875. *Cyclodehydrogenation of* o,o′-*Quaterphenyl and* 4-(*Bicyclohex*-1-*en*-2-*yl*)*biphenyl.*

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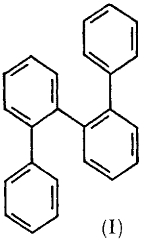
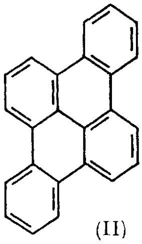
When passed over palladium–platinum–charcoal at 490°, *o,o′*-quaterphenyl was cyclodehydrogenated, giving dibenzo[*fg,op*]naphthacene, triphenylene, and 2-phenyltriphenylene. Treatment with aluminium and stannic chlorides yielded only isomerisation products. Cyclodehydrogenation of 4-(bicyclohex-1-en-2-yl)biphenyl yielded *p*-terphenyl, 2-phenyltriphenylene, and *o,p′*-quaterphenyl. A synthesis of 1-phenyltriphenylene is also described.

The cyclodehydrogenation over palladium–platinum–charcoal of *o*-terphenyl, 1-2′-biphenylyl-3,4-dihydronaphthalene, and the binaphthyls has been reported in previous papers.[1] This reaction has now been extended to the preparation of dibenzo[*fg,op*]naphthacene (II) from *o,o′*-quaterphenyl (I). Decalin was used as carrier in all these reactions. The value of this, and tetralin, in dehydrogenation was first established by Baker *et al.* in their preparation of azulene from its decahydro-derivative.[2] Its use in cyclodehydrogenation does not appear to have been reported before the present work.


(I)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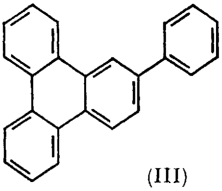
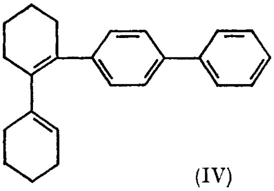

(III)


(IV)

The yield of dibenzonaphthacene now obtained (25%) represents a marked improvement over existing methods.[3] After removal of naphthalene from the crude product, extraction with light petroleum gave an insoluble fraction identified as the dibenzonaphthacene by its ultraviolet spectrum. Chromatography of the fraction soluble in petroleum separated triphenylene (33%) and a compound (7·4%) which was expected to be 1-phenyltriphenylene. The infrared spectrum of this compound showed an absorption band in the region expected for a phenyl group but its intensity was considerably lower than would be expected from an examination of the spectra of other phenyl polynuclear compounds, and hence the presence of a phenyl group could not be confirmed by this means. That this compound was not the 1-phenyl isomer was established by comparison with an authentic specimen prepared by dehydrogenation of the product formed on treating 1,2,3,4-tetrahydro-1-oxotriphenylene with phenyl-lithium. The same compound, however, was formed by the cyclodehydrogenation of 4-(bicyclohex-1-en-2-yl)-biphenyl (IV), prepared by dehydrating the product from 2-cyclohex-1′-enylcyclohexanone and 4-biphenyl-lithium. It is therefore considered to be 2-phenyltriphenylene (III).

A small amount of *o,p′*-quaterphenyl was also formed in the cyclodehydrogenation of the bicyclohexenylbiphenyl; dehydrogenation at a lower temperature with 10% palladium–charcoal in *p*-cymene gave a much improved yield (78%), thus offering an alternative synthesis to that described by Dale.[4]

Considerable breakdown of the carbon skeleton occurred in both cyclodehydrogenations,

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[1] Copeland, Dean, and McNeil, *J.*, 1960, **1687**, 1689.

[2] Baker, Warburton, and Breddy, *J.*, 1953, 4149.

[3] Sako, *Bull. Chem. Soc. Japan*, 1934, **9**, 55; Clar, *Ber.*, 1943, **76**, 609; Schubert, *Pharmazie*, 1954, **9**, 395.

[4] Dale, *Acta Chem. Scand.*, 1957, **11**, 640.

the quaterphenyl and the bicyclohexenylbiphenyl yielding triphenylene and *p*-terphenyl, respectively, by loss of a terminal phenyl or cyclohexenyl group. This, together with the apparent isomerisation of 1- to 2-phenyltriphenylene, has not been observed by us in previous work with this catalyst. The 1-phenyl isomer appears to achieve stability at the high temperature of reaction by loss of a phenyl group, isomerisation, and possibly by cyclisation. The tendency of a similar compound, 4-phenylphenanthrene, to cyclise to benzo[*e*]pyrene with palladium–charcoal at 310° has been reported by Campbell.[5] 1-Phenyltriphenylene does not form a picrate, thus resembling 4-phenylphenanthrene; [5] the 2-phenyl-isomer forms a picrate.

In an attempt to improve the yield of the dibenzonaphthacene from *o,o'*-quaterphenyl, the latter was treated with aluminium and stannic chlorides in refluxing benzene. This method, although successfully used by Clar and Zander [6] to cyclise 9,9'-biphenanthryl to dibenzo[*b,n*]perylene resulted in our case in extensive isomerisation yielding *p,p'*-, *m,m'*-, and possibly *m,p'*-quaterphenyl. The identity of the last isomer was based on elementary analysis, melting point (the melting points of the six possible isomeric quaterphenyls are known), and its infrared spectrum. The spectrum suggests the presence of a *meta*-substituted ring, but the type of substitution in the remaining ring is not easy to establish. Examination of the published spectra of a number of monosubstituted terphenyls showed that some of these containing a *para*-substituted ring absorb at a wavelength lower than, *e.g.*, the *p,p'*-isomer but at about the same wavelength as that of the one band in the spectrum of our material.

EXPERIMENTAL

Light petroleum refers to material of b. p. 60—80°.

o,o'-*Quaterphenyl*.—Reaction between 2-iodobiphenyl and copper powder gave the required compound, m. p. 118°, in 69% yield [7] (Found: C, 94·2; H, 6·0. Calc. for $C_{24}H_{18}$: C, 94·1; H, 5·9%).

Cyclodehydrogenation of o,o'-*Quaterphenyl*.—The apparatus has been described elsewhere.[1] In a typical experiment, a solution of the quaterphenyl (4 g.) in decalin (15 ml.) was passed over palladium–platinum–charcoal (25 ml.) at 490° together with hydrogen (7—8 l./hr.). The product, after removal of naphthalene in steam, was repeatedly extracted with boiling light petroleum to give an insoluble fraction, which, on crystallisation from xylene, gave dibenzo-[*fg,op*]naphthacene (0·52 g., 25%) as pale yellow cubes, m. p. 365—366° (Found: C, 95·4; H, 4·8. Calc. for $C_{24}H_{14}$: C, 95·3; H, 4·7%). No infrared spectrum was available for comparison but the ultraviolet spectrum was identical with that previously published.[8] Chromatography of the petroleum-soluble fraction on activated alumina gave unchanged quaterphenyl (1·9 g.) on elution with the same solvent. Elution with increasing amounts of benzene in light petroleum gave triphenylene (0·52 g., 33·2%), m. p. and mixed m. p. 199°, and elution with benzene yielded 2-*phenyltriphenylene* (0·15 g., 7·2%) as colourless needles (from light petroleum), m. p. 185° (Found: C, 94·5; H, 5·4. $C_{24}H_{16}$ requires C, 94·7; H, 5·3%). The *picrate* separated from benzene–light petroleum as orange needles, m. p. 164° (Found: N, 8·2. $C_{30}H_{19}N_3O_7$ requires N, 7·9%).

3,4-*Dihydro*-1-*phenyltriphenylene*.—1,2,3,4-Tetrahydro-1-oxotriphenylene,[9] m. p. 98—99° (5 g.), as a fine suspension in ether (200 ml.), was added dropwise to a solution of phenyl-lithium from lithium (0·7 g.) and bromobenzene (7 g.) in ether (70 ml.). After 4 hours' stirring under reflux the mixture was decomposed with ice and dilute acid. The ether layer was separated, washed, and dried ($MgSO_4$) and the solvent removed, leaving 3,4-*dihydro*-1-*phenyltriphenylene* which crystallised from benzene–light petroleum as colourless prisms (3·2 g., 51·4%), m. p. 196° (Found: C, 94·1; H, 6·0. $C_{24}H_{18}$ requires C, 94·1; H, 5·9%). Attempts to isolate the intermediate alcohol in this reaction failed.

1-*Phenyltriphenylene*.—A slow stream of carbon dioxide was passed through a boiling

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[5] Campbell, *J.*, 1954, 3659.
[6] Clar and Zander, *J.*, 1958, 1861.
[7] Bowden, *J.*, 1931, 1111.
[8] Wittig and Lehmann, *Chem. Ber.*, 1957, **90**, 875.
[9] Fieser and Joshel, *J. Amer. Chem. Soc.*, 1939, **61**, 2958.

mixture of the above dihydro-compound (0·5 g.), 10% palladium–charcoal (0·4 g.), and *p*-cymene (15 ml.) for 2 days. The catalyst was then removed by filtration, and the solvent by distillation. Crystallisation of the residue from ethanol gave 1-*phenyltriphenylene* (0·41 g., 82·5%) as colourless needles, m. p. 162° (Found: C, 94·5; H, 5·3. $C_{24}H_{16}$ requires C, 94·7; H, 5·3%).

4-(*Bicyclohex*-1-*en*-2-*yl*)*biphenyl*.—2-Cyclohex-1′-enylcyclohexanone [10] (b. p. 143—146°/15 mm.; 13 g.) in ether (50 ml.) was added dropwise to a solution of 4-biphenyl-lithium from lithium (1·3 g.) and 4-iodobiphenyl (15 g.) in ether (200 ml.). After 6 hours' stirring under reflux the mixture was poured on ice and dilute acid. The ethereal layer was separated, the solvent removed, and the unchanged ketone removed by distillation in steam. Treatment of the oily residue with light petroleum (b. p. 40—60°) gave a white solid (8·8 g.), m. p. 95°. Crystallisation from the same solvent gave prisms of 1-(4-*biphenylyl*)-2-(*cyclohex*-1-*enyl*)*cyclohexan*-1-*ol* (7·1 g., 40·5%), m. p. 100° (Found: C, 86·7; H, 8·6. $C_{24}H_{28}O$ requires C, 86·7; H, 8·5%).

This alcohol (5 g.) was distilled (b. p. 267—275°/10 mm.); it gave 4-(*bicyclohex*-1-*en*-2-*yl*)-*biphenyl* (4·2 g., 89%) as a colourless syrup. No suitable solvent could be found for crystallisation; it was deposited from light petroleum (b. p. 40—60°) or methanol as a white wax, m. p. ~75° (Found: C, 91·5; H, 8·4. $C_{24}H_{26}$ requires C, 91·7; H, 8·3%).

Dehydrogenation of the last hydrocarbon as previously described for 3,4-dihydro-1-phenyltriphenylene yielded *o,p*′-quaterphenyl (78%) as colourless needles (from ethanol), m. p. 118° (Found: C, 93·9; H, 6·0. Calc. for $C_{24}H_{18}$: C, 94·1; H, 5·9%). Its infrared spectrum was identical with that published.[4]

Cyclodehydrogenation of 4-(*Bicyclohex*-1-*en*-2-*yl*)*biphenyl*.—This compound (4 g.) in decalin (15 ml.) was cyclodehydrogenated as described for quaterphenyl. Fractional crystallisation of the product from benzene–light petroleum gave the following fractions: (*a*) *p*-terphenyl, plates (0·64 g., 21·8%), m. p. and mixed m. p. 210°; (*b*) 2-phenyltriphenylene, needles (0·55 g., 14·2%), m. p. and mixed m. p. with the suspected 2-isomer from quaterphenyl, 185° (the infrared spectra are identical); (*c*) an intermediate fraction (0·42 g.), m. p. 155—160°, probably consisting of the two previous compounds; (*d*) *o,p*′-quaterphenyl (0·21 g., 5·4%), m. p. and mixed m. p. 118°; and (*e*) an unidentified fraction (0·23 g.), m. p. 95—102°.

Isomerisation of o,o′-*Quaterphenyl*.—This compound (5 g.), stannic chloride (5 g.), aluminium chloride (5 g.), and benzene (50 ml.) were stirred together under reflux for 1 hr. Decomposition of the purple-black complex with 10% hydrochloric acid (200 ml.), followed by removal of the benzene in steam, gave an orange semisolid residue. This was dried and extracted with warm benzene, leaving *p,p*′-quaterphenyl (0·40 g.), crystallising from xylene as leaflets, m. p. 316—317°, mixed m. p. 318° (correct infrared spectrum). Chromatography of the benzene-soluble portion on alumina gave a solid (0·7 g.), m. p. ~70°, and a solid (1·77 g.), m. p. 163—166°, on elution with light petroleum and benzene respectively. Fractional crystallisation of the former solid from light petroleum gave (*a*) *m,m*′-quaterphenyl as white leaflets (0·35 g., 7·0%), m. p. 85—86° (Bowden [7] gives m. p. 86°) (its identity was confirmed by infrared analysis), and (*b*) *m,p*′-quaterphenyl, white plates (0·15 g.), m. p. 168° (Woods and Tucker [11] give m. p. 166°) (Found: C, 94·0; H, 6·0. Calc. for $C_{24}H_{18}$: C, 94·1; H, 5·9%). Crystallisation of the higher-melting solid from benzene–light petroleum gave more of the *m,p*′-isomer (1·44 g., total yield 32%). Elution of the column with ether yielded a further quantity of the *p,p*′-isomer (0·02 g.; total yield 8·4%).

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[10] Rapson, *J.*, 1941, 15.
[11] Woods and Tucker, *J. Amer. Chem. Soc.*, 1948, **70**, 3340.