572. *Eight- and Higher-membered Ring Compounds. Part IX.* Improved Synthesis of Coronene.*

By Wilson Baker, J. F. W. McOmie, and W. K. Warburton.

The synthesis of coronene described in Part V (*J.*, 1951, 1118) from 2 : 7-dimethylnaphthalene (III) *via* di(naphthalene-2 : 7-dimethylene) (IV) has been improved.

In Part V of this series (Baker, Glockling, and McOmie, *J.*, 1951, 1118) was described a synthesis of coronene from 2 : 7-dimethylnaphthalene (III), *via* di(naphthalene-2 : 7-dimethylene) (IV). Improvements in this synthesis are now reported.

2 : 7-Dimethylnaphthalene (III) may be prepared in five steps from toluene and methylsuccinic anhydride in 50% (reproducible) yield. The most critical stage, the formation of di(naphthalene-2 : 7-dimethylene) (IV) from 2 : 7-bisbromomethylnaphthalene, was previously brought about in 16·3% yield by reaction with sodium in dioxan, but the isolation of (IV) in the pure state was tedious owing to the necessity of hand-picking it from 1 : 2-di-(7-methyl-2-naphthyl)ethane (V) which was simultaneoulsy formed in some 4% yield. By working in more dilute solution (100 c.c. of dioxan for each 1 g. of the dibromo-compound, instead of the approximately 20 c.c. of dioxan previously employed) the yield

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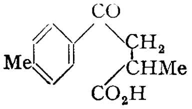
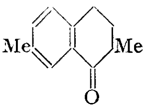
* Part VIII, *J.*, 1952, 1452.

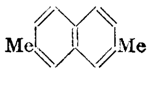
of (IV) unexpectedly fell to 4·4%, the major product being (V). A considerable improvement has now been effected in the Würtz–Fittig type reaction by adding a benzene solution of the dibromide to a solution of phenyl-lithium in ether; a 20% yield of (IV) was readily isolated, and none of the compound (V) was produced. The final yield of coronene is 5% from 2 : 7-dimethylnaphthalene in three steps, or 2·5% in eight steps from toluene. The synthesis of coronene due to Newman (*J. Amer. Chem. Soc.*, 1940, **62**, 1683) gave a 1·7% yield in six steps from 7-methyltetralone.



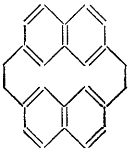
(I)



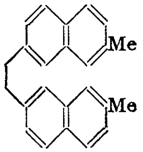
(II)



(III)



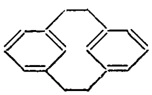
(IV)



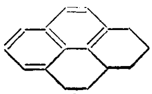
(V)

Methylsuccinic acid was prepared from methyl methacrylate by reaction with sodium cyanide and hydrolysis, and the derived anhydride was condensed with toluene to give β-*p*-toluoyl*iso*butyric acid (I), which was then reduced by Clemmensen's method to α-methyl-γ-*p*-tolylbutyric acid. Cyclisation of α-methyl-γ-*p*-tolylbutyric acid with technical fluorosulphonic acid in carbon disulphide gave 2 : 7-dimethyltetralone (II) in very high yield, and a further Clemmensen reduction followed by catalytic dehydrogenation gave 2 : 7-dimethylnaphthalene (III). The bromination of (III) with *N*-bromosuccinimide, and the final conversion of (IV) into coronene, were carried out as previously described.

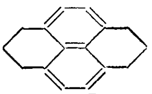
Although only indirectly concerned with the present synthesis of coronene, the opportunity may be taken to add some observations relating to the similar synthesis of pyrene from *m*-xylylene dibromide *via* di-*m*-xylylene (VI) (Part IV of this series, Baker, McOmie, and Norman, *J.*, 1951, 1114). The possibility existed that di-*m*-xylylene (rhombs, m. p. 132—133°), which is easily dehydrogenated to pyrene and isomerised by aluminium chloride to *as*-1 : 2 : 2*a* : 3 : 4 : 5-hexahydropyrene, might be identical with *s*-3 : 4 : 5 : 8 : 9 : 10-hexahydropyrene (needles, m. p. 131—133°; Cook and Hewett, *J.*, 1933, 404), but this is excluded by the fact that a mixture of the two compounds melted over the range 90—97°. Moreover *s*-hexahydropyrene gives a red-brown picrate, whilst



(VI)



(VII)



(VIII)

di-*m*-xylylene forms no picrate. We are greatly indebted to Professor J. W. Cook, F.R.S., for specimens of *s*- and *as*-hexahydropyrene.

EXPERIMENTAL

Methylsuccinic Acid and Anhydride.—This is conveniently prepared (61% yield) from commercial methyl methacrylate by reaction with sodium cyanide and subsequent hydrolysis, following the directions given in *Org. Synth.* (**26**, 54) for its preparation from ethyl crotonate. The final extraction of the methylsuccinic acid is best carried out by ethyl acetate instead of ether. The anhydride (b. p. 127—129°/30 mm.; 83% yield) was prepared from the acid by reaction with acetyl chloride (Dev and Guha, *J. Indian Chem. Soc.*, 1948, **25**, 16).

*α-Methyl-γ-*p*-tolylbutyric Acid.*—β-*p*-Toluoyl*iso*butyric acid (I) was prepared in 80—83% yield from methylsuccinic anhydride, toluene, and aluminium chloride in nitrobenzene (Dev, *J. Indian Chem. Soc.*, 1948, **25**, 69). Reduction of the keto-acid for 36 hours by the

Clemmensen–Martin method with the addition of acetic acid (5 c.c. for each 50 g. of the keto-acid) gave α-methyl-γ-*p*-tolylbutyric acid, m. p. 54—56°, b. p. 143—144·5°/0·8 mm., in 95% yield (Bailey, Bryant, Hancock, Morrell, and Smith, *J. Inst. Petroleum*, 1947, **33**, 503, record m. p. 50—51°, b. p. 150°/0·8 mm.).

2 : 7-*Dimethyltetralone* (II).—To α-methyl-γ-*p*-tolylbutyric acid (15 g.) in carbon disulphide (50 c.c.) was added during 15 minutes with vigorous stirring technical fluorosulphonic acid (13 c.c.; containing some free sulphur trioxide). The mixture was then boiled for 1 hour, cooled, and poured into ice and water, and excess of sodium carbonate added. Extraction with ether then yielded 2 : 7-dimethyltetralone (II) (13·1 g., 97%), b. p. 93—95°/0·3 mm., giving a 2 : 4-dinitrophenylhydrazone, m. p. 251° (Bailey *et al.*, *loc. cit.*, record b. p. 122°/0·5 mm.; 2 : 4-dinitrophenylhydrazone, m. p. 251°).

2 : 7-*Dimethyltetralin.*—Clemmensen–Martin reduction of the tetralone as in the case of the keto-acid (above) gave 2 : 7-dimethyltetralin, b. p. 80—84°/1 mm. (85%) (Bailey *et al.*, *loc. cit.*, record b. p. 95—110°/0·27 mm.).

2 : 7-*Dimethylnaphthalene* (III).—The dimethyltetralin was dehydrogenated in the vapour phase at 30 mm. over a charcoal catalyst containing 0·5% each of palladium and platinum. The charcoal column (1 × 35 cm.) was kept at 440°, and the dimethyltetralin introduced at the rate of 5 c.c. per hour. 2 : 7-Dimethylnaphthalene was obtained directly (86% yield), of m. p. and mixed m. p. with an authentic specimen, 95·5—96° (picrate, m. p. 135·5—136°).

Di(*naphthalene*-2 : 7-*dimethylene*) (IV).—To a stirred solution of phenyl-lithium prepared from lithium (0·70 g.) and bromobenzene (7·8 g.) in anhydrous ether (100 c.c.) was added in an atmosphere of nitrogen during 2 hours a solution of 2 : 7-bisbromomethylnaphthalene (Part V, Baker, Glockling, and McOmie, *loc. cit.*) (6·24 g.) in benzene (700 c.c.). The temperature was then raised to 60° and stirring continued for ½ hour; the mixture was cooled, water added, and the whole shaken and filtered, leaving some benzene-insoluble material (*ca.* 1 g.). The washed benzene solution was then distilled to dryness under reduced pressure, and finally heated at 150°/20 mm. for 2 hours to remove most of the bromobenzene. The solid residue was sublimed on to a cold finger, at temperatures rising to 250°/0·1 mm., and was then resublimed. After ½ hour at 120°/0·5 mm. was obtained low-melting material (0·2 g.) containing a trace of bromobenzene, followed at 220°/0·5 mm. by a solid (m. p. >180°), which after one crystallisation from benzene gave di(naphthalene-2 : 7-dimethylene) (IV) as either long, thick needles, or hexagonal plates, m. p. 235—236·5° (628 mg., 20%), identical (mixed m. p.) with the substance previously described, m. p. 237—238°.

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