270. *The Chloromethylation of Naphthalene and of Tetralin.*

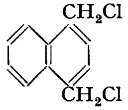
By G. M. Badger, J. W. Cook, and G. W. Crosbie.

Chloromethylation of naphthalene with boiling aqueous formaldehyde and hydrochloric acid gives a mixture from which 1 : 4-bischloromethylnaphthalene and 1 : 5-*bischloromethylnaphthalene* have been isolated. From tetralin, 5 : 8-*bischloromethyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene* has been obtained.

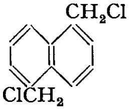
From the products of the chloromethylation of 1-chloromethylnaphthalene, Anderson and Short (*J.*, 1933, 485) obtained a crude bischloromethylnaphthalene, m. p. 130—145°, which they were unable to purify. They regarded this as being largely the 1 : 5-derivative because, on reduction, they isolated and characterised 1 : 5-dimethylnaphthalene. Furthermore, on oxidation of the crude bischloromethylnaphthalene, they obtained the corresponding 1 : 5-dicarboxylic acid. Manske and Ledingham (*Canadian J. Res.*, 1939, **17**, 14) investigating the high-boiling residues resulting from Cambron's (*ibid.*, p. 10) chloromethylation of naphthalene, obtained a supposedly pure bischloromethylnaphthalene, m. p. 144°, which they regarded as the 1 : 5-derivative. Evidence for this was obtained by conversion into the dinitrile, hydrolysis to the diacetic acid, and decarboxylation to dimethylnaphthalene. The hydrocarbon was an oil, giving a picrate, m. p. 138°. As 1 : 5-dimethylnaphthalene is a solid, and as the picrates of the 1 : 5- and 1 : 4-dimethylnaphthalenes have closely similar melting points, this evidence was inconclusive.

However, supposing the major product of the bischloromethylation of naphthalene to be the 1 : 5-derivative, we decided to attempt the synthesis of *s*-hexahydropyrene by condensing bischloromethylnaphthalene with ethyl malonate, followed by hydrolysis, decarboxylation, ring-closure and reduction. While this work was in progress, two papers by Lock and Walter (*Ber.*, 1942, **75**, 1158; 1944, **77**, 286) became available to us, and we found that the main object of our work had already been achieved. In the second paper, these authors state that the bischloromethylnaphthalene, for which they give m. p. 150°, is not the 1 : 5- but the 1 : 4-derivative; no evidence of this was presented. Our work has confirmed this conclusion of Lock and Walter, and we have also isolated the 1 : 5-derivative from the crude bischloromethylnaphthalenes resulting from the chloromethylation both of naphthalene and of 1-chloromethylnaphthalene.

Naphthalene was chloromethylated with boiling aqueous formaldehyde and hydrochloric acid (B.P. 345,146; Lock and Walter, *loc. cit.*). Taking advantage of solubility differences in ether, the crude product was separated into several fractions, from which 1 : 5-*bischloromethylnaphthalene* (II), m. p. 172°, and 1 : 4-bischloromethylnaphthalene (I), m. p. 150°, were obtained by repeated recrystallisation. The constitution of each product was shown by reduction to the dimethylnaphthalene, which was characterised by the formation of the picrate and *s*-trinitrobenzene complex. The major mixed fraction resulting from the treatment with ether had m. p. 128—130°. That this contained some 1 : 5-bischloromethylnaphthalene was shown by the isolation, in poor yield, of crystalline 1 : 5-dimethylnaphthalene after reduction, a result which is in agreement with the work of Anderson and Short (*loc. cit.*). However, that this fraction consisted largely of the 1 : 4-isomer was shown by its conversion into 1 : 4-bis-(ωω-dicarbethoxyethyl)naphthalene (III) (Lock and Walter, *loc. cit.*). The constitution of this product was shown by hydrolysis, followed by oxidation with potassium ferricyanide, to naphthalene-1 : 4-dicarboxylic acid. 1 : 4-Bischloromethylnaphthalene has also been converted into the corresponding dinitrile. This appears to be the same as the dinitrile described as the 1 : 5-derivative by Manske and Ledingham (*loc. cit.*), and we therefore believe that these authors were in error in attributing the 1 : 5-configuration to their products, which should all be described as 1 : 4-derivatives. To confirm this conclusion we have also prepared *naphthalene*-1 : 5-*diacetonitrile* from pure 1 : 5-bischloromethylnaphthalene.



(I.)



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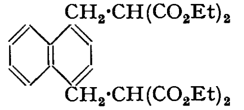

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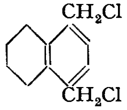

(IV.)

The patent literature (D.R.-P. 533,850) describes the preparation of a bischloromethyltetralin. We have also prepared this, and have shown that it is 5 : 8-*bischloromethyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene* (IV). Reduction with zinc and hydrochloric acid, or with hydrogen and palladium, gave 5 : 8-dimethyl-1 : 2 : 3 : 4-tetrahydronaphthalene, which on dehydrogenation with sulphur, or with palladised asbestos, gave 1 : 4-dimethylnaphthalene, characterised by the formation of the picrate and *s*-trinitrobenzene complex.

EXPERIMENTAL.

Chloromethylation of Naphthalene.—(*a*) A mixture of naphthalene (80 g.), aqueous formaldehyde (40%; 220 g.), and concentrated hydrochloric acid (220 g.) was boiled under reflux with vigorous stirring for 16 hours, while a current of hydrogen chloride was introduced through a tube leading to the bottom of the flask. After cooling, the aqueous layer was decanted, and the pasty mass triturated with ether (100 c.c.). In one run, this ethereal solution deposited, on standing, 1 : 4-bischloromethylnaphthalene (30 mg.) as colourless needles from alcohol, m. p. 149—150° (Found : C, 64·1; H, 4·5. Calc. for $C_{12}H_{10}Cl_2$: C, 64·0; H, 4·4%). This compound was later obtained pure in considerable quantity. The ethereal solution, after evaporation, gave 1-chloromethylnaphthalene (43 g.), b. p. 150—152°/13 mm., and crude bischloromethylnaphthalenes, b. p. 180—200°/13 mm., m. p. 128—130°.

The solid obtained after this ether washing was extracted with ether (200 c.c.) in a Soxhlet apparatus. The ether deposited, on cooling, crude bischloromethylnaphthalene (19 g.), m. p. 128—130°. Recrystallisation from alcohol did not raise the m. p., although later work showed that this fraction contained both the 1 : 4- and the 1 : 5-isomer. The ethereal filtrate, on evaporation, gave a further impure fraction, m. p. 105—115° (2 g.). The residue (4·0 g.), m. p. 153—159°, remaining in the Soxhlet thimble gave, after several recrystallisations from alcohol, colourless needles of 1 : 5-*bischloromethylnaphthalene*, m. p. 171·5—172·5° (Found : C, 64·0; H, 4·4. $C_{12}H_{10}Cl_2$ requires C, 64·0; H, 4·4%).

The above experiment was successfully repeated several times, but in two large scale runs naphthalene (700 g.) gave crude bischloromethylnaphthalene (300 g.) from which no pure 1 : 5-bischloromethylnaphthalene could be isolated by the above procedure. The crude product was soluble in ether (500 c.c.) and, after several recrystallisations, gave pure 1 : 4-bischloromethylnaphthalene.

(*b*) Crude bischloromethylnaphthalene was also obtained by chloromethylating 1-chloromethylnaphthalene (250 g.) in light petroleum (b. p. 100—120°; 300 c.c.) with paraformaldehyde (60 g.) and anhydrous zinc chloride (15 g.), by the method of Anderson and Short, except that the reaction was carried out on the steam-bath, and that hydrogen chloride was passed for 24 hours. The product, obtained in *ca.* 60% yield, was separated as above, and gave 1·5 g. of pure 1 : 5-bischloromethylnaphthalene, m. p. 171·5—172·5°.

Reduction of fraction, m. p. 128—130°. A mixture of bischloromethylnaphthalene, m. p. 128—130° (1·2 g.), in a little alcohol, and zinc dust (1·5 g.) was boiled for 1 hour, concentrated hydrochloric acid being added at intervals. After distillation (b. p. 60—65°/0·2 mm.), the product was dissolved in 50% acetone. After standing, the crystalline product which separated (75 mg.) was recrystallised from alcohol, and had m. p. 79·5—80·5°. The orange-red picrate had m. p. 138—139°, and the product isolated was therefore 1 : 5-dimethylnaphthalene, in agreement with Anderson and Short (*loc. cit.*).

Reduction of 1 : 4-*bischloromethylnaphthalene.* 1 : 4-Bischloromethylnaphthalene (m. p. 149°) was reduced in about 50% yield as above. The product formed a colourless oil, b. p. 132—134°/15 mm. (Found : C, 92·4; H, 7·4. Calc. for $C_{12}H_{12}$: C, 92·3; H, 7·7%). The picrate crystallised from methanol in long orange-red needles, m. p. 142—144° (Found : N, 10·9. Calc. for $C_{18}H_{15}O_7N_3$: N, 10·9%); Kloetzel (*J. Amer. Chem. Soc.*, 1940, **62**, 1708) gives m. p. 143—144°. The *s*-trinitrobenzene complex formed yellow needles, from methanol, m. p. 164—166° (Found : N, 11·6. Calc. for $C_{18}H_{15}O_6N_3$: N, 11·4%); Kloetzel (*loc. cit.*) gives m. p. 165—166°. The reduction product was therefore 1 : 4-dimethylnaphthalene.

The reduction was also carried out in almost quantitative yield by hydrogenation over palladium black in acetone.

Reduction of 1 : 5-*bischloromethylnaphthalene.* 1 : 5-Bischloromethylnaphthalene (m. p. 172°) was reduced as above with zinc and hydrochloric acid. The 1 : 5-dimethylnaphthalene, which crystallised from the reaction mixture, was purified by sublimation at 100°/13 mm., and formed colourless lustrous plates, m. p. 80—81° (Found : C, 92·2; H, 7·6. Calc. for $C_{12}H_{12}$: C, 92·3; H, 7·7%); Butz (*J. Amer. Chem. Soc.*, 1940, **62**, 2557) gives m. p. 80°, and Anderson and Short (*loc. cit.*) give m. p. 80—80·5°. The picrate formed orange-red needles, from methanol, m. p. 138—139° (Found : N, 10·9. Calc. for $C_{18}H_{15}O_7N_3$: N, 10·9%); Butz (*loc. cit.*) gives m. p. 137°, and Anderson and Short (*loc. cit.*) give m. p. 138—139°. The s-*trinitrobenzene* complex formed yellow needles, from alcohol, m. p. 158—159° (Found : N, 11·3. $C_{18}H_{15}O_6N_3$ requires N, 11·4%).

1 : 4-*Bis*-(*ωω-dicarboxyethyl*)*naphthalene*.—Ethyl malonate (200 g.) was added to a solution of sodium (18 g.) in alcohol (300 c.c.). After cooling, bischloromethylnaphthalene, m. p. 128—130° (23 g.), suspended in alcohol (200 c.c.) was added. After 10 hours' refluxing the product was worked up in the usual way. The ester (20 g.) formed colourless needles, from alcohol, m. p. 68·5—69° (Found : C, 65·8; H, 6·7. Calc. for $C_{26}H_{32}O_8$: C, 66·1; H, 6·8%); Lock and Walter (*loc. cit.*) give m. p. 66·5°. A solution of this ester (20 g.) in methanol (75 c.c.), water (150 c.c.), and sodium hydroxide (36 g.) was refluxed for 8 hours, a further quantity (10 g.) of sodium hydroxide being added after the first 4 hours. The bismalonic acid (9 g.) was recrystallised from water. It decomposed at about 140° with evolution of gas, finally melting at 255—256°.

Proof of constitution. A solution of this acid (2 g.), potassium ferricyanide (300 g.), potassium hydroxide (43 g.), and water (1 l.) was heated at 70—80°, with stirring, for 24 hours. A further quantity (80 g.) of potassium ferricyanide and potassium hydroxide (14 g.) in a little water was then added, and the heating continued for 8 hours. After cooling, the filtered solution was acidified, and the precipitate collected, suspended in water, and extracted with ether. The ethereal extract on evaporation gave an acid, m. p. 309—310° (75 mg.). The methyl ester had m. p. 63—64°. These constants are in agreement with the published figures for naphthalene-1 : 4-dicarboxylic acid.

Naphthalene-1 : 4-*diacetonitrile*.—The following procedure was found superior to that of Manske and Ledingham (*loc. cit.*). A mixture of 1 : 4-bischloromethylnaphthalene, m. p. 148—150° (0·5 g.), potassium cyanide (0·5 g.) in a little water, and alcohol (30 c.c.) was boiled under reflux for 2 hours. After addition of water, the naphthalene-1 : 4-diacetonitrile (0·3 g.) was recrystallised from alcohol, and formed colourless prisms, m. p. 140—142° (Found : C, 81·7; H, 4·75. Calc. for $C_{14}H_{10}N_2$: C, 81·55; H, 4·85%). The same compound was obtained following a similar experiment with crude bischloromethylnaphthalene, m. p. 128—130°. This compound is evidently identical with the derivative, m. p. 140°, described by Manske and Ledingham (*loc. cit.*) as the 1 : 5-derivative.

Naphthalene-1 : 5-*diacetonitrile*.—This was prepared as above, using 1 : 5-bischloromethylnaphthalene. The *naphthalene*-1 : 5-*diacetonitrile* formed colourless small needles, m. p. 188—189° (Found : C, 81·4; H, 4·6. $C_{14}H_{10}N_2$ requires C, 81·55; H, 4·85%).

Chloromethylation of Tetralin.—Freshly distilled tetralin (90 g.), concentrated hydrochloric acid (210 g.), and aqueous formaldehyde (40%; 220 g.) were boiled under reflux, with stirring, for 48 hours, while hydrogen chloride was passed in. The cooled mixture was extracted with ether, and the ethereal solution dried and evaporated. The oily residue partly crystallised. The solid was collected, washed with a little ether, and recrystallised from alcohol. 5 : 8-*Bischloromethyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene* (10 g.) was obtained as colourless lustrous needles, m. p. 117—118° (Found : C, 62·9; H, 6·0. $C_{12}H_{14}Cl_2$ requires C, 62·9; H, 6·1%). The oil was collected in two fractions, b. p. 150—180°/17 mm. (65 g.), and 180—195°/13 mm. (12 g.). The latter deposited a further quantity (2 g.) of bischloromethyltetralin on standing.

5 : 8-*Dimethyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*. 5 : 8-Bischloromethyl-1 : 2 : 3 : 4-tetrahydronaphthalene (4·5 g.) was reduced with zinc and hydrochloric acid, in alcohol, as described for the bischloromethylnaphthalenes. The 5 : 8-dimethyl-1 : 2 : 3 : 4-tetrahydronaphthalene (0·8 g.) was obtained as a colourless oil, b. p. 125°/14 mm. (Found : C, 90·1; H, 10·25. Calc. for $C_{12}H_{16}$: C, 90·0; H, 10·0%) (cf. Barnett and Sanders, *J.*, 1933, 434). The reduction was also carried out, in almost quantitative yield, by hydrogenation over palladium black in acetone.

Dehydrogenation of 5 : 8-*dimethyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*. The above dimethyltetrahydronaphthalene (0·5 g.) was dehydrogenated with sulphur (0·3 g.) at 230—250° for 2 hours. The product was converted into the picrate (0·6 g.), which formed orange-red needles, m. p. 142—143°, alone, or mixed with the picrate of 1 : 4-dimethylnaphthalene. The *s*-trinitrobenzene complex formed yellow needles, m. p. 163—165°, alone, or mixed with the *s*-trinitrobenzene complex of 1 : 4-dimethylnaphthalene. The same results were obtained when the dehydrogenation was carried out with palladised asbestos at 240° for 5 hours.

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