NOTES.

1 : 3-*Dichloroanthraquinone*. By ALAN AUGUST GOLDBERG.

THIS substance, which was prepared by Meyer and Zahn (*Annalen*, 1913, **396**, 152) and by Junghaus (*ibid.*, 1913, **399**, 316), who gave no satisfactory proof of its structure, is best obtained in quantity by the following method, which leaves no doubt as to its constitution.

Aluminium chloride (100 g.) was added to a solution of phthalic anhydride (50 g.) in *m*-dichlorobenzene (208 g.), and the mixture stirred at 100—110° for 7 hours with exclusion of moisture (compare Eng. Pat. 288884). Water was then added, and the excess of *m*-dichlorobenzene (144 g.) distilled in steam. The residual oil was separated from the aqueous layer, pulverised after it had become friable, and extracted with a boiling solution of sodium carbonate (6 hours). The extract was concentrated, cooled, and acidified with dilute hydrochloric acid. The dichlorobenzoylbenzoic acid, precipitated as a nearly white gum which slowly solidified, was dissolved in aqueous ammonia (charcoal) and reprecipitated with cold dilute hydrochloric acid (yield, 72 g.). The acid is very soluble in alcohol and insoluble in ligroin, but crystallises from chloroform or benzene in hard white cubes, m. p. 106—107° (Found : Cl, 24·0. Calc. : Cl, 24·1%).

The above dichlorobenzoylbenzoic acid (20 g.) was dissolved in 5%

fuming sulphuric acid (80 c.c.) and heated at 155—160° for 2½ hours. The dark red melt was poured into ice-water, the product heated over-night on the steam-bath, and the coagulated dichloroanthraquinone collected and freed from dichlorobenzoylbenzoic acid by extraction with dilute aqueous sodium hydroxide. The residue was dissolved in acetic acid and purified by treatment with chromic acid. The addition of water precipitated the dichloroanthraquinone (which must be the 1 : 3-dichloro-compound) in bright yellow flocks (17 g.), m. p. 206°, which crystallised from acetic acid in long, stout, yellow needles, m. p. 209—210° alone and in admixture with a specimen obtained from 2-aminoanthraquinone (Junghaus, *loc. cit.*; Goldberg, this vol., p. 1789) (Found : Cl, 25·6. Calc. : Cl, 25·6%).

In conclusion the author wishes to thank Professor J. F. Thorpe, C.B.E., F.R.S., and Dr. H. King for their valuable advice and kind interest in this work; also the Department of Scientific and Industrial Research for permission to publish the results and for a grant which made the investigation possible.—IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY, LONDON, S.W.7. [*Received, July 20th*, 1931.]

Tribenzylsilicane. By WALTER ERIC EVISON and FREDERIC STANLEY KIPPING.

FROM the complex product of the interaction of sodium and benzylsilicon dichloride, Steele and Kipping (J., 1928, 1431) isolated small proportions of tetrabenzylsilicane and tribenzylsilicyl oxide, and suggested that their formation probably occurred as follows :

$$>Si(CH_2Ph)_2 + 2Na = >Si(CH_2Ph)Na + Na\cdot CH_2Ph : \quad Si(CH_2Ph)_2Cl_2 + 2Na\cdot CH_2Ph = Si(CH_2Ph)_4 + 2NaCl.$$

$$Si(CH_2Ph)_2Cl_2 + Na\cdot CH_2Ph = Si(CH_2Ph)_3Cl + NaCl : \quad 2Si(CH_2Ph)_3Cl + Na_2O = [Si(CH_2Ph)_3]_2O + 2NaCl.$$

Some pure tetrabenzylsilicane being required for another investigation, a sample of Steele and Kipping's crude silicohydrocarbon was fractionally crystallised from light petroleum; the mother-liquors gave deposits which were mixtures, but their further fractionation from the same or from a different solvent did not afford a separation of their components. When crystallised very slowly from cold light petroleum, the mixtures gave long needles of tetrabenzylsilicane and a small proportion of six-sided plates; the latter were separated mechanically and recrystallised until constant in melting point. The compound so obtained formed well-defined six-sided plates, m. p. 91°, readily soluble in benzene, chloroform, acetone, and hot light petroleum. On treatment with acetone and potassium hydroxide solution, it gave hydrogen and was converted into a sparingly soluble product, which was proved to be tribenzylsilicyl oxide (m. p. 205°) by its properties and by a mixed melting-point determination.

The compound, m. p. 91°, therefore, is *tribenzylsilicane* [Found : Si, 9·7 ; hydrogen value (c.c. per g.), 71·1 ; *M*, cryoscopic in benzene, 279. $C_{21}H_{22}Si$ requires Si, 9·4% ; H.V., 74 ; *M*, 303].

It is probably the first product of the action of water on a sodium compound, $Si(CH_2Ph)_3Na$, produced from tetrabenzylsilicane, and the tribenzylsilicyl oxide isolated by Steele and Kipping was possibly formed from it by the action of alkali.

The fact that tribenzylsilicane is a solid whereas triphenylsilicane (Kipping and Murray, J., 1929, 364) is a liquid at the ordinary temperature is noteworthy; in most cases a phenyl derivative of silicane has a melting point considerably higher than that of the corresponding benzyl compound, but tribenzylsilicyl chloride, m. p. 141°, and triphenylsilicyl chloride, m. p. 110°, dibenzylsilicon dichloride, m. p. 50°, and diphenylsilicon dichloride (oil), like the silico-hydrocarbons, $SiHR_3$, are exceptions to the general rule.—

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