800. *Intramolecular Acylation. Part II.*[1] *The Cyclisation of* β-(7-tert.-*Butyl*-1-*naphthyl*)*propionic Acid.*

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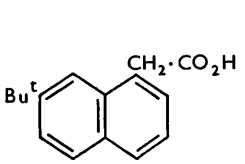
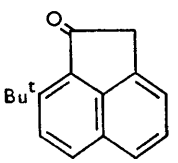
Cyclisation of β-(7-*tert.*-butyl-1-naphthyl)propionic acid occurs predominantly by angular cyclisation to the benzindanone. An attempted synthesis of 9-*tert.*-butylperinaphthan-1-one by cyclisation of hydroaromatic intermediates was not successful.

In Part I [1] the cyclisation of β-7-methyl-, -ethyl-, and -*iso*propyl-1-naphthylpropionic acids to give only the products of *peri*-ring closure was reported. We now record the results obtained with the 7-*tert.*-butyl analogue. It was made by the same route as the others. The acid chloride of the intermediate acid (I) yielded the acenaphthenone (II) when treated with aluminium chloride but the free acid could not be cyclised with polyphosphoric acid.



(I)



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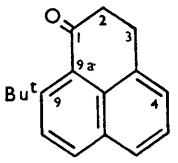

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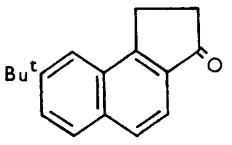


(IV)

The behaviour of β-(7-*tert.*-butyl-1-naphthyl)propionic acid to cyclising agents was quite different from that of the other alkyl compounds. It was largely unaffected by polyphosphoric acid although traces of two high-melting substances, one soluble in aqueous mineral acid, were obtained, but in amounts too small to be characterised. The acid chloride with stannic chloride in benzene or aluminium chloride in ethylene chloride gave a compound, m. p. 186—187·5°, and an oil, which were separated chromatographically. The oil resisted further purification and a dinitrophenylhydrazone could not be obtained from it.

[1] Part I, Wenham and Whitehurst, *J.*, 1956, 3857.

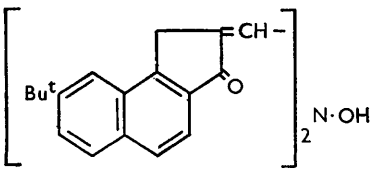
Attempted dehydrogenation with bromine–triethylamine gave an impure yellow substance partially soluble in dilute hydrochloric acid. These results do not exclude the possibility that the original oil might have contained some of the perinaphthanone (III).

Cyclisation in nitrobenzene produced relatively more of the substance, m. p. 186—187·5°, and only a trace of the oil. In hydrogen fluoride the acid afforded two solid compounds with m. p.s 186—187·5° and 166—168° respectively, and some oil which on this occasion contained material soluble in dilute hydrochloric acid.

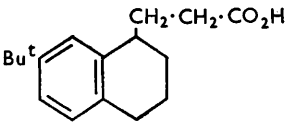
Analysis of compound, m. p. 186—187·5°, showed it to be either the perinaphthanone (III) or the isomeric benzindanone (IV). Attempts at dehydrogenation were unsuccessful. The ultraviolet absorption spectrum agreed fairly closely with those of the benzindanones recorded by Ansell and Berman.[2] The high melting point also indicates the benzindanone structure (IV). Johnson and Shelberg [3] devised a chemical method for distinguishing five- from six-membered cyclanones provided there is one α-methylene group. The hydroxymethylene derivative of a *cyclo*hexanone on treatment with hydroxylamine and sodium methoxide yields a nitrile through an intermediate *iso*oxazole. A *cyclo*pentanone however gives a disubstituted hydroxylamine. Only the latter gives highly coloured salts. This elegant test applied to our compound gave the deep red hydroxylamine derivative (V) soluble in alcoholic (but not in aqueous) potassium hydroxide to a deep violet solution. The compound, m. p. 186—187·5°, thus has structure (IV).

The substance with m. p. 166—168° had an ultraviolet absorption almost identical with that of (IV). Analysis indicated the presence of two butyl groups. As these are almost certain to be tertiary it appears to be 2′ : *x*-di-*tert.*-butyl-4 : 5-benzindanone. The formation of such a compound is a further instance of the well-known acid-catalysed transfer of *tert.*-butyl groups.[4]

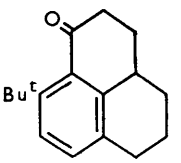
As attempts to isolate the perinaphthanone (III) had proved abortive, experiments were undertaken to synthesise the compound from the hydroaromatic acid (VI), prepared by hydrogenation and subsequent homologation of the unsaturated acid obtained by a Reformatsky reaction. The action of aluminium chloride on its acid chloride according to the " inverse " Friedel–Crafts procedure of Johnson and Glenn [5] gave an intractable oil. Hydrogen fluoride also produced an oil, from which, however, a dinitrophenylhydrazone was secured. Unfortunately, this proved to be that of tetrahydroperinaphthan-1-one, the *tert.*-butyl group having been lost during cyclisation.



(V)



(VI)



(VII)

According to molecular models it is only just possible to construct the perinaphthanone (III) and the tetrahydro-derivative (VII). It is necessary for two of the methyl groups to be arranged skew with respect to the $C_{(9a)}$–CO bond, and for the C–H linkages in two of the methyl groups to eclipse the linkages attached to the central carbon atom of the butyl group.

It has been mentioned [1] that the products from Reformatsky reactions on the tetralones under the more usual conditions were low-boiling oils. That from 7-methyl-1-tetralone has been examined. The substance gave fairly satisfactory analyses for 1 : 2 : 3 : 4-tetrahydro-6-methylnaphthalene but gave positive unsaturation tests, and both the refractive

[2] Ansell and Berman, *J.*, 1954, 1792.
[3] Johnson and Shelberg, *J. Amer. Chem. Soc.*, 1945, **67**, 1745.
[4] See, for example, Schlatter, *ibid.*, 1954, **76**, 4952.
[5] Johnson and Glenn, *ibid.*, 1949, **71**, 1092.

index and ultraviolet absorption were widely different from those of authentic 1 : 2 : 3 : 4-tetrahydro-6-methylnaphthalene prepared by Wolff–Kishner reduction (Huang-Minlon modification) of the tetralone. It was inferred that some of the 1 : 2-dihydronaphthalene was present. For comparison the dihydro-compound was made by reduction of the tetralone with lithium aluminium hydride followed by dehydration. A comparison of the ultraviolet spectra showed very clearly that the oil was a mixture of these two components. As far as we know, this is the first recorded example of a reduction $>CO \longrightarrow >CH_2$ under Reformatsky conditions and was all the more surprising as an attempted reduction of the tetralone by Clemmensen's method (Martin modification) proceeded poorly, yielding as the main product a viscous oil (which was not further investigated).

Experimental

Deactivated alumina contained 1% (w/w) of added water.

By the general method previously described, *tert.*-butylbenzene gave β-*p-tert.*-butylbenzoylpropionic acid (91·5% crude; 76% once crystallised from benzene), m. p. 125—127°. Fieser and Price [6] record m. p. 121—122°. Wolff–Kishner reduction afforded γ-*p-tert.*-butylphenylbutyric acid, b. p. 147°/0·2 mm., m. p. 56—59° (82%) (Martin [7] gives m. p. 57—60°), sufficiently pure for cyclisation to 7-*tert.*-butyl-1-tetralone, b. p. 108—110°/0·3—0·4 mm., m. p. 95—98° (90%). Bromby *et al.*[8] record m. p. 101—102°.

7-tert.-*Butyl*-1-*naphthylacetic Acid.*—With the precautions mentioned previously,[1] a Reformatsky reaction on the above tetralone yielded 84% of distilled unsaturated ester, b. p. 125—140°/0·3 mm., hydrolysed to the crude acid, m. p. 64—78°. 7-tert.-*Butyl*-x : y-*dihydro*-1-*naphthylacetic acid* (or isomer) separated from light petroleum (b. p. 40—60°) in prisms, m. p. 80·5—81·5° (Found: C, 78·5; H, 8·3. $C_{16}H_{20}O_2$ requires C, 78·7; H, 8·3%). Heating the distilled unsaturated ester (35·4 g.) with sulphur (4·4 g.) for 2 hr. at 220—260° gave methyl 7-*tert.*-butyl-1-naphthylacetate, b. p. 127—128°/0·04 mm., which on hydrolysis afforded the *acid* (21·45 g.; m. p. 64—68°, which crystallised from hexane as elongated rhombs, m. p. 78—79·5° (Found: C, 78·9; H, 7·4. $C_{16}H_{18}O_2$ requires C, 79·3; H, 7·5%).

β-(7-tert.-*Butyl*-1-*naphthyl*)*propionic Acid.*—This was made as for the 7-methyl compound. The methyl ester, b. p. 140—142°/0·07 mm. (74%), was hydrolysed to the *acid* which crystallised from benzene in blunt needles, m. p. 146·5—149° (Found: C, 79·8; H, 7·8. $C_{17}H_{20}O_2$ requires C, 79·7; H, 7·9%).

8-tert.-*Butylacenaphthen*-1-*one* (II).—7-*tert.*-Butyl-1-naphthylacetic acid (1 g.) in ether (10 ml.) containing pyridine (1 drop) was treated with thionyl chloride (2 ml.) and refluxed (3 hr.). The solvent and excess reagent were removed completely and the residue stirred with aluminium chloride (0·63 g.) in dry ethylene chloride (20 ml.) for 1 hr. After addition of dilute hydrochloric acid the organic layer was separated, washed and dried ($MgSO_4$). 8-tert.-*Butylacenaphthen*-1-*one* formed platelets (0·45 g., 49%), m. p. 89—91°, from hexane. An analytical sample (from hexane) melted at 85—87°, solidified, and remelted at 90—91·5° (Found: C, 85·0; H, 7·1. $C_{16}H_{16}O$ requires C, 85·7; H, 7·2%).

Cyclisation of β-(7-tert.-*butyl*-1-*naphthyl*)*propionic Acid.*—(a) *With stannic chloride.* The acid (5 g.) in benzene (50 ml.) was converted into its acid chloride with phosphorus pentachloride (6 g.) and treated with stannic chloride (15 g.) as described previously. The crude oil containing some crystalline material (4·29 g.), crystallised from *cyclo*hexane, gave 2′-tert.-*butyl*-4 : 5-*benzindan*-1-*one* (IV) (compound A) (2·31 g., m. p. 184—186°). An analytical specimen had m. p. 186—187·5° (Found: C, 85·3; H, 7·6. $C_{17}H_{18}O$ requires C, 85·7; H, 7·6%), $\lambda_{min.}$ (log ε in parentheses here and below) 253 (4·82), 273 (4·02), 282 (4·07), 334 (3·46), 347 (3·52), $\lambda_{max.}$ 267 (3·96), 277 (4·00), 307 (2·95), 338 mμ (3·44). The mother-liquors were evaporated to dryness and the residue chromatographed over alumina in benzene. Elution gave first a dark oil (0·70 g.) which could not be further purified, then compound A (0·28 g.), m. p. and mixed m. p. 185—187°.

(b) *With aluminium chloride.* (i) In ethylene chloride. The acid (5 g.) was treated with thionyl chloride (5 ml.) in benzene (25 ml.). After repeated evaporation with benzene, the residue was dissolved in ethylene chloride (100 ml.), cooled to 0°, and treated, whilst being stirred, with aluminium chloride (3·2 g.) during 5 min. After 1¼ hr. at room temperature the

[6] Fieser and Price, *J. Amer. Chem. Soc.*, 1936, **58**, 1838.
[7] Martin, *ibid.*, p. 1438.
[8] Bromby, Peters, and Rowe, *J.*, 1943, 144.

deep green solution was worked up. The brown sticky product was crystallised once from *cyclo*hexane, to give compound A (2·2 g., 47%). The mother-liquors were evaporated, and the residue was chromatographed in benzene on deactivated alumina: elution and evaporation gave intractable pale brown oils (2·11 g.).

(ii) In nitrobenzene. The acid (0·5 g.) was treated with thionyl chloride (5 ml.) in ether (5 ml.) containing pyridine (1 drop). The acid chloride, freed from sulphur compounds, was treated in nitrobenzene (10 ml.) with aluminium chloride (0·32 g.) at room temperature (stirring). The product was isolated as before. Compound A (0·31 g.), m. p. and mixed m. p. 185—187°, and a trace of oil were isolated.

(c) *With hydrogen fluoride.* The acid (12·23 g.) was added to anhydrous hydrogen fluoride (120 ml.), and the solution allowed to evaporate spontaneously during 24 hr. Dilute sodium hydroxide solution was added and the organic material extracted with benzene–ether, washed and dried. Evaporation left a dark brown sticky solid which was treated with cold concentrated hydrochloric acid (this removed only intractable material), and the residue in dry benzene ($MgSO_4$) chromatographed on alumina (65 g.). Four fractions were eluated. Fractions (2), (3), and (4) yielded after evaporation and crystallisation from *cyclo*hexane 2′-*tert.*-butyl-4 : 5-benzindan-1-one (2·55 g., 22·2%), m. p. and mixed m. p. 178—184°. Fraction (1), together with the mother-liquors from the crystallisation of fraction (2), was evaporated and the residue chromatographed in light petroleum (b. p. 40—60°) on alumina (60 g.). The first 50 ml. of eluate (the column being developed with light petroleum) yielded, after evaporation and crystallisation from *cyclo*hexane, colourless needles of a *di*-tert.-*butyl*-4 : 5-*benzindanone* (0·36 g.), m. p. 166—168° (Found: C, 85·1; H, 8·6. $C_{21}H_{26}O$ requires C, 85·7; H, 8·9%), $\lambda_{max.}$ 255 (4·82), 273 (4·01), 288 (4·05), 343 (3·42) (shoulder), 353 (3·46), $\lambda_{min.}$ 269 (3·98), 278 (3·98), 307·5 mμ (2·79).

2′-tert.-*Butyl*-2-*hydroxymethylene*-4 : 5-*benzindan*-1-*one*.—This was made by adding 2′-*tert.*-butyl-4 : 5-benzindan-1-one (2·50 g., 0·0105 mol.) in benzene (100 ml.) to a swirled mixture of ethyl formate (1·56 g., 0·0210 mol.), benzene (10 ml.), and sodium methoxide [from sodium (0·48 g., 0·21 mol.) and dry methanol (8 ml.), finally evaporated and baked in a vacuum at 200°] under dry oxygen-free nitrogen at *ca.* 10°. The solution became red and after 6 hr. the cake was broken up, and the mixture warmed to 40° and set aside overnight. Dilute sulphuric acid was added, and the organic layer removed and extracted with cold 5% aqueous potassium hydroxide. From the aqueous layer, by treatment with dilute hydrochloric acid, there was obtained the crude, almost colourless, hydroxymethylene compound [1·98 g., m. p. 186—188° (decomp.)]. Crystallisation from benzene furnished fibrous needles (1·19 g.), m. p. 179—181°. Further recrystallisation caused unusual changes in the appearance of this compound and it was not possible to purify it to constant m. p.

NN-*Di*-(2′-tert.-*butyl*-1-*oxo*-4 : 5-*benzindan*-1-*ylidenemethyl*)*hydroxylamine* (V).—The above hydroxymethylene compound (1 g.) was stirred vigorously with hydroxylamine hydrochloride (0·31 g., 20% excess) and glacial acetic acid (15 ml.). After 24 hr. the red solid was collected, triturated with water, and dried [0·92 g.; m. p. 234—236° (decomp.)]. Crystallisation from tetrachloroethane furnished the *hydroxylamine* (0·25 g.), m. p. 255—257° (decomp.) (Found: C, 82·5; H, 6·7; N, 2·8. $C_{36}H_{35}O_3N$ requires C, 81·6; H, 6·7; N, 2·6%), as fine red needles with a green sheen.

β-(7-tert.-*Butyl*-1 : 2 : 3 : 4-*tetrahydro*-1-*naphthyl*)*propionic Acid*.—7-*tert.*-Butyldihydro-1-naphthylacetic acid (from 25·44 g. of dehydrated Reformatsky ester) was shaken with hydrogen and platinic oxide (400 mg.) in acetic acid (150 ml.) (uptake 2240 ml.; theor. 2400 ml.). The filtered mixture was evaporated at reduced pressure, and the residue dissolved in ether, washed with water, dried ($MgSO_4$), and distilled. The main fraction (17·56 g.), b. p. 144—146°/0·03 mm., was impure 7-*tert.*-butyl-1 : 2 : 3 : 4-tetrahydro-1-naphthylacetic acid (Found: C, 77·0; H, 9·2. Calc. for $C_{16}H_{22}O_2$: C, 78·0; H, 9·0%). It (17·50 g.) was converted into its acid chloride with thionyl chloride (20 ml.) in benzene (20 ml.) and after complete removal of solvents and excess of reagent, was added in dry ether (50 ml.) dropwise to diazomethane (from 35 g. of methylnitrosourea) in dry ether (*ca.* 250 ml.). Evaporation at reduced pressure left the yellow oily diazo-ketone which was treated in dry methanol (150 ml.) with silver benzoate (2 g.) in triethylamine (10 ml.), and the product was isolated as before. The distilled product (14·34 g. of pale yellow oil, b. p. 116—118°/0·04 mm.) was hydrolysed with 20% aqueous potassium hydroxide. Acidification, extraction with ether, and distillation furnished the *tetrahydro-propionic acid* (12·21 g.), b. p. 148—152°/0·04 mm. (Found: C, 78·8; H, 9·7. $C_{17}H_{24}O_2$ requires C, 78·4; H, 9·3%), which solidified.

Attempted cyclisation. The propionic acid (9·39 g.) was treated with phosphorus pentachloride (8·28 g.) in benzene (20 ml.) and after 1 hr. the solution was repeatedly evaporated with benzene at reduced pressure. The residue in benzene (105 ml.) was added dropwise to aluminium chloride (6·27 g.) and benzene (120 ml.) at 0° and left for 2 hr. Working up in the usual way gave the following arbitrary fractions (at 0·05 mm.): (*a*) up to 114° (0·18 g.), smell of *tert.*-butylbenzene; (*b*) 114—124° (4·21 g.), pale yellow, aromatic odour; (*c*) 124—160° (1·62 g.). From fraction (*b*) was isolated the 2 : 4-*dinitrophenylhydrazone* of 3*a* : 4 : 5 : 6-tetrahydroperinaphthan-1-one as deep red plates (from xylene), m. p. 243—244° (decomp.) (Found: C, 62·5; H, 4·8; N, 14·9. $C_{19}H_{18}O_4N_4$ requires C, 62·3; H, 5·0; N, 15·3%). No pure material could be isolated by attempted dehydrogenation of (*b*) with sulphur or 30% palladium–charcoal.

1 : 2 : 3 : 4-*Tetrahydro*-7-*methyl*-1-*naphthol and* 1 : 2-*Dihydro*-6-*methylnaphthalene.*—The alcohol was prepared by adding 7-methyl-1-tetralone (10 g.) in ether (100 ml.) to a gently refluxing solution of lithium aluminium hydride (1·0 g.) in ether (100 ml.) during 20 min. After ethyl acetate (1 ml.) had been added, the product was worked up in the usual way. Crystallisation of a portion from hexane gave long colourless needles of the *alcohol*, m. p. 52—53° (Found: C, 81·0; H, 8·7. $C_{11}H_{14}O$ requires C, 81·4; H, 8·7%).

The remaining material was heated with potassium hydrogen sulphate (1 g.) at 160° for ½ hr. After addition of water, the *hydrocarbon* was isolated with ether. It was finally distilled (at 0·07 mm.) from potassium hydrogen sulphate (1 g.) and then redistilled (*ca.* 6 g.), having b. p. 48°/0·05 mm., n_D^{14} 1·5752 (Found: C, 91·7; H, 8·3. $C_{11}H_{12}$ requires C, 91·6; H, 8·4%), $\lambda_{max.}$ 265 (3·95), 303 (3·02), $\lambda_{min.}$ 238 (3·47), 299 mμ (2·93).

Authentic 1 : 2 : 3 : 4-tetrahydro-6-methylnaphthalene had n_D^{14} 1·5388 and $\lambda_{max.}$ 271 (2·87), 280 (2·94), $\lambda_{min.}$ 240 (1·68), 277 mμ (2·65).

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