180. *Side-chain Bromination of Some Alkylnaphthalenes with* N-*Bromosuccinimide.*

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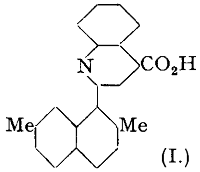
It is shown that the reaction between *N*-bromosuccinimide and some alkylnaphthalenes results in every instance in the formation of side-chain brominated compounds. Convenient methods for the synthesis of sapotalene (1 : 2 : 7-trimethylnaphthalene) and other derivatives of 2 : 6- and 2 : 7-dimethylnaphthalene are described.

It was found by one of us (Buu-Hoï, *Annalen*, 1944, **556**, 1) that when *N*-bromosuccinimide reacted with β-methylnaphthalene, bromination took place exclusively in the methyl group. This observation leads to a convenient method for the preparation of β-bromomethylnaphthalene, which was not hitherto readily accessible. Since those preliminary studies, a broader investigation has been made to ascertain whether this method would prove of value for the synthesis of similar unknown side-chain brominated compounds of the type Ar·CH_2Br. This paper deals with the behaviour of some alkylnaphthalenes towards *N*-bromosuccinimide. α-Methylnaphthalene could be converted into α-bromomethylnaphthalene in very high yield, and this suggests that no differences in the reactivity of the methyl group exist between the two isomeric methylnaphthalenes. α-Ethylnaphthalene has been found to be far more reactive than its lower homologue, but the bromide of the α-1-bromoethylnaphthalene thus obtained was very unstable towards heat, and spontaneously decomposed in the reaction medium to give significant amounts of α-vinylnaphthalene. It is noteworthy that, in analogous experimental conditions, acenaphthene, which is closely related to α-ethylnaphthalene, has been shown (Buu-Hoï, *loc. cit.*) to undergo nuclear substitution.

2 : 6-Dimethylnaphthalene could easily be brominated in one of the methyl groups, giving 2-*methyl*-6-*bromomethylnaphthalene* in excellent yield. The mobility of the bromine atom in this compound is shown by its transformation into 2-*methyl*-6-*naphthylacetonitrile*, saponification of which gave 2-*methyl*-6-*naphthylacetic acid.* When a similar sequence of reactions was applied to 2 : 7-dimethylnaphthalene, the corresponding 2 : 7-*analogues* were successively obtained. For purpose of comparison, 1-bromo-2 : 7-dimethylnaphthalene has been prepared by direct treatment of 2 : 7-dimethylnaphthalene with bromine (cf. Clar and Wallenstein, *Ber.*, 1931, **64**, 2076). The Grignard compound prepared from it gave sapotalene (1 : 2 : 7-trimethylnaphthalene) on treatment with methyl sulphate, and 2 : 7-dimethyl-1-naphthol on spontaneous oxidation during its formation. Work in this field is being pursued.



(I.)

The reactivity of the position 1 in the molecule of 2 : 7-dimethylnaphthalene is further shown by the results of acetylation, the sole ketone obtained being 1-*acetyl*-2 : 7-*dimethylnaphthalene.* A cinchoninic *acid* (I) could readily be obtained by condensing the aforementioned substance with isatin in alkaline medium; but, as expected from previous observations on the influence of steric hindrance upon Pfitzinger's reactions (Buu-Hoï and Cagniant, *Bull. Soc. chim.*, 1946, **13**, 123), no cinchoninic acid could be obtained from α-naphthisatin.

EXPERIMENTAL.

Bromination of α-Methylnaphthalene.—A mixture of *N*-bromosuccinimide (12·5 g.), α-methylnaphthalene (10 g.), and carbon tetrachloride (65 g.) was gently refluxed on a water-bath; after 2 hours' heating, the heavy yellowish microcrystalline bromoimide had almost completely disappeared, and was replaced by white crystals of succinimide. Boiling was continued for 12 hours more, the mixture cooled in ice, and the crystals of succinimide separated by suction. The last traces of the imide were removed by shaking the filtrate with an ice-cooled dilute aqueous solution of sodium hydroxide, and then with water. The organic layer was dried (Na_2SO_4), the solvent removed, and the residue distilled in a good vacuum. α-Bromomethylnaphthalene (9 g.) was thus collected as a slightly lachrymatory yellow oil, b. p. 175/10 mm., which quickly solidified; after a single crystallisation from ligroin (b. p. 60—80°), colourless prisms, m. p. 56°, were obtained. Schmidlin and Massini (*Ber.*, 1909, **42**, 2389) described this compound as an oil; Wislicenus and Elvert (*ibid.*, 1916, **49**, 2822) and Shoesmith and Rubli (*J.*, 1927, 3098) recorded respectively m. p. 45—46° and 53°. As the direct bromination of α-methylnaphthalene requires a combined action of high temperature and irradiation with ultra-violet light, the present method is the best for preparation.

Bromination of α-Ethylnaphthalene.—The hydrocarbon used was obtained from α-acetylnaphthalene by Clemmensen reduction. α-Ethylnaphthalene (11 g.), dissolved in dry carbon tetrachloride (50 g.), was treated with *N*-bromosuccinimide (9·5 g.) under the same conditions as above. After removal of the solvent, the slightly brown oil thus obtained was strongly unsaturated towards bromine, and was vigorously shaken with a hot concentrated solution of potassium carbonate in order to decompose the last traces of brominated products. On distillation, α-vinylnaphthalene (6 g.) was isolated as an almost colourless oil, b. p. 125—135°/15 mm., which instantly decolourised a solution of bromine in carbon disulphide (cf. Brandis, *Ber.*, 1889, **22**, 2158).

Bromination of 2 : 6-*Dimethylnaphthalene.*—The reaction of *N*-bromosuccinimide (11 g.) with 2 : 6-dimethylnaphthalene (10 g., dissolved in 95 g. of carbon tetrachloride) was carried exactly as for α-methylnaphthalene. 2-*Methyl*-6-*bromomethylnaphthalene* (7·5 g.) had b. p. 195—200°/14 mm., and formed silky colourless needles, m. p. 90° (decomp.), from ligroin (Found : Br, 34·2. $C_{12}H_{11}Br$ requires Br, 34·0%). These were extremely soluble in benzene and much less so in ethanol.

2-*Methyl*-6-*naphthylacetonitrile.*—A mixture of the above bromide (5 g.) and a solution of potassium cyanide (2·5 g.) in aqueous alcohol (25 c.c.) was refluxed during two hours; after dilution with water and extraction by means of ether, the organic layer was washed with water and dried (Na_2SO_4). On vacuum distillation, 2-*methyl*-6-*naphthylacetonitrile* (4 g.) was obtained as a viscous oil, b. p. 205°/10 mm., which readily solidified on cooling, and gave silky colourless needles, m. p. 111°, after recrystallisation in alcohol (Found : N, 7·5. $C_{13}H_{11}N$ requires N, 7·7%). Saponification of this nitrile by alcoholic potassium hydroxide gave the *acid*, which separated from aqueous ethanol in glistening plates, m. p. 168° (Found : *M*, by titration, 201. $C_{13}H_{12}O_2$ requires *M*, 200). The corresponding *amide* (prepared from the viscous acid chloride by treatment with aqueous ammonia) crystallised from benzene in yellowish needles, m. p. 185° (decomp.) (Found : N, 7·4. $C_{13}H_{13}ON$ requires N, 7·0%).

Side-chain Bromination of 2 : 7-*Dimethylnaphthalene.*—A mixture of bromosuccinimide (11 g.), 2 : 7-dimethylnaphthalene (10 g.), and carbon tetrachloride (95 g.) was heated during 12 hours and treated as previously described. 2-*Methyl*-7-*bromomethylnaphthalene* was obtained after two crystallisations from ligroin (b. p. 60—80°) as silky colourless needles, m. p. 100° (decomp.). This product (6 g.) had b. p. 200°/15 mm., and was strongly lachrymatory and irritating to the skin (Found : Br, 34·3. $C_{12}H_{11}Br$ requires Br, 34·0%).

2-*Methyl*-7-*naphthylacetonitrile.*—This substance was readily obtained on heating the foregoing bromide (3 g.) with potassium cyanide (2 g.) dissolved in aqueous ethanol. After distillation (b. p. 200°/10 mm.) and crystallisation from alcohol, glistening colourless prisms, m. p. 92°, were obtained (2·8 g.) (Found : N, 7·4. $C_{13}H_{11}N$ requires N, 7·7%). This *nitrile* on alkaline saponification afforded the *acid*, which crystallised from dilute alcohol in glinting plates, m. p. 166° (Found : *M*, by titration, 198. $C_{13}H_{12}O_2$ requires *M*, 200). The corresponding *amide* separated from benzene–alcohol as slightly yellowish needles, m. p. 205° (Found : N, 7·2. $C_{13}H_{13}ON$ requires N, 7·0%).

Synthesis of Sapotalene from 2 : 7-*Dimethylnaphthalene.*—1-Bromo-2 : 7-dimethylnaphthalene was prepared in almost theoretical yield by treating a carbon disulphide solution of 2 : 7-dimethylnaphthalene (10 g.) with bromine (10 g.) at room temperature. The product thus obtained boiled at 170°/10 mm., and melted at 52° after recrystallisation from ligroin. Clar and Wallenstein (*loc. cit.*) gave b. p. 174—180°/16 mm., m. p. 48°. The corresponding *picrate* crystallised from alcohol in bright yellow needles, m. p. 112°, extremely soluble in benzene (Found : N, 8·6. $C_{12}H_{11}Br,C_6H_3O_7N_3$ requires N, 9·0%). A solution prepared from magnesium (1·3 g.), ethyl bromide (2 g.), and 1-bromo-2 : 7-dimethylnaphthalene (13 g.) in ether (heating was prolonged to 12 hours to effect complete reaction of magnesium) was treated with excess of pure methyl sulphate, and the mixture obtained was refluxed during two hours on a water-bath. After treatment by ice-cooled dilute hydrochloric acid, the ethereal layer was shaken with 10% aqueous sodium hydroxide (fraction A), then with water, and dried (Na_2SO_4). After removal of the solvent, the remaining oil was fractionated, and yielded 2 g. of a liquid fraction, b. p. 150—155°/10 mm., which gave an orange-yellow picrate, m. p. 128°. Späth and Hromatka (*Monatsh.*, 1932, **60**, 117) recorded m. p. 129° for the picrate of sapotalene. The alkaline fraction (A) gave on acidification with hydrochloric acid a precipitate (0·2 g.) which was extracted by means of chloroform and recrystallised from hot water. The straw-coloured silky needles of 2 : 7-dimethyl-1-naphthol thus obtained had a strong phenolic odour, melted at 95°, and gave a *picrate*, which formed red needles, m. p. 147°, from alcohol (Found : N, 10·7. $C_{12}H_{12}O,C_6H_3O_7N_3$ requires N, 10·4%).

Acetylation of 2 : 7-Dimethylnaphthalene.—An ice-cooled mixture of 2 : 7-dimethylnaphthalene (6 g.), acetyl chloride (3 g.), and carbon disulphide (50 c.c.) was slowly treated with finely powdered aluminium chloride (8 g.). The greenish-yellow solid thus obtained was decomposed with water and gave after standard treatment 1-*acetyl*-2 : 7-*dimethylnaphthalene* (5 g.) as a mobile, pale yellow liquid, $n^{22.5^\circ}$ 1·6050, b. p. 190—191°/15 mm. (Found : C, 84·6; H, 7·3. $C_{14}H_{14}O$ requires C, 84·8; H, 7·0%). A mixture of this ketone (2 g.), isatin (1·4 g.), sodium hydroxide (1·1 g. dissolved in 2 c.c. of water), and ethanol (10 c.c.) was refluxed during 12 hours. After dilution with water, removal of the neutral impurities by extraction with ether, and treatment with acetic acid, 2-(2′ : 7′-*dimethyl*-1′-*naphthyl*)*cinchoninic acid* (I) was obtained (1 g.). It crystallised from acetic acid as almost colourless needles, m. p. 305° (efferv.) (Found : N, 4·5. $C_{22}H_{17}O_2N$ requires N, 4·3%). On decarboxylation, this afforded the corresponding quinoline which gave a *picrate* crystallising from nitrobenzene in microscopic yellow needles, m. p. 245—247° (Found : N, 11·2. $C_{21}H_{17}N,C_6H_3O_7N_3$ requires N, 10·9%).

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