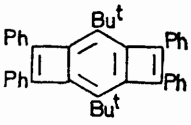
Isolation of Stable Benzocyclobutenes†

By FUMIO TODA* and NOBUYUKI DAN

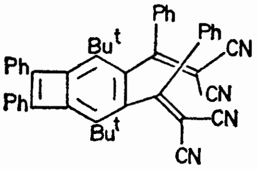
(*Department of Chemistry, Faculty of Engineering, Ehime University, Matsuyama 790, Japan*)

Summary Highly stable benzocyclobutenes (**2**), (**3**), and (**5**), and naphtho[*b*]cyclobutenes (**10**), (**11a**), and (**11b**) have been isolated.

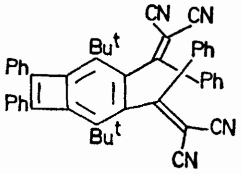
IN spite of many attempts,[1] only one benzocyclobutene[2] and two naphtho[*b*]cyclobutenes[1,3] have been isolated so far. In addition, it has been reported[2] that the former derivative (**7**), is sensitive to oxygen. We now report a new route to extremely stable benzocyclobutenes and naphtho[*b*]cyclobutenes starting from the highly reactive (**1**).[4]



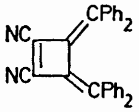
(1)



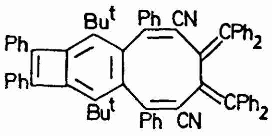
(2) *syn*



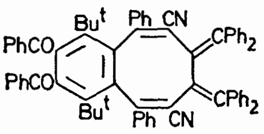
(3) *anti*



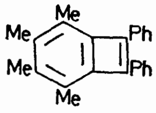
(4)



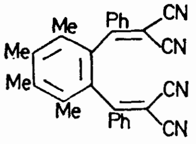
(5)



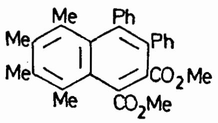
(6)



(7)

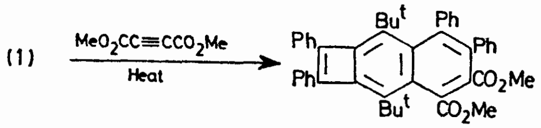


(8)

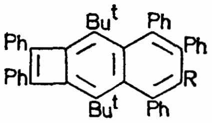


(9)

Treatment of (**1**) with an equimolar amount of tetracyanoethylene (TCNE) in *o*-xylene under N_2 for 1 h at room temperature gave *syn*-(**2**) as red prisms, in almost quantitative yield, m.p. 206–207 °C; λ_{max} 258 (ϵ 33,800), 310sh (9000), and 410 nm (1300); τ 2·68 (20H, s, Ph) and 9·06 (18H, s, Bu^t).‡ This reaction is similar to that of unisolated (**7**) with TCNE which affords the *syn*-form of (**8**).[5] Heating (**2**) under reflux in *o*-xylene for 1 h gave its *anti*-isomer (**3**) as red needles in quantitative yield, m.p. 229–231 °C; λ_{max} 266 (ϵ 38,200), 309 (31,900), and 410sh nm (2200); τ 2·61 (20H, s, Ph) and 8·94 (18H, s, Bu^t). This isomerisation is similar to that of the *syn*-form of (**8**) into its *anti*-form.[5]



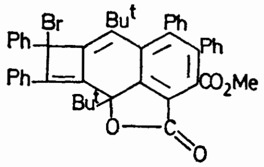
(10)



(11)

a; R = H

b; R = CN



(12)

Heating a 1 : 1 mixture of (**1**) and (**4**) under reflux in *o*-xylene under N_2 for 3 h afforded (**5**), red prisms, 55%, m.p. 280 °C; λ_{max} (ϵ 44,700), 334 (49,900), and 400sh nm (20,000); τ 2·1–2·8 (26H, m, Ph), 2·9–3·3 (14H, m, Ph), and 9·25 and 9·45 (each 9H, s, Bu^t). The two Bu^t groups are non-equivalent presumably because the molecule is unsymmetrical. Molecular models of (**5**) show that it is twisted between the two diphenylmethylene groups because of steric hindrance.

Compounds (**2**), (**3**), and (**5**) are extremely stable, not only in the crystalline state, but also in solution. This is in contrast to (**1**)[4] and (**7**),[2] which are very sensitive to oxygen. However, (**2**), (**3**), and (**5**) were easily photo-oxidised. For example, irradiation of (**5**) in benzene under O_2 gave (**6**) as yellow needles in quantitative yield, m.p. 267–269 °C; ν_{max} 1650 cm^{-1} (C=O).‡

Reaction of (**1**) with acetylene derivatives gives naphtho[*b*]cyclobutenes. Thus, heating (**1**) with an equimolar amount of dimethyl acetylenedicarboxylate under reflux in *o*-xylene under N_2 for 30 min gave (**10**), orange prisms, 67%, m.p. 244 °C; ν_{max} 1735 and 1725 cm^{-1} (ester); λ_{max} 262sh

---

† Such compounds have been incorrectly termed 'benzocyclobutadienes' in the past. According to the I.U.P.A.C. nomenclature rules, the ending 'ene' denotes the system with the maximum number of non-cumulative double bonds. The name 'benzocyclobutene' has been widely used in the past for the compound which should correctly be named 1,2-dihydrobenzocyclobutene.

‡ I.r., u.v., and n.m.r. spectra were measured for Nujol mulls and solutions in $CHCl_3$, and $CDCl_3$, respectively. All new compounds gave satisfactory elemental analyses and mass spectral data.

(ϵ 31,300), 335 (33,600), and 400 nm (5600); τ 2·79 (20H, m, Ph), 6·17 and 6·60 (3H, s, Me), and 8·83 and 9·38 (9H, s, Bu^t). This reaction is similar to that of unisolated (**7**) with dimethyl acetylenedicarboxylate to give (**9**).[6] Similar treatment of (**1**) with phenylacetylene and phenylcyanoacetylene gave (**11a**), orange-red prisms, 59%, m.p. 280 °C, and (**11b**), orange prisms, 70%, m.p. 250–251 °C, respectively.

Compounds (**2**), (**3**), (**5**), (**10**), (**11a**), or (**11b**) did not react further with TCNE, (**4**), or acetylene derivatives presumably because of steric hindrance. This assumption receives support from the following experiment. Treatment of (**10**) with Br_2 in $CHCl_3$ at room temperature gave the γ-lactone (**12**); 68%, m.p. 260 °C; ν_{max} 1770 (lactone) and 1730 cm^{-1} (ester); λ_{max} 363 (ϵ 23,700) and 382sh nm (18,500); τ 2·64 (20H, m. Ph), 6·38 (3H, s, Me), and 8·77 and 9·38 (9H, s, Bu^t), and not the normal Br_2 addition product which would be sterically difficult to form.

(*Received*, 8*th October* 1975; *Com.* 1148.)

---

[1] M. P. Cava and M. J. Mitchell, 'Cyclobutadiene and Related Compounds', Academic Press, New York, 1967.

[2] H. Straub, *Angew. Chem. Internat. Edn.*, 1974, **13**, 405.

[3] M. P. Cava, H. Firouzabadi, and M. Krieger, *J. Org. Chem.*, 1974, **39**, 480.

[4] F. Toda and M. Ohi, *J.C.S. Chem. Comm.*, 1975, 506.

[5] A. Huth, H. Straub, and E. Müller, *Tetrahedron Letters*, 1973, 2845.

[6] A. Huth, H. Straub, and E. Müller, *Annalen*, 1973, 1893.