750. *Intramolecular Acylation. Part I. Ring Closure of Some β-(7-Alkyl-1-naphthyl)propionic Acids.*

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Cyclisation of β-7-methyl-, β-7-ethyl-, and β-7-*iso*propyl-1-naphthylpropionic acids and of their acid chlorides gives only the products of *peri*-ring closure.

CYCLISATION of β-1-naphthylpropionic acid (I; R = H, R′ = H) can be made to yield perinaphthan-1-one (II), perinaphthen-1-one (III), or 4 : 5-benzindan-1-one (IV).[1] The present investigation concerned the effect of a 7-substituent, and this paper presents the results obtained with the methyl, ethyl, and *iso*propyl compounds. We also investigated the preparation of the methoxy-acid (I; R = OMe) but discontinued it when a paper by Hey and Green [2] appeared.

All the syntheses started from the readily available tetralones (V; R = Alkyl). Clemmensen reduction of the β-*p*-alkylbenzoylpropionic acids to the butyric acids [the precursors of (V)] was, in our hands, more tedious and less reliable than the Wolff–Kishner reduction (Huang-Minlon modification). Cyclisation of the butyryl chlorides by a modification of the method of Newman, Anderson, and Takemura [3] gave the tetralone in over 90% yield.

The first attempts to complete the synthesis involved conversion of 7-methoxy-1-tetralone into 1-formyl-1 : 2 : 3 : 4-tetrahydro-7-methoxynaphthalene. Unfortunately, the initial Darzens condensation gave only a viscous yellow oil (containing much unchanged tetralone) which did not appear to undergo hydrolysis under Claisen conditions,[4] but did

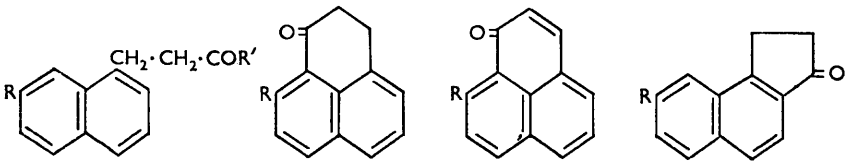
[1] (*a*) Mayer and Sieglitz, *Ber.*, 1922, **55**, 1835; von Braun, Manz, and Reinsch, *Annalen*, 1929, **468**, 277; Darzens and Levy, *Compt. rend.*, 1935, **201**, 902; Buu-Hoï and Cagniant, *ibid.*, 1943, **216**, 346; (*b*) Cook and Hewett, *J.*, 1934, 365; (*c*) Fieser and Gates, *J. Amer. Chem. Soc.*, 1940, **62**, 2335.

[2] Hey and Green, *J.*, 1954, 4306.

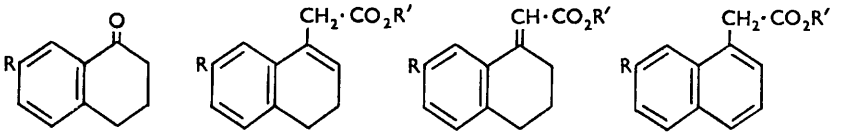
[3] Newman, Anderson, and Takemura, *J. Amer. Chem. Soc.*, 1953, **75**, 347; cf. Bachmann and Horton, *ibid.*, 1947, **69**, 58.

[4] Claisen, *Ber.*, 1905, **38**, 693; Johnson, Belew, Chinn, and Hunt, *J. Amer. Chem. Soc.*, 1953, **75**, 4995.

yield an acid on more vigorous treatment. Decarboxylation of this acid proceeded poorly, yielding no detectable aldehyde. It is noteworthy that benzosuberone is reported to undergo a Darzens condensation normally.[5]



The second attempt was a modified Reformatsky reaction involving the tetralone and methyl β-bromopropionate as for the similar case of 6-methoxy-1-tetralone.[6] Whereas the latter yielded 30%, our compound gave less than 10% of the desired product. Hey and Green [2] also report a low yield for this reaction.



The remaining compounds (I; R′ = H) were prepared from the tetralones by means of the Reformatsky reaction and homologation. Ruzicka and Hofmann [7] prepared the methyl derivative (VI*a* or *b*; R = Me, R′ = Et). Our Reformatsky reactions, effected in ether–benzene,[8] required extreme precautions in drying in order to avoid predominant formation of neutral, low-boiling oils. Dehydration of the hydroxy-esters formed was achieved with hot 90% formic acid,[9] and hydrolysis then furnished the acids (VI). Of these only the methyl and ethyl derivatives gave pure compounds (VI*a* or *b*) on crystallisation.

After exploratory experiments, dehydrogenation of the dihydronaphthylacetic acids (VI; R′ = H) was achieved with palladium–charcoal (on a small scale) or, best, by heating the methyl esters with sulphur at 240°. Overall yields from the tetralones to the naphthylacetic acids were 34—41%. The naphthylacetyl chlorides were fairly readily cyclised to the corresponding acenaphthenones by aluminium chloride but not by stannic chloride. Polyphosphoric acid failed to cyclise the free acids. In the Arndt–Eistert chain-lengthening of acids (VII; R′ = H), Newman and Beal's [10] improvement of the Wolff rearrangement gave 40—62% yields.

The two main types of cyclisation were examined, *viz.*, cyclodehydration by acid, and internal Friedel–Crafts reaction on the acid chlorides. During separation and purification of the products by chromatography on alumina, prolonged contact with the absorbent and exposure to strong light had to be avoided as both caused much decomposition. The initial products from these reactions must be either perinaphthanones (II) or benzindanones (IV). Such compounds differ sufficiently in ultraviolet light absorption to be characterised.[2,11] Thus for ethanol solutions perinaphthanones show maximum absorption at 248, 322, and 331 mμ whereas benzindanones have peaks at 250, 275, 284, 294, 331, and 334 mμ. Moreover, the former on dehydrogenation should yield perinaphthenones (III), which besides being soluble in, and recoverable from, aqueous mineral acid [1b]

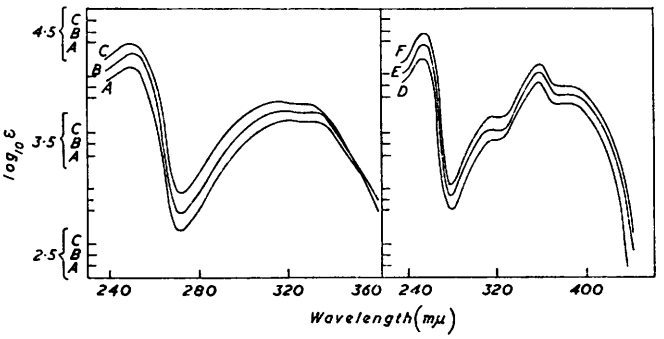
[5] Horton and Walker, *ibid.*, 1952, **74**, 758.
[6] Haberland and Heinrich, *Ber.*, 1939, **72**, 1222.
[7] Ruzicka and Hofmann, *Helv. Chim. Acta*, 1937, **20**, 1155.
[8] Cf. Bachmann, Cole, and Wilds, *J. Amer. Chem. Soc.*, 1940, **62**, 824.
[9] Johnson and Glenn, *ibid.*, 1949, **71**, 1087.
[10] Newman and Beal, *ibid.*, 1950, **72**, 5163.
[11] Ansell and Berman, *J.*, 1954, 1792.

have a characteristic band at 358 mμ.[11,12] It is perhaps conceivable that benzindanones could be converted into benzindenones [isomers of (III)] under conditions described in this work. However, such compounds, unsubstituted in the *cyclo*pentadienone ring, should be very unstable. Indenone [13] itself rapidly polymerises to a colourless high-melting product on storage or in contact with mineral acids. The properties of our dehydro-compounds can only be accounted for by a perinaphthenone structure.

The reaction between polyphosphoric acid and β-(7-methyl-1-naphthyl)propionic acid at 140° (45 minutes) furnished 9-methylperinaphthenone as sole product, whereas at 110—120° (15 minutes) the chief product was the perinaphthanone. The latter conditions were extended to the other two acids with similar results. 85% Sulphuric acid gave only water-soluble material. Anhydrous hydrogen fluoride gave the alkylperinaphthanones in very high yields (87—94%) along with traces of the perinaphthenones.

Aluminium chloride with ethylene chloride solutions of the acid chlorides at 15° furnished only (74—96%) the perinaphthanones, but yields fell to 57—81% when nitro-benzene was used as solvent. The stannic chloride method, giving 90—93% yields of perinaphthanones, was the preparative reaction of choice. Chromatography and spectro-graphic examination showed that not more than traces of the isomeric benzindanones

Light absorption, in EtOH, *of*: FIG. 1, 9-*methyl-* (*curve A*), 9-*ethyl-* (*B*), *and* 9-iso*propyl-perinaphthanone* (*C*); FIG. 2, 9-*methyl-* (*D*), 9-*ethyl-* (*E*), *and* 9-iso*propyl-perinaphthenone* (*F*).



For FIG. 2 (right) the vertical scales for curves *D*, *E*, and *F* correspond to those for curves *A*, *B*, and *C*, respectively, in FIG. 1 (left).

could have been formed. This is surprising as β-1-naphthylpropionic acid (I; R = H, R′ = H), treated with stannic chloride [1b] or hydrogen fluoride,[1c] gives a small yield of benzindanone (IV; R = H). Evidently, the electron-releasing properties of the alkyl groups outweigh their steric effect.

Few examples of deliberate dehydrogenations of perinaphthanones have been cited. Ansell and Berman,[11] having regard to the incidental dehydrogenation which often accompanies cyclisations with aluminium chloride–nitrobenzene, treated some 3-alkyl-perinaphthanones in this way and obtained small yields of the desired product. Loudon and Razdan [14] used palladium–charcoal on 9-hydroxyperinaphthan-1-one. In our work palladium–charcoal, alone or in the presence of *cyclo*hexane, had little effect on 9-methyl-perinaphthan-1-one. The 9-ethyl isomer behaved similarly but with the same catalyst in hot trimethylene glycol [15] it gave a 34% yield of dehydro-product. As 9-methyl-perinaphthen-1-one had been formed by a cyclisation in hot polyphosphoric acid, it was considered likely that the latter might dehydrogenate the perinaphthanone. This was the case, the yield (13%) being doubled on addition of palladium–charcoal. If the acidity of the medium is an important factor, then the use of the still stronger trichloroacetic acid should enhance the process and it was found that yields were increased thus to 33—65%. The best of the methods tried was the dehydrobromination of the 2-bromo-derivatives

[12] Cromwell and Hudson, *J. Amer. Chem. Soc.*, 1953, **75**, 872.
[13] Marvel and Hinman, *ibid.*, 1954, **76**, 5435.
[14] Loudon and Razdan, *J.*, 1954, 4299.
[15] Leonard and Berry, *J. Amer. Chem. Soc.*, 1953, **75**, 4989.

of these perinaphthanones. During bromination in carbon tetrachloride orange precipitates appeared, probably related to the dibromoperinaphthenones investigated by Lukin,[16] but these disappeared when the solutions were boiled. Evaporation and treatment with triethylamine gave the perinaphthenones in 46—78% yield.

Experimental

Aroylpropionic Acids.—Finely powdered anhydrous aluminium chloride (240 g., 1·8 moles) was added to a stirred mixture of the hydrocarbon (0·88 mole), succinic anhydride (80 g., 0·8 mole), and tetrachloroethane (300 ml.). After 3 hr. at room temperature the mixture was poured on ice and hydrochloric acid, and the organic layer washed and steam-distilled. Dissolution of the crude acids in sodium carbonate solution followed by precipitation with mineral acid gave 86—92% of slightly impure products, and crystallisation from benzene afforded 72—77% of pure materials.

γ-p-*Tolylbutyric Acid.*—β-*p*-Toluoylpropionic acid (109·5 g.), potassium hydroxide (96 g.), 90% w/w hydrazine hydrate (76 ml.), and ethylene glycol (500 ml.) were refluxed for 3 hr., distilled until the temperature had risen to 198°, and refluxed again for a further 12 hr. Working up in the usual way gave *γ*-*p*-tolylbutyric acid (82·9 g., 82%), b. p. 144—146°/1 mm., m. p. 60—62°. Analogous compounds were prepared in a similar manner.

7-*Methyltetralone.*—*γ*-*p*-Tolylbutyric acid (82·9 g., 0·465 mole) in benzene (200 ml.) was added to phosphorus pentachloride (127 g., 0·613 mole) under benzene (200 ml.). After 15 min. the solution was warmed on the water-bath for 5 min, then cooled to 0°. Anhydrous stannic chloride (132 ml., 1·05 moles) was added rapidly to the well-stirred solution (frothing) and after 6 hr. the dark brown solution was poured on ice and hydrochloric acid. The benzene layer was washed with hydrochloric acid–water (1 : 1), water, dilute aqueous alkali, and water, dried ($MgSO_4$), and distilled, giving 7-methyltetralone (67 g., 90%), b. p. 122—124°/1 mm., m. p. 34—36°. 7-Ethyltetralone (b. p. 95°/0·18 mm., 92%) and 7-*iso*propyltetralone (b. p. 98°/0·1 mm., 32—36°, 92%) were obtained similarly.

Reformatsky Reactions.—Apparatus used was heated at 120° for 4 hr. before use. Zinc foil, cleaned with sand-paper and cut into 1/8 in. squares, was etched with 6N-hydrochloric acid, washed with distilled water and with acetone, and dried at 120°. Pure benzene and pure ether, prepared according to Fieser,[17] were dried with sodium wire for 2 days before use.

To a boiling stirred mixture of 7-methyltetralone (32 g., 0·2 mole), zinc (20 g.), methyl bromoacetate (10 ml.), and 1 : 1 benzene–ether (400 ml.) a crystal of iodine was added, and at intervals of 20 min. two further additions of zinc (20 g.) and methyl bromoacetate (8 ml., 10 ml.), together with a crystal of iodine. After 12 hours' refluxing the precipitated complex was decomposed by 50% aqueous acetic acid (60 ml.), the organic layer was washed with water, saturated sodium hydrogen carbonate solution, water, and saturated brine, dried ($MgSO_4$), and evaporated.

The crude oily hydroxy-ester was refluxed for 30 min. with 90% formic acid (65 ml.), the latter then removed at reduced pressure, and the residue washed in ether with water and dilute sodium hydroxide solution. The ether extract (A) was evaporated and the residue heated for $3\frac{1}{2}$ hr. with 10% (w/v) potassium hydroxide in aqueous methanol (1 : 1) (180 ml.). The methanol was then distilled off at reduced pressure, and the solution diluted with water (2 vol.), and extracted with ether, the extract being rejected. Acidification gave the mixed unsaturated acids as a tan solid (23 g., 57%). Crystallisation from ether–light petroleum (b. p. 40—60°) gave an *acid* as colourless needles, m. p. 84—85° (Found: C, 77·3; H, 6·8. $C_{13}H_{14}O_2$ requires C, 77·2; H, 7·0%).

Distillation of the extract (A) gave a small forerun of colourless neutral oil, b. p. 80—125°/0·4 mm., and then unsaturated ester (26·5 g., 61·4%), b. p. 128—132°/0·4 mm.

Similar reactions with 7-ethyl- and 7-*iso*propyl-tetralone gave crude mixed acids in yields of 70 and 72% respectively. In the case of the ethyl compound, crystallisation from *n*-hexane furnished an unsaturated *acid* as colourless needles, m. p. 81—83° (Found: C, 77·6; H, 7·3. $C_{14}H_{16}O_2$ requires C, 77·8; H, 7·5%).

7-*Methyl*-1-*naphthylacetic Acid.*—The dehydrated, distilled ester (47 g.) from the Reformatsky reaction was heated with sulphur (6·9 g.), the temperature being raised from 210° to 270° during $3\frac{3}{4}$ hr. The product was taken into ether and washed with 2N-sodium hydroxide

[16] Lukin, *Bull. Acad. Sci. U.R.S.S.*, 1941, 565, 695; *Chem. Abs.*, 1943, **37**, 2734.
[17] Fieser, "Experiments in Organic Chemistry," D. C. Heath and Co., New York, 1941.

and water, then dried ($MgSO_4$). Distillation yielded a liquid (38·0 g.), b. p. 117—121°/0·3 mm., which was hydrolysed with boiling 20% aqueous potassium hydroxide (190 ml.) After ether-extraction the aqueous solution was acidified, yielding the crude acid (31·9 g.), m. p. 150—160°. Crystallisation from benzene furnished *7-methyl-1-naphthylacetic acid* (27·8 g., 64%) as colourless rhombs, m. p. 160—163°. A specimen, further crystallised, had m. p. 164—165° (Found: C, 77·6; H, 5·8. $C_{13}H_{12}O_2$ requires C, 78·0; H, 6·0%).

7-Ethyl- and *7-iso*propyl-*1-naphthylacetic acid* were obtained similarly, as rhombs (from benzene), m. p. 139—141° (Found: C, 78·7; H, 6·8. $C_{14}H_{14}O_2$ requires C, 78·5; H, 6·6%), and needles (from *cyclo*hexane–benzene), m. p. 126—127·5°, respectively (Found: C, 78·8; H, 7·2. $C_{15}H_{16}O_2$ requires C, 78·9; H, 7·1%). The latter was obtained in 57% yield by heating the distilled dehydrated Reformatsky ester (23·2 g.) with 25% palladium–charcoal (4·6 g.) under nitrogen at 230—270° and working up in the usual way. The yields of methyl and ethyl compound by this method were lower (25—36%).

β-(*7-Methyl-1-naphthyl*)*propionic Acid*.—7-Methyl-1-naphthylacetic acid (27·8 g.) was refluxed with thionyl chloride (30 ml.) and anhydrous ether (170 ml.) containing a drop of pyridine. The solvent and excess of reagent were removed under reduced pressure and the residue was freed from sulphur compounds by repeated evaporation with benzene. The acid chloride was added in ether (50 ml.) dropwise to stirred ice-cold ethereal diazomethane (from 63 g. of methylnitrosourea). Next day, removal of the solvent under reduced pressure at 20—30° left the crude diazo-ketone as yellow crystals, m. p. 65—80° (decomp.), which were dissolved in absolute methanol (320 ml.) and treated with 10 ml. portions of a solution of silver benzoate (10 g.) in dry triethylamine (60 ml.). Reaction was not entirely homogeneous, most of the nitrogen being evolved from the precipitate. After being left overnight the mixture was refluxed for 10 min., filtered, and evaporated. The residue was taken up in ether, washed with N-nitric acid, water, and sodium hydrogen carbonate solution, and dried ($MgSO_4$). Distillation gave methyl β-(7-methyl-1-naphthyl)propionate (21·6 g.), b. p. 140—146°/0·5 mm. Hydrolysis with 20% aqueous potassium hydroxide (110 ml.) and acidification gave the acid which from benzene afforded colourless plates (16·27 g.), m. p. 135—138°. The pure *acid* had m. p. 139—140° (Found: C, 78·2; H, 6·7. $C_{14}H_{14}O_2$ requires C, 78·5; H, 6·6%). β-(*7-Ethyl-1-naphthyl*)*propionic acid* (19·8 g., crude) was obtained similarly from the corresponding naphthylacetic acid (39·8 g.), and had m. p. 121·5—123° (from benzene) (Found: C, 79·0; H, 7·2. $C_{15}H_{16}O_2$ requires C, 79·0; H, 7·1%).

*7-iso*Propyl-1-naphthylacetic acid (15·2 g.) furnished the corresponding ester (9·7 g.), b. p. 146—152°/0·3 mm., hydrolysed to the *acid*, needles (8·58 g., crude), m. p. 130—131° (from *cyclo*hexane) (Found: C, 79·3; H, 7·6. $C_{16}H_{18}O_2$ requires C, 79·3; H, 7·5%).

Cyclisation of the Naphthylacetic Acids.—Details of the acenaphthenones are shown in Table 1. They were crystallised from *cyclo*hexane.

TABLE 1. *Acenaphthenones.*

			Found (%)			Required (%)	
Deriv.	Form	M. p.	C	H	Formula	C	H
8-Me	Plates	92—92·5°	85·6	5·5	$C_{13}H_{10}O$	85·7	5·5
8-Et	Needles	79—80	85·7	6·2	$C_{14}H_{12}O$	85·7	6·2
8-Pr^i	,,	113—114	85·4	6·4	$C_{15}H_{14}O$	85·7	6·7

8-Methylacenaphthenone. (1) 7-Methyl-1-naphthylacetic acid (0·2 g.) was converted into the acid chloride with thionyl chloride (0·5 ml.) in ether (5 ml.) containing a trace of pyridine. The residue, after removal of solvents and excess of reagent, was dissolved in benzene (6 ml.) and stirred with aluminium chloride (0·15 g.) for 2½ hr. at room temperature. After chromatography on alumina there was isolated 8-methylacenaphthenone (76 mg., 42%), m. p. 82—85°.

(2) Reaction of the above but in nitrobenzene yielded 25 mg., m. p. 91—92°.

(3) Cyclisation of the acid chloride from the acid (1 g.) with aluminium chloride (0·73 g.) in ethylene dichloride (25 ml.) (2 hr.) gave a solid (0·62 g.) purified by chromatography on alumina and collected in fractions (*a*) 0·13 g., m. p. 85—90°, and (*b*) 0·23 g., m. p. 91—92°.

8-Ethylacenaphthenone. 7-Ethyl-1-naphthylacetic acid (0·2 g.), converted into the acid chloride and treated with aluminium chloride (0·2 g.) in benzene (3 ml.), yielded 70 mg. (36%) of the acenaphthenone.

8-iso*Propylacenaphthenone* was prepared similarly (25%).

Cyclisation of the Naphthylpropionic Acids.—Details of the perinaphthanones are contained in Table 2. The first two were crystallised from light petroleum. 9-iso*Propylperinaphthanone*,

purified by two passages in light petroleum solution (b. p. 40—60°) through alumina, had n_D^{20} 1·6172.

(A) *With polyphosphoric acid* (85% P_2O_5). (1) β-(7-Methyl-1-naphthyl)propionic acid. (*a*) The acid (0·5 g.) and the reagent (5 g.) were heated together at 140°. The acid formed a molten layer on the surface at this temperature. The reagent layer was red after 3 min., brown after 15 min., and dark brown after 45 min. The mixture was cooled, then quenched with water, and the organic material isolated with benzene, yielding 0·40 g. of dark oil. Chromatography in benzene on alumina (16 × 1·3 cm.) gave yellow crystals (0·18 g.) which from *cyclo*hexane (charcoal) furnished yellow flakes of 9-*methylperinaphthenone*, m. p. 91—93° (Found: C, 86·1; H, 5·0. $C_{14}H_{10}O$ requires C, 86·6; H, 5·2%).

TABLE 2. *Perinaphthanones.*

			Found (%)			Required (%)	
Deriv.	Form	M. p.	C	H	Formula	C	H
9-Me	Prisms	39—41°	85·1	6·1	$C_{14}H_{12}O$	85·7	6·2
9-Et	Plates	61·5—62·5	85·3	7·0	$C_{15}H_{14}O$	85·7	6·7
9-Pr^i	Oil	—	86·0	7·3	$C_{16}H_{16}O$	85·7	7·2

(*b*) The acid (0·5 g.) and reagent (11·5 g.) were heated at 118° for 10 min. The crude product was chromatographed on alumina, yielding 9-*methylperinaphthanone* (0·22 g., 48%), m. p. 33—39°.

(2) β-(7-Ethyl-1-naphthyl)propionic acid. The acid (0·5 g.) was treated as in 1(*b*). 9-*Ethylperinaphthanone* (0·20 g.), m. p. 56—62·5°, was obtained.

(3) β-(7-*iso*Propyl-1-naphthyl)propionic acid. This was heated (0·5 g.) with polyphosphoric acid as already described but for 20 min., and afforded 9-*iso*propylperinaphthanone (0·15 g.).

(B) *With stannic chloride on the acid chloride.* The requisite acid (usually 0·5 g.) was converted into the acid chloride with phosphorus pentachloride (1·1 equiv.) in benzene (usually 10 ml.) and then treated, with stirring, with anhydrous stannic chloride (*ca.* 2·4 equiv.) in benzene (usually 2 ml.) in one portion. After 1 hr., ether was added and the whole poured on ice and hydrochloric acid. The organic layer was washed with 2N-hydrochloric acid, water, 2N-sodium hydroxide, and water, dried ($MgSO_4$), and chromatographed on alumina.

(1) β-(7-Methyl-1-naphthyl)propionyl chloride. The acid chloride (from 0·5 g.) of the acid was treated as described above. Isolation without chromatography afforded the perinaphthanone as crystals (0·36 g., 79%), m. p. 36—38·5°. The pale yellow colour was readily removed by passing its solution in light petroleum through alumina. On a larger scale, 2·8 g. gave 2·23 g. (87%), m. p. 34—38°, and 5·6 g. gave 4·48 g. (86·5%), m. p. 38—40°.

(2) β-(7-Ethyl-1-naphthyl)propionyl chloride. Obtained as above, the results were: 0·5 and 8·28 g. of acid gave 0·40 and 5·82—7·44 g., m. p. 60—62° and 60·5—62° (or 57—61·5°), respectively.

(3) β-(7-*iso*Propyl-1-naphthyl)propionyl chloride. Treated as above, 0·50 g. of acid gave 0·20 g. of pure product (43·6%).

(C) *With aluminium chloride on the acid chlorides in ethylene chloride or nitrobenzene.* The acid was converted into its acid chloride with thionyl chloride (2 ml. per g.) in ether (10 ml. per g.) containing pyridine (one drop). Excess of reagent and solvent were removed by evaporation with benzene, and the residue in pure ethylene chloride or nitrobenzene (20 ml. per g. of acid) was treated with aluminium chloride (1·1 equivs.) whilst being stirred at 15°. After 5 min. the solutions were allowed to reach room temperature during 1 hr. and poured on ice and hydrochloric acid. Ethylene chloride was removed by evaporation, nitrobenzene by steam-distillation. Acid washings of the products were pale yellow, but no pure organic material could be isolated from them. Final purification was usually carried out by chromatography on alumina. The results are in Table 3; they refer to 0·5 g. of acid.

TABLE 3.

	Reaction in $(CH_2Cl)_2$			Reaction in $Ph{\cdot}NO_2$		
Deriv.	State	M. p.	Yield (%)	State	M. p.	Yield (%)
7-Me	Crude	34—36°	74·3	—	—	—
	Chromatd.	34—37	56·7	Chromatd.	38—39·5°	57·6[c]
7-Et	Crude	58—60	74·8	—	—	—
	Chromatd.	59—61	82·5	Cryst.[a]	61—62	41·8
7-Pr^i	Crude[b]	Oil	96·4	Crude[b]	Oil	81·5

[a] From light petroleum (b. p. 40—60°). [b] No isomeric material found. [c] From 2·5 g. of acid.

(D) *With hydrogen fluoride.* The acid (1 g.) was treated with hydrogen fluoride (25 ml.), the latter being allowed to evaporate during 24 hr. The residue was washed with 2N-sodium hydroxide, and the product isolated with ether and purified by chromatography. The products were: Me, m. p. 35—39° (crude, 93·8% yield), 39—41° (pure, 44·8%); Et, m. p. 60—61·5° (crude, 92·8%), 61—62·5° (60·1%); Pr^{i}, oil (86·4% crude, 75·6% pure).

Dehydrogenation of the Perinaphthanones.—Details of the perinaphthenones (all yellow) are shown in Table 4. They were more strongly absorbed on alumina than the parent ketones and formed clear lemon-yellow bands easily eluted with benzene.

TABLE 4. *Perinaphthenones.*

		Found (%)			Required (%)	
Deriv.	Form	M. p.	C	H	Formula	C	H
9-Me	Flakes	91—93°	86·1	5·0	$C_{14}H_{10}O$	86·6	5·2
9-Et	,,	65—66	85·6	5·6	$C_{15}H_{12}O$	86·5	5·8
9-Pr^{i}	Oil[a]	—	86·1	6·4	$C_{16}H_{14}O$	86·5	6·4

[a] n_D^{18} 1·6378. Decomposes when heated.

(1) 9-*Methylperinaphthanone.* (*a*) The ketone (0·30 g.) was heated with polyphosphoric acid (from 88% orthophosphoric acid, 2·5 g., and phosphoric oxide, 3·25 g.) for 1 hr., the mixture assuming a clear deep red colour. After working up in the usual way 9-methylperinaphthenone (0·040 g.), m. p. 84—88°, was obtained.

(*b*) The above method, with the addition of 25% palladised charcoal (0·3 g.), gave the unsaturated ketone (0·07 g.), m. p. 85—90°.

(*c*) The perinaphthanone (0·3 g.), 25% palladium–charcoal (0·3 g.), and glacial acetic acid (5 ml.) were refluxed together overnight. After cooling, water was added, the mixture filtered, the acid neutralised by the addition of 2N-sodium hydroxide, and the whole extracted with ether. Evaporation of the washed (water, saturated brine) and dried ($MgSO_4$) solution gave a yellow-brown solid. By absorption from benzene on alumina and elution with, first, 1 : 20 and then 1 : 10 ether–benzene the perinaphthenone (0·08 g.), m. p. 85—90°, was obtained.

(*d*) The ketone (0·3 g.), palladium–charcoal (0·3 g.), and trichloroacetic acid (10 g.) were refluxed together for 5 min. (evolution of hydrogen chloride). 9-Methylperinaphthenone (0·10 g., 33%), m. p. 85—90°, was isolated in the usual way.

(*e*) Bromine (theoretical amount) in carbon tetrachloride (2 ml.) was added dropwise to the ketone (0·3 g.) in hot carbon tetrachloride (15 ml.). An orange precipitate separated but disappeared on refluxing (5 min.). The solution was slowly evaporated, and the residual dark oil taken up in chloroform (5 ml.) and treated with anhydrous triethylamine (10 ml.). After 2 hr. the precipitated triethylamine hydrobromide was removed and washed with ether. Evaporation of the solution and washings left a dark solid which was thoroughly extracted with cold concentrated hydrochloric acid; the extract was diluted with water until turbidity appeared and then shaken with ether. The washed and dried ether solution was treated in the cold with a little charcoal and filtered. Evaporation and chromatography of the product from benzene on alumina furnished 9-methylperinaphthenone (0·11 g.).

(2) 9-*Ethylperinaphthanone.* Method 1(*d*), applied to the ethyl isomer, gave 30% of material, m. p. 61—64°. Method 1(*e*) gave 65% of material, m. p. 64—66°.

(3) 9-iso*Propylperinaphthanone.* (*a*) The ketone (0·51 g.), 25% palladium–charcoal (0·51 g.), and trichloroacetic acid (2 g.) were heated together at 100° overnight. Working up in the usual way furnished pure 9-*iso*propylperinaphthenone as a yellow acid-soluble oil (0·33 g.) which did not form a picrate.

(*b*) The perinaphthanone (0·65 g.) was treated with bromine and triethylamine as described above. The crude brownish-yellow oil (0·63 g.) was chromatographed on alumina (15 g. of active material, supplied by Savory and Moore Ltd.), and the product immediately rechromatographed in the same manner, elution being as rapid as possible. 9-*iso*Propylperinaphthenone was obtained as an analytically pure oil (0·56 g., 78%).

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