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ISOLATION OF TETRAPHENYL-, PENTAPHENYL-, HEXAPHENYL-, AND HEPTAPHENYL-SUBSTITUTED TETRAMETHYLENECYCLOBUTANES.

STABLE TETRARADIALENES

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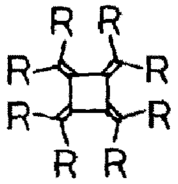
Summary: The title polyphenyl-substituted tetramethylenecyclobutanes were isolated and their propeller structures were studied by means of NMR spectra.

Tetramethylenecyclobutane (tetraradialene **1**) has been of interest for its unique π-electron system and ring strain.[1] Nevertheless, neither the parent compound (**1a**)[2] nor aryl-substituted derivative of **1a** has been isolated. As we are aware, perchloro derivative (**1b**)[3a] and three alkyl-substituted derivatives of **1a**[3b-d] have only been isolated so far. Polyphenyl-substituted derivatives of **1a**, particularly the octaphenylradialene (**1c**)[4] are interesting compounds, since phenyl groups of these might be arranged so as to form propeller. We now report isolation of the title polyphenyl-substituted radialenes and structural study of these propellers.



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a: R = H
b: R = Cl
c: R = Ph

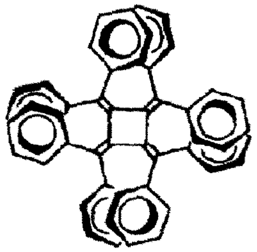
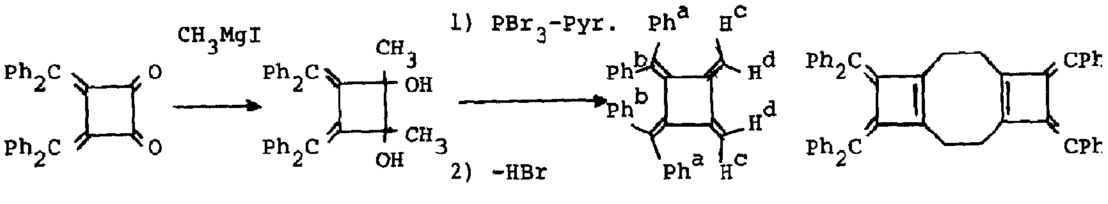


Fig. 1. An Imaginary Propeller Structure of **1c**

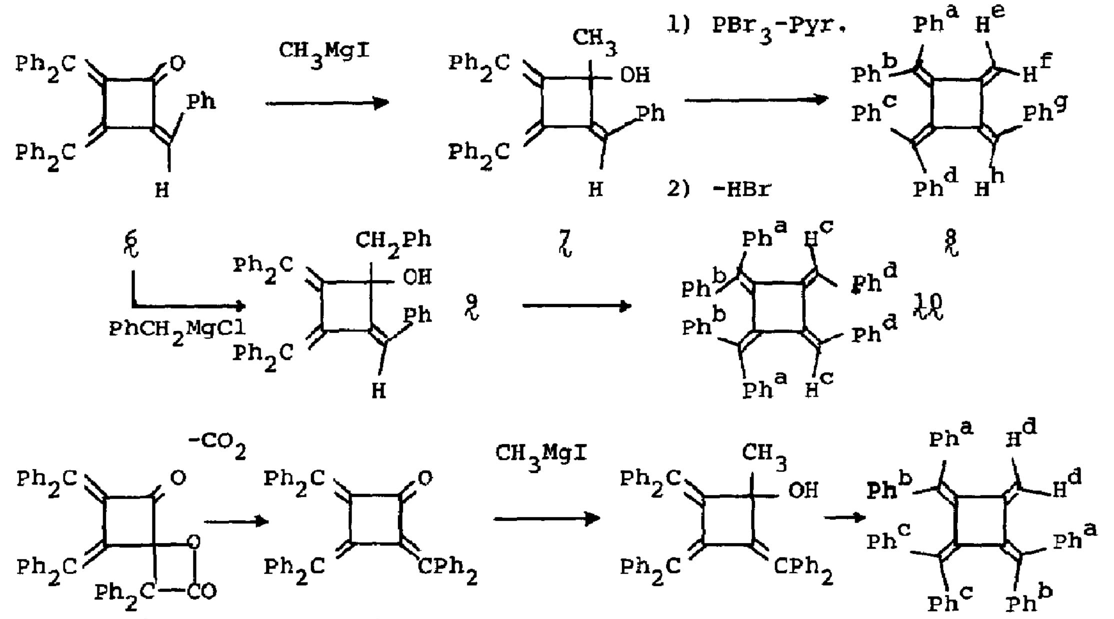


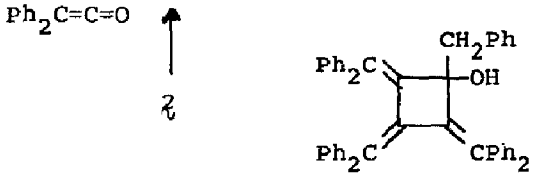
2 3 4 5

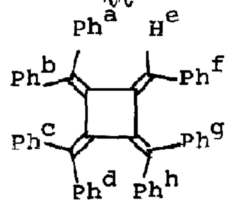
3,4-Bis(diphenylmethylene)-1,2-dimethylenecyclobutane (4) was derived fron the trans-diol (3) (mp 135 °C; 34% yield) which was obtained together with its cis-isomer (mp 187 °C; 23% yield) by the reaction of 3,4-bis(diphenylmethylene) cyclobutanedione (2)[5] with CH_3MgI. Treatment of 3 with PBr_3-pyridine in benzer at room temperature afforded 4, after purification by column chromatography on alumina, as yellow needles (11% yield); $\nu(=CH_2)$ 870 cm^{-1}; λ_{max} 262 (32600), 32C sh (9400), 405 nm (ε 5700); NMR δ 7.35 (s, Ph^a, 10H), 6.78 (s, Ph^b, 10H), 4.88 (s, H^d, 2H), 4.26 (s, H^c, 2H).[6] The radialene 4 is thermally labile and easil dimerizes by heating at 60 °C in $CHCl_3$ for 1 h to afford its dimer 5 (mp 274-27 °C; quantitative yield). The NMR spectral data of 4 clearly show that two Ph^b rings are located so that they overlap and shield each other.

Reaction of 2-(Z)-benzylidene-3,4-bis(diphenylmethylene)cyclobutanone (6)[7] with CH_3MgI gave alcohol (7) (mp 219-221 °C; 64% yield), which upon treatment with PBr_3-pyridine afforded 2-(E)-benzylidene-3,4-bis(diphenylmethylene)-1-methylenecyclobutane (8) as yellow needles (mp 190-192 °C; 49% yield); $\nu(=CH_2)$ 890 cm^{-1}; λ_{max} 280 (24800), 310 sh (18200), 350 sh (9300), 425 nm (ε 5300); NMF 7.42, 7.38, and 7.24 (each s, $Ph^{a,d,g}$, 5H), 6.85 (s, $Ph^{b,c}$, 10H), 5.85 (s, H^h, 5.12 and 4.27 (each s, $H^{e,f}$, 1H). The radialene 8 is thermally stable and can recrystallized from benzene. Reaction of 6 with $PhCH_2MgCl$ gave alcohol (9) (mɪ 191-193 °C; 19% yield), which upon treatment with PBr_3-pyridine afforded 1,2-(E dibenzylidene-3,4-bis(diphenylmethylene)cyclobutane (10) as yellow needles (mp 270-273 °C; 53% yield); λ_{max} 306 (40200), 373 (18100), 450 sh nm (ε 5400); NMR 7.44 (s, Ph^a, 10H), 7.0-6.5 (m, $Ph^{b,d}$, 20H), 5.90 (s, H^c, 2H).

Tris(diphenylmethylene)methylenecyclobutane (14), an isomeric hexaphenyl-radialene of 10, and benzylidene-tris(diphenylmethylene)cyclobutane (16) were







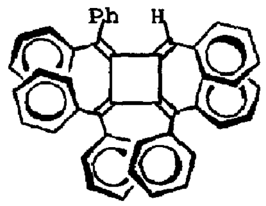


Fig. 2. An Imaginary Propeller Structure of 16

derived from tris(diphenylmethylene)cyclobutanone (12) which was prepared by the following method. Heating of 2 and diphenylketene in p-xylene under reflux for 1 h gave 12 as dark red prisms (mp 239-240 °C; 43% yield); ν(C=O) 1750 cm^{-1}; λ_{max} 402 (20000), 548 nm (ε 4800); NMR δ 7.35 (s, Ph, 10H), 6.88 (s, Ph, 20H). This reaction probably proceeds via the cycloaddition product (11). Treatment with PBr$_3$-pyridine of the alcohol (13) (mp 163-164 °C; 46% yield) obtained by the reaction of 12 with CH$_3$MgI, afforded 14 as red prisms (mp 181-183 °C; 30% yield); ν(=CH$_2$) 870 cm^{-1}; λ_{max} 284 (28300), 310 sh (24900), 340 sh (19600), 480 sh nm (ε 2800); NMR δ 7.20 (s, Ph^a, 10H), 6.82 (s, Ph^{b,c}, 20H), 4.12 (s, H^d, 2H). Similar treatment of the alcohol (15) (mp 233-235 °C; 28% yield) prepared from 12 and PhCH$_2$MgCl, afforded 16 as red prisms (mp 179-181 °C; 29% yield); λ_{max}

298 (31900), 320 sh (29000), 400 sh (13800), 490 nm (ϵ 2500); NMR δ 7.40 (s, Ph 5H), 6.92, 6.87, 6.78 (each s, Ph^{b,c,d,f,g,h}, 10H), 6.05 (s, H^{e}, 1H).

The aromatic proton signal at higher magnetic field (δ 6.85) in the NMR spectrum of **8** shows that Ph^{b} and Ph^{c} groups are located so that they overlap an shield each other. The following Ph overlappings can also be deduced from NMR spectral data, Ph^{b} and Ph^{b}, and Ph^{d} and Ph^{d} in **10**, Ph^{b} and Ph^{c} in **14**, Ph^{b} and P Ph^{d} and Ph^{h}, and Ph^{f} and Ph^{g} in **16**. The results support propeller structures o these compounds. An imaginary propeller structure of **16** is shown in Fig. 2.

Although all attempts to prepare the octaphenyltetraradialene (**1c**) failed far, further efforts are now in progress.

REFERENCES AND NOTES

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