Synthesis of 2,7-Di-*t*-butyl-4,5,9,10-tetraphenyltricyclo[6.2.0.0^{3,6}]deca-1,3(6),4,7,9-pentaene. A Benzo[1,2: 4,5]dicyclobutene[1]

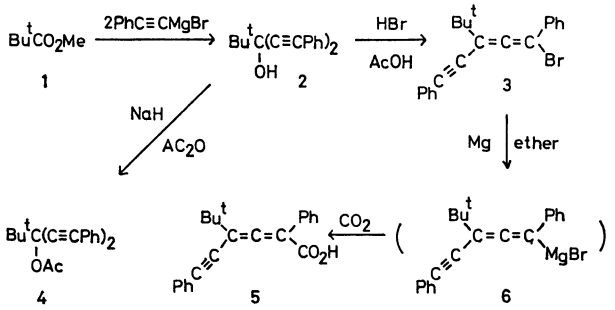
Fumio TODA and Yutaka TAKAHARA

Department of Industrial Chemistry, Faculty of Engineering, Ehime University, Matsuyama 790

(Received March 29, 1976)

The title compound (**15**) which has two cyclobutadienes fused to a benzene ring, was synthesized by heating *dl*- (**7**), *meso*-3,8-di-*t*-butyl-1,5,6,10-tetraphenyldeca-3,4,6,7-tetraene-1,9-diyne (**8**), or *E,Z*-3,4-bis(1-*t*-butyl-3-phenyl-2-propynylidene)-1,2-diphenyl-1-cyclobutene (**12**).

Benzocyclobutene has been an interesting subject in relating to antiaromatic cyclobutadiene,[2] and some derivatives of benzocyclobutadiene have been isolated.[3-5] It is, however, much more interesting to fuse an additional cyclobutadiene further to the benzene ring of benzocyclobutadiene, because the resulting carbocycle which has two antiaromatic cyclobutadienes is formally a 10π electrons system. As the first example of this carbocycle, the title compound (**15**) was prepared according to the following routes.



3-*t*-Butyl-1,5-diphenylpenta-1,4-diyn-3-ol (**2**) was prepared by the reaction of methyl pivalate (**1**) with two molar amounts of phenylethynylmagnesium bromide. The treatment of **2** with hydrobromic acid and acetic anhydride afforded 1-bromo-3-*t*-butyl-1,5-diphenylpenta-1,2-dien-4-yne (**3**) and the acetate of **2** (**4**), respectively. The reaction of **3** with magnesium in ether resulted in an ethereal solution of the Grignard reagent (**6**), which on treatment with carbon dioxide afforded 1-carboxy derivative (**5**).

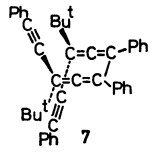
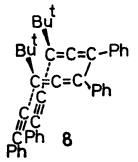
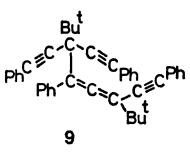
Both the treatments of **3** and **4** with CuCl in *N,N*-dimethylformamide (DMF) according to the previously-reported procedure,[6] afforded *dl*- (**7**)[7] and *meso*-3,8-di-*t*-butyl-1,5,6,10-tetraphenyldeca-3,4,6,7-tetraene-1,9-diyne (**8**), and 3,6-di-*t*-butyl-1,5,8-triphenyl-6-phenylethynylocta-3,4-diene-1,7-diyne (**9**)[7] in the yields summarized in Table 1. The treatment of an ethereal solution of **6** with CuCl also gave **7**, **8**, and **9** in the yields shown in Table 1.

In order to characterize the structure of **9**, the following reactions were carried out. The oxidation of **9** with potassium permanganate afforded 3,6-di-*t*-butyl-1,5,8-triphenyl-6-phenylethynylocta-3,4-diene-7-yne-1,3-dione (**10**). An evidence for the α-diketone structure of **10** was obtained by its sodium borohydride reduction into 3,6-di-*t*-butyl-1,5,8-triphenyl-6-phenylethynylocta-3,4-dien-7-yne-1,2-diol (**11**) which shows NMR signals of two vicinal methine protons. Furthermore, the fact that the stretching frequencies of allene of **10** (1930 cm^{-1}) are lower than those of **11** (1940 cm^{-1}), supported the structure of **10** in which a conjugation between the α-diketone and allene moieties is possible.

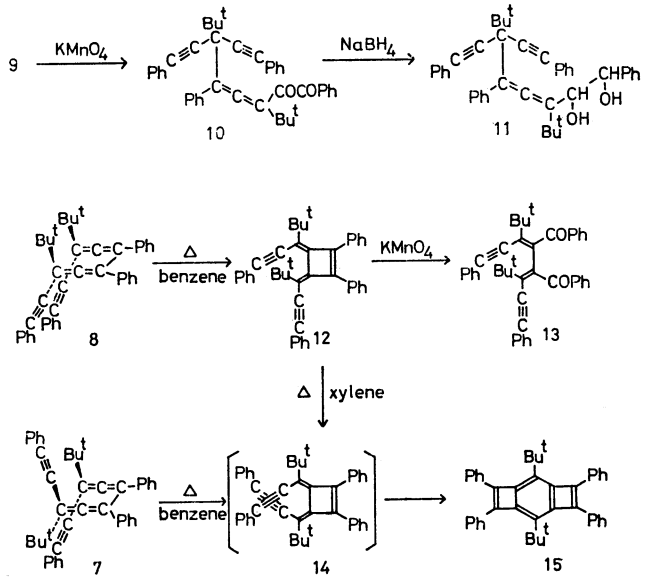
The *meso* structure of **8** was elucidated on the basis of its thermal conversion into *E,Z*-3,4-bis(1-*t*-butyl-3 phenyl-2-propynylidene)-1,2-diphenyl-1-cyclobutene (**12**). The *E,Z*-structure of **12** was determined by means of its NMR spectrum which shows two *t*-butyl signals. The *E,Z*-structure of **12** was further confirmed by its oxidation with potassium permanganate which affords thermally stable *E,Z*-4,5-dibenzoyl-3,6-di-*tert*-butyl-1,8-diphenylocta-3,5-diene-1,7-diyne (**13**).

Because it has been well established that thermal 2+2 cyclization of diallene proceeds by conrotatory manner,[8,9] the diallene (**8**) which affords *E,Z*-dimethylenecyclobutene (**12**) by heating should be *meso*-form. Finally, the another diallene (**7**) would be *dl*-form.

Table 1. Yields (%) of **7**, **8**, and **9**

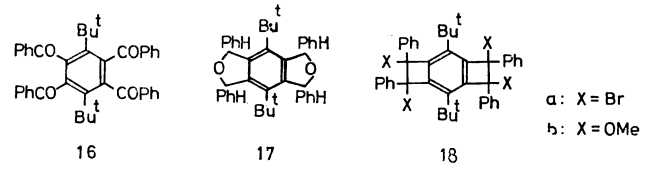
	 **7**	 **8**	 **9**
3 $\xrightarrow[DMF]{CuCl}$	11	11	54
4 $\xrightarrow[DMF]{CuCl}$	19	16	41
6 $\xrightarrow[ether]{CuCl}$	13	13	69

Heating of **7** in benzene under reflux in nitrogen atmosphere for 30 min gave the title compound (**15**) as greenish blue needles in almost quantitative yield. The UV spectrum of **15** showed the absorption bands at 394 and 643 nm. These bands at longer wavelength region are typical for benzocyclobutene derivatives.[3,4] In the mass spectrum, **15** showed a divalent ion peak at *m/e* 271. The thermal conversion of **7** into **15** presumably proceeds *via* the *E,E*-isomer of **12** (**14**) which was initially formed by a conrotatory cyclization of **7**. In the cyclization of **7**, formation of the *Z,Z*-isomer of **14** would be prohibited because of a steric repulsion between the two *t*-butyl groups. The formation of **15** by a thermal cycloaddition between the two acetylene moieties of **14** is reasonable because such cycloaddition of acetylenes has been reported.[3] Nevertheless, such the cycloaddition reaction which forms two cyclobutadienes and one benzene ring at a time has not been reported, even though this reaction is probably not a



concerted one.

The heating of **8** in *o*-xylene under reflux also afforded **15** in almost quantitative yield. This reaction probably proceeds *via* **12** and **14** successively, because the same treatment of **12** which was prepared from **8** gave **15**. Nevertheless, **12** was inert to the thermal reaction in benzene. This result shows that the conversion of the *E,Z*-geometry of **12** into the *E,E*-one can be performed in boiling *o*-xylene but not in boiling benzene.



In solution, **15** was immediately oxidized but in the crystalline state it was fairly stable and turned gradually into 2,3,5,6-tetrabenzoyl-1,4-di-*t*-butylbenzene (**16**). The treatment of **16** with sodium borohydride followed by hydrogen bromide afforded 1,7-dioxa-4,10-di-*t*-butyl-2,6,8,12-tetraphenyltricyclo[7.3.0.0^{3,11}]dodeca-3,5(9),10-triene (**17**) in almost quantitative yield. The addition of bromine to **15** afforded 4,5,9,10-tetrabromo-2,7-di-*t*-butyl-4,5,9,10-tetraphenyltricyclo[6.3.0.0^{3,6}]deca-1,3(6),7-triene (**18a**), which on treatment with methanol gave the tetramethoxy derivative (**18b**).

Experimental

All the melting points are uncorrected. The IR, UV, and NMR spectra were measured in Nujol mull, $CHCl_3$, and $CDCl_3$, respectively, unless otherwise stated. The mass spectra were measured with an ionization energy of 75 eV.

Synthesis of **2**. To an ethereal solution of ethylmagnesium bromide prepared from Mg (50 g), ethyl bromide (220 g), and ether (1 l), was added a solution of phenylacetylene (208 g) in ether (1 l) under stirring during the period of 1 h. This solution was stirred for further 2 h, and then heated under reflux for 1 h. Into this solution, was added a solution of methyl pivalate (113 g) in ether (500 ml) during the period of 1 h. The reaction mixture was heated under reflux for 2 h, decomposed with dil HCl, and then extracted with ether. The ethereal solution was washed with water and dried over anhydrous Na_2SO_4. The crude crystals left after the evaporation of the solvent were recrystallized from hexane to afford **2** as colorless needles; 196 g (71%); mp 59 °C. IR: 3540 (OH) and 2210 cm^{-1} (C≡C); NMR: 2.3—2.7 (m, Ph, 10H), 7.36 (s, OH, 1H), and 8.72 τ (s, Bu^t, 9H).

Found: C, 87.23; H, 6.75%. Calcd for $C_{21}H_{20}O$: C, 87.46; H, 6.99%.

Synthesis of **3** *and* **5**. To an ice-cooling solution of **2** (144 g) in acetic acid (140 ml), was added concd HBr (72 ml). The reaction mixture was stirred for 1 h under ice-cooling, decomposed with water, and then extracted with petroleum ether. The organic solution was washed with aqueous $NaHCO_3$ and water successively, and dried over anhydrous Na_2SO_4. The evaporation of the solvent afforded **3** as colorless oil; 160 g (91 %), which was used without further purification for all the following synthesis. IR (liquid): 1940 cm^{-1} (C=C=C).

A mixture of **3** (15 g), Mg (1 g), and ether (200 ml) was stirred under N_2 atmosphere for 1 hr, and then heated under reflux for 0.5 h. Into the ethereal solution, CO_2 was bubbled for 2 h. The reaction mixture was decomposed with dil HCl and extracted with ether. The ethereal solution was washed with water and dried over anhydrous Na_2SO_4. The crude crystals left after the evaporation of the solvent were recrystallized from petroleum ether–CCl_4 (10: 1) to afford **5** as colorless needles; 10.1 g (74%); mp 150—152 °C. IR: 1930 (C=C=C) and 1700 cm^{-1} (C=O); λ_{max} 274 nm (ε, 31600); NMR: −1.0 (s, CO_2H, 1H), 2.3—2.8 (m, Ph, 10H), and 8.80 τ (s, Bu^t, 9H).

Found: C, 83.46; H, 6.35%. Calcd for $C_{22}H_{20}O_2$: 83.51; H, 6.37%.

Synthesis of **4**. A mixture of **2** (5 g), NaH (0.44 g), and benzene (25 ml) was kept to stand at room temperature for 1 h. Into this solution, Ac_2O (1.8 g) was added, and the mixture was heated under reflux for 15 min. The crude crystals left after the evaporation of the solvent were recrystallized from hexane to afford **4** as colorless needles; 5.2 g (91%); mp 105 °C. IR: 2210 (C≡C) and 1740 cm^{-1} (C=O); λ_{max}: 254 (35300) and 279 nm (ε, 1440); NMR: 2.2—2.8 (m, Ph, 10H), 7.87 (s, Me, 3H), and 8.70 τ (s, Bu^t, 9H).

Found: C, 83.76; H, 6.57%. Calcd for $C_{23}H_{22}O_2$: C, 83.60; H, 6.71%.

Synthesis of **7**,**8**, *and* **9**. *Procedure A)*. A solution of **2** (253 g) and CuCl (130 g) in DMF (630 ml) was kept to stand at room temperature for 12 h. The crude crystals formed were filtered, washed with MeOH, and dried. The crude crystals were dissolved in acetone (300 ml). The crystals formed after th acetone solution was kept to stand for 5 h were recrystallized from AcOEt to afford **7** as colorless needles; 21.5 g (11%). This compound turned into **15** immediately when melted at 145 °C, and melted again at 296—297 °C. This melting point was measured in N_2 atmosphere[7]. IR ($CHCl_3$): 2200 (C≡C) and 1940 cm^{-1} (C=C=C); λ_{max}: 275 (52900) and 297 nm (ε, 41000); NMR: 2.1—2.8 (m, Ph, 20H) and 8.79 τ (s, Bu^t, 18H); MS *m/e*: 542 (M$^+$).

Found: C, 92.75; H, 6.78%. Calcd. for $C_{42}H_{38}$: C, 92.94; H, 7.06%.

The crystals formed after the acetone mother liquor was kept to stand for further 5 h were recrystallized from acetone to afford **9** as colorless prisms; 104.4 g (54%); mp 149—151 °C. IR ($CHCl_3$): 2200 (C≡C) and 1940 cm^{-1} (C=C=C); λ_{max}: 280 (30,900) and 297 nm (ε, 26600); NMR: 2.1—2.8 (m, Ph, 20H) and 8.69 and 8.83 τ (each s, Bu^t, 9H); MS *m/e*: 542 (M$^+$).

Found: C, 92.97; H, 6.81%. Calcd for $C_{42}H_{38}$: C, 92.94; H, 7.06%.

The DMF solution left after the separation of **7** and **9** was decomposed with water and extracted with ether. The ethereal solution was washed with water and dried over anhydrous Na_2SO_4. The crude crystals left after the evaporation of the solvent were recrystallized from acetone to afford **8** as colorless

prisms; 21.1 g (11%); mp 123—124 °C. IR ($CHCl_3$): 2200 (C≡C) and 1940 cm^{-1} (C=C=C); λ_{max}: 276 (59000) and 316 sh nm (ε, 28700); NMR: 2.4—3.7 (m, Ph, 20H) and 8.79 τ (s, Bu^t, 18H); MS *m/e*: 542 (M^+).

Found: C, 92.81; H, 6.84%. Calcd for $C_{42}H_{38}$: C, 92.94; H, 7.06%.

Procedure B). A solution of **4** (50 g) and CuCl (25 g) in DMF (120 ml) was heated at 50 °C for 6 h, and then kept to stand for 12 h. The treatment of the reaction mixture by the same procedure as that used in *Procedure A*, afforded **7** (8.1 g, 19%), **8** (6.8 g, 16%), and **9** (17.5 g, 41%).

Procedure C). To an ethereal solution of **6** prepared from **2** (15 g), Mg (1 g), and ether (200 ml), was added CuCl (7.5 g) under stirring at room temperature during the period of 1 h. The reaction mixture was decomposed with dil HCl and extracted with ether. Fractional recrystallization of the crude crystals left after the evaporation of the solvent by the same procedure as that used in *Procedure A*, afforded **7** (1.5 g, 13%), **8** (1.5 g, 13%), and **9** (8 g, 69%).

*Oxidation of **9** with $KMnO_4$.* A solution of **9** (1 g) and $KMnO_4$ (3 g) in acetone (30 ml) was heated under reflux for 6 h. After excess $KMnO_4$ was decomposed with EtOH, MnO_2 formed was filtered off. The crude crystals left after the evaporation of the solvent were recrystallized from AcOEt–MeOH (1: 1) to afford **10** as colorless prisms; 0.74 g (70%); mp 120—121 °C. IR: 1930 (C=C=C) and 1670 cm^{-1} (C=O); λ_{max}: 255 nm (ε, 53400): NMR: 2.1—2.9 (m, Ph, 20H), and 8.75 and 9.10 τ (s, Bu^t, 9H). Ms *m/e*: 578(M^+).

Found: C,87.54; H, 6.38%. Calcd for $C_{42}H_{38}O_2$: C, 87.77; H, 6.66%.

The reduction of **10** (0.5 g) with $NaBH_4$ (0.5 g) in MeOH–THF (1: 1) (20 ml) afforded, **11** as colorless needles after recrystallization from MeOH; 0.41 g (82%); mp 160—161 °C. IR: 3530 (OH), 1940 (C=C=C), and 1020 cm^{-1} (C–O); λ_{max}: 250 (35000) and 257 nm (ε, 35000); NMR: 2.0—2.9 (m, Ph, 20H), 5.10 and 5.80 (d, J=9 Hz, CH, 1H), 6.60 (s, OH, 2H), and 8.80 τ (s, Bu^t, 18H); MS *m/e*: 578 (M^+).

Found: C, 86.88; H, 7.22%. Calcd for $C_{42}H_{42}O_2$: C, 87.16; H, 7.31%.

*Synthesis of **12**.* A solution of **8** (1 g) in benzene (20 ml) was heated under reflux for 2 h. The crude crystals left after the evaporation of the solvent were recrystallized from acetone to afford **12** as pale yellow needles; 0.98 g (98%); mp 161—162 °C. IR: 2200 cm^{-1} (C≡C); λ_{max}: 318 nm (ε, 40600); NMR: 2.3—3.0 (m, Ph, 20H), and 8.47 and 8.90 τ (s, Bu^t, 9H); MS *m/e*: 542 (M^+).

Found: C, 92.72; H, 6.87%. Calcd for $C_{42}H_{38}$: C, 92.94; H, 7.06%.

*Oxidation of **12**.* A solution of **12** (1 g) and $KMnO_4$ (3 g) in acetone (30 ml) was heated under reflux for 2 h. The reaction mixture was treated by the same procedure as that used for the oxidation of **9** afforded **13** as colorless prisms; 0.86 g (81%); mp 129—130 °C. IR: 2160 (C≡C) and 1640 cm^{-1} (C=O); λ_{max} 270 nm (ε, 40900); NMR: 2.4—4.0 (m, Ph, 20H), and 8.50 and 8.80 τ (s, Bu^t, 9H); MS *m/e*: 574 (M^+).

Found: C, 87.54; H, 6.39%. Calcd for $C_{42}H_{38}O_2$: C, 87.77; H, 6.66%.

*Synthesis of **15**.* When a solution of **7** (2 g) in benzene (15 ml) was heated under reflux in N_2 for 1 h, greenish blue needles were formed. Filtration of the crystals under N_2 atmosphere afforded **15**; 1.96 g (98%); mp 296—297 °C. λ_{max}: 394 and 643 nm; NMR: 2.65 (s, Ph, 20H) and 8.88 τ (s, Bu^t, 18H); MS *m/e* (relative intensity): 543 (M^++1, 53), 542 (M^+, 100), 271.5 ($(M+1)^{2+}$, 12), and 271 (M^{2+}, 23). Since **15** was sensitive to oxygen, its melting point, UV, and NMR spectra were measured in N_2 atmosphere, and its correct molecular coefficient in the UV spectrum could not be obtained.

Found: C, 92.85; H, 6.99%. Calcd for $C_{42}H_{38}$: C, 92.94; H, 7.06%.

When **8** and **12** were heated in *o*-xylene under reflux in N_2 for 1 h, **15** was obtained in 97 and 98% yield, respectively.

*Oxidation of **15** into **16**.* When powdered **15** (1 g) was allowed to keep in the air at room temperature for 1 day, **16** was obtained, after recrystallization from acetone, as yellow prisms; 1.06 g (95%); mp 246—247 °C. IR: 1660 and 1640 cm^{-1} (C=O); λ_{max}: 300 (29000), 330 sh (19800), and 350 sh nm (ε, 9400); NMR: 2.5—2.9 (m, Ph, 20H) and 9.20 τ (s, Bu^t, 18H); MS *m/e*: 606 (M^+).

Found: C, 83.06; H, 6.15%. Calcd for $C_{42}H_{38}O_4$: C, 83.14; H, 6.31%.

*Conversion of **16** into **17**.* A mixture of **16** (0.1 g), sodium borohydride (0.6 g), MeOH (15 ml), and tetrahydrofuran (5 ml) was kept to stand at room temperature for 1 h. The reaction mixture was decomposed with water, and then extracted with ether. The ethereal solution was washed with water, and dried over anhydrous Na_2SO_4. The evaporation of the solvent left crude crystals (IR: 3400 and 1070 cm^{-1} (OH)), which were dissolved in $CHCl_3$ (5 ml). Through this solution, HBr was bubbled for 10 min at room temperature. The crude crystals left after the evaporation of the solvent were recrystallized from MeOH to afford **17** as colorless needles; 0.09 g (94%); mp 173—175 °C. IR: 1075 cm^{-1} (ether); λ_{max}: 297 nm (ε, 22600) NMR: 2.5—3.1 (m, Ph, 20H), 7.06 (s, CH, 4H), and 9.32 τ (s, Bu^t, 18H); MS *m/e*: 578 (M^+).

Found: C, 86.88; H, 7.09%. Calcd for $C_{42}H_{42}O_2$: C, 87.16; H, 7.31%.

*Formation of **18a** and **18b**.* To a solution of Br_2 (1.8 g) in $CHCl_3$ (10 ml), was added **15** (2.7 g) under N_2 atmosphere. The colorless prisms formed were filtered, washed with $CHCl_3$ to result in **18a**, 3.87 g (90%); mp>300 °C. λ_{max}: 305 nm (ε, 5800).

Heating of a mixture of **18a** (1.7 g) and MeOH (20 ml) under reflux for 1 h afforded **18b**, after recrystallization from AcOEt, 1.06 g (82%); mp 271—273 °C. IR: 1100 cm^{-1} (ether); λ_{max}: 273 (3700) and 284 nm (ε, 2500); NMR: 2.65 (s, Ph, 20H), 7.20 (s, OMe, 12H), and 8.85 τ (s, Bu^t, 18H); MS *m/e*: 666 (M^+).

Found: C, 82.78; H, 7.48%. Calcd for $C_{46}H_{50}O_4$: C, 82.84; H, 7.56%.

References

1) A preliminary communication has been reported: F. Toda and M. Ohi, *J. Chem. Soc., Chem. Commun.*, **1975**, 506.

2) M. P. Cava and M. J. Mitchell, "Cyclobutadiene and Related Compounds," Academic Press, New York and London (1967), pp. 181—218.

3) H. Straub, *Angew. Chem.*, **86**, 412 (1974).

4) F. Toda and N. Dan, *J. Chem Soc., Chem. Commun.*, **1976**, 30.

5) Very recently, the IR and UV spectra of benzocyclobutene itself have been recorded: O. L. Chapman, C. C. Chang, and N. R. Rosenquist, *J. Am. Chem. Soc.*, **98**, 261 (1976).

6) F. Toda and Y. Takehira, *J. Chem. Soc., Chem. Commun.*, **1975**, 174.

7) In the preliminary communication,[1] we have incorrectly reported that the structures of **7** and **9** are *E,E*- (**14**) and *E,Z*-3,4-bis(1-*t*-butyl-3-phenyl-2-propynylidene)-1,2-diphenyl-1-cyclobutene (**12**), respectively. However, the structures of **7** and **9** should be corrected to read as those depicted in this report. We have also reported[1] that **7** melts at 243—245 °C. However, the data should be corrected to read as those described in this paper (measured in N_2 atmosphere), because the previously-reported data are those obtained by the measurement in the air.

8) R. B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.*, **87**, 395 (1965).

9) K. Kleveland and L. Skattebøl, *J. Chem Soc., Chem. Commun.*, **1973**, 432.