Intramolecular Acylation. Part II. The Ring Closure of Some β-Substituted β-1-Naphthylpropionic Acids.*

By M. F. Ansell and A. M. Berman.

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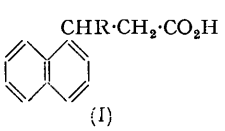
The ring closure of each of four β-substituted β-1-naphthylpropionic acids by the action of anhydrous hydrogen fluoride yields a mixture of the corresponding 3-substituted perinaphthan-1-one, 3-substituted perinaphthen-1-one, and 3-substituted 4 : 5-benzindan-1-one.

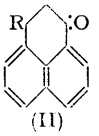
In Part I * it was shown that cyclisation of α-alkyl-substituted β-1-naphthylpropionic acids gives a mixture of the corresponding 2-substituted perinaphthan-1-one and 2-substituted 4 : 5-benzindan-1-one. In an attempt to establish the generality of these results four β-alkyl-substituted β-1-naphthylpropionic acids (I), prepared by the general method of Bachmann and Edgerton (*J. Amer. Chem. Soc.*, 1940, **62**, 2219) outlined below, were cyclised. One of these acids, β-1-naphthylbutyric acid (I; R = Me), has been previously

$$1\text{-}C_{10}H_7\cdot COR \longrightarrow 1\text{-}C_{10}H_7\cdot CHR\cdot OH \longrightarrow 1\text{-}C_{10}H_7\cdot CHRBr \longrightarrow 1\text{-}C_{10}H_7\cdot CHR\cdot CH(CO_2Et)_2 \longrightarrow 1\text{-}C_{10}H_7\cdot CHR\cdot CH_2\cdot CO_2H.$$

cyclised by Boekelheide and Larrabee (*ibid.*, 1950, **72**, 1243) and Lock and Gergely (*Monatsh.*, 1948, **79**, 521), using anhydrous hydrogen fluoride. In both cases the only isolated product was 3-methylperinaphthan-1-one (II; R = Me). On repeating the experiment and chromatographing the crude product, we have isolated in addition 3-methyl-4 : 5-benzindan-1-one (IV; R = Me) together with a small amount of 3-methylperinaphthen-1-one (III; R = Me). The latter compound has been previously prepared by the action of piperidine on 1 : 8-diacetylnaphthalene (Criegee, Kraft, and Rank, *Annalen*, 1933, **507**, 159).



(I)



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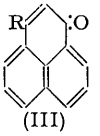

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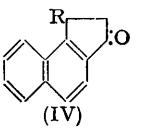

(IV)

The formation of perinaphthen-1-ones by the action of anhydrous hydrogen fluoride on β-1-naphthylpropionic acids has not been previously recorded, although it has been observed that the products are often yellow (Part I; Boekelheide and Larrabee, *loc. cit.*; Fieser *et al.*, *J. Amer. Chem. Soc.*, 1940, **62**, 1855, 2335), probably owing to contamination with the corresponding perinaphthen-1-one. Cyclisation of β-1-naphthylpropionyl chloride with aluminium chloride in nitrobenzene does however give perinaphthen-1-one (von Braun, Manz, and Reinsch, *Annalen*, 1929, **468**, 277). This reaction presumably involves dehydrogenation of the first formed perinaphthan-1-one, for we have found that 3-methyl- and 3-ethyl-perinaphthan-1-one (see below) can be dehydrogenated to the corresponding perinaphthen-1-one under these conditions.

Similar results were obtained in the cyclisation of β-1-naphthylvaleric acid (I; R = Et), 3-ethylperinaphthan-1-one (II; R = Et), 3-ethyl-4 : 5-benzindan-1-one (IV; R = Et), and 3-ethylperinaphthen-1-one (III; R = Et) being isolated. On cyclising 3-1′-naphthylhexanoic acid † (I; R = Pr^n) it was found that when the chromatography was carried out slowly (elution with light petroleum) considerable decomposition occurred on the column and only 24% of 3-*n*-propylperinaphthan-1-one (II; R = Pr^n) was isolated together with 14% of 3-*n*-propyl-4 : 5-benzindan-1-one (IV; R = Pr^n) and 4% of 3-*n*-propylperinaphthen-1-one (III; R = Pr^n). When the chromatography was carried out more rapidly (elution with light petroleum–ether) no decomposition occurred and the yields were respectively 75, 15, and 0·2%. It therefore appears that the perinaphthan-1-one was oxidised by atmospheric oxygen to the perinaphthen-1-one. It has been observed that perinaphthan-1-ones darken in contact with air.

* Part I, *J.*, 1954, 575.

† Geneva nomenclature, $CO_2H = 1$.

The cyclisation of 3-1′-naphthylheptanoic acid (I; R = Bu^n) was analogous to that of the previous examples, yielding 3-*n*-butylperinaphthan-1-one (II; R = Bu^n), 3-*n*-butylperinaphthen-1-one (III; R = Bu^n), and 3-*n*-butyl-4 : 5-benzindan-1-one (IV; R = Bu^n).

Absorption maxima (mμ) *in ethanol.*

	Perinaphthan-1-one					Perinaphthen-1-one						4 : 5-Benzindan-1-one					
2-Me	(220)	248	320	330	—	—	—	—	—	—	—	250	274	283	294	332	344
3-Me	(220)	248	322	331	—	(225)	248	254	322	360	(382)	250	275	284	294	331	344
3-Et	(223)	(240)	250	320	331	(225)	248	254	322	360	(382)	250	274	284	294	331	344
3-Pr^n	(221)	250	322	331	—	(225)	248	256	322	360	(382)	250	274	284	294	332	344
3-Bu^n	(221)	248	322	332	—	(225)	250	256	324	360	(382)	250	275	284	294	331	344

The structures of the various cyclisation products were assigned on the basis of their ultra-violet absorption spectra, which fell into three distinct groups (see Table). Authentic samples were available of 2-methylperinaphthan-1-one and 2-methyl-4 : 5-benzindan-1-one (Part I), and the structure of 3-methylperinaphthen-1-one was known from its previous preparation. Additional evidence for the structures of the perinaphthen-1-ones was their formation of yellow solutions in hydrochloric acid (Cook and Hewett, *J.*, 1934, 365).

Experimental

In all 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 perinaphthen-1-ones gave yellow solutions in hydrochloric acid and black precipitates of indeterminate m. p. with 2 : 4-dinitrophenylhydrazine.

Preparation of 1-*Acylnapthalenes.*—1-Acetylnaphthalene, see Baddeley, *J.* 1949, S 99; 1-propionylnaphthalene, see Kloetzel and Wildman, *J. Org. Chem.*, 1946, **11**, 390; 1-butyrylnaphthalene and 1-valerylnaphthalene were prepared in yields of 80 and 78% respectively by the method of Kloetzel and Wildman (*loc. cit.*; cf. Nunn and Henze, *ibid.*, 1947, **12**, 540).

*Preparation of Alkyl-*1-*naphthylcarbinols.*—The 1-acylnaphthalene (0·13 mole) was added to a suspension of lithium aluminium hydride (2 g., 0·05 mole) in dry ether (60 c.c.) at such a rate that the ether refluxed, and then heated under reflux for 30 min. The mixture, cooled in ice, was decomposed with water, and poured into 10% sulphuric acid (1 l.). The ethereal layer was separated and the aqueous layer extracted with ether. Evaporation of the dried (Na_2SO_4) extracts gave the alcohol in a high state of purity. In this way were prepared: 1-1′-naphthylethanol (92%; m. p. 66°) (cf. Lund, *Ber.*, 1937, **70**, 1520); 1-1′-naphthylpropan-1-ol (77%; b. p. 168°/11 mm., n_D^{20} 1·6099) (cf. Levina, *J. Gen. Chem. U.S.S.R.*, 1940, **10**, 913); 1-1′-*naphthylbutan*-1-*ol* (80%; b. p. 198°/19 mm., n_D^{20} 1·6042) (Found: C, 84·0; H, 8·1. $C_{14}H_{16}O$ requires C, 84·0; H, 8·1%) [3 : 5-*dinitrobenzoate*, m. p. 129—130° (from ether) (Found: C, 63·8; H, 4·4; N, 7·1. $C_{21}H_{18}O_6N_2$ requires C, 63·9; H, 4·6; N, 7·1%)]; and 1-1′-*naphthylpentan*-1-*ol* (80%; m. p. 65—66°) (Found: C, 84·1; H, 8·2. $C_{15}H_{18}O$ requires C, 84·1; H, 8·2%) [3 : 5-*dinitrobenzoate*, m. p. 96—97° (from alcohol) (Found: C, 64·8; H, 4·8; N, 6·9. $C_{22}H_{20}O_6N_2$ requires C, 64·7; H, 4·9; N, 6·9%)].

Preparation of α-*Alkyl-*1-*naphthylmethyl Bromides.*—1-Bromo-1-1′-naphthylethane was prepared from the corresponding alcohol by the method of Bachmann and Edgerton (*loc. cit.*). Similarly were prepared 1-*bromo*-1-1′-*naphthylpropane* (78%; m. p. 38—39°) (Found: C, 62·8; H, 5·4; Br, 32·0. $C_{13}H_{13}Br$ requires C, 62·6; H, 5·4; Br, 32·1%), 1-bromo-1-1′-naphthylbutane (79%; b. p. 134°/2 mm.) (decomposes on storage), and 1-bromo-1-1′-naphthylpentane (80%; b. p. 122/4 mm.) (decomposes on storage).

Preparation of β-*Alkyl-*β-1-*naphthylpropionic Acids.*—β-1-Naphthylbutyric acid was prepared by the method of Bachmann and Edgerton (*loc. cit.*). Similarly were prepared β-1-*naphthylvaleric acid* [75%; m. p. 70—70·5° (from light petroleum)] (Found: C, 78·9; H, 7·1. $C_{15}H_{16}O_2$ requires C, 78·9; H, 7·1%), 3-1′-*naphthylhexanoic acid* [88·2%; m. p. 64—65° (from light petroleum–benzene)] (Found: C, 79·3; H, 7·3. $C_{16}H_{18}O_2$ requires C, 79·3; H, 7·4%), and 3-1′-*naphthylheptanoic acid* [73%; b. p. 188—190°/2 mm., m. p. 35—36° (Found: C, 79·7; H, 7·9. $C_{17}H_{20}O_2$ requires C, 79·7; H, 7·8%)]. The intermediate malonic esters were not purified.

Cyclisation of β-1-*Naphthylbutyric Acid.*—A solution of this acid (20 g.) 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 yellow-brown solid (17·1 g.). The

latter was dissolved in light petroleum and chromatographed through alumina (5 × 60 cm.). Elution was carried out with light petroleum. The first fractions yielded 3-methylperinaphthan-1-one (14·9 g.), m. p. 61—61·5°. Crystallisation from light petroleum gave colourless prisms, m. p. 61·5—62° (oxime, m. p. 129—130°). Lock and Gergely (*loc. cit.*) record m. p.s 62° and 130°. The 2 : 4-*dinitrophenylhydrazone* had m. p. 229—230° (Found : C, 63·9; H, 4·4; N, 14·8. $C_{20}H_{16}O_4N_4$ requires C, 63·8; H, 4·3; N, 14·9%). The second series of fractions from the chromatography yielded 3-*methyl*-4 : 5-*benzindan*-1-*one* (1·0 g.), m. p. 40—43°. Crystallisation from light petroleum at −10° gave colourless crystals, m. p. 48—48·5° (Found : C, 85·7; H, 6·1. $C_{14}H_{12}O$ requires C, 85·7; H, 6·2%) [2 : 4-*dinitrophenylhydrazone*, m. p. 280—282° (Found : C, 63·7; H, 4·4; N, 14·8. $C_{20}H_{16}O_4N_4$ requires C, 63·8; H, 4·3; N, 14·9%)]. Final elution with benzene gave 3-methylperinaphthen-1-one (0·03 g.), m. p. 150—154°. Crystallisation from benzene yielded bright yellow crystals, m. p. 156—157° (Found : C, 86·5; H, 5·1. Calc. for $C_{14}H_{10}O$: C, 86·6; H, 5·2%). Criegee, Kraft, and Rank (*loc. cit.*) record m. p. 156°.

Dehydrogenation of 3-*Methylperinaphthan*-1-*one*.—A mixture of this ketone (0·5 g.) and anhydrous aluminium chloride in nitrobenzene (10 c.c.) was heated on a water-bath for 1 hr., then poured into water (100 c.c.), and ether (100 c.c.) was added. After filtering, the ethereal layer was separated and the aqueous layer extracted with ether. The residue obtained on evaporation, under reduced pressure, of the dried (Na_2SO_4) combined extracts, was dissolved in light petroleum and chromatographed (alumina). Elution with light petroleum–ether (4 : 1) gave 3-methylperinaphthen-1-one (0·1 g.), m. p. 156—157° after recrystallisation.

Cyclisation of β-1-*Naphthylvaleric Acid*.—This acid (20 g.) was cyclised as in the preceding case, to yield a yellow oil (12·5 g.). Chromatography in light petroleum through alumina (5 × 60 cm.) and elution with light petroleum gave 3-*ethylperinaphthan*-1-*one* (8·2 g.) as a viscous yellow liquid, b. p. 126/2 mm. (Found : C, 86·0; H, 6·6. $C_{15}H_{14}O$ requires C, 85·7; H, 6·7%) [2 : 4-*dinitrophenylhydrazone* (scarlet crystals from benzene), m. p. 183—184° (Found : C, 64·5; H, 4·7; N, 14·1. $C_{21}H_{18}O_4N_4$ requires C, 64·6; H, 4·6; N, 14·3%)]. Further elution with light petroleum yielded 3-*ethyl*-4 : 5-*benzindan*-1-*one* (3·8 g.), m. p. 44—45° after recrystallisation from light petroleum (Found : C, 85·9; H, 6·7. $C_{15}H_{14}O$ requires C, 85·7; H, 6·7%) [2 : 4-*dinitrophenylhydrazone* (scarlet crystals from glacial acetic acid), m. p. 248—249° (Found : C, 64·5; H, 4·7; N, 14·1. $C_{21}H_{18}O_4N_4$ requires C, 64·6; H, 4·6; N, 14·3%)]. Final elution with light petroleum–benzene (1 : 1) gave 3-*ethylperinaphthen*-1-*one* (3·7 mg.), m. p. 90°. Crystallisation from light petroleum–benzene yielded yellow crystals, m. p. 94—95° (Found : C, 86·6; H, 6·2. $C_{15}H_{12}O$ requires C, 86·5; H, 5·8%).

Dehydrogenation of 3-*Ethylperinaphthan*-1-*one*.—This ketone (0·5 g.) was dehydrogenated, as for the 3-methyl analogue, to 3-ethylperinaphthen-1-one (0·2 g.).

Cyclisation of 3-1′-*Naphthylhexanoic Acid*.—(*A*) This acid (20 g.) was cyclised as in the previous case, to a pale yellow oil (17·0 g.). Chromatography in light petroleum through alumina (5 × 60 cm.) and elution with light petroleum–benzene (9 : 1) gave 3-n-*propylperinaphthan*-1-*one* (5·2 g.) (b. p. 154—156°/2 mm.) which at 0° yielded pale yellow crystals, m. p. 21—22° (Found : C, 85·7; H, 7·1. $C_{16}H_{16}O$ requires C, 85·7; H, 7·2%) [2 : 4-*dinitrophenylhydrazone*, m. p. 201—202° (scarlet crystals from acetic acid) (Found : C, 65·4; H, 5·0; N, 13·9. $C_{22}H_{20}O_4N_4$ requires C, 65·3; H, 5·0; N, 13·8%)]. Further elution gave a yellow solid, m. p. 58—68°, which on fractional crystallisation from light petroleum gave 3-n-*propyl*-4 : 5-*benzindan*-1-*one* (3·0 g.), m. p. 69·5—70° (Found : C, 85·7; H, 5·1. $C_{16}H_{16}O$ requires C, 85·7; H, 7·2%) [2 : 4-*dinitrophenylhydrazone*, m. p. 259—260° (scarlet crystals from acetic acid) (Found : C, 65·4; H, 5·0; N, 13·8. $C_{22}H_{20}O_4N_4$ requires C, 65·3; H, 5·0; N, 13·8%)], and 3-n-*propylperinaphthen*-1-*one* (0·9 g.), m. p. 84—85° (Found : C, 87·0; H, 6·1. $C_{16}H_{14}O$ requires C, 86·5; H, 6·3%). Final elution with ether gave a considerable amount of tar. (*B*) The cyclisation product (8·6 g.) was chromatographed in light petroleum through alumina (5 × 15 cm.) and eluted successively with light petroleum–ether mixtures in the ratio of 9 : 1, 8 : 2, 7 : 3, 6 : 4, and 5 : 5, to yield 3-*n*-propylperinaphthan-1-one (7·0 g.), 3-*n*-propyl-4 : 5-benzindan-1-one (1·4 g.), and 3-*n*-propylperinaphthen-1-one (0·02 g.).

Cyclisation of 3-1′-*Naphthylheptanoic Acid*.—This acid (20 g.) was cyclised as in the previous case, to yield a yellow oil (17·1 g.). Chromatography in light petroleum–ether (9 : 1) through alumina (5 × 15 cm.) and elution with the same solvent nixture gave 3-n-*butylperinaphthan*-1-*one* (14·0 g.), b. p. 178°/3·5 mm. (Found : C, 85·6; H, 7·5. $C_{17}H_{18}O$ requires C, 85·7; H, 7·6%) [2 : 4-*dinitrophenylhydrazone*, m. p. 212—214° (scarlet crystals from acetic acid) (Found : C, 66·0; H, 5·2; N, 13·0. $C_{23}H_{22}O_4N_4$ requires C, 66·0; H, 5·3; N, 13·4%)]. Further elution with light petroleum–ether (8 : 2) yielded 3-n-*butyl*-4 : 5-*benzindan*-1-*one* (2·8 g.), m. p. 29—30° after recrystallisation from light petroleum–benzene (9 : 1) at −20° (Found : C, 85·7; H, 7·7%)

[2 : 4-*dinitrophenylhydrazone*, m. p. 253—254° (scarlet crystals from acetic acid) (Found : C, 65·9; H, 5·3; N, 13·0. $C_{23}H_{22}O_4N_4$ requires C, 66·0; H, 5·3; N, 13·4%)]. Final elution with light petroleum–ether (1 : 1) gave 3-n-*butylperinaphthen*-1-*one* as pale yellow crystals, m. p. 82—84° after crystallisation from light petroleum–benzene (9 : 1) (Found : C, 86·5; H, 6·7. $C_{17}H_{16}O$ requires C, 86·4; H, 6·8%).

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QUEEN MARY COLLEGE (UNIVERSITY OF LONDON),
MILE END ROAD, LONDON, E.1.

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