Intramolecular Acylation. Part I. The Ring Closure of Some α-Substituted β-1-Naphthylpropionic Acids.

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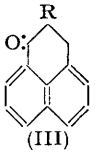
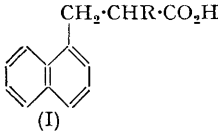
The ring closure of four α-substituted β-1-naphthylpropionic acids by the action of anhydrous hydrogen fluoride has been shown to yield in each case a mixture of the corresponding 2-substituted perinaphthan-1-one and 2-substituted 4 : 5-benzindan-1-one.

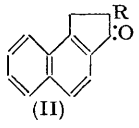
THE products formed when four α-substituted β-1-naphthylpropionic acids (I) were cyclised with anhydrous hydrogen fluoride have been examined chromatographically to determine whether they contained any of the corresponding 2-substituted 4 : 5-benzindan-1-one (II). For although the main product, and often the only product isolated, from such a reaction is the 2-substituted perinaphthan-1-one (III) (Johnson, "Organic Reactions," Vol. II, p. 126), Fieser and Gates (*J. Amer. Chem. Soc.*, 1940, **62**, 2335) have shown that the cyclisation of β-1-naphthylpropionic acid (I; R = H) yields both perinaphthan-1-one (III; R = H) and 4 : 5-benzindan-1-one (II; R = H). The apparent preferential formation of a 4 : 5-benzindan-1-one has been reported by Ansell and Hey (*J.*, 1950, 2874) who found that when α-1-naphthylmethylglutaric acid (I; R = $\cdot CH_2 \cdot CH_2 \cdot CO_2H$) was treated with anhydrous hydrogen fluoride the only isolatable product was β-(1-oxo-4 : 5-benzindan-2-yl)propionic acid (II; R = $CH_2 \cdot CH_2 \cdot CO_2H$).



(III)



(I)



(II)

The cyclisation of α-1-naphthylmethylpropionic acid (I; R = Me) with anhydrous hydrogen fluoride has been reported by Fieser and Novello (*J. Amer. Chem. Soc.*, 1940, **62**, 1855) to yield 2-methylperinaphthan-1-one (a liquid) as the sole product. It has now been shown that Fieser and Novello's product was a mixture of 2-methylperinaphthan-1-one (III; R = Me) (m. p. 50—51°) and 2-methyl-4 : 5-benzindan-1-one (II; R = Me) (m. p. 71—72°), which can be separated by chromatography. The structures of these products were established by oxidation to naphthalic and naphthalene-1 : 2-dicarboxylic acid respectively.

α-1-Naphthylmethylbutyric acid (I; R = Et), prepared by the hydrolysis and decarboxylation of ethyl ethyl-1-naphthylmethylmalonate, is a solid, m. p. 85—86°, and not a liquid as reported by Mayer and Sieglitz (*Ber.*, 1922, **55**, 1835). The cyclisation of this acid, by the action of aluminium chloride on the acid chloride, to 2-ethylperinaphthan-1-one (III; R = Et) (liquid) has been recorded by Mayer and Sieglitz (*loc. cit.*). With anhydrous hydrogen fluoride, the initial product is a liquid, which was separated by chromatography into 2-ethylperinaphthan-1-one (III; R = Et) (liquid) and 2-ethyl-4 : 5-benzindan-1-one (II; R = Et) (solid). The structures were proved as for the methyl analogues.

Cyclisation of α-1-naphthylmethylvaleric acid (I; R = Pr^n), prepared as for the butyric acid, with anhydrous hydrogen fluoride yielded a mixture of 2-*n*-propylperinaphthan-1-one (III; R = Pr^n) and 2-*n*-propyl-4 : 5-benzindan-1-one (II; R = Pr^n), which was separated by chromatography. The structure of the former was proved by oxidation to naphthalic acid. Naphthalene-1 : 2-dicarboxylic acid could not be isolated on oxidation of the latter, but its structure is considered to be certain.

When 2-1'-naphthylmethylhexanoic acid * (I; R = Bu^n), prepared as above, was cyclised with anhydrous hydrogen fluoride, a mixture of 2-*n*-butylperinaphthan-1-one

* Geneva nomenclature, CO_2H = 1.

(III; R = Bu^n) and 2-*n*-butyl-4 : 5-benzindan-1-one (II; R = Bu^n) was obtained together with a considerable amount of viscous unidentified material. In this cyclisation the yield of the 4 : 5-benzindane derivative exceeded that of the perinaphthan-1-one derivative. This appears to provide an example of the preferential formation of a five-membered ring (cf. Ansell and Hey, *loc. cit.*). It is possible however that some of the 2-*n*-butyl perinaphthan-1-one had undergone self-condensation to yield the tarry by-product.

Experimental

In all the reactions with anhydrous hydrogen fluoride "Polythene" beakers were used and the reactions carried out in the open under shelter. Light petroleum used had b. p. 60—80°.

The yellow ketones described below could not be obtained colourless by recrystallisation; they probably owe their colour to contamination by perinaphthenones (Ansell and Berman, unpublished work).

Cyclisation of α-1-*Naphthylmethylpropionic Acid.*—A solution of the acid (20 g.) (Fieser and Novello, *loc. cit.*) in anhydrous hydrogen fluoride (100 g.) was kept for 24 hr. at room temperature, then poured on ice and extracted with ether. After being washed with water and 5% sodium hydrogen carbonate solution and dried (Na_2SO_4), the ethereal extract was evaporated to a viscous yellow oil (17·7 g.). The latter was dissolved in light petroleum (250 c.c.) and chromatographed through alumina (44 × 4 cm.). Elution was carried out with light petroleum. The first fractions yielded 2-*methylperinaphthan*-1-*one* (13·0 g.), m. p. 46—50°. Crystallisation from ice-cold alcohol yielded pale yellow plates, m. p. 50—51° (Found: C, 85·3; H, 5·8. $C_{14}H_{12}O$ requires C, 85·7; H, 6·1%) [oxime, m. p. 150—152°; Fieser and Novello (*loc. cit.*) record m. p. 147·2—148·2°]. The second series of fractions from the chromatography yielded 2-*methyl*-4 : 5-*benzindan*-1-*one* (1·9 g.), m. p. 66—72°. Crystallisation from ice-cold alcohol gave yellow prisms, m. p. 71—72° (Found: C, 85·1; H, 6·0. $C_{14}H_{12}O$ requires C, 85·7; H, 6·1%) [*oxime*, m. p. 168—170° (needles from alcohol) (Found: N, 6·7. $C_{14}H_{13}ON$ requires N, 6·6%)].

Oxidation of 2-*methylperinaphthan*-1-*one.* A solution of 2-methylperinaphthan-1-one (1·0 g.) and sodium dichromate (7·5 g.) in glacial acetic acid (25 c.c.) was heated under reflux for 30 min. and then poured into water. The precipitated solid was collected and sublimed at 230° under reduced pressure, to give naphthalic anhydride, m. p. 272—274°, raised to 274—278° on admixture with an authentic specimen.

Oxidation of 2-*methyl*-4 : 5-*benzindan*-1-*one.* 2-Methyl-4 : 5-benzindan-1-one (0·8 g.), was heated at 60—70° for 24 hr. with potassium ferricyanide (50 g.) and potassium hydroxide (9·0 g.) in water (180 c.c.). When cold the solution was filtered and acidified. The precipitated acid was collected and sublimed at 180—200° under reduced pressure, to yield naphthalene-1 : 2-dicarboxylic anhydride in needles, m. p. 166—167° raised to 167—168° on admixture with an authentic specimen.

Ethyl Ethyl-1-*naphthylmethylmalonate.*—To a solution of sodium ethoxide prepared from anhydrous alcohol (250 c.c.) and sodium (15 g., 0·65 mole) was added ethyl ethylmalonate (131·6 g., 0·7 mole), followed by 1-naphthylmethyl chloride (Grummitt and Buck, *J. Amer. Chem. Soc.*, 1943, **65**, 295) (88·3 g., 0·5 mole). The whole was heated under reflux for 4 hr., cooled, diluted with water, and neutralised with 2N-hydrochloric acid. The organic layer was separated and the aqueous layer extracted twice with ether. The combined extracts were washed with dilute sodium carbonate solution, followed by 2N-hydrochloric acid, and dried (Na_2SO_4). Removal of the ether, followed by distillation at 15 mm. to remove unchanged ethyl ethylmalonate, left a residue which on distillation yielded ethyl ethyl-1-naphthylmethylmalonate (133 g.), b. p. 160—162°/0·02 mm. Mayer and Sieglitz (*loc. cit.*) record b. p. 227°/12 mm.

α-1-*Naphthylmethylbutyric Acid.*—The above ester (133 g.) in alcohol (133 c.c.) was heated under reflux for 6 hr. with potassium hydroxide (133 g.) in water (133 c.c.). After removal of the alcohol the residue was diluted with water and acidified. The solid which separated was collected and decarboxylated at 170—180° for 45 min. A solution of the resulting acid in aqueous sodium hydroxide solution was extracted with ether, and the aqueous solution was acidified and extracted with ether. Evaporation of the final dried (Na_2SO_4) ethereal solution yielded an oil which when cooled and scratched solidified. Recrystallisation from light petroleum (b. p. 60—80°) containing a trace of benzene gave α-1-*naphthylmethylbutyric acid* (83·5 g.), m. p. 79—83°. Further recrystallisation raised the m. p. to 85—86° (Mayer and Sieglitz, *loc. cit.*, reported this acid as a liquid, b. p. 223—227°/15 mm.) (Found: C, 78·9; H, 7·2. $C_{15}H_{16}O_2$ requires C, 78·95; H, 7·1%).

Cyclisation of α-1-*Naphthylmethylvaleric Acid.*—This acid (20 g.) was cyclised as in the preceding case, to yield a yellow oil (17·7 g.). The latter was chromatographed in light petroleum through alumina (44 × 4 cm.). Elution was carried out with light petroleum and finally with light petroleum–ether (9 : 1). The first fractions yielded 2-ethylperinaphthan-1-one (11·5 g.) as a viscous yellow liquid, b. p. 160—168°/1·0 mm. (Mayer and Sieglitz, *loc. cit.*, record b. p. 195°/15 mm.) (Found: C, 86·4; H, 6·9. Calc. for $C_{15}H_{14}O$: C, 85·7; H, 6·7%), which gave a *semicarbazone*, small needles (from alcohol), m. p. 212° (Found: N, 15·5. $C_{16}H_{17}ON_3$ requires N, 15·7%). The later fractions from the chromatography solidified, to yield 2-*ethyl*-4 : 5-*benzindan*-1-*one* (2·0 g.), m. p. 54—58°. Recrystallisation raised the m. p. to 64—65° (Found: C, 85·9; H, 6·6%) [*semicarbazone*, small needles (from alcohol), m. p. 232—234° (Found: N, 15·7%)].

2-Ethylperinaphthan-1-one (0·8 g.) was oxidised, as was 2-methyl-4 : 5-benzindan-1-one, to naphthalic anhydride, m. p. 272—274°, raised to 274—278° on admixture with an authentic specimen.

2-Ethyl-4 : 5-benzindan-1-one (0·8 g.) was oxidised, as was 2-methyl-4 : 5-benzindan-1-one, to naphthalene-1 : 2-dicarboxylic anhydride, m. p. 166—167°, raised to 167—168° on admixture with an authentic specimen.

Ethyl 1-*Naphthylmethyl*-(n-*propyl*)*malonate.*—This *ester* was prepared in the same way as ethyl ethyl-1-naphthylmethylmalonate (yield, 123 g.) and had b. p. 168—170°/0·6 mm. (Found: C, 74·1; H, 7·6. $C_{21}H_{26}O_4$ requires C, 73·7; H, 7·6%).

α-1-*Naphthylmethylvaleric Acid.*—Ethyl 1-naphthylmethyl-(*n*-propyl)malonate (120 g.) was hydrolysed and decarboxylated as was ethyl ethyl-1-naphthylmethylmalonate to yield, after recrystallisation from light petroleum, α-1-*naphthylmethylvaleric acid* (66·0 g.), m. p. 84—85°. Further recrystallisation raised the m. p. to 85—86° (Found: C, 79·6; H, 7·4. $C_{16}H_{18}O_2$ requires C, 79·3; H, 7·4%).

Cyclisation of α-1-*Naphthylmethylvaleric Acid.*—This acid (20 g.) was cyclised as was α-methyl-β-1-naphthylpropionic acid, to yield a yellow oil (17·5 g.). Chromatography in light petroleum through alumina, and elution with light petroleum, gave, first, 2-n-*propylperinaphthan*-1-*one* (13·5 g.; m. p. 60—62°), needles, m. p. 62—63° (from ice-cold alcohol) (Found: C, 85·7; H, 7·0. $C_{16}H_{16}O$ requires C, 85·7; H, 7·1%) [*semicarbazone* (needles from alcohol), m. p. 202—204° (Found: N, 14·8. $C_{17}H_{19}ON_3$ requires N, 15·0%)], then 2-n-*propyl*-4 : 5-*benzindan*-1-*one* (2·1 g.; m. p. 32—35°), pale yellow crystals (from ice-cold alcohol), m. p. 35—36° (Found: C, 85·7; H, 7·0%) [*semicarbazone* (needles from alcohol), m. p. 218—220° (Found: N, 14·7%)].

2-*n*-Propylperinaphthan-1-one (1·0 g.) was oxidised as above to naphthalic anhydride, m. p. 272—274° raised to 274—276° on admixture with an authentic specimen.

Ethyl n-*Butyl*-1-*naphthylmethylmalonate.*—This *ester*, prepared from ethyl *n*-butylmalonate and 1-naphthylmethyl chloride as above (yield, 130 g.), had b. p. 154—156°/0·002 mm. (Found: C, 74·7; H, 7·9. $C_{22}H_{28}O_4$ requires C, 74·5; H, 7·8%). On hydrolysis it (110 g.) gave 2-1′-*naphthylmethylhexanoic acid* (61·0 g.), m. p. 64—66° (from light petroleum plus a trace of benzene) (Found: C, 79·4; H, 7·7. $C_{17}H_{20}O_2$ requires C, 79·7; H, 7·8%).

Cyclisation of 2-1′-*Naphthylmethylhexanoic Acid.*—This acid was cyclised as above to a reddish oil (17·8 g.). Chromatography in light petroleum (200 c.c.) through alumina (44 × 4 cm.), elution with light petroleum, and recrystallisation from ice-cold alcohol gave 2-*n*-*butylperinaphthan*-1-*one* (1·7 g.), m. p. 30—31° (Found: C, 85·8; H, 7·5. $C_{17}H_{18}O$ requires C, 85·7; H, 7·6%) [*semicarbazone* (small needles from alcohol), m. p. 196—198° (Found: C, 73·0; H, 6·9; N, 14·6. $C_{18}H_{21}ON_3$ requires C, 73·0; H, 7·0; N, 14·2%)]. Further elution with light petroleum–benzene (9 : 1) yielded a semi-solid fraction (0·3 g.), followed by 2-n-*butyl*-4 : 5-*benzindan*-1-*one* (4·0 g.), m. p. 46—48°. Recrystallisation from ice-cold alcohol yielded colourless plates, m. p. 52—53° (Found: C, 85·6; H, 7·5%); the *semicarbazone* formed needles (from alcohol), m. p. 222—223° (introduced at 200°) (Found: C, 73·2; H, 7·2; N, 14·1%). Continued elution yielded a viscous red oil (10·3 g.) which did not solidify.

2-*n*-Butylperinaphthan-1-one (1·0 g.) was oxidised as above to naphthalic anhydride, m. p. 273—275° raised to 274—276° on admixture with an authentic specimen.

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