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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); 7 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, $[\lambda_{max} 394 \text{ and } 643 \text{ nm}; \tau 2.65]$ (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 N2 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, But); m/e 606 (M+) and 105 (PhCO)].

Treatment of (8) with NaBH₄ 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 $(\epsilon 22,600); \tau 2.5-3.1$ (20H, m, Ph), 7.06 (4H, s, CH), and 9.32 (18H, s, But)]. 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.



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[†] The i.r., u.v., and n.m.r. spectra were measured for Nujol mulls and solutions in CHCl₃ and CDCl₃ 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.