515. *Acenaphthene Series. Part VII.* The Three Isomeric* tert.-*Butylacenaphthenes. Migration of* tert.-*Butyl Groups and Disproportionation. Preparation and Orientation of* 1 : 3 : 6-*Tri*-tert.-*butylacenaphthene.*

By Eric Illingworth and Arnold T. Peters.

Migration of the *tert.*-butyl group occurred when 1- or 3-*tert.*-butylacenaphthene was treated with aluminium chloride in carbon disulphide at 46°; the products were 2-*tert.*-butyl- and 2 : 5-di-*tert.*-butyl-acenaphthene and acenaphthene. In similar manner, 1 : 6-di-*tert.*-butylacenaphthene afforded 2 : 5-di-*tert.*-butylacenaphthene.

Mechanisms of normal and abnormal orientation in Friedel–Crafts reactions in this series are postulated.

1 : 5-Di-*tert.*-butyl- and 1 : 3 : 6-tri-*tert.*-butyl-acenaphthene were prepared and orientated.

Effect of Aluminium Chloride on the Three Isomeric tert.-*Butylacenaphthenes.*—It has been shown (Part V *) that, when aluminium chloride is used as catalyst in the *tert.*-butylation of acenaphthene, the products are abnormally orientated but that when ferric chloride is employed normal orientation results.

In this investigation, 1-, 2-, and 3-*tert.*-butylacenaphthene were individually treated with finely ground aluminium chloride in carbon disulphide for 40 minutes. Small amounts of hydrogen chloride were evolved, and the products in each case were 2 : 5-di-*tert.*-butylacenaphthene and acenaphthene, with some 2-*tert.*-butylacenaphthene in the experiments with 1- and 3-*tert.*-butylacenaphthene. The 2 : 5-di-*tert.*-butylacenaphthene and acenaphthene were probably present in equimolecular proportions; on the assumption that

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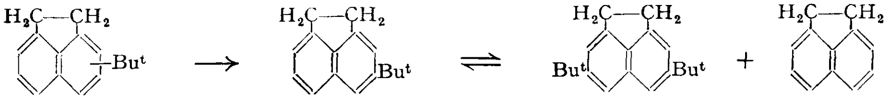
* Parts V and VI, *J.*, 1951, 1602 and 2508.

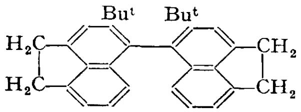
*iso*butene and tri-*tert.*-butylacenaphthene were not formed to any great extent, the reaction can be formulated as :



Thus, the aluminium chloride-catalysed migration of the *tert.*-butyl group gave not only the abnormally orientated 2-mono-*tert.*-butyl derivative, but also caused a considerable amount of disproportionation, to give the abnormally orientated 2 : 5-disubstituted compound. Under similar conditions, 1 : 6-di-*tert.*-butylacenaphthene and aluminium chloride gave 30% of 2 : 5-di-*tert.*-butylacenaphthene. Smith and Perry (*J. Amer. Chem. Soc.*, 1939, **61**, 1411) showed that in presence of aluminium chloride 4-*tert.*-butyl-*m*-xylene was converted into the 5-*tert.*-butyl isomer.

Effect of Ferric Chloride on the Three Isomeric tert.*-Butylacenaphthenes.*—1-, 2-, and 3-*tert.*-Butylacenaphthene were treated with ferric chloride in boiling carbon disulphide for 3 hours. In each experiment, the reaction mixture was deeply coloured, but no migration of the *tert.*-butyl group could be detected, and no acenaphthene or di-*tert.*-butylacenaphthene was isolated; 1-, 2-, and 3-*tert.*-butylacenaphthene were recovered in 78, 76, and 56% yield, respectively. Some loss was attributed to formation of yellow resin and to other reactions such as dehydrogenation.

Although ferric chloride caused no group migration, a small amount of hydrogen chloride was evolved, and after distillation of the mono-*tert.*-butylacenaphthene under reduced pressure a high-boiling residue remained, which set to a yellow glass. This residue, in the experiment with 2-*tert.*-butylacenaphthene, was crystallised from ethyl acetate to give a cream-coloured solid, m. p. 230—232°, b. p. 260°/8 mm., with a blue fluorescence in ethyl acetate. Molecular-weight determination and analysis suggest that the compound was formed by the condensation of two molecules of 2-*tert.*-butylacenaphthene by the elimination of two atoms of hydrogen, to give 2 : 2′-di-*tert.*-butyl-3 : 3′-diacenaphthyl.



A similar product, m. p. 229—230°, was obtained from 1-*tert.*-butylacenaphthene, but on admixture with the foregoing compound it melted at 190°.

Thus there is little doubt that the high-boiling products obtained by the action of ferric chloride on the three isomeric *tert.*-butylacenaphthenes are isomeric di-*tert.*-butyldiacenaphthyls.

Low-temperature tert.*-Butylation of Acenaphthene in Presence of Aluminium Chloride.*—Conditions of alkylation of acenaphthene can be made less vigorous, not only by substituting ferric chloride for aluminium chloride, but also by a reduction in reaction temperature. For example, Smith and Perry (*loc. cit.*) quote an analogous case with 4-*n*-propyl-*m*-xylene, which is unaffected by aluminium chloride at 15°, whereas at 100° conversion into 5-*iso*propyl-*m*-xylene occurs readily (cf. Nightingale and Carton, *J. Amer. Chem. Soc.*, 1940, **62**, 280).

tert.-Butylation of acenaphthene was therefore carried out at −10° to −5°, with aluminium chloride as catalyst; the low temperature was maintained until the reaction product had been completely separated from the aluminium chloride. The resulting mixture was fractionated as described in Part V and the mono-*tert.*-butylacenaphthene fraction gave 2-*tert.*-butylacenaphthene as the main product; from the more soluble fractions, 1-*tert.*-butylacenaphthene was isolated. The mixed isomers were not separable completely by crystallisation, and the remaining residue was oxidised by chromic acid in boiling acetic acid to the *tert.*-butylnaphthalic anhydrides; these were separated by refluxing their alcoholic solution with concentrated aqueous ammonia; under these conditions 3- and 4-*tert.*-butylnaphthalic anhydride readily form the corresponding imide, whereas the 2-isomer is unchanged. 3-*tert.*-Butylnaphthalimide and 2-*tert.*-butylnaphthalic anhydride were thus isolated; no 4-*tert.*-butyl derivative was found. Thus, the original mono-*tert.*-butylacenaphthene was a mixture of the 1- and the 2-isomer.

The di-*tert.*-butylacenaphthene fraction yielded a new di-*tert.*-butylacenaphthene, m. p. 86—87° (from alcohol), raised to 97·5—98° (from acetic acid); this gave a picrate and a *s*-trinitrobenzene complex. It is most probably the 1 : 5-derivative (see below). Some 1 : 6-di-*tert.*-butylacenaphthene, m. p. 135—136·5°, was obtained from the more soluble fractions.

Thus, when the *tert.*-butylation of acenaphthene is carried out at −10° to −5°, even in presence of aluminium chloride, the conditions are sufficiently mild to allow a certain amount of normally orientated products to be isolated.

Orientation of 1 : 5-*Di*-tert.-*butylacenaphthene.*—The above-mentioned di-*tert.*-butylacenaphthene, m. p. 97·5—98°, is accompanied by some 1-*tert.*-butylacenaphthene, but no 3-isomer. As it is unlikely that two *tert.*-butyl groups will enter positions *ortho* to each other, and as the new di-*tert.*-butyl derivative differs from the 1 : 6- and the 2 : 5-isomer, there is little doubt that it is 1 : 5-di-*tert.*-butylacenaphthene. This is supported by preparation of the same compound from 2-*tert.*-butylacenaphthene at 10—15° in presence of anhydrous ferric chloride: as no migration of the 2-*tert.*-butyl group could have taken place under these conditions, and as substitution in the 1-position is favoured at 10—15° (see Part V) when ferric chloride is the catalyst, it is almost certain that the 1 : 5-derivative would be formed.

When 1-, 2-, or 3-*tert.*-butylacenaphthene is refluxed at atmospheric pressure for 8 hours, no isomerisation occurs, and the starting material is recovered.

Explanation of Migration Reactions.—The orientation of the products from Friedel–Crafts alkylations is dependent on many factors, the most important being (i) identity of the catalyst, (ii) quantity of catalyst, (iii) temperature of reaction, (iv) duration of reaction, (v) activity of alkylating agent, (vi) activity of the aromatic nucleus being substituted, and (vii) identity of the solvent; other factors, such as the rate of stirring (Francis, *Chem. Reviews*, 1948, **43**, 257) influence the reaction less.

The normal orientating effect of the alkyl group is *ortho-para*, but in many cases it is so weak, in view of the lability of the group, that it is readily superseded by the effect of thermodynamic stability. Hence, in a reaction where the alkyl group is cleaved from the nucleus, the proportions of isomers formed will approximate to those obtained at thermodynamic equilibrium, and any divergencies from the equilibrium composition will be those due to the directive influence, indicating that the time or temperature allowed for the reaction was not vigorous enough to give the equilibrium mixture.

When aluminium chloride was used as catalyst at 46° in the condensation of *tert.*-butyl chloride and acenaphthene, 2-*tert.*-butyl- and 2 : 5-di-*tert.*-butyl-acenaphthene were formed mainly, if not solely. As aluminium chloride can readily cleave the *tert.*-butyl group from the acenaphthene nucleus under the conditions of the reaction, it appears that the products substituted in the *m*-position are most stable and are formed at the expense of the less stable *o*- and *p*-isomers (*o*-, *m*-, and *p*- relative to $-CH_2-$).

When the conditions of reaction were made less vigorous by carrying out the reaction at −10° to −5°, a certain amount of normally orientated products, *viz.*, 1-*tert.*-butyl- and 1 : 6-di-*tert.*-butyl-acenaphthene, was formed, although the mono-*tert.*-butyl fraction still consisted largely of the 2-isomer. The 1 : 5-isomer was partly normally and partly abnormally orientated. Therefore, under milder conditions, as was expected, when the products of reaction were not able to reach thermodynamic equilibrium so quickly, the amount of abnormal *m*-substitution was decreased.

The absence of the 3-isomer, although the 1-isomer is present, may be attributed to either or both of the following factors: (i) In presence of ferric chloride, the proportion of 1-*tert.*-butylacenaphthene increased from 50 to 80% at the expense of the 3-isomer as the temperature of alkylation of acenaphthene was reduced from 46° to 10—15°. Thus, at −10°, it is to be expected that the *tert.*-butyl group will be even more likely to enter the 1-position. (ii) At the low temperature, the 3-isomer may not be stable enough to exist in presence of aluminium chloride, whereas the 1-isomer may be more stable and not be completely isomerised by the aluminium chloride. In this connexion, Norris and Vaala (*J. Amer. Chem. Soc.*, 1939, **61**, 2131) showed that *o*-xylene is more stable to aluminium chloride than the *m*- or the *p*-isomer.

On the other hand, when ferric chloride was used as catalyst in the *tert.*-butylation of acenaphthene, only the normally orientated products were obtained, *viz.*, *o*- and *p*- to the $-CH_2 \cdot CH_2-$ bridge; as ferric chloride does not cleave the *tert.*-butyl group from the nucleus, the products originally formed are also the final products of reaction.

1 : 3 : 6-*Tri-*tert.*-butylacenaphthene.*—*tert.*-Butylation of acenaphthene, with *tert.*-butyl chloride and ferric chloride in carbon disulphide, gave 1- and 3-*tert.*-butyl- and 1 : 6-di-*tert.*-butyl-acenaphthene (Part V); careful distillation of the higher-boiling fractions at 0·6 mm. has now afforded a tri-*tert.*-butylacenaphthene, m. p. 133·5—134°, b. p. 210—220°/0·6 mm., 390—400°/758 mm. If the products of reaction are distilled at 1 atmosphere, the di- and tri-*tert.*-butylacenaphthene are not separated, as crystallisation gives di-*tert.*-butylacenaphthene and an uncrystallisable resin.

The same tri-*tert.*-butylacenaphthene was also prepared by further *tert.*-butylation of 1- or 3-*tert.*-butyl- or 1 : 6-di-*tert.*-butyl-acenaphthene with *tert.*-butyl chloride and ferric chloride. Under the conditions employed, ferric chloride has been shown not to cause migration of the *tert.*-butyl group, and the only tri-substituted derivative which would be formed from all the above compounds is the 1 : 3 : 6-isomer. This indeed is the derivative which would be expected from *tert.*-butylation of the parent acenaphthene in presence of ferric chloride.

EXPERIMENTAL

Micro-analyses were carried out by Drs. Weiler and Strauss, of Oxford.

Effect of Aluminium Chloride on tert.*-Butylacenaphthenes.*—(*a*) 1-*tert.*-Butylacenaphthene (5 g.), anhydrous aluminium chloride (0·6 g.), and dry carbon disulphide (50 c.c.) were refluxed for 40 minutes. After filtration and removal of solvent, the residue afforded 2 : 5-di-*tert.*-butylacenaphthene (0·7 g.), which crystallised from absolute alcohol in colourless needles, m. p. and mixed m. p. 162—163°; the alcoholic mother-liquors were treated with picric acid to yield orange solids, m. p. 159—161°, and m. p. 118—121°, which on hydrolysis yielded, respectively, acenaphthene (0·4 g.), m. p. and mixed m. p. 96°, and 2-*tert.*-butylacenaphthene (0·5 g.), m. p. and mixed m. p. 87—88°.

(*b*) 2-*tert.*-Butylacenaphthene (5 g.) in similar manner gave a small amount of aluminium chloride complex and a carbon disulphide filtrate; decomposition of the complex with dilute hydrochloric acid gave a solid which on extraction with carbon disulphide, removal of solvent, and crystallisation from alcohol furnished colourless needles of 2 : 5-di-*tert.*-butylacenaphthene (0·3 g.), m. p. and mixed m. p. 162—163°. The original carbon disulphide filtrate afforded a further amount of the same di-*tert.*-butyl derivative (0·4 g.), and conversion of the more soluble fractions into picrates yielded orange-red needles (0·5 g.), m. p. and mixed m. p. with acenaphthene picrate, 160—161°; no starting material was recovered.

(*c*) 3-*tert.*-Butylacenaphthene (5 g.) similarly afforded 2 : 5-di-*tert.*-butylacenaphthene (0·8 g.), 2-*tert.*-butylacenaphthene (0·3 g.), and acenaphthene (as picrate. 0·4 g., m. p. 160—161°).

(*d*) 1 : 6-Di-*tert.*-butylacenaphthene (5 g.), treated as above, gave 2 : 5-di-*tert.*-butylacenaphthene (1·4 g.), m. p. and mixed m. p. 162—163°, and an unidentified mixture.

Effect of Ferric Chloride on tert.*-Butylacenaphthenes.*—(*a*) Anhydrous ferric chloride (2·2 g.) was added to 1-*tert.*-butylacenaphthene (10 g.) in boiling dry carbon disulphide (30 c.c.) and the mixture refluxed for 3 hours. 1-*tert.*-Butylacenaphthene (7·8 g.), b. p. 144°/2 mm., m. p. and mixed m. p. 65—66°, was recovered, together with a high-boiling resin, which on repeated treatment with ethyl acetate afforded minute pale yellow prisms (0·4 g.), m. p. 229—230° (Found: C, 90·0; H, 7·9. $C_{32}H_{34}$ requires C, 91·9; H, 8·1%), which show a strong blue fluorescence in ultra-violet light; it is possibly 1 : 1′-*di-*tert.*-butyldiacenaphthyl*, by analogy with the 2 : 2′-derivative.

(*b*) 2-*tert.*-Butylacenaphthene (10 g.), treated as in (*a*), afforded a fraction (7·6 g.), b. p. 165°/8 mm., m. p. and mixed m. p. with 2-*tert.*-butylacenaphthene, 87—88°, and cream-coloured needles (0·5 g.), m. p. 230—232° (from ethyl acetate), unchanged in m. p. on repeated crystallisation [Found: C, 91·0; H, 8·1%; *M* (Rast), 433. $C_{32}H_{34}$ requires C, 91·9; H, 8·1%; *M*, 418), and showing a strong blue fluorescence in ultra-violet light in ethyl acetate. This product is probably 2 : 2′-*di-*tert.*-butyl-*3 : 3′-*diacenaphthyl.*

(*c*) 3-*tert.*-Butylacenaphthene (10 g.) and ferric chloride, as above, gave 5·6 g. of unchanged product, m. p. and mixed m. p. 101—102°, and a high-boiling resin which was not further investigated.

tert.*-Butylation of Acenaphthene at* −10° *to* 15°, *with Aluminium Chloride as Catalyst.*—

Throughout the reaction and during removal of the catalyst, the temperature was maintained at $-10°$ to $-5°$. Acenaphthene (308 g., 1 mol.), dissolved in dry carbon disulphide (750 c.c.) at room temperature, was cooled to $-10°$, and anhydrous aluminium chloride (54 g., 0·2 mol.) was added at such a rate (during 1 hour) as to keep the temperature below $-5°$. After a further 4 hours' stirring, the mixture was filtered and the solvent removed from the filtrate; fractionation gave (i) 71 g., b. p. 274°, (ii) 12·5 g., b. p. 277—318°, (iii) 130 g., b. p. 318—320°, and (iv) 80 g., b. p. *ca.* 360°. Fraction (i) was acenaphthene, (ii) was a mixture of (i) and (iii); fraction (iii) comprised mixed mono-*tert.*-butylacenaphthenes, which were fractionally crystallised from methanol, to give (*a*) 26 g. of 2-*tert.*-butylacenaphthene, colourless plates, m. p. 90° (not depressed on admixture with a specimen of m. p. 88—88·5°, recorded by Nursten and Peters, *J.*, 1950, 729), (*b*) 9·5 g. of the more soluble 1-*tert.*-butylacenaphthene, colourless plates, m. p. and mixed m. p. 65—66°, and (*c*) 64 g. of a mixture (*M*), m. p. 46—54° (Found: C, 91·3; H, 8·7. Calc. for $C_{16}H_{18}$: C, 91·4; H, 8·6%), containing 1- and 2-*tert.*-butylacenaphthene (see below). Fraction (iv) was a viscous liquid, which flowed at *ca.* 60° and afforded 15·5 g. of colourless prismatic needles (from alcohol), m. p. 86—87°, unchanged in m. p. on crystallising from alcohol; after crystallising from acetic acid three times, and then from methanol, it gave similar crystals, m. p. 97·5—98° (Found: C, 90·3; H, 9·8. $C_{20}H_{26}$ requires C, 90·2; H, 9·8%). This product is almost certainly 1 : 5-*di*-tert.-*butylacenaphthene*. The original alcoholic mother-liquors from (iv), after separation of the 1 : 5-isomer, yielded 8·2 g. of 1 : 6-di-*tert.*-butylacenaphthene, colourless prismatic needles, m. p. 135—136·5° (mixed m. p. with above product, m. p. 97·5—98°, was 70—75°).

1 : 5-Di-*tert.*-butylacenaphthene gave a *picrate*, scarlet needles (from absolute alcohol), m. p. 113—114° (Found: C, 63·6; H, 6·0; N, 8·5. $C_{20}H_{26},C_6H_3O_7N_3$ requires C, 63·0; H, 5·9; N, 8·5%), and a s-*trinitrobenzene* complex, orange needles (from alcohol), m. p. 132—133° (Found: C, 64·9; H, 6·1; N, 9·3. $C_{20}H_{26},C_6H_3O_6N_3$ requires C, 65·1; H, 5·85; N, 8·8%).

Oxidation of Mixture (*M*).—The above mixture (*M*) (15 g.) was heated under reflux with sodium dichromate (45 g.) and acetic acid (400 c.c.) for 5 hours, and then added to water; the collected solid was extracted with boiling 5% aqueous sodium carbonate (three successive extractions), and the alkaline extracts were acidified, to give a colourless solid (12 g.), m. p. 145—146°, comprising mixed butylnaphthalic anhydrides. This was dissolved in alcohol and boiled with excess of aqueous ammonia (*d* 0·88) for 1 hour, further aqueous ammonia being added at intervals; from the boiling solution crystals separated which were shown to be 3-*tert.*-butylnaphthalimide, colourless prismatic needles (from alcohol), m. p. and mixed m. p. 254—256°. The alkaline filtrate from this product was then acidified to give, after crystallisation of the resulting precipitate from acetic acid, colourless needles, m. p. and mixed m. p. 162—163°, of 2-*tert.*-butylnaphthalic anhydride. Thus the mixture (*M*) contained 1- and 2-*tert.*-butylacenaphthene.

tert.-*Butylation of* 2-tert.-*Butylacenaphthene.*—Anhydrous ferric chloride (2·2 g.) was added to a stirred solution of 2-*tert.*-butylacenaphthene (10 g., 1 mol.) in carbon disulphide (30 c.c.) at 10—15°, and *tert.*-butyl chloride (7·3 c.c., 1·3 mols.) was added during 5 minutes. After 5 hours at 10—15°, the mixture was filtered, washed, dried, and distilled, to give (i) 4·5 g., b. p 120—150°/0·7 mm., and (ii) 4 g., b. p. 150—165°/0·7 mm.; fraction (i) contains much unchanged material, but fraction (ii) was crystallised from alcohol, to yield colourless needles, m. p. 86—87°, which on crystallisation from acetic acid gave similar needles, m. p. 97·5—98°, identical with the 1 : 5-di-*tert.*-butylacenaphthene prepared above.

x-*Bromo*-1-tert.-*butylacenaphthene.*—Bromine (1·3 c.c.; 1·1 mols.) in dry chloroform (60 c.c.) was added to 1-*tert.*-butylacenaphthene (6 g.) in dry chloroform (60 c.c.), and the mixture was left at room temperature for 1 hour; hydrogen bromide was evolved and the solution became deep yellow. Concentration to 40 c.c., followed by addition of absolute alcohol (50 c.c.), gave an oil, which afforded colourless prisms (from absolute alcohol) (4·2 g., 51%), m. p. 89·5—90·5°, of the *monobromo*-derivative (Found: Br, 27·3. $C_{16}H_{17}Br$ requires Br, 27·7%).

x-*Bromo*-1 : 6-*di*-tert.-*butylacenaphthene.*—In similar manner, 1 : 6-di-*tert.*-butylacenaphthene (5 g.) and bromine (1·2 c.c.) gave colourless prisms, m. p. 138—139° (from alcohol) (4·5 g., 82%) (Found: Br, 23·4. $C_{20}H_{25}Br$ requires Br, 23·2%), of the *monobromo*-derivative, together with a small amount (0·5 g., 9%) of an *isomer*, more soluble long colourless needles, m. p. 212—213° (Found: Br, 22·6%). No dibromo-derivative was isolable even when 2—3 mols. of bromine were used, the products again being the above two isomers.

1 : 3 : 6-*Tri*-tert.-*butylacenaphthene.*—(*a*) In the *tert.*-butylation of acenaphthene with ferric chloride in boiling carbon disulphide (Part V), a fraction, b. p. 210—220°/0·6 mm., was obtained, which set to a yellow glass. Repeated crystallisation from alcohol gave almost colourless plates, m. p. 133·5—134°, b. p. *ca.* 390°, of 1 : 3 : 6-*tri*-tert.-*butylacenaphthene* (Found: C, 89·3;

H, 10·7. $C_{24}H_{34}$ requires C, 89·4; H, 10·6%). The m. p. 135—136·5°, of 1 : 6-di-*tert*.-butylacenaphthene, was depressed to 115—118°. The new hydrocarbon does not form a picrate in dry alcohol.

(*b*) Ferric chloride (2·2 g.) was added to 1-*tert*.-butylacenaphthene (5 g., 1 mol.) in boiling carbon disulphide (30 c.c.), *tert*.-butyl chloride (6·5 c.c., 2·5 mols.) was introduced slowly, and the mixture was boiled for 1 hour. In the usual way, fractions, 4·6 g. of b. p. 180—208°/0·6 mm. (mixture) and 5·1 g. of b. p. 208—216°/0·6 mm., were obtained. The latter fraction crystallised from alcohol, to yield almost colourless plates of 1 : 3 : 6-tri-*tert*.-butylacenaphthene, m. p. and mixed m. p. with the product from (*a*) 133·5—134°.

(*c*) 3-*tert*.-Butylacenaphthene (5 g.) similarly afforded a fraction, b. p. 212—220°/0·6 mm., and thence 3·4 g. of pure 1 : 3 : 6-tri-*tert*.-butylacenaphthene, m. p. 133·5—134°.

(*d*) 1 : 6-Di-*tert*.-butylacenaphthene (20 g., 1 mol.), *tert*.-butyl chloride (15 c.c., 1·4 mols.), and ferric chloride (4·2 g.) in boiling carbon disulphide afforded a fraction, b. p. 180—185°/0·3 mm. (17·3 g.), and thence 1 : 3 : 6-tri-*tert*.-butylacenaphthene (13·8 g.), m. p. 133·5—134°.

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