Isolation of a Tricyclo[6,2,0,$0^{2,5}$]deca-1,3,5,7,9-pentaene

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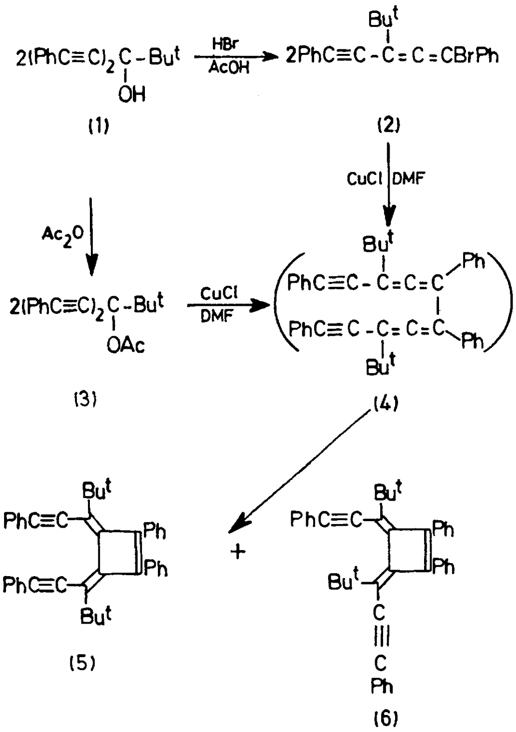
Summary The compound (**7**), containing two cyclobutadiene rings, was isolated as blue needles by heating *E,E*-1,2-diphenyl-3,4-bis(t-butylphenylethynylmethylene)cyclobut-1-ene (**5**).

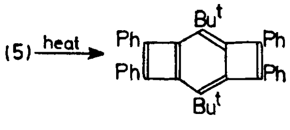
The only example of a benzocyclobutadiene which has been isolated so far is 3,4,5,6-tetramethyl-1,2-diphenylbenzocyclobutadiene.[1] We now report the isolation of the compound (**7**) which has two cyclobutadienes fused to a benzene ring.

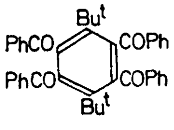
Treatment of the ethynylbromoallene (**2**), derived from the diethynyl alcohol (**1**), with CuCl in dimethylformamide (DMF) according to previously reported procedure,[2] gave *E,E*-1,2-diphenyl-3,4-bis-(t-butylphenylethynylmethylene)-cyclobut-1-ene (**5**), m.p. 243—245 °C [λ_{max} 275 (ϵ 52,900) and 297 nm (41,000); τ 2·1—2·8 (20H, m, Ph) and 8·79 (18H, s, Bu^t); *m/e* 542 (M^+, base) and 486 ($M^+ - C_4H_8$)†] and its *Z,E*-isomer (**6**), m.p. 149—151 °C [λ_{max} 280 (ϵ 30,900) and 297 nm (26,600); τ 2·1—2·8 (20H, m, Ph), 8·69 (9H, s, Bu^t), and 8·83 (9H, s, Bu^t); *m/e* 542 (M^+) and 486 ($M^+ - C_4H_8$, base)], in 18 and 29% yields respectively. Similar treatment of the acetate (**3**) gave (**5**) and (**6**) in 15 and 23% yields respectively. Both the reactions proceed *via* cyclisation of the initially formed conjugated diallene(**4**).

Heating (**5**) under reflux in *o*-xylene under N_2 atmosphere for 30 min gave (**7**) as blue needles, m.p. 296—297 °C, in almost quantitative yield, [λ_{max} 394 and 643 nm; τ 2·65 (20H, s, Ph) and 8·88 (18H, s, Bu^t); *m/e* (relative intensity) 543 ($M^+ + 1$, 53), 542 (M^+, 100), 271·5 ($M^{2+} + 1$, 12), and 271 (M^{2+}, 23)]. The appearance of the divalent ion agrees well with the structure of (**7**). Since (**7**) was very sensitive to oxygen, its melting point, u.v., and n.m.r. spectra were measured in N_2 atmosphere, and its correct molecular coefficient in the u.v. spectrum could not be obtained. A solution of (**7**) in air was immediately oxidised but in the crystalline state it was fairly stable and turned gradually into 1,2,4,5-tetrabenzoyl-2,6-di-t-butylbenzene (**8**), m.p. 246—247 °C [ν_{max} 1660 and 1640 cm^{-1} (C=O); λ_{max} 300 (ϵ 29,000), 330 sh (19,800), and 350 sh nm (9400); τ 2·5—2·9 (20H, m, Ph) and 9·20 (18H, s, Bu^t); *m/e* 606 (M^+) and 105 (PhCO)].

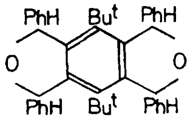
Treatment of (**8**) with NaBH$_4$ followed by HBr gave the dihydrofuran derivative (**9**) in almost quantitative yield, m.p. 173—175 °C [ν_{max} 1075 cm^{-1} (furan); λ_{max} 297 nm (ϵ 22,600); τ 2·5—3·1 (20H, m, Ph), 7·06 (4H, s, CH), and 9·32 (18H, s, Bu^t)]. Hydrogenation of (**7**) over Pd–C gave the tetrahydro derivative (**10**) in almost quantitative yield, m.p. 143 °C [λ_{max} 255 (ϵ 10,700) and 282 sh nm (7,600); τ 3·03 (20H, s, Ph), 4·84 (4H, s, CH), and 8·95 (18H, s, Bu^t). However, the configuration of (**9**) and (**10**) is not clear.



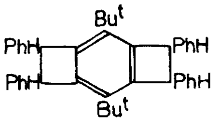




(**8**)



(**9**)



(**10**)

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† The i.r., u.v., and n.m.r. spectra were measured for Nujol mulls and solutions in $CHCl_3$ and $CDCl_3$ respectively. The mass spectra were measured with an ionisation energy of 75 eV, except for compound (**8**), 15 eV. All new compounds gave satisfactory elemental analyses.

[1] H. Straub, *Angew. Chem. Internat. Edn.*, 1974, **13**, 405.
[2] F. Toda and Y. Takehira, *Chem. Comm.*, 1975, 174.