

ISOLATION OF *o*-XYLYLENE (*o*-QUINODIMETHANE) DERIVATIVES.

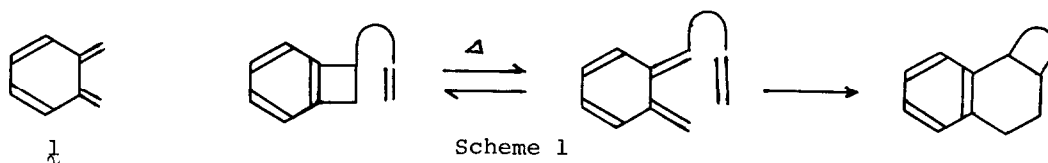
A STRONG THROUGH-BOND INTERACTION IN 2,3-BENZOBICYCLO[2.2.0]HEXANE SYSTEM

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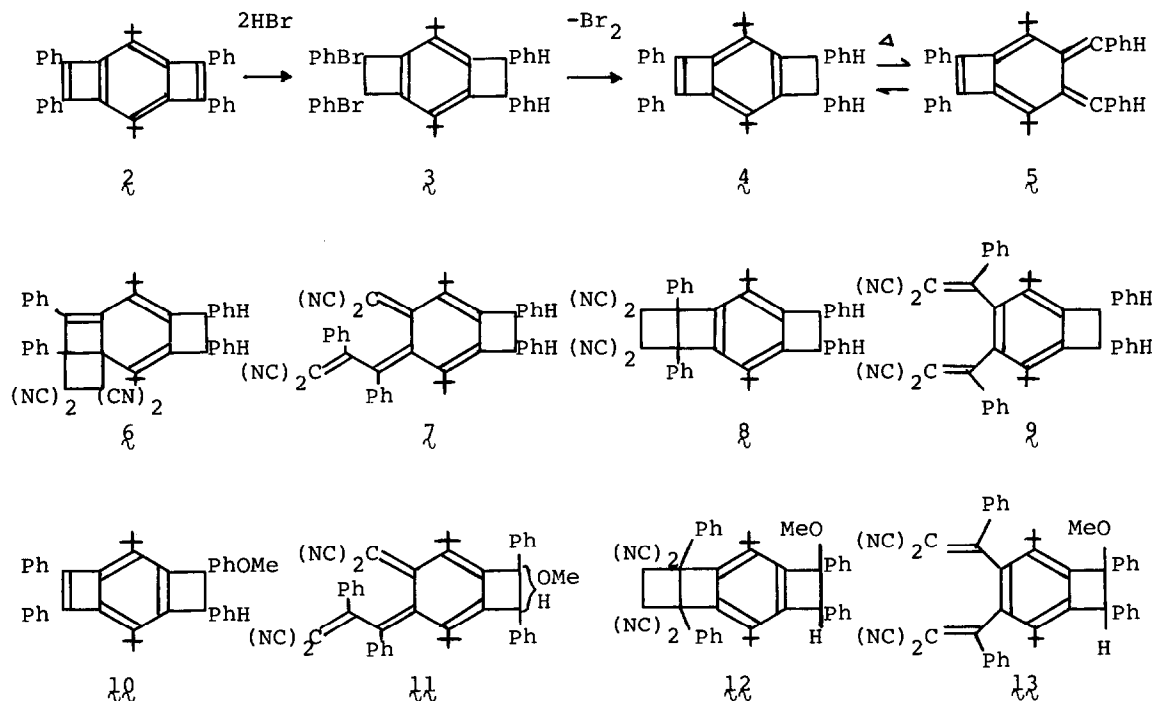
*Summary:* Some *o*-xylylene (*o*-quinodimethane) derivatives were isolated as stable crystalline materials. A strong through-bond interaction in tetracyanoethylene addition product of tetraphenylbenzodicyclobutadiene ( $\lambda_1^1$ ) is suggested.

Attentions have been focused on the reactive species, *o*-xylylene (*o*-quinodimethane) ( $\lambda$ ), for instance, *o*-xylylene which is produced as an intermediate of the recently developed synthetic reaction of steroid (Scheme 1).<sup>1</sup> Nevertheless, neither  $\lambda$  itself nor its derivative has been isolated so far, even though some derivatives have been observed spectroscopically.<sup>2</sup> We now wish to report the isolation of some derivatives of  $\lambda$  as stable crystalline materials. We also report a strong through-bond interaction in 2,3-benzobicyclo[2.2.0]hexane ( $\lambda_1^1$ ).



Debromination by heating with Zn in THF of the dibromide ( $\lambda_3^3$ )<sup>3</sup> which was prepared by the addition of two HBr to benzodicyclobutadiene ( $\lambda$ ),<sup>4</sup> afforded *cis*-dihydro derivative of  $\lambda$  ( $\lambda_4^4$ ). Thermal conversion of  $\lambda_4^4$  into  $\lambda_5^5$  seems to be probable, because this process involves a release from the anti-aromatic benzocyclobutadiene system. However,  $\lambda_5^5$  was not obtained by heating  $\lambda_4^4$  and  $\lambda_4^4$  was recovered unchanged. In order to trap  $\lambda_5^5$  with dienophile,  $\lambda_4^4$  and tetracyanoethylene (TCNE) were heated in xylene under N<sub>2</sub> for 1.5 h, and *o*-xylylene derivative ( $\lambda_7^7$ , 18%) and

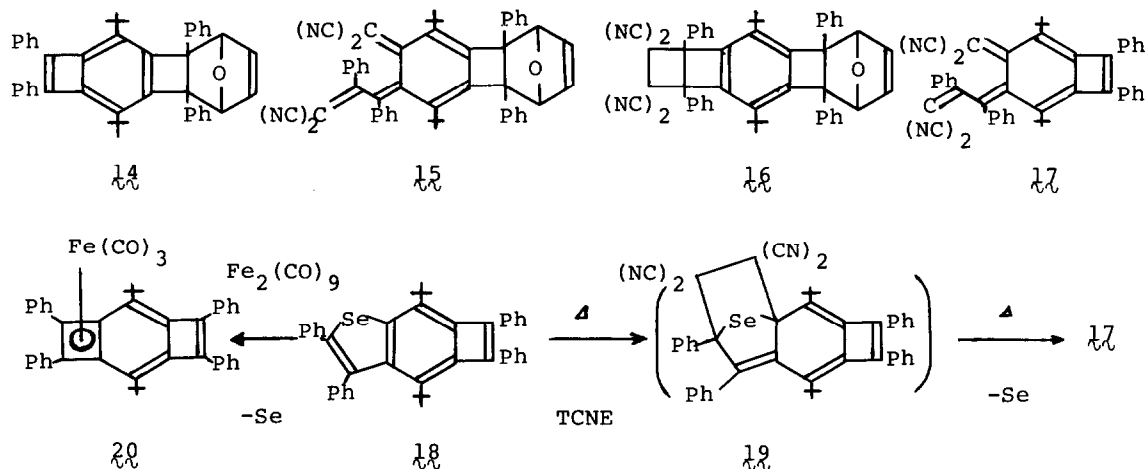
9 (31 %) were obtained instead of the TCNE adduct of 5. The reaction also occurred at room temperature, and 7 and 8 were obtained in 2 and 39% yields, respectively. 8 was easily converted into 9 by heating. The addition compound (6) which is formed by an attack of TCNE from the angular direction of 4, is probably the precursor of 7. In the case of 10, yield of *o*-xylylene (11) increased from 2 to 44% by raising the reaction temperature from room temperature to 140 °C. Binding positions of OMe and H in 11 are not clear. Reason for the increase of the angular addition by raising the reaction temperature is also not clear.



We have recently reported that TCNE attacks 2 at room temperature from the linear direction to afford 6.<sup>5,6</sup> This time, the reaction was carried out at 140 °C, in expectation of the angular attack which may give finally the *o*-xylylene condensed with cyclobutadiene ring (11). Nonetheless, this reaction gave only the ring-cleaved derivative of 2.<sup>5,6</sup> This result is contrasted with the angular attack of TCNE to 4 and 10. However, 11 could be prepared easily by the following method. Reaction of TCNE at room temperature with 12 which was initially prepared by thermal cycloaddition of furan to 2, afforded *o*-xylylene derivative (13, 23%) and 14 (18%). Heating of 15 in diglyme under reflux for 5 h

Table 1. Physical Properties of *o*-Xylylene Derivatives

Compound	State	mp (°C)	$\lambda_{\text{max}}^{\text{CHCl}_3}$ nm ( $\epsilon \times 10^{-2}$ )	m/e (%)
2	crimson needles	>300	250 (292), 345 (167) 386 (157), 526 (150)	672 (M <sup>+</sup> , 48) 57 (t-Bu, 100)
11	crimson needles	>300	245 (244), 342 (135) 380 (127), 515 (104)	
15	crimson prisms	216	257 (165), 300 (152) 352 (117), 403 (95) 510 (104)	738 (M <sup>+</sup> , 7) 670 (M <sup>+</sup> -furan, 100)
17	purple needles	296-298	260 (354), 332 (365) 555 (123)	670 (M <sup>+</sup> , 76) 57 (t-Bu, 100)



afforded **17** in 71% yield. Physical properties of all the *o*-xylylene derivatives are summarized in Table 1. We found that **17** can also be easily prepared in 64% yield by heating the benzenoselenophene (**18**) which had been prepared by Se insertion into **2**<sup>7</sup> with TCNE in xylene for 5 h under N<sub>2</sub>. This reaction may proceed by deselenation and ring cleavage of the initially formed Diels-Alder adduct (**19**). However, **18** did not react with TCNE at room temperature. A similar deselenation reaction was observed in the thermal reaction of **18** with diiron nonacarbonyl to afford iron tricarbonyl complex of **2** (**20**)<sup>8</sup> and Se metal in 85 and 99% yields, respectively.

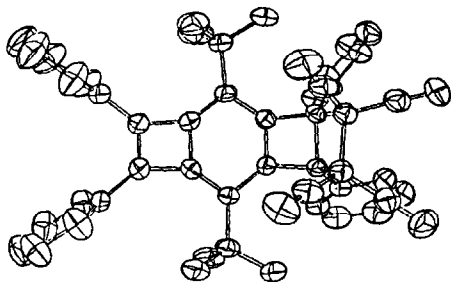
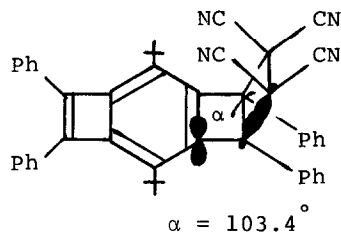


Figure 1. Molecular Structure of  $21$ .



$21$

All the *o*-xylylenes ( $7$ ,  $11$ ,  $15$ ,  $17$ ) are stable and intramolecular [4+2] cycloaddition was not observed even at the temperature of their melting points. The stability is probably due to CN groups which decrease electron density of diene moiety and increase steric crowding around dienophile and diene moieties.

In contrast with high reactivity of  $4$ ,  $10$ , and  $14$  to TCNE at room temperature,  $21$  was inert to TCNE under the same reaction conditions. The molecular structure (Figure 1) does not show the presence of serious steric crowding around the cyclobutadiene moiety which prevents an approach of TCNE. However, the observed small dihedral angle,  $103.4^\circ$ , of the two cyclobutane rings suggests that electronic effect of CN is transmitted to the benzene and then the cyclobutadiene through strained cyclobutane  $\sigma$ -bonds which may have high p-character. Evidence for similar through-bond interaction in the cyclic dimer of cyclobutadiene and benzene has been obtained by photoelectron spectrometry.

#### REFERENCES AND NOTES

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