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

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Benzoyl peroxide easily added to 2,7-di-tert-butyl-4,5,9,10-tetraphenyltricyclo[6.2.0.0^{3,6}]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^{3,6}]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^{3,6}]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^{3,6}]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 2 and 3

Compound	Mp (°C)	Yield (%)	ν_{Nujol} (cm ⁻¹)	$\lambda_{\text{max}}^{\text{CHCl}_3}$ nm (x10 ⁻²)	τ_{CDCl_3}
<u>2a</u>	256	62	1730 (C=O)	265 (120), 360 (390)	2.1 (m, Ph), 9.06 (s, Bu ^t)
<u>2b</u>	260	55	1735 (C=O)	275 (135), 360 (365)	3.1 (m, Ar), 9.13 (s, Bu ^t)
<u>3a</u>	296	18	2220 (C≡N)	282 (103), 387 (436)	2.1 (m, Ph), 8.22 and 8.68 (s, Me), 9.05 (s, Bu ^t)
<u>3b</u>	289	31	2220 (C≡N)	287 (115), 372 (366)	2.8 (m, Ar), 8.28 and 8.70 (s, Me), 9.07 (s, Bu ^t)

ethyl)-analogs of 2a (3a) and of 2b (3b), respectively, both as pale yellow prisms. Both 2 and 3 were stable. Melting points, yields, and spectral data of 2 and 3 are summarized in Table 1. The possibility that these products are 1,2-addition ones is excluded, because it has been reported^{1,3)} 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 2 and 3 was uncertain.

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

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