Cycloaddition of Dienophiles to the Benzene Nucleus of Tricyclo[6.2.0.$0^{3,6}$]deca-1,3(6)4,7,9-pentaene

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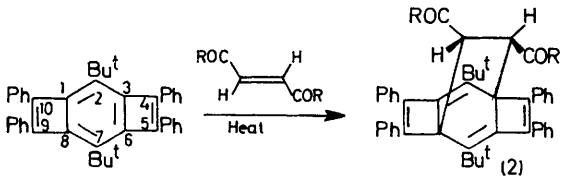
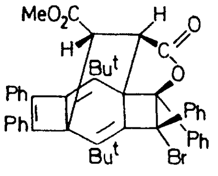
Summary Cycloaddition of dimethyl fumarate, *trans*-1,2-dibenzoylethylene, dimethyl maleate, and maleic anhydride to the benzene nucleus of (**1**) afforded (**2a**), (**2b**), (**5a**), and (**5b**), respectively.

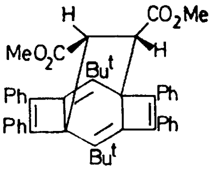


(1)

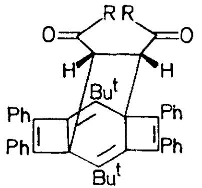
(2)
a; R = OMe
b; R = Ph



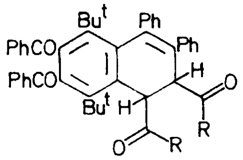
(3)



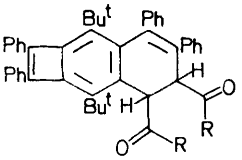
(4)



(5)
a; R = OMe
b; RR = O



(7)
a; R = OMe
b; RR = O



(6)
a; R = OMe
b; RR = O

Cycloadditions of dienophiles to the cyclobutene ring of (**1**)[1] and benzocyclobutene[2] have been reported. However, it might be expected that a dienophile could add to the 3,8-positions of the benzene nucleus of (**1**), because such attack would destroy the antiaromatic nature of both the four-membered rings of (**1**). We now report examples of such cycloadditions.

Heating a 1 : 1 mixture of (**1**) and dimethyl fumarate under reflux in *o*-xylene under N_2 for 0·5 h afforded *syn*-(**2a**)† in 75% yield, m.p. 222—223 °C; ν_{max} 1735 cm^{-1} (ester); λ_{max} 248 (ϵ 21,000) and 320 nm (35,800); τ 2·5—3·2 (20H, m, Ph), 5·75 (2H, s, CH), 6·53 (6H, s, Me), and 9·10 (18H, s, Bu^t). Similarly, reaction of (**1**) with *trans*-1,2-dibenzoylethylene afforded (**2b**) (49%), m.p. 251—252 °C.

The spatial relationship between the CO_2Me groups and the cyclobutene ring in (**2a**) was shown by its reaction with Br_2 which afforded the γ-lactone (**3**) (89%), m.p. 211 °C (decomp.); ν_{max} 1795 (lactone) and 1730 cm^{-1} (ester). The two Ph groups on the cyclobutane ring in (**3**) must be ***trans***, because a mutual shielding was not observed in the n.m.r. spectrum. Molecular models of the alternative structure (**4**) show that it cannot give the γ-lactone because the CO_2Me group is too far from the cyclobutene carbon to react. Molecular models also show that the stereospecificity of the addition of dimethyl fumarate to (**1**) is due to steric repulsion between the CO_2Me and Bu^t groups. This assumption is supported by the following experiments.

Similar treatment of (**1**) with dimethyl maleate as with dimethyl fumarate afforded (**6a**) as the major product, orange needles (79%), m.p. 239—240 °C; ν_{max} 1760 and 1740 cm^{-1} (ester); λ_{max} (tetrahydrofuran) 316 (ϵ 38,400) and 414 nm (2100); τ 2·5—3·5 (20H, m, Ph), 5·58 and 6·12 (1H, d, *J* 3 Hz, CH), 6·49 and 6·65 (3H, s, Me), and 8·88 and 9·43 (9H, s, Bu^t), in addition to (**5a**), (7%), m.p. 265—266 °C; ν_{max} 1740 and 1715 cm^{-1} (ester), λ_{max} 250 (ϵ 20,400) and 320 nm (30,600); τ 2·2—3·2 (20H, m, Ph), 5·50 and 6·02 (1H, d, *J* 12 Hz, CH), 6·25 and 6·45 (3H, s, Me), and 9·05 and 9·10 (9H, s, Bu^t). This result shows that approach of dimethyl maleate to the benzene nucleus of (**1**) is sterically hindered. This is again supported by the reaction of (**1**) with the sterically less hindered maleic anhydride which affords (**5b**) as the major product (46%), m.p. 241—242 °C, in addition to (**6b**), orange prisms (19%), m.p. 231—232 °C.

In contrast with the previously reported stable benzocyclobutenes,[1] (**6a**) and (**6b**) were slightly sensitive to oxygen even in the crystalline state and gradually changed into (**7a**), m.p. 214—215 °C; which showed a new CO i.r. absorption at 1680 cm^{-1}, and (**7b**), m.p. 263—264·5 °C, with new i.r. absorptions at 1670 and 1650 cm^{-1}. However, the conformations of (**6**) and (**7**) were not determined.

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† I.r., u.v., and n.m.r. spectra were measured for Nujol mulls and solutions in $CHCl_3$, and $CDCl_3$, respectively, unless otherwise noted. All new compounds gave satisfactory elemental analyses and mass spectral data. In their mass spectra, (**2a**), (**2b**), (**5a**), and (**5b**) all showed the fragment ion at *m/e* 542 as the base peak, which is presumably attributable to (**1**) formed by a retro-Diels–Alder reaction.

[1] F. Toda and N. Dan, *J.C.S. Chem. Comm.*, 1976, 30.
[2] A. Huth, H. Straub, and E. Müller, *Annalen*, 1973, 1893.