671. *Synthesis of Fluoranthenes. Part III. Cyclisation of Arylbutadienes. Syntheses of* 1 : 3-*Dimethyl- and of* 1 : 2 : 3-*Trimethylnaphthalene.*

By S. Horwood Tucker, (Miss) Margaret Whalley, and (in part) James Forrest.

Phenylbutadienes have been cyclised by means of hydrogen bromide and stannic chloride. The products have been converted, by dehydrogenation–demethylation, into 1 : 3-dimethylnaphthalene. This and 1 : 2 : 3-trimethylnaphthalene can be synthesised from the condensation product of benzyl methyl ketone and cyanoacetic ester. 1 : 2 : 3-Trimethylnaphthalene has been synthesised from hemimellitene.

Michael addition products from benzyl cyanide and of mesityl oxide and ethylideneacetone have been isolated.

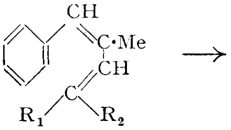
The following work describes new and improved methods for synthesing methylated naphthalenes which were required for use in synthesis of methylated fluoranthenes (Forrest and Tucker, *J.*, 1948, 1137; Tucker and Whalley, this vol., pp. 50, 632).

1 : 3-Dimethylnaphthalene has already been synthesised from *m*-xylene and succinic anhydride (Krollpfeiffer and Schäfer, *Ber.*, 1923, **56**, 620; Barnett and Sanders, *J.*, 1933, 434; Heilbron and Wilkinson, *J.*, 1930, 2539; Ruzicka and Ehmann, *Helv. Chim. Acta*, 1932, **15**, 140).

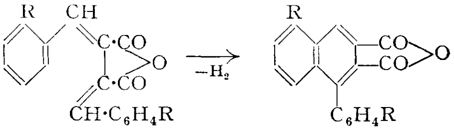
The same method when applied to hemimellitene (1 : 2 : 3-trimethylbenzene) gave 1 : 2 : 3-trimethylnaphthalene (low overall yield). We assume that hemimellitene condenses with succinic anhydride to give β-(2 : 3 : 4-*trimethylbenzoyl*)*propionic acid* although the possibility of formation of the 3 : 4 : 5-trimethyl analogue cannot be excluded. Since the end product, 1 : 2 : 3-trimethylnaphthalene, will be the same from either isomer, no attempt was made to separate them. Reduction of the above by the Clemmensen method gave rise to γ-*hemimellitylbutyric acid*, cyclised by 80% sulphuric acid to 1-*keto*-5 : 6 : 7-*trimethyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, which was reduced to 1 : 2 : 3-*trimethyl*-5 : 6 : 7 : 8-*tetrahydronaphthalene*, dehydrogenated by selenium to 1 : 2 : 3-trimethylnaphthalene.

1 : 3-Dimethylnaphthalene can be readily prepared by cyclisation of butadiene derivatives by the method first used by Tucker and Whalley (*loc. cit.*, p. 632) in the synthesis of fluoranthene derivatives. Mesityl oxide and benzylmagnesium chloride give 1-phenyl-2 : 4 : 4-trimethylbutadiene (I; $R_1 = R_2 =$ Me) (Fellenberg, *Ber.*, 1906, **39**, 2064), cyclised by either (*a*) treatment of its benzene solution with hydrogen bromide, followed by addition of stannic chloride, to give 1 : 1 : 3-*trimethyl*-1 : 2(or 1 : 4)-*dihydronaphthalene* (II) (83% yield); or, (*b*) by boiling with hydriodic acid in glacial acetic acid, to give, presumably, 1 : 1 : 3-trimethyl-1 : 2 : 3 : 4-tetrahydronaphthalene. Of the two possible isomeric forms of the dihydronaphthalene (II), 1 : 2- is

more probable than 1 : 4-dihydro- since in the former the double bond is conjugated with the benzene ring, a mesomerically more stable configuration than that in the 1 : 4-dihydro-isomer in which the double bond is isolated. 1 : 2-Dihydronaphthalene has a higher resonance energy, *i.e.*, is more stable than 1 : 4-dihydronaphthalene (Fieser in Gilman's " Organic Chemistry," 1938, p. 94; Syrkin and Diatkina, *Acta Physicochim.* U.R.S.S., 1941, **14**, 105). The dihydronaphthalene (II), as also the corresponding tetrahydronaphthalene, underwent dehydrogenation–demethylation to give 1 : 3-dimethylnaphthalene.



(I.) (II.)



(III.) (IV.)

Similarly, ethylideneacetone reacted with benzylmagnesium chloride to give 1-*phenyl*-2 : 4-*dimethylbutadiene* (I; $R_1 = H$, $R_2 = Me$), which, by means of hydrogen bromide and stannic chloride followed by dehydrogenation, gave 1 : 3-dimethylnaphthalene (poor yield). Under this treatment 1-phenylbutadiene gave a polymer.

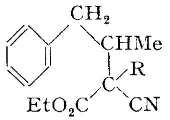
As far as we are aware, the only comparable cyclisation of a phenylated butadiene—and the resemblance is formal only—is the conversion of dibenzylidenesuccinic anhydride (III; R = H), by exposure to sunlight in presence of iodine, into 1-phenylnaphthalene-2 : 3-dicarboxylic anhydride (IV; R = H) (Stobbe, *Ber.*, 1907, **40**, 3372). Baddar, El-Assal, and Gindy (*J.*, 1948, 1270) converted, by light or heat treatment, the corresponding methoxyl derivative (III; R = OMe) into the compound (IV; R = OMe), but it will be noted that in this cyclisation a molecule of hydrogen is simultaneously eliminated (see also Baddar and El-Assal, *ibid.*, p. 1267).

In the cyclisation we are now reporting—as in the comparable diene-cyclisation of 4-fluorenylidene-2-methylpent-2-ene to 2 : 4 : 4-trimethyl-1 : 4-dihydrofluoranthene (Tucker and Whalley, *loc. cit.*)—there is no migration of methyl groups. Cyclisation of (I; $R_1 = R_2 = Me$) by means of hydriodic acid in acetic acid, followed by dehydrogenation and demethylation, gave 1 : 3-dimethylnaphthalene, but no trimethylnaphthalene was detected; although in the comparable cyclisation of the above-mentioned 4-fluorenylidene-2-methylpent-2-ene the hydriodic acid treatment gave directly 2 : 3 : 4-trimethylfluoranthene—a result paralleled in the work of Kloetzel (*J. Amer. Chem. Soc.*, 1940, **62**, 3405), who found that cyclisation of diols by means of acidic reagents (hydrogen fluoride, sulphuric acid, and even 85% phosphoric acid) gave rise to the expected *gem*-dimethylnaphthalene derivatives and simultaneously to the corresponding trimethylnaphthalenes produced by migration of a methyl group from the *gem*-dimethyl grouping to an adjoining unmethylated carbon atom. Kloetzel also found that heating 1 : 1 : 4-trimethyl-1 : 2 : 3 : 4-tetrahydronaphthalene with sulphur or selenium effected dehydrogenation and removal of methyl of the *gem*-dimethyl grouping to give 1 : 4-dimethylnaphthalene—a result corresponding to our synthesis of 1 : 3-dimethylnaphthalene. Jitkow and Bogert (*J. Amer. Chem. Soc.*, 1941, **63**, 1979) demethylated analogous compounds to 1 : 3-dimethylnaphthalene (cf. also Ruzicka and Rudolph, *Helv. Chim. Acta*, 1927, **10**, 918).

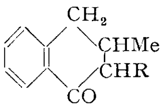
The preparation of benzylmagnesium chloride has been considered troublesome (Houben, *Ber.*, 1903, **36**, 3084; Hell, *ibid.*, 1904, **37**, 455; cf. Klages, *ibid.*, 1904, **37**, 1449; 1905, **38**, 2220, footnote 5). Hilpert and Grüttner (*Ber.*, 1914, **47**, 178) indicated that dibenzyl is produced if the reagents are pure: in comparable reactions they recommend incompletely dried ether and non-activated magnesium (see also Brown and Jones, *J.*, 1946, 781). There certainly is a definite tendency towards dibenzyl formation, more marked still with *p*-alkoxy-derivatives of benzyl chloride (Van Campen, Meisner, and Parmerter, *J. Amer. Chem. Soc.*, 1948, **70**, 2296). Gilman, Zoellner, and Dickey (*ibid.*, 1929, **51**, 1576, 1583; *Rec. Trav. chim.*, 1935, **54**, 584) found that, by using six equivalents of ether, benzylmagnesium chloride could be obtained in 93% yield (see also Austin and J. R. Johnson, *J. Amer. Chem. Soc.*, 1932, **54**, 647). We find that by using *pure* reagents, and no magnesium activator, slightly opalescent solutions containing >90% yields of benzylmagnesium chloride can be obtained (cf. Cusa and Kipping, *J. Soc. Chem. Ind.*, 1934, **53**, 213).

Another method of synthesis of 1 : 3-dimethylnaphthalene, which can be adapted for the synthesis of 1 : 2 : 3-trimethylnaphthalene, was suggested by the work of Cope (*J. Amer. Chem. Soc.*, 1941, **63**, 3452), who condensed benzyl methyl ketone with ethyl cyanoacetate to give ethyl (1-benzylethylidene)cyanoacetate which by hydrogenation gave ethyl α-cyano-β-benzylbutyrate

(V; R = H). Cope's method of simultaneous condensation and hydrogenation (*ibid.*, 1944, **66**, 886) gave a lower yield. Hydrolysis of (V; R = H) with a mixture of aqueous sulphuric and acetic acids, and decarboxylation to give β-benzylbutyric acid, followed by cyclisation, yielded 1-keto-3-methyl-1 : 2 : 3 : 4-tetrahydronaphthalene (VI, R = H). The Grignard reaction on (VI; R = H) of methylmagnesium iodide gave 1-*hydroxy*-1 : 3-*dimethyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene* (VII; R = H). In this preparation excess of Grignard reagent had to be used: when theoretical quantities of reactants were used the 3-methyltetralone (VI, R = H) was recovered unchanged. Dehydration and dehydrogenation gave 1 : 3-dimethylnaphthalene.



(V.)



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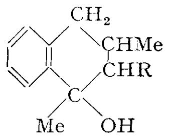

(VII.)

The synthesis of 1 : 2 : 3-trimethylnaphthalene has been accomplished from (V; R = H) by treatment with sodium ethoxide and methyl iodide (2 mols.) to give *ethyl* α-*cyano*-β-*benzyl*-α-*methylbutyrate* (V; R = Me). Hydrolysis and cyclisation, as above, led to 1-*keto*-2 : 3-*dimethyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene* (VI; R = Me) which, by the action of methylmagnesium iodide, gave 1-hydroxy-1 : 2 : 3-trimethyl-1 : 2 : 3 : 4-tetrahydronaphthalene (VII; R = Me), with accompanying dehydration product. The mixture on dehydrogenation by selenium gave 1 : 2 : 3-trimethylnaphthalene.

Attempts were made to prepare 1 : 3-dimethylnaphthalene from the condensation product of benzyl cyanide and mesityl oxide, *viz.*, 4-*keto*-1-*phenyl*-2 : 2-*dimethylamyl cyanide*, but it could not be cyclised. Benzyl cyanide and ethylideneacetone gave the corresponding 4-*keto*-1-*phenyl*-2-*methylamyl cyanide*: it likewise failed to cyclise. Ethyl phenylacetate did not react with mesityl oxide. This investigation is being continued.

EXPERIMENTAL.

1 : 3-Dimethylnaphthalene was synthesised by Barnett and Sanders's method (*loc. cit.*) with slight improvements. β-(2 : 4-Dimethylbenzoyl)propionic acid was prepared in the usual way from *m*-xylene (11·7 g., 0·11 g.-mol.), succinic anhydride (10 g., 0·1 g.-mol.), and aluminium chloride (30 g., 0·28 g.-mol.) in *s*-tetrachloroethane (36 ml.) and crystallised from benzene; m. p. 111—112° (lit. 114°) (84%). γ-(2 : 4-Dimethylphenyl)butyric acid was prepared by boiling the above acid (20·6 g.), lightly amalgamated zinc (65 g.), concentrated hydrochloric acid (240 ml.), and glacial acetic acid (100 g.) under reflux for 6 hours. The acid was crystallised from petroleum (b. p. 60—80°), m. p. 74° (lit. 77°) (18 g., 93%).

1-Keto-5 : 7-dimethyl-1 : 2 : 3 : 4-tetrahydronaphthalene was prepared by keeping γ-(2 : 4-dimethylphenyl)butyric acid (2·4 g.), phosphorus pentachloride (2·9 g.), and benzene (12 ml.) at room temperature for 15 minutes and then on the boiling water-bath for 30 minutes, adding this mixture to a cold solution of stannic chloride (3 ml.) in benzene (3 ml.), and leaving the whole for 15 minutes. Working up in the usual way gave, after distillation (b. p. 164°/10 mm.) and freezing, 1-keto-5 : 7-dimethyl-1 : 2 : 3 : 4-tetrahydronaphthalene (1·35 g., 62%), m. p. 46°. It gave a 2 : 4-*dinitrophenylhydrazone* in dark scarlet prisms from methylene dichloride; m. p. 270—271° (decomp.) (Found: C, 60·8; H, 5·0; N, 15·7. $C_{18}H_{18}O_4N_4$ requires C, 61·0; H, 5·1; N, 15·8%).

5 : 7-Dimethyl-1 : 2 : 3 : 4-tetrahydronaphthalene was prepared from the keto-compound by reduction as given above for β-(2 : 4-dimethylbenzoyl)propionic acid (yield 75%; in absence of acetic acid, 50%). It was dehydrogenated by heating with sulphur at $\not>$220° for 3 hours to give 1 : 3-dimethylnaphthalene (60%), b. p. 125—135°/10 mm. (Jitkow and Bogert, *loc. cit.*, give 126—142°/10 mm.; Herzenberg and Ruhemann, *Ber.*, 1927, **60**, 889, give 121—126°/10 mm.). It afforded a picrate, m. p. 115—117° (Barnett and Sanders, *loc. cit.*, give m. p. 118°), and a *s*-trinitrobenzene complex.

[With JAMES FORREST.] 1 : 2 : 3-*Trimethylnaphthalene from Hemimellitene*.—β-(2 : 3 : 4-*Trimethylbenzoyl*)*propionic acid*. Hemimellitene (17 g.) and succinic anhydride (17 g.) in chlorobenzene were treated with aluminium chloride (54 g.). After standing overnight the complex was treated with ice and hydrochloric acid (and ether, 10 ml.). The organic layer was washed as usual, sodium carbonate added, the chlorobenzene removed in steam, and the aqueous residue acidified to give β-(2 : 3 : 4-*trimethylbenzoyl*)*propionic acid*, which crystallised from benzene–petroleum (b. p. 60—80°) in needles, m. p. 142—145° (10·5 g., 30%) (Found: C, 70·8; H, 7·5. $C_{13}H_{16}O_3$ requires C, 70·9; H, 7·3%).

γ-(2 : 3 : 4-*Trimethylphenyl*)*butyric Acid*.—The above acid (10·5 g.) was heated for 7 hours with zinc (80 g.) in concentrated hydrochloric acid and acetic acid (2 : 1 by vol.; 450 ml.), the solution being saturated at intervals with hydrogen chloride. The *butyric acid* crystallised from petroleum (b. p. 60—80°) in rhombs, m. p. 95° (7 g., 80%) (Found: C, 75·6; H, 8·7. $C_{13}H_{18}O_2$ requires C, 75·7; H, 8·7%).

1-*Keto*-5 : 6 : 7-*trimethyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*. The above acid (7 g.) was heated with 80% sulphuric acid (83 ml.) on the boiling water-bath, with frequent shaking, for 15 hours, the mixture poured into water and extracted with chloroform, and unchanged acid recovered by shaking the chloroform extract with sodium carbonate solution. After removal of chloroform the residue solidified, and the *ketone* crystallised from methanol in pale yellow rhombs, m. p. 52—53° (4·5 g., 70%) (Found: C, 82·8; H, 8·7. $C_{13}H_{16}O$ requires C, 83·0; H, 8·5%). The 2 : 4-*dinitrophenylhydrazone* was obtained as dark orange crystals (from anisole), m. p. ~210° (Found : C, 61·7; H, 5·2; N, 15·3. $C_{19}H_{20}O_4N_4$ requires C, 61·9; H, 5·4; N, 15·2%).

5 : 6 : 7-Trimethyl-1 : 2 : 3 : 4-tetrahydronaphthalene was obtained from the above keto-compound (4·5 g.) (Clemmensen method, as above) as an oil, b. p. 135—137°/11 mm. (2·3 g., 55%).

1 : 2 : 3-*Trimethylnaphthalene.* 5 : 6 : 7-Trimethyl-1 : 2 : 3 : 4-tetrahydronaphthalene (2·3 g.) was heated with selenium (2·05 g.) at 300° for 3 hours. 1 : 2 : 3-Trimethylnaphthalene (0·8 g., 35%) was obtained, b. p. 155—160°/10 mm. The picrate, styphnate, and *s*-trinitrobenzene complex corresponded in properties with those reported in the literature.

Synthesis of 1 : 3-*Dimethylnaphthalene from* 1-*Phenyl*-2 : 4 : 4-*trimethylbutadiene* (I; $R_1 = R_2 =$ Me).—Benzylmagnesium chloride was prepared in the usual way from *pure* magnesium (24 g., 1 atom), benzyl chloride (126·5 g., 1 mol.), and ether (622 ml., 6 mols.). The benzyl chloride was prepared by saturating commercial benzyl chloride with dry hydrogen chloride, washing with water, drying ($CaCl_2$), and distilling twice in vacuum. The ether was purified by shaking with a small amount of alkaline silver nitrate solution for 10 minutes (Werner, *Analyst*, 1933, **58**, 335), washing with water, drying ($CaCl_2$), distilling, drying over sodium wire, distilling, and preserving in filled bottles containing a copper wire reaching to the top. It was distilled from phosphoric oxide before use. With these reagents there was no need to activate the magnesium (by iodine or other means) and the solution of benzylmagnesium chloride obtained was clear of black particles and only faintly opalescent. Estimation by Gilman's method showed that the yield of reagent was >90%.

1-*Phenyl*-2 : 4 : 4-*trimethylbutadiene* (I; $R_1 = R_2 =$ Me). Mesityl oxide (32·6 g.) was added to the benzylmagnesium chloride solution with stirring and at such a rate that the mixture boiled gently. After boiling for 10 minutes longer, the cooled mixture was treated with hydrochloric acid (1 : 1) and washed with water in the usual way, then, without drying, the whole was distilled. After ether and dissolved water had passed over, the residual carbinol decomposed to give the required diene, which distilled at 235—250°/765 mm.; redistillation in vacuum gave 1-phenyl-2 : 4 : 4-trimethylbutadiene, b. p. 116—118°/10 mm. (39·5 g.; 70% calculated on benzyl chloride), n_D^{18} 1·555 (Found : C, 90·6; H, 9·1. Calc. for $C_{13}H_{16}$: C, 90·7; H, 9·3%). It gave a scarlet solution when added to a yellow solution of 2 : 4 : 7-trinitrofluorenone in xylene, but no stable complex could be isolated. It did not give an addition product with maleic anhydride. Oxidation with sodium dichromate in dilute sulphuric acid solution gave benzoic acid. It could not be hydrogenated in presence of Raney nickel, but in presence of palladium–charcoal (5%) (Cheronis and Levin, *J. Chem. Educ.*, 1944, **21**, 603) (2 g.) in ethanol (10 ml., treated with Raney nickel) the diene (1·72 g.) absorbed 432 ml. of hydrogen (theory, 448 ml.) in 5 hours, after which absorption ceased. The isolated 2 : 4-*dimethyl*-1-*amylbenzene* (4-*amyl*-m-*xylene*) has b. p. 105°/10 mm. (Found : C, 88·7; H, 11·3. $C_{13}H_{20}$ requires C, 88·6; H, 11·4%), n_D^{23} 1·488.

Cyclisation of 1-*phenyl*-2 : 4 : 4-*trimethylbutadiene* (I; $R_1 = R_2 =$ Me) *to* 1 : 1 : 3-*trimethyl*-1 : 2(or 1 : 4)-*dihydronaphthalene* (II). (*a*) 1-Phenyl-2 : 4 : 4-trimethylbutadiene (I; $R_1 = R_2 =$ Me) (8·6 g.) in sodium-dried benzene (20 ml.) containing phenyl-β-naphthylamine (0·01 g.) (Grummitt and Becker, *J. Amer. Chem. Soc.*, 1948, **70**, 149) was cooled in ice–salt and saturated with hydrogen bromide (from tetralin and bromine and passed over red phosphorus and phosphoric anhydride) in *ca.* 20 minutes : the gas was passed for another 20 minutes. Then cooled stannic chloride (6 ml.) in benzene (10 ml.) was added in portions, and the black-red solution left for 2·5 hours in the freezing mixture and finally for 0·5 hour at room temperature. The liquid was treated with concentrated hydrochloric acid (and ether) several times, then with 5% sodium hydroxide solution, and washed thoroughly with water. The pale yellow liquid when heated under atmospheric pressure evolved much hydrogen bromide and gave 1 : 1 : 3-*trimethyl*-1 : 2(or 1 : 4)-*dihydronaphthalene* (II), which distilled at 235—240°/ 760 mm.; it was redistilled, b. p. 116—120°/11 mm. (7·15 g., 83%); n_D^{18} 1·551 (Found : C, 90·5; H, 9·4. $C_{13}H_{16}$ requires C, 90·7; H, 9·3%). It gave a deep red coloration when mixed with an acetic acid solution of 2 : 4 : 7-trinitrofluorenone. Hydrogenation of 1 : 1 : 3-trimethyl-1 : 2-dihydronaphthalene (II) (1·72 g.) in presence of 5% palladium–charcoal (224 ml. of hydrogen absorbed, *i.e.*, theoretical for one double bond) gave rise to 1 : 1 : 3-*trimethyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, b. p. 116°/10 mm., n_D^{23} 1·515 (Found : C, 89·5; H, 10·3. $C_{13}H_{18}$ requires C, 89·6; H, 10·4%). It gave no colour change when mixed with an acetic acid solution of 2 : 4 : 7-trinitrofluorenone.

(*b*) 1-Phenyl-2 : 4 : 4-trimethylbutadiene (I; $R_1 = R_2 =$ Me) (10 g.) was boiled under reflux with a solution of hydriodic acid (*d* 1·70; 8 ml.) in glacial acetic acid (25 ml.) for 10 hours. The mixture was treated with sulphurous acid and extracted with ether. Distillation gave a colourless oil which, after being heated with sulphur at 220°, gave 1 : 3-dimethylnaphthalene (0·9 g.; 10%).

Dehydrogenation–demethylation of 1 : 1 : 3-*trimethyl*-1 : 2(*or* 1 : 4)-*dihydronaphthalene* (II). The naphthalene (II) (6·88 g.) was boiled with selenium (3·16 g.) for 12 hours. The liquid was distilled, then distilled from copper, and heated in benzene with sodium for 3 hours. Distillation gave 1 : 3-dimethylnaphthalene, b. p. 125—135°/10 mm. (3·2 g., 51%) (overall yield from benzyl chloride, 30%). With 2 : 4 : 7-trinitrofluorenone it gave a *complex*, orange-red prisms, which, after repeated recrystallisation from ethyl acetate, had m. p. 142—145° (Found : C, 58·1; H, 3·0; N, 10·6. $C_{12}H_{12},2C_{13}H_5O_7N_3$ requires C, 58·0; H, 2·8; N, 10·7%).

1 : 3-*Dimethylnaphthalene from* 1-*Phenyl*-2 : 4-*dimethylbutadiene.*—An ethereal solution of benzylmagnesium chloride (containing $\frac{1}{6}$ g.-mol. of the reagent, prepared from benzyl chloride, 22·1 g.; magnesium, 4·25 g.; and ether, 100 ml.) was treated with ethylideneacetone (14 g., $\frac{1}{6}$ g.-mol.), and the mixture left overnight. After the usual treatment 1-*phenyl*-2 : 4-*dimethylbutadiene*, b. p. 110—115°/20 mm. (13·7 g., 48%), was isolated (Found : C, 91·1; H, 8·6. $C_{12}H_{14}$ requires C, 91·1; H, 8·9%). Cyclisation, followed by dehydrogenation by selenium (at 300°), gave a small amount of 1 : 3-dimethylnaphthalene, identified as its *s*-trinitrobenzene complex.

Synthesis of 1 : 3-*Dimethylnaphthalene from Benzyl Methyl Ketone and Ethyl Cyanoacetate.—Ethyl* (1-*benzylethylidene*)*cyanoacetate.* Benzyl methyl ketone (Newman and Booth, *J. Amer. Chem. Soc.*, 1945, **67**, 154) (2 : 4-*dinitrophenylhydrazone*, orange needles from ethyl acetate, m. p. 150—152°. Found : C, 57·5; H, 4·6; N, 17·75. $C_{15}H_{14}O_4N_4$ requires C, 57·3; H, 4·5; N, 17·8%) was condensed with ethyl cyanoacetate in presence of glacial acetic acid, ammonium acetate, and benzene (Cope, 1941, *loc. cit.*), the water produced being removed in a separator (Dean and Stark, *Ind. Eng. Chem.*, 1920, **12**, 456) containing a long-legged funnel which forced condensed benzene and water to run to the bottom of the separator.

Replacement, in the above, of acetic acid and acetate by trichloroacetic acid and ammonium trichloroacetate reduced the reaction time but did not improve the yield (73%).

Ethyl α-cyano-β-benzylbutyrate (V; R = H). Ethyl (1-benzylethylidene)cyanoacetate (18 g.) was hydrogenated in ethanol by use of palladium–strontium carbonate (Polgar and Robinson, *J.*, 1945, 393) or of palladium–charcoal (Cheronis and Levin, *loc. cit.*). The oil obtained, after filtration of catalyst and evaporation of ethanol, was washed with dilute hydrochloric acid (to remove traces of amine produced by reduction of the cyano-group), extracted with benzene, and distilled to give *ethyl α-cyano-β-benzylbutyrate* (V; R = H), b. p. 168—170°/7 mm. (14·8 g., 82%) (Found: C, 72·9; H, 7·2; N, 6·3. $C_{14}H_{17}O_2N$ requires C, 72·7; H, 7·4; N, 6·1%). Simultaneous condensation and hydrogenation effected by shaking benzyl methyl ketone (13·4 g.), ethyl cyanoacetate (11·3 g.), ammonium acetate (0·8 g.), glacial acetic acid (2 g.), ethanol (25 ml.), and palladium–charcoal (1 g.) with hydrogen until the theoretical volume had been absorbed (25 hours) gave a greatly reduced yield (7·0 g., 30%).

β-Benzylbutyric acid (V; H for R, CN, and Et). Ethyl α-cyano-β-benzylbutyrate (10 g.), glacial acetic acid (20 ml.), concentrated sulphuric acid (10 ml.), and water (10 ml.) were heated under reflux together (7 hours). Dilution with water, extraction with carbon tetrachloride, and distillation gave β-benzylbutyric acid, a pale yellow oil, b. p. 275—277° (7·1 g.; 84%) (Found: C, 74·3; H, 7·7. Calc. for $C_{11}H_{14}O_2$: C, 74·2; H, 7·9%).

1-*Keto*-3-*methyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene* (VI; R = H). Phosphorus pentachloride (11·2 g.) was added in portions to a solution of β-benzylbutyric acid (8 g.) in dry benzene (80 ml.). After standing for 1 hour at room temperature, the mixture was heated on a steam-bath for 5 minutes, cooled in a freezing mixture, and a solution of anhydrous stannic chloride (12·4 g.) in benzene (12·4 ml.) added rapidly with swirling; an orange-red complex separated. After standing for 15 minutes in ice-water, the mixture was decomposed by a mixture of hydrochloric acid (40 ml.), ice, and ether (5 ml.). The benzene layer was washed with dilute acid, water, and then with 5% sodium hydroxide solution, and again with water. Distillation gave 1-keto-3-methyl-1 : 2 : 3 : 4-tetrahydronaphthalene (VI; R = H) (6·8 g., 94%). The 2 : 4-dinitrophenylhydrazone crystallised from benzene in scarlet needles, m. p. 241—242° (Found: C, 60·1; H, 4·5. Calc. for $C_{17}H_{16}O_4N_4$: C, 60·0; H, 4·7%). Its semicarbazone crystallised from methanol in salmon-brown, rectangular plates, m. p. 179—188° (Found: C, 66·1; H, 6·8; N, 19·4. Calc. for $C_{12}H_{15}ON_3$: C, 66·4; H, 6·9; N, 19·4%) (Jones and Ramage, *J.*, 1938, 1857, give 242° and 189°, respectively, for these two derivatives, cf. Weygand and Schröder, *Ber.*, 1941, **74**, 1848).

1-*Hydroxy*-1 : 3-*dimethyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene* (VII; R = H). An ethereal solution of methylmagnesium iodide [magnesium (6 g., 0·25 g.-atom), methyl iodide (35·5 g., 0·25 g.-mol.), and ether (150 ml.)] was added slowly to a cooled solution of 1-keto-3-methyl-1 : 2 : 3 : 4-tetrahydronaphthalene (10 g., 0·06 g.-mol.) in ether (10 ml.). After standing overnight, the mixture was decomposed with ammonium chloride solution, and the ethereal layer separated. Distillation gave 1-*hydroxy*-1 : 3-*dimethyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene* (VII; R = H), a pale yellow liquid, b. p. 103—105°/0·9 mm. (7·25 g., 66%) (Found: C, 82·0; H, 8·8. $C_{12}H_{16}O$ requires C, 81·8; H, 9·1%).

1 : 3-*Dimethylnaphthalene.* The above carbinol (VII; R = H) (9·0 g.) and anhydrous potassium hydrogen sulphate (9·0 g.) were heated at 150° till no more water collected in the upper part of the tube (3 hours). On cooling, the potassium hydrogen sulphate was removed, and the liquid product dehydrogenated (palladium–charcoal; 220—260°; 3 hours). The product was extracted with ether and 1 : 3-dimethylnaphthalene obtained (7·0 g., 86%) (picrate, m. p. 115—117°; *s*-trinitrobenzene complex, m. p. 132—134°).

Synthesis of 1 : 2 : 3-*Trimethylnaphthalene.*—*Ethyl α-cyano-β-benzyl-α-methylbutyrate* (V; R = Me). Ethyl α-cyano-β-benzylbutyrate (V, R = H) (18 g.) was slowly added to a solution of sodium ethoxide prepared from sodium (3 g.) and ethanol (63 ml.). Methyl iodide (18 g.) was then added, and the mixture heated under reflux for 2 hours. After removal of ethanol and treatment with water, an oil was obtained which after distillation, b. p. 160—162°/12 mm., consisted essentially of the *ester* (V; R = Me) (16 g., 84%). It was impure, as shown by analysis (Found: C, 75·5; H, 6·9. $C_{15}H_{19}O_2N$ requires C, 73·5; H, 7·8%).

β-Benzyl-α-methylbutyric acid (V; R = Me, H for CN and Et) was prepared by hydrolysis of the above butyrate (V; R = Me) (16 g.) with sulphuric acid (16 ml.), acetic acid (32 ml.), and water (16 ml.) by boiling for 24 hours. It was obtained as a yellow oil, b. p. 278—281°/754 mm. (12 g., 95%). A white solid separated from this oil: it proved to be an acid amide, since on treatment with sodium nitrite and 80% sulphuric acid it gave 1-keto-2 : 3-dimethyl-1 : 2 : 3 : 4-tetrahydronaphthalene.

1-*Keto*-2 : 3-*dimethyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene.* Cyclisation of β-benzyl-α-methylbutyric acid by means of phosphorus pentachloride and stannic chloride, as above, yielded this *ketone*, b. p. 155—160°/11 mm. (yield 92%) (Found: C, 82·5; H, 8·0. $C_{12}H_{14}O$ requires C, 82·8; H, 8·0%). Its 2 : 4-*dinitrophenylhydrazone* crystallised (ethyl acetate) in small red needles, m. p. 201—203° (Found: C, 60·9; H, 5·0; N, 16·0. $C_{18}H_{18}O_4N_4$ requires C, 61·0; H, 5·1; N, 15·8%).

1-*Hydroxy*-1 : 2 : 3-*trimethyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene.* The action of excess of methylmagnesium iodide on 1-keto-2 : 3-dimethyl-1 : 2 : 3 : 4-tetrahydronaphthalene (10 g.), as above, gave mainly 1-hydroxy-1 : 2 : 3-trimethyl-1 : 2 : 3 : 4-tetrahydronaphthalene, mixed with its dehydration product, as an oil, b. p. 120—125°/9 mm. (6 g.).

1 : 2 : 3-*Trimethylnaphthalene.* The above, crude 1-hydroxy-1 : 2 : 3-trimethyl-1 : 2 : 3 : 4-tetrahydronaphthalene (10 g.) was heated with selenium for 5 hours at 300°. The residue was extracted with benzene; distillation gave 1 : 2 : 3-trimethylnaphthalene (5 g., 55%) (picrate, m. p. 141—142°; styphnate, m. p. 142—144°). The s-*trinitrobenzene* complex crystallised (ethanol) in yellow needles, m. p. 154—156° (Found: N, 10·9. $C_{19}H_{17}O_6N_3$ requires N, 11·0%).

Michael Addition of Benzyl Cyanide to αβ-Unsaturated Ketones.—4-*Keto*-1-*phenyl*-2 : 2-*dimethylamyl cyanide.* Benzyl cyanide (6 g.) was added slowly with vigorous shaking to a mixture of mesityl oxide (5 g.) and benzyltrimethylammonium hydroxide (35% solution, 2 ml.). The reaction mixture was heated on the boiling water-bath for 20 minutes and then set aside for 2 hours. Dilute hydrochloric acid precipitated the *keto-cyanide*, m. p. 94—96° (ethanol) (85% yield) (Found : C, 78·0 ; H, 7·8 ; N, 6·7. $C_{14}H_{17}ON$ requires C, 78·1 ; H, 7·9 ; N, 6·5%). It gave a *semicarbazone*, m. p. 185—187°, from benzene (Found : C, 66·4 ; H, 7·4 ; N, 20·6. $C_{15}H_{20}ON_4$ requires C, 66·2 ; H, 7·3 ; N, 20·6%), also a 2 : 4-*dinitrophenylhydrazone*, m. p. 187—188°, orange prisms from benzene (Found : C, 61·0 ; H, 5·4 ; N, 17·7. $C_{20}H_{21}O_4N_5$ requires C, 60·7 ; H, 5·3 ; N, 17·7%). When the base used in the above condensation was replaced by 50% potassium hydroxide solution or by powdered potassium hydroxide (vigorous reaction), yields of condensation product were 75% and 70%, respectively. The cyanide (2 g.) was hydrolysed by heating on a boiling water-bath for 1 hour with glacial acetic acid (4 ml.), concentrated sulphuric acid (4 ml.) and water (4 ml.), and gave prisms from benzene–petroleum (b. p. 60—80°) of δ-*keto-α-phenyl-ββ-dimethylhexoic acid*, m. p. 84—86° (Found : C, 71·6 ; H, 7·6. $C_{14}H_{18}O_3$ requires C, 71·8 ; H, 7·7%). Unsuccessful attempts were made to cyclise 4-keto-1-phenyl-2 : 2-dimethylamyl cyanide by means of hydrogen bromide in a mixture of glacial acetic acid and its anhydride (cf. France, Tucker, and Forrest, *J.*, 1945, 7 ; Forrest and Tucker, *J.*, 1948, 1137) and also by means of hydriodic acid solution in glacial acetic acid.

4-*Keto*-1-*phenyl*-2-*methylamyl cyanide* was prepared (yield, 25%) from benzyl cyanide and ethylideneacetone as described for the homologous cyanide. It crystallised from ethanol, m. p. 92—94° (Found : C, 77·7 ; H, 7·6 ; N, 7·0. $C_{13}H_{15}ON$ requires C, 77·6 ; H, 7·5 ; N, 7·0%). It gave a 2 : 4-*dinitrophenylhydrazone* in light orange, feathery clusters of needles from ethyl acetate, m. p. 186—188° (Found : C, 60·0 ; H, 5·2 ; N, 18·1. $C_{19}H_{19}O_4N_5$ requires C, 59·9 ; H, 5·0 ; N, 18·4%).

Ethyl phenylacetate and mesityl oxide did not combine under the conditions above-mentioned.

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