

THE REACTION OF TRICYCLO[6.2.0.0<sup>3,6</sup>]DECA-1,3(6)4,7,9-PENTAENE  
WITH BENZOYL PEROXIDE AND AZOISOBUTYRONITRILE TO AFFORD A NEW  
QUINODIMETHANE, TRICYCLO[6.2.0.0<sup>3,6</sup>]DECA-2,5,7,10-TETRAENE

Fumio TODA, Koichi TANAKA, and Takayuki YOSHIOKA

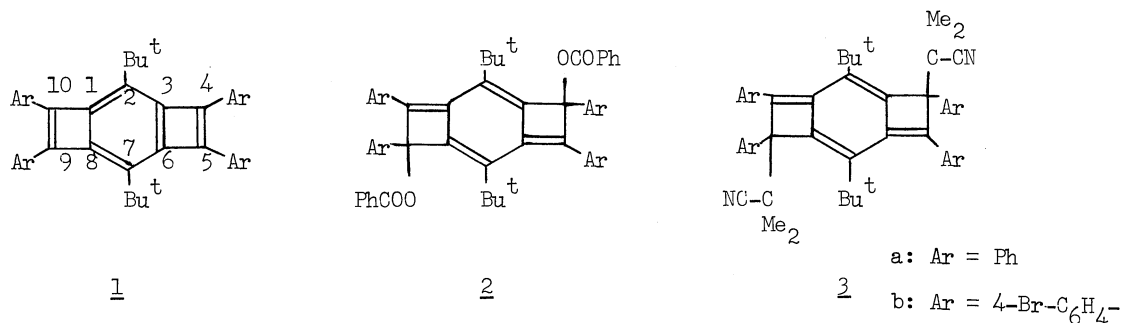
Department of Industrial Chemistry, Faculty of Engineering, Ehime University,

Matsuyama 790

Benzoyl peroxide easily added to 2,7-di-tert-butyl-4,5,9,10-tetraphenyltricyclo[6.2.0.0<sup>3,6</sup>]deca-1,3(6)4,7,9-pentaene (1a) and its tetrabromo derivative (1b), affording new quinodimethanes, 4,9-dibenzoyloxy-2,7-di-tert-butyl-4,5,9,10-tetraphenyltricyclo[6.2.0.0<sup>3,6</sup>]deca-2,5,7,10-tetraene (2a) and its tetrabromo derivative (2b), respectively. Similarly the reactions of 1a and 1b with azoisobutyronitrile afforded 4,9-di(1-cyano-1-methylethyl)-analogs of 2a (3a) and 2b (3b), respectively.

1)  
We reported the cycloaddition of dimethyl fumarate and trans-1,2-dibenzoyl ethylene to the 3,8-positions of the benzene nucleus of 2,7-di-tert-butyl-4,5,9,10-tetraphenyltricyclo[6.2.0.0<sup>3,6</sup>]deca-1,3(6)4,7,9-pentaene (1a). We now report the reaction of benzoyl peroxide (BPO) and azoisobutyronitrile (AIBN) to the 4,9-positions of 1a and its tetrabromo derivative (1b).

2)  
When a mixture of 1a, an equimolar amount of BPO, and o-xylene was allowed to keep at room temperature for 2 hr, 4,9-dibenzoyloxy-2,7-di-tert-butyl-4,5,9,10-tetraphenyltricyclo[6.2.0.0<sup>3,6</sup>]deca-2,5,7,10-tetraene (2a) was obtained as pale yellow needles. Similarly the tetrabromo derivative of 1a (1b) reacted with BPO and afforded the 1,8-addition product (2b) as pale yellow prisms. The reactions of 1a and 1b with AIBN in o-xylene at 100 °C for 1.5 hr afforded 4,9-di(1-cyano-1-methyl-

Table 1. Melting points, yields, and spectral data of  $\underline{2}$  and  $\underline{3}$ 

Compound	Mp (°C)	Yield (%)	$\nu_{\text{Nujol}}$ (cm <sup>-1</sup> )	$\lambda_{\text{max}}^{\text{CHCl}_3}$ nm (εx10 <sup>-2</sup> )	$\tau_{\text{CDCl}_3}$
$\underline{2a}$	256	62	1730 (C=O)	265 (120), 360 (390)	2.1 (m, Ph), 9.06 (s, Bu <sup>t</sup> )
$\underline{2b}$	260	55	1735 (C=O)	275 (135), 360 (365)	3.1 (m, Ar), 9.13 (s, Bu <sup>t</sup> )
$\underline{3a}$	296	18	2220 (C≡N)	282 (103), 387 (436)	2.1 (m, Ph), 8.22 and 8.68 (s, Me), 9.05 (s, Bu <sup>t</sup> )
$\underline{3b}$	289	31	2220 (C≡N)	287 (115), 372 (366)	2.8 (m, Ar), 8.28 and 8.70 (s, Me), 9.07 (s, Bu <sup>t</sup> )

ethyl)-analogs of  $\underline{2a}$  ( $\underline{3a}$ ) and of  $\underline{2b}$  ( $\underline{3b}$ ), respectively, both as pale yellow prisms. Both  $\underline{2}$  and  $\underline{3}$  were stable. Melting points, yields, and spectral data of  $\underline{2}$  and  $\underline{3}$  are summarized in Table 1. The possibility that these products are 1,2-addition ones is excluded, because it has been reported<sup>1,3)</sup> that benzocyclobutadiene is sensitive to oxygen and shows electronic absorption band at the wavelength region longer than 400 nm. However, stereochemical relationship between the two groups at the 4,9-positions in  $\underline{2}$  and  $\underline{3}$  was uncertain.

The electronic absorption bands at longer wave-length region of  $\underline{2}$  and  $\underline{3}$ , 360-387 nm, are comparable to those of 7,7,8,8-tetracyano- [395 (63600)]<sup>4)</sup> and tetrakis(methoxycarbonyl)quinodimethane [363 nm (ε, 38000)]<sup>4)</sup>. The magnetic nonequivalence of the two Me groups of each 1-cyano-1-methylethyl moiety of  $\underline{3}$  is probably due to an asymmetric effect, because the NMR spectrum of  $\underline{2}$  was not affected by raising temperature to 80 °C.

## References

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