NOTES.

The Preparation of Halogenated Methoxybenzaldehydes and the Demethylation of the Corresponding Benzil Derivatives. By HARRY SHAPIRO and KENNETH A. SMITH.

5-BROMO-2-METHOXYBENZALDEHYDE may be prepared most conveniently by the methylation of 5-bromosalicylaldehyde in acetone solution by dimethyl sulphate and a suitable metal carbonate. 5-Bromosalicylaldehyde (Auwers and Bürger, *Ber.*, 1904, **37**, 3934) is simpler to obtain as a starting material than 2-methoxybenzaldehyde, which may be brominated directly (Perkin, *Annalen*, 1868, **145**, 304). The demethylation of 5 : 5′-dibromo-2 : 2′-dihydroxybenzil described by Kuhn, Moller, and Went (*Ber.*, 1943, **76**, 900) is not practicable for amounts larger than 2 g. A modification of their process using chlorobenzene as a solvent gives excellent yields.

Both the methylation and demethylation procedure is applicable to the corresponding 5-chloro- and 3 : 5-dichloro-compounds.

5-Bromo-2-methoxybenzaldehyde. 5-Bromosalicylaldehyde (12·6 g.) is dissolved in acetone (100 c.c.) in which is suspended anhydrous potassium carbonate (7 g.). Dimethyl sulphate (12·6 g.) is added and the mixture is refluxed with stirring for 2 hours on the water-bath. The solvent is removed from the colourless solution and the residue treated with hot water (150 c.c.). After cooling, the colourless crystalline *compound* is separated, washed with 2N-NaOH and then with water until the washings are neutral. The product is then dried at 70° (13·4 g., 99·3%), m. p. 116·4° (corr.) (Found : C, 44·8; H, 3·5; Br, 37·5; MeO, 14·6. $C_8H_7O_2Br$ requires C, 44·7; H, 3·3; Br, 37·2; MeO, 14·4%).

5 : 5′-Dibromo-2 : 2′-dihydroxybenzil. 5 : 5′-Dibromo-2 : 2′-dimethoxybenzil (21·4 g.) is dissolved in dry chlorobenzene (100 c.c.) to which is added powdered anhydrous aluminium chloride (214 g.). The mixture is stirred for 7 hours at 60° on a water-bath. The dark liquid is then poured into an equal volume of N-hydrochloric acid and the chlorobenzene removed by steam distillation. The dark residue is dissolved in 2N-NaOH (400 c.c.) and filtered from a small amount of insoluble material. On acidifying with concentrated hydrochloric acid (Congo red), the canary yellow demethylated *product* is obtained. This is collected, washed with water and dried at 90° (19·2 g., 96%). After crystallis-

ation from alcohol or glacial acetic acid, it has m. p. 214° (corr.) (Found: C, 42·0; H, 2·0; Br, 39·9. $C_{14}H_8O_4Br_2$ requires C, 42·0; H, 2·0; Br, 40·0%).—RESEARCH DIVISION, BAYER PRODUCTS, LONDON. [*Received, November 23rd,* 1945.]

Chloromethylation of 1- *and* 2-*Chloronaphthalenes.* By DENIS H. S. HORN and FRANK L. WARREN.

VARIOUS methods, designed to increase the yield, have been described for the chloromethylation of aromatic nuclei. We have been unable to confirm the 90% conversion reported by Darzens and Levy (*Compt. rend.*, 1936, **202**, 73; cf. Grummit and Buck, *J. Amer. Chem. Soc.*, 1943, **65**, 295). The essential details—without which, the yield is reduced by more than 50%—of any method seem to be the removal of acids and the drying of the crude product with anhydrous potassium carbonate prior to distillation as recommended by Grummit and Buck (*loc. cit.*).

The chloromethylation of 1-chloronaphthalene gave 1-*chloro*-4-*chloromethylnaphthalene*, m. p. 78—79°, which was oxidised by dilute nitric acid (cf. Weissgerber and Kurber, *Ber.*, 1919, **52B**, 346) to 4-chloro-1-naphthoic acid, m. p. 221—223°, identical with that of the acid synthesised from 1-chloro-4-bromonaphthalene, although Friedlander and Weisberg (*Ber.*, 1895, **28**, 1843) give m. p. 210°.

The chloromethylation of 2-chloronaphthalene gave a mixture of difficultly separable isomers. Catalytic hydrogenation experiments in the presence of palladium black on calcium carbonate (Busch and Stöve, *Ber.*, 1916, **49**, 1063) caused the reduction of the alkyl-chlorine without the elimination of the halogen attached to the nucleus, and the velocity of the reaction indicated a break in the curve when 85% of the hydrogen had been absorbed. By stopping the reduction at 60—67% absorption and distilling the product, 2-*chloro*-1-*chloromethylnaphthalene*, m. p. 67—68°, was separated. Amination of the reduction product, 2-chloro-1-methylnaphthalene, and acetylation gave an acetyl derivative, m. p. 188—189°, recorded by Fries and Hubner (*Ber.*, 1906, **39**, 444) for 1-methyl-2-acetnaphthalide, but the yield was too small for analysis. The structure was confirmed by oxidation to 2-chloro-1-naphthoic acid; the slow rate of catalytic reduction may be explained by steric hindrance. The other isomer, 7-*chloro*-1-*chloromethylnaphthalene*, m. p. 75°, was obtained by crystallisation of the mixture from ligroin. The structure was established by direct oxidation with dilute nitric acid, or *via* 7-*chloro*-1-*hydroxymethylnaphthalene*, to 7-*chloro*-1-*naphthoic acid*, synthesised from 7-chloro-1-bromonaphthalene, m. p. 67°. This latter compound has been designated as 6(or 7)-chloro-1-bromonaphthalene by Guareschi (*Jahrb. Fortsch. Chemie*, 1888, 921); but the acid, m. p. 238—240°, obtained from it by the Grignard reaction, and its p-*bromophenacyl ester*, m. p. 144—145°, are different respectively from 6-chloro-1-naphthoic acid, m. p. 189° [synthesised by the method of Price *et al.* (*J. Amer. Chem. Soc.*, 1941, **63**, 1861)] and its p-*bromophenacyl ester*, m. p. 142—143°.

Chloromethylation of 1- *and* 2-*Chloronaphthalenes.*—Dry hydrogen chloride was passed to saturation into a suspension of paraformaldehyde (12·5 g., 0·14 mol.) in glacial acetic acid (80 ml.) at room temperature and finally at 0°; the chloronaphthalene (40·6 g., 0·25 mol.) and syrupy phosphoric acid (20 ml.; *d* 1·72) were added and the mixture rapidly stirred and kept at 95° for 10 hours and then poured into water, the oil washed with 5% sodium carbonate and water, taken up in ether and dried with potassium carbonate. The solvent was removed and the product distilled under reduced pressure.

(*a*) 1-Chloronaphthalene gave unchanged material (11 g., b. p. 115—140°/2 mm.) and a fraction (12 g., b. p. 140—180°/2 mm.) which redistilled at 145—158°/0·5 mm. to give a solid which, crystallised twice from ligroin and then from methanol, gave 1-*chloro*-4-*chloromethylnaphthalene* as transparent needles, m. p. 78—79° (Found: Cl, 33·5. $C_{11}H_8Cl_2$ requires Cl, 33·7%).

(*b*) 2-Chloronaphthalene gave unchanged material (10·5 g., b. p. 110—130°/1·5 mm.) and a fraction (26·3 g., b. p. 130—170°/2 mm.) which redistilled at 195—198°/10 mm. (Found: Cl, 33·2%) to give a mixture of isomeric chlorochloromethylnaphthalenes. (i) Crystallisation from a large volume of ligroin gave needles of 7-*chloro*-1-*chloromethylnaphthalene*, m. p. 75° (yield 5 g.) (Found: Cl, 33·2%); but an isomer was not obtained by fractional crystallisation. (ii) Freshly distilled isomeric mixture (20 g.) in alcohol (300 ml.) containing 10% alcoholic potash (60 ml.) and palladium black on calcium carbonate (2 g.), prepared according to Busch and Stöve (*loc. cit.*), was shaken with hydrogen until 60% of the theoretical had been absorbed. The reaction mixture was poured into water, the oil dissolved in ether and dried over sodium sulphate. The oil obtained by the removal of the solvent gave 7-*chloro*-1-*methylnaphthalene* as a mobile oil (13 g.), b. p. 158—170°/10 mm. (Found: Cl, 20·6. $C_{11}H_9Cl$ requires Cl, 20·1%), and a solid (4·5 g.), m. p. 46°, b. p. 186—194°/10 mm., which twice crystallised from ethanol gave colourless needles (2 g.) of 2-*chloro*-1-*chloromethylnaphthalene* (2 g.), m. p. 67—68° (Found: Cl, 33·5%).

7-*Chloro*-1-*hydroxymethylnaphthalene.*—7-Chloro-1-chloromethylnaphthalene (0·5 g.), potassium carbonate (0·3 g.), water (25 ml.), and benzene were refluxed for 8 hours and the benzene evaporated. The crystals, which separated on cooling, recrystallised from water to give 7-*chloro*-1-*hydroxymethylnaphthalene* as large plates, m. p. 101·5—103° (Found: Cl, 18·2. $C_{11}H_9OCl$ requires Cl, 18·4%).

p-*Bromophenacyl Ester of* 4-*Chloro*-1-*naphthoic Acid.*—1-Chloro-4-chloromethylnaphthalene (2 g.) was refluxed with water (187 ml.), nitric acid (15 ml.), dioxan (20 ml.), and benzene (5 ml.) for 48 hours. The acid, isolated from the unoxidised material, was crystallised twice from aqueous dioxan to give 4-chloro-1-naphthoic acid (0·4 g.) as long needles, m. p. 221—223° (Found: Cl, 17·8; Eq. Wt., 206·8. Calc. for $C_{11}H_7O_2Cl$: Cl, 17·2%; Eq. Wt., 206·5). The p-*bromophenacyl ester* crystallised from alcohol in soft needles, m. p. 130—131° (Found: C, 56·6; H, 3·2. $C_{19}H_{12}O_3ClBr$ requires C, 56·5; H, 3·0%). Mixed m. ps. of both acid and ester with authentic specimens (below) showed no depression. The acid was synthesised from 1-chloro-4-bromonaphthalene (2·5 g., b. p. 150—156°/0·7 mm., m. p. 66·5—67·5°) by the Grignard reaction, as described for 1-bromonaphthalene by Gilman, St. John, and Schulz (*Org. Syn.*, 1931, **11**, 80), and crystallised from ethanol to give 4-chloro-1-naphthoic acid (1·1 g., m. p. 221—223°) (Friedlander and Weisberg, *Ber.*, 1895, **28**, 1843, give m. p. 210°) (Found: Cl, 17·9%; Eq. Wt., 208·3). The *p*-bromophenacyl ester had m. p. 130·5—131° (Found: C, 56·2; H, 3·1%).

2-Chloro-1-chloromethylnaphthalene (0·5 g.) was refluxed with water (50 ml.) and nitric acid (4 ml.) for 15 days to give a small quantity of acid, which after distillation under reduced pressure had m. p. 151°. Rabe (*Ber.*, 1889, **22**, 394) gives 2-chloro-1-naphthoic acid, m. p. 150—152°.

7-*Chloro*-1-*naphthoic Acid.*—2-Chloro-8-chloromethylnaphthalene (1 g.) was refluxed with water (100 ml.) and nitric acid (8 ml.) for 24 hours. The acid was separated from unchanged material and crystallised from toluene to give soft needles of 7-*chloro*-1-*naphthoic acid* (0·36 g.), m. p. 235° (Found: Cl, 17·3; Eq. Wt., 203·4. $C_{11}H_7O_2Cl$ requires Cl, 17·2%; Eq. Wt., 206·5). Its p-*bromophenacyl ester* crystallised from alcohol in soft needles, m. p. 145—146° (Found: C, 56·3; H, 3·0%). Mixed m. p.s of both acid and ester with authentic specimens showed no depression. The acid was synthesised from 7-chloro-1-bromonaphthalene (cf. Gilman, St. John, and Schulz, *loc. cit.*) to give 7-chloro-1-naphthoic acid, m. p. 238—240° (Found: Cl, 17·5%; Eq. Wt., 205·8). Its *p*-bromophenacyl ester had m. p. 144—145° (Found: C, 56·2; H, 3·1%).

6-Chloro-1-naphthoic acid, prepared by the method of Price *et al.* (*J. Amer. Chem. Soc.*, 1941, **63**, 1861), had m. p. 188—189°. Its *p*-bromophenacyl ester crystallised from alcohol as soft needles, m. p. 142—143° (Found: C, 56·5; H, 3·1%).

M. ps. are corrected.—NATAL UNIVERSITY COLLEGE (UNIVERSITY OF SOUTH AFRICA), PIETERMARITZBURG, NATAL. [*Received, November 23rd,* 1945.]