113. *The Synthesis of Some Homologous Naphthalenes.*

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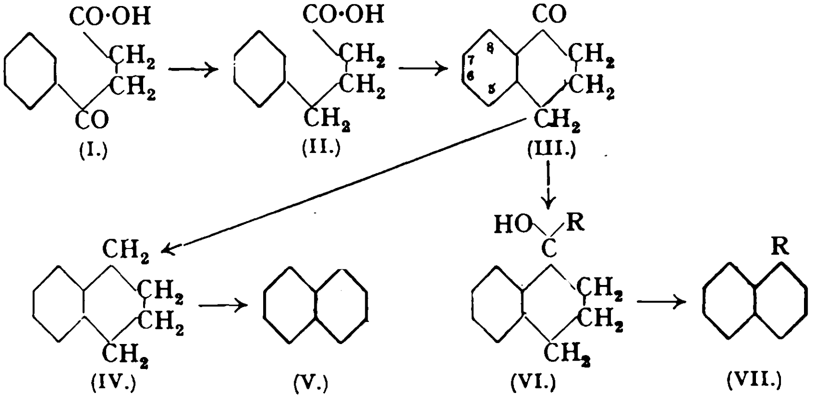
The condensation of succinic anhydride with a benzene hydrocarbon takes place easily and results in the β-aroylpropionic acid (I), from which the γ-aryl-*n*-butyric acid (II) can be obtained and cyclised to the 1-ketotetrahydronaphthalene (III). Reduction of this and subsequent dehydrogenation leads to the naphthalene hydrocarbon (V), or a new alkyl group can be introduced by the action of a Grignard reagent and the resulting carbinol (VI) submitted to simultaneous dehydration and dehydrogenation (VII).

It was by this method that Ruzicka and Ehmann (*Helv. Chim. Acta*, 1932, **15**, 140) synthesised 1 : 3 : 5-trimethylnaphthalene, and it has also been applied by Weisz and Woidich (*Monatsh.*, 1926, **46**, 453) for the preparation of 1-phenylnaphthalene. With these exceptions the method does not seem to have been employed for the preparation of homologous naphthalenes, although in many cases it affords a shorter path than the syntheses which have actually been used.

The keto-acid obtained from toluene gives a cyclic ketone (III, Me at 7), from which 1 : 7-dimethylnaphthalene was prepared by the action of methylmagnesium iodide and subsequent dehydration and dehydrogenation. This was found to agree with the description of the liquid 1 : 7-dimethylnaphthalene given by Darzens and Heinz (*Compt. rend.*, 1927, **184**, 33) but to differ widely from the solid 1 : 7-dimethylnaphthalenes of Veselý and Medvedeva (*Coll. Czech. Chem. Comm.*, 1931, **3**, 440) and of Zelinsky, Titz, and Fatejew

(*Ber.*, 1926, **59**, 2580). From the same cyclic ketone by the use of *iso*propylmagnesium bromide 7-methyl-1-*iso*propylnaphthalene was prepared and this agreed with the description given by Ruzicka and Mingazzini (*Helv. Chim. Acta*, 1922, **4**, 710) of the apocadalene obtained by them by the elimination of one of the methyl groups from cadalene. These investigators were apparently unable to synthesise this hydrocarbon and relied for orientation on its difference from 1-methyl-4-*iso*propylnaphthalene, which they synthesised and which has been synthesised recently by a shorter and more reliable method by one of us (Barnett and Cook, this vol. p. 22).



Cumene with succinic anhydride gives a keto-acid (I, Pr^{β} at 4), the orientation being proved by its oxidation to cumic acid. This by reduction and cyclisation gives a ketone, from which 1-methyl-7-*iso*propylnaphthalene (eudalene) was prepared easily. This synthesis is shorter and easier than either the method used by Ruzicka and Stoll (*Helv. Chim. Acta*, 1922, **5**, 923) or the more recent method of Darzens and Levy (*Compt. rend.*, 1932, **194**, 2056).

The reduction product of the keto-acid derived from *o*-xylene might be expected to undergo cyclisation in two directions (cf. Barnett and Marrison, *Ber.*, 1931, **64**, 535), but only one ketone was isolated, and as the yield of pure recrystallised substance was 85% any isomeride could only have been formed to a very small extent. The conversion of this ketone into 2 : 3-dimethylnaphthalene (guajen) shows that it must be 1-keto-6 : 7-dimethyl-1 : 2 : 3 : 4-tetrahydronaphthalene (III, Me at 6 and 7), the positions of the methyl groups in guajen having been established synthetically by Schroeter, Lichtenstadt, and Irineu (*Ber.*, 1918, **51**, 1587). By means of methylmagnesium iodide the cyclic ketone was converted into 1 : 6 : 7-trimethylnaphthalene, which has previously been obtained by Wilkinson (J., 1931, 1333) and by Ruzicka and Ehmann (*loc. cit.*) by very much longer syntheses. Wilkinson did not obtain sufficient for complete purification, and the product of Ruzicka and Ehmann was probably also impure, as they apparently only obtained it as a liquid, whereas in reality the hydrocarbon is a well-crystallised solid.

The cyclic ketone derived from *m*-xylene (III, Me at 5 and 7) was reduced to the dimethyltetrahydronaphthalene (Krollpfeiffer and Schäfer, *Ber.*, 1923, **56**, 620), and from this the hitherto unknown 1 : 3-dimethylnaphthalene was prepared. The conversion of the ketone into 1 : 5 : 7-trimethylnaphthalene has already been described by Heilbron and Wilkinson (J., 1930, 2537) and by Ruzicka and Ehmann (*loc. cit.*).

From *p*-xylene, 1 : 4-dimethylnaphthalene has been prepared by a shorter method than that recently employed by Darzens (*Compt. rend.*, 1930, **190**, 1562 ; cf. Robinson and Thompson, J., 1932, 2015), and the cyclic ketone has also been converted into 1 : 4 : 5-trimethylnaphthalene, here again the synthesis being very much shorter than that of Ruzicka and Ehmann (*loc. cit.*).

EXPERIMENTAL.

Keto-acids (β-*Aroylpropionic Acids*, I).—$C_2H_2Cl_4$ was found to be more suitable than the solvents (CS_2, $PhNO_2$, C_6H_6, and petroleum) employed by previous workers, but was unsuitable in the case of naphthalene. In all cases, finely powdered $AlCl_3$ (60 g.) was slowly added to succinic anhydride (20 g.; 0·2 mol.), the hydrocarbon (0·22 mol.), and $C_2H_2Cl_4$ (75 c.c.). Reaction was rapid at room temp. and was complete in 2 to 3 hr., except with *p*-xylene, when keeping over-night was necessary. The products were worked up as usual, and after being pptd. from Na_2CO_3 aq. were sufficiently pure for most purposes. Further purification was best effected from C_6H_6, with or without the addition of a little C_6H_{12}. The yields were 80—90%. The following β-benzoylpropionic acids were prepared : 4-Methyl, m. p. 129° (literature, m. p. 117°, 120°, 127°); 4-*iso*propyl, m. p. 142° (literature, m. p. 72°) (Found : C, 70·9; H, 7·4. Calc.: C, 70·9; H, 7·3%); 3 : 4-dimethyl, m. p. 129° (literature, m. p. 105°) (Found : C, 69·9; H, 6·9. Calc.: C, 69·9; H, 6·8%); 2 : 4-dimethyl, m. p. 114° (literature, m. p. 108°, 111—112°); 2 : 5-dimethyl, repeated crystn. failed to yield a product with a sharp m. p., but this was easily achieved after distillation in vac. (b. p. 215°/1 mm.), m. p. 86° (literature, m. p. 84°).

γ-Aryl-n-*butyric Acids* (II).—Contrary to statements by other workers (*e.g.*, Krollpfeiffer and Schäfer, *loc. cit.*; Borsche, *Ber.*, 1919, **52**, 2083; Mayer and Stamm, *ibid.*, 1923, **56**, 1424) reduction of the keto-acids by Clemmensen's method did not require any modification of the usual conditions, and was smoothly effected by using 2—3 parts of Zn wool. After being pptd. from Na_2CO_3 aq., the acids were sufficiently pure for cyclisation, but were easily purified from light petroleum. The yields were 70—90%. The following acids were prepared : γ-*p*-tolyl-*n*-butyric acid (II, Me at 4), m. p. 59° (literature, m. p. 59°, 60°); *γ-*p*-cumyl-*n*-butyric acid* (II, Pr^{β} at 4), m. p. 50° (Found : C, 75·7; H, 8·8. $C_{13}H_{18}O_2$ requires C, 75·7; H, 8·8%); *γ-*o*-xylyl-*n*-butyric acid* (II, Me at 3 and 4), m. p. 53° (Found : C, 74·9; H, 8·4. $C_{12}H_{16}O_2$ requires C, 75·0; H, 8·3%); γ-*m*-xylyl-*n*-butyric acid (II, Me at 2 and 4), m. p. 79° (literature, m. p. 70°, 71°, 78—79°); γ-*p*-xylyl-*n*-butyric acid (II, Me at 2 and 5), repeated recrystn. failed to yield a product with sharp m. p., but this was easily achieved by distillation in vac. (b. p. 175°/2 mm.), m. p. 70° (literature, m. p. 70°).

Cyclic Ketones (III).—Cyclisation of the above acids was effected by adding 20 g. to 100 c.c. of 80% H_2SO_4 and then heating the whole on the water-bath for 1—1½ hr. After cooling and dilution with H_2O the ketone was extracted with Et_2O, and the Et_2O solution washed with dil. NaOH aq. (which removed much colour). The ketone was purified by distillation in vac. and by recrystn. from light petroleum. The yields averaged over 70%, but the yield from the *m*-xylene product was only 30%. The following 1-keto-1 : 2 : 3 : 4-tetrahydronaphthalenes were prepared : 7-Methyl, m. p. 35° (literature, m. p. 33—35°); 7-iso*propyl*, m. p. 36° (Found : C, 83·0; H, 8·5. $C_{13}H_{16}O$ requires C, 83·0; H, 8·5%); 6 : 7-*dimethyl*, m. p. 49° (Found : C, 82·7; H, 7·8. $C_{12}H_{14}O$ requires C, 82·7; H, 8·0%); 5 : 7-dimethyl, m. p. 50° (literature, m. p. 50°); 5 : 8-*dimethyl*, m. p. 33° (Found : C, 82·7; H, 8·2. $C_{12}H_{14}O$ requires C, 82·7; H, 8·0%).

Carbinols (VI).—The cyclic ketone, dissolved in anhyd. Et_2O, was added slowly to the Grignard solution prepared from 1·25 mols. of Mg and cooled in a freezing mixture. After warming to room temp. and then boiling for 5—10 min., the solution was poured on ice and NH_4Cl. The washed and dried (Na_2SO_4) solution was evaporated, and the residue recrystallised from light petroleum or C_6H_{12} or a mixture of these. The yields were about 70%. The following 1 : 2 : 3 : 4-tetrahydro-1-naphthols were prepared : 1 : 7-*dimethyl*, m. p. 90° (Found : C, 81·7; H, 9·2. $C_{12}H_{16}O$ requires C, 81·8; H, 9·1%); 1-*methyl*-7-iso*propyl*, m. p. 83° (Found : C, 82·2; H, 9·8. $C_{14}H_{20}O$ requires C, 82·3; H, 9·8%); 7-methyl-1-*iso*propyl and 1 : 6 : 7-trimethyl, both of which could not be crystallised; 1 : 5 : 8-*trimethyl*, m. p. 136° (Found : C, 82·1; H, 9·5. $C_{13}H_{18}O$ requires C, 82·1; H, 9·5%).

Tetrahydronaphthalenes (IV).—Reduction of the cyclic ketones was effected by the usual Clemmensen method, using 5 parts of Zn wool. The products, obtained in 70—90% yield, were extracted with Et_2O and purified by distillation in vac. 6 : 7-*Dimethyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene* had b. p. 128°/7 mm. (Found : C, 90·0; H, 10·0. $C_{12}H_{16}$ requires C, 90·0; H, 10·0%), and 5 : 8-*dimethyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, b. p. 120°/1 mm. and 254°/760 mm. (Found : C, 89·8; H, 10·0%).

Dehydrogenation.—Dehydrogenation was effected with a slight excess of Se for 20—40 hr. An electrically heated air-bath was used and adjusted to give a temp. of 300° inside the reaction vessel, although the b. p. of the liquids did not permit this being reached. Dehydrogenation appeared to take place chiefly in the vapour phase, as, unless the vessel was immersed sufficiently deeply for the walls above the level of the liquid to be heated, scarcely any H_2Se was evolved. This was particularly noticeable with the dimethyltetrahydronaphthalenes (b. p. about 254°). Carbinols were heated until evolution of H_2O had ceased before the Se was added. In all cases the naphthalene hydrocarbon was isolated as its picrate and then liberated from this, after purification, by NH_3. The following naphthalenes were prepared: 1 : 3-*Dimethyl*, b. p. 107°/1 mm. (Found: C, 91·9; H, 7·8. $C_{12}H_{12}$ requires C, 92·3; H, 7·7%); *picrate*, m. p. 118° (Found: N, 11·0. $C_{12}H_{12},C_6H_3O_7N_3$ requires N, 10·9%). 1 : 4-Dimethyl, b. p. 264°/760 mm.; picrate, m. p. 144° (literature, 139—144°). 1 : 7-Dimethyl, b. p. 258°/760 mm.; picrate, m. p. 120°, unaltered by repeated crystn. (Darzens and Heinz, *loc. cit.*, give b. p. 147—149°/15 mm. and 123—124° as m. p. of the picrate). 2 : 3-Dimethyl, m. p. 104°, alone or mixed with an authentic sample, for which the authors thank Dr. J. W. Cook. 1-Methyl-7-*iso*propyl (eudalene), b. p. 281°; picrate, m. p. 95°, styphnate, m. p. 122° (literature, eudalene, b. p. 281°, picrate, m. p. 90—91°, 91·8°, styphnate, m. p. 119—120°, 119·8°). 7-Methyl-1-*iso*propyl (apocadalene), b. p. 282°; picrate, m. p. 102°, styphnate, m. p. 166° (Ruzicka and Mingazzini, *loc. cit.*, give picrate, m. p. 101—102°, styphnate, m. p. 163—164°). 1 : 4 : 5-Trimethyl, m. p. 63°; picrate, m. p. 146°, styphnate, m. p. 146° (Ruzicka and Ehmann, *loc. cit.*, give the same figures). 1 : 6 : 7-Trimethyl, m. p. 28° (from MeOH) (Found: C, 91·7; H, 8·3. Calc.: C, 91·8; H, 8·2%); picrate, m. p. 125°, styphnate, m. p. 149° (Ruzicka and Ehmann, *loc. cit.*, describe the hydrocarbon as a liquid, b. p. 138°/12 mm., the picrate, m. p. 122·5°, and the styphnate, m. p. 146°. Wilkinson, *loc. cit.*, describes the picrate, m. p. 122°, and the styphnate, m. p. 148—149°, but did not obtain the hydrocarbon pure).

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