solution of the silicol containing a few drops of a 10% solution of sodium hydroxide is evaporated on the water-bath, and the residue heated during about an hour. It crystallises well from chloroform-acetone in rhomboidal plates, m. p. 223—224° (Found: Si, 9·2. $C_{42}H_{42}OSi_2$ requires Si, 9·15%). It dissolves freely in chloroform and fairly readily in benzene, but is only sparingly soluble in light petroleum and acetone.—UNIVERSITY COLLEGE, NOTTINGHAM. [Received, January 9th, 1929.]

The Influence of Colloids on the Precipitation of Salts. By ROBERT DICKINSON.

PREVIOUS workers (Williams and Mackenzie, J., 1920, **117**, 844; Bolam and Mackenzie, *Trans. Faraday Soc.*, 1926, **22**, 151, 162; Bolam and Desai, *ibid.*, 1928, **24**, 50; Bolam, *ibid.*, p. 463) have shown that silver chromate and lead iodide can be maintained in supersaturated solutions by the presence of gelatin and of agar-agar respectively.

A striking example of the above phenomenon has now been observed in the case of *lead sozoiodolate* (3:5-di-iodo-4-hydroxy-benzenesulphonate) [Found: Pb, 30·6, 30·3. $C_6H_2O_4I_2SPb$ requires Pb, 32·8. $(C_6H_3O_4I_2S)_2Pb$ requires Pb, 19·6%], in which sozoiodol acts as a dibasic acid. The low values for lead are probably due to partial volatilisation of lead iodide.

When equivalent solutions of lead acetate and sodium sozoiodolate were mixed to give a volume of 50 c.c. containing 0·5% Pb, no change was observed for about 10 seconds. Nuclei then appeared, and these rapidly increased in size and number until the liquid finally became a semi-solid mass of minute lemon-yellow needles. The amount of precipitate was 0·5058 g. (calc., 0·762 g.), hence the solubility of lead sozoiodolate in water is 0·512 g. per 100 c.c. of solution.

On repeating the above experiment, but having 2% of gum acacia also present in the solution, no change was observed for at least 2 hours. Minute yellow nodules then appeared on the bottom of the flask and slowly increased in size; they were not numerous (less than 100), and some attained a diameter of nearly 1 mm. When equilibrium had been reached, the weight of solid was found

to be 0.204 g., and hence the solubility of lead sozoiodolate in 2% gum acacia solution is 1.116 g. per 100 c.c. of solution. Thus gum acacia prevents the precipitation of more than half the expected amount of this lead salt.

The behaviour of gelatin in this connexion could not be studied, since it reacts with sodium sozoiodolate to give a white rubber-like precipitate; and despite an extensive examination of many other lead salts, no further example of this phenomenon has been observed.

This work was carried out on behalf of the Liverpool Medical Research Organisation.—THE UNIVERSITY, LIVERPOOL. [Received, November 22nd, 1928.]

On the Individuality of Humulene. By A. CHASTON CHAPMAN.

IN his reply to my paper entitled "On the Individuality of Humulene" (J., 1928, 785) Deussen (*J. pr. Chem.*, 1928, **120**, 133) gives certain tables illustrating the fractional distillation of specimens of caryophyllene, and shows the relation between the boiling ranges, optical rotations and yields of nitrosochloride, nitrosite and nitrosate. His results are not altogether easy to understand, but so far as they go they are quite consistent with the presence in the caryophyllene of a proportion of humulene.

I may incidentally point out two instances in which Deussen has evidently misunderstood me. In my paper I stated that the 5 lb. of caryophyllene with which I actually worked was a portion of 40 lb. of the crude hydrocarbon itself, and not, as Deussen appears to have thought, of clove oil.

In the second place, I need scarcely say that I made a large number of fractional distillations (not two, as stated by Deussen), using in the end, for the purposes of my examination, the two fractions which differed most widely in their boiling points.

Both Deussen's results and mine appear to indicate very clearly that the inactive hydrocarbon which is present in clove oil is, in fact, identical with the hydrocarbon which I obtained in 1895 from hop oil, and to which I gave the name "humulene." That this hydrocarbon is not caryophyllene is shown by the fact that it does not yield a crystalline alcohol, and further that its nitrosite differs from that of caryophyllene. There need be no confusion in nomenclature such as that to which Deussen refers, and in any case it does not constitute an argument of any weight, and may be disregarded.

In conclusion, no inactive hydrocarbon having all the properties of caryophyllene has ever been obtained, and I see no reason to modify the view I have always held—and which has been confirmed by

others—that humulene is not identical with caryophyllene. In the terpene series identity of derivatives is by no means to be regarded as definite evidence of the identity of the parent hydrocarbons. On the other hand, differences in behaviour in respect of the formation of derivatives is strong evidence that the parent hydrocarbons are not the same. It is tolerably clear that humulene and caryophyllene are closely related, and it is not impossible that in certain reactions intramolecular change occurs, the one being transformed into the other.—CHEMICAL LABORATORIES, 8, DUKE STREET, E.C. 3. [*Received, January 18th, 1929.*]
