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REACTIONS OF CYCLO-OCTATETRAENE AND ITS DERIVATIVES - X[1]

1,2,3,8-TETRAPHENYLCYCLO-OCTATETRAENE AND 2,3,4,5-TETRAPHENYLCYCLO-OCTA-1,3,5-TRIENE

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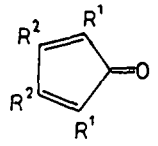
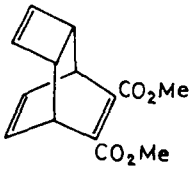
Abstract - The reaction of tetracyclone 1b with the cyclo-octatetraene-dimethyl acetylenedicarboxylate adduct 2 at ca. 110° produces, in addition to the exo[4+2]π cycloadduct 3b (49%), 1,2,3,8-tetraphenylcyclo-octatraene 5 (11%), together with the diketone 11 (5%). In a similar reaction with the esterified cyclo-octatetraene-maleic anhydride adduct 13a, the major product 14 (82%) is accompanied by the cyclohexa-1,3-diene 15 and the dihydrosemibullvalene derivative 16. Thermolysis of 3b at ca. 145° leads to the cyclobutene 12, which on catalytic hydrogenation followed by decarbonylation at 180-190° gives 2,3,4,5-tetraphenylcyclo-octa-1,3,5-triene 19. Attempted thermal conversion of 19 into a dihydrosemi-bullvalene failed.

It has been shown that the reaction of hemi-cyclone 1a with an excess of the cyclo-octatetraene-dimethyl acetylenedicarboxylate adduct 2 proceeds slowly at ca. 60°(refluxing $CHCl_3$) to afford a 9:1[†] mixture of the exo and endo[4+2]π cyclo-addition products, 3a and 4a respectively.[2] In our hands a similar reaction using tetracyclone 1b at ca. 110° (refluxing toluene) analogously gave the exo carbonyl-bridged adduct 3b as the major product (49%), the illustrated stereochemistry being confirmed by the ^{13}C NMR spectrum,[‡] but no adduct corresponding to 4a was isolated. Instead there was obtained 1,2,3,8-tetraphenylcyclo-octatetraene 5[5] (11%), identical with a specimen prepared by zinc dechlorination of the bicyclo-octadiene 6a.[6] The tetraphenylcyclo-octatetraene 5 presumably derived from 4b [which should decarbonylate more easily than the exo isomer 3b (cf. Ref. 7)] via the cyclohexa-1,3-diene 7.[§] A [4+2] cycloreversion in 7 would lead to dimethyl phthalate and 9, a valence tautomer of 5, but an alternative route to 5 would involve ring-opening in 7,



1a : R^1 = Me, R^2 = Ph
1b : R^1 = R^2 = Ph



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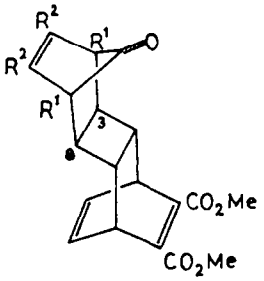
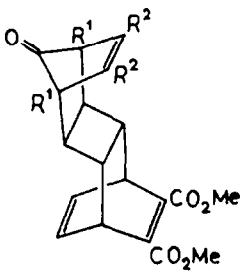
[†]The original (preliminary) report[3] recorded the ratio as ca. 6:1.

[‡]The endo stereochemistry of the protons in positions 3 and 8 was revealed by the proton-coupled spectrum, in which the signal due to the ^{13}C atom in the carbonyl-bridge appeared as a triplet.[4]

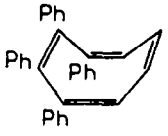
[§]For an analogous sequence employing acecyclone 8, see Ref. 8.



3a : R^1 = Me, R^2 = Ph
3b : R^1 = R^2 = Ph



4a : R^1 = Me, R^2 = Ph
4b : R^1 = R^2 = Ph



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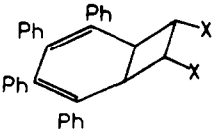
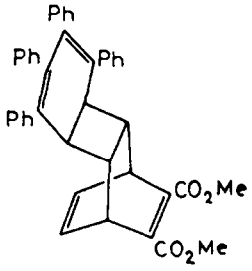


6a : X = Cl
6b : X = H



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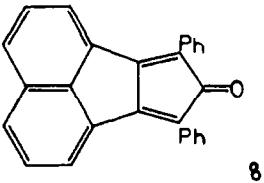

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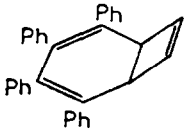

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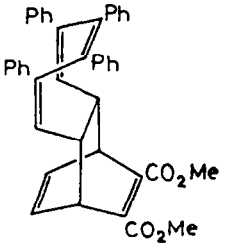

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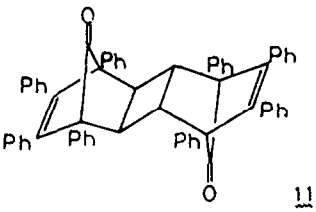
facilitated by the presence of the phenyl substituents,[1] to form the cyclo-octa-1,3,5-triene 10, which might be expected to extrude dimethyl phthalate more readily than 7. A third product of the tetracyclone reaction was the diketone 11 (5%), the basic structure of which followed from its thermolysis at ca. 250° to give 1,2,3,4-tetraphenylbenzene, decarbonylation being followed by fragmentation in the known manner.[9-11] Although the low solubility of 11 precluded the determination of its stereochemistry by ^{13}C NMR spectroscopy, its reluctance to undergo thermal decarbonylation indicated an exo-anti-exo configuration. Its formation must have resulted from the reaction of tetracyclone with the cyclobutene 12, produced from 3b by loss of dimethyl phthalate (see below).

With the hope of improving our understanding of the thermal transformations leading to the cyclo-octatetraene 5, we examined the reaction of tetracyclone with the dimethyl ester 13a, prepared by esterification of the cyclo-octatetraene-maleic anhydride adduct 13b. A 1:1 ratio of the



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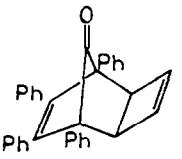

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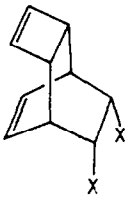
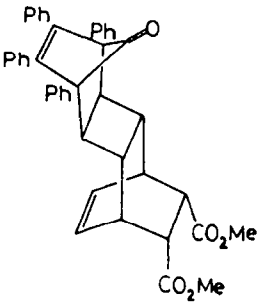


13a : X = CO_2Me

13b : XX = CO.O.CO



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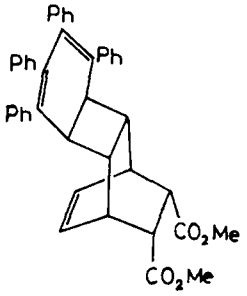

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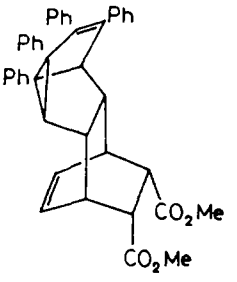

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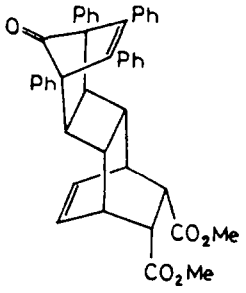

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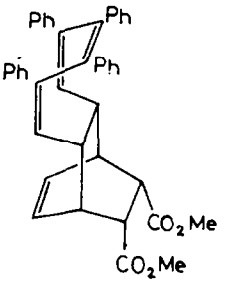

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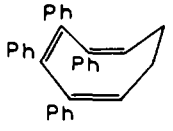
reactants in refluxing toluene was employed, and the reaction was continued until no starting materials remained (ca. 1 week). Cycloaddition again occurred predominantly in the exo mode, affording the carbonyl-bridged adduct 14‡ (86%), but minor products were the cyclohexa-1,3-diene 15 and the (known[1]) dihydrosemibullvalene derivative 16. It may be inferred that 15 was formed by decarbonylation of an initial endo adduct 17 (cf. Ref. 7), and that 16 resulted from 15 via the cyclo-octa-1,3,5-triene 18 (thermal treatment of analogous tetra-arylcyclohexa-1,3-dienes has been shown[1,11] to lead to the corresponding cyclo-octa-1,3,5-trienes, which when heated separately yield dihydrosemibullvalenes[12]). Although attempts to detect the cyclo-octa-1,3,5-triene 18 failed, when the cyclohexa-1,3-diene 15 was kept at ca. 145° (refluxing xylene) for 24 hr., it was converted into 16 in high yield. The facility with which the rearrangement 18 → 16 must occur is striking, and may be contrasted with the failure of 2,3,4,5-tetraphenylcyclo-octa-1,3,5-triene 19 to undergo such a process (see below).

Examples of the thermally activated cyclo-octa-1,3,5-triene → dihydrosemibullvalene transformation reported up to the present time have all involved structures of the type 20.[1,10-12]** The parent cyclo-octa-1,3,5-triene does not undergo this rearrangement[14,15] (though dihydrosemibullvalene is a photolysis product[15,16]) and it was naturally of interest to examine the behaviour of 2,3,4,5-tetraphenylcyclo-octa-1,3,5-triene 19 in this respect. The required compound was obtained as follows. Extrusion of dimethyl phthalate from the adduct 3b occurred in refluxing xylene and led to the cyclobutene 12, previously obtained[6] by dechlorination of the cis-3,4-dichlorocyclobutene adduct 22a. Catalytic hydrogenation of 12 then gave the cyclobutane 22b, which on thermal decarbonylation at 180-190° in tetralin formed the cyclo-octa-1,3,5-triene 19 via its bicyclic valence tautomer 6b.



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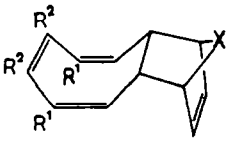
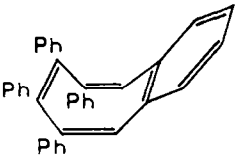


20 : X = 1C, 2C or 2N bridge
R¹ = Me or Ar, R² = Ar



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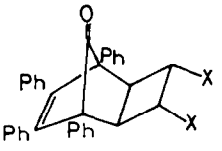

22a : X = Cl
22b : X = H

Attempts to effect the thermal rearrangement of 19 to a dihydrosemibullvalene failed. A solution of 19 in hexachlorobutadiene darkened when kept at ca. 145° for 5 days, but examination of its ^{1}H NMR spectrum showed that it was substantially unchanged. Whatever the mechanism of the thermal cyclo-octa-1,3,5-triene → dihydrosemibullvalene rearrangement,[1,10,11] it appears that it is greatly facilitated by fusion of the 7,8-positions of the eight-membered ring to a rigid bicyclic system, as in structures of type 20.

EXPERIMENTAL

Light petroleum refers to the fraction of b.p. 60-80°; IR spectra were determined for Nujol mulls; ^{1}H and ^{13}C NMR spectra were measured at 100 and 25.15 MHz respectively, using solutions in $CDCl_3$ with Me_4Si as internal standard. The m.ps of some of the products described below were diffuse and varied with the rate of heating.

Reaction of the triene-diester 2 with tetracyclone. A mixture of 2[17] (9.0 g) and tetracyclone (7.0 g) in toluene (100 ml) was heated under reflux until the colour of the solution had faded to a light brown (ca. 15 hr.). Concentration of the solution (at atmos. pressure) followed by cooling afforded the highly insoluble diketone 11 (0.35 g, 5%); m.p. ca. 250° (dec) (from toluene) (Found: C, 90.9; H, 5.5. $C_{62}H_{44}O_2$ requires: C, 90,7; H, 5.4%); IR ν_{max} 1765, 1600 cm^{-1}.

The mother liquors were evaporated under reduced pressure, and the residue was taken up in Et_2O. Addition of light petroleum then gave the carbonyl-bridged adduct 3b (5.6 g, 49%); m.p. ca. 200° (dec) (from CH_2Cl_2-Et_2O) (Found: C, 81.6; H, 5.5. $C_{43}H_{34}O_5$ requires: C, 81.9; H, 5.4%); IR ν_{max} 1775, 1710, 1635, 1600 cm^{-1}. NMR δ_H 7.4-7.05(10H), 7.0-6.8(6H), 6.8-6.5(6H), 4.3-4.15(2H), 3.68(6H, s), 2.64 (2H, d, J 3Hz), 2.2-2.0(2H); δ_C 202.4 [bridge C=O; removal of proton-decoupling gave a t, J(^{13}C-H) 7.3 Hz], 165.9 (ester C=O), 143.5, 142.3, 134.2, 133.9, 133.0, 129.9, 129.5, 128.4, 127.5, 127.2, 126.9 (11 >C= resolved), 66.4, 52.1, 42.7, 42.1, 38.2 (5 saturated C) ppm.

The material remaining in the mother liquors was chromatographed on silica.

** A closely analogous rearrangement, apparently involving the benzo-derivative 21, has been observed by the Bristol research group of Dr. J.W. Barton.[13]

Toluene eluted a fraction which, after being washed with Et_2O, furnished 1,2,3,8-tetraphenylcyclo-octatetraene 5 (0.8 g, 11%), identical with the sample described below. All the other chromatographic fractions were oils.

1,2,3,8-Tetraphenylcyclo-octatetraene 5. cis-anti-7,8-Dichloro-2,3,4,5-tetraphenylbicyclo [4.2.0]octa-2,4-diene 6a[6] (0.40 g) in refluxing EtOH (60 ml) was stirred with activated Zn powder[2] (10 g) for 48 hr. To the resulting mixture was added CH_2Cl_2, and the solids were removed by filtration through celite. The filtrate was poured into water, and the organic layer was separated, washed with water, dried ($MgSO_4$), and evaporated. Recrystallisation of the residue from EtOH then yielded 5 (0.275 g, 71%), m.p. 168-169°; IR ν_{max} 1600 cm^{-1}; NMR (cf. Ref. 5) δ_H 7.7-7.4(4H), 7.4-7.1(6H), 7.1-6.8(10H), 6.5-6.4(2H), 6.4-6.25(2H) ppm.

Thermolysis of the diketone 11 [with Akhtar[18]]. The diketone 11 (1.0 g) was heated at 250° (bath) until gas-evolution ceased (2-3 min). Chromatography of the residue on silica (elution with light petroleum), followed by recrystallisation from C_6H_6-light petroleum, gave 1,2,3,4-tetraphenylbenzene (0.4 g, 44%), identical with an authentic specimen.[19]

Reaction of the diene-diester 13a with tetracyclone. A mixture of 13a[17] (3.1 g) and tetracyclone (4.8 g) in toluene (30 ml) was heated under reflux until the colour of the solution had faded to a pale pink-brown (ca. 1 week). The solvent was removed under reduced pressure, and the residue was extracted with cold Et_2O. The insoluble fraction was the carbonyl-bridged adduct 14 (6.5 g, 82%), m.p. ca. 240° (dec) after recrystallisation from CH_2Cl_2-Et_2O [Found: (M-28) (mass spectrum), 604.2612. $C_{43}H_{36}O_5$ requires: (M-28), 604.2611];†† IR ν_{max} 1780, 1745, 1600 cm^{-1}. NMR δ_H 7.5-7.15(10H), 7.0-6.8(6H), 6.8-6.6(6H), 3.59(6H, s), 3.3-3.1(2H), 2.9-2.7(4H), 2.0-2.15(2H); δ_C 203.1 [bridge C=O; removal of proton-decoupling gave a t, $J(^{13}C\text{-}H)$ 6.1Hz], 172.9(esterC=O), 142.7, 133.9, 133.1, 132.5, 129.9, 129.5, 128.9, 128.3, 127.4, 127.1, 126.8 (11 >C= resolved), 66.5, 51.7, 46.0, 43.0, 36.6, 36.2 (6 saturated C) ppm.

The Et_2O-soluble fraction was chromatographed on silica. Elution with toluene-Et_2O (1:1) and then Et_2O gave a gum, which on treatment with Et_2O-light petroleum afforded the cyclohexa-1,3-diene 15 (0.25 g), m.p. 188-190° (dec) after repeated recrystallisation from CH_2Cl_2-Et_2O (Found: C, 83.5; H, 5.9. $C_{42}H_{36}O_4$ requires: C, 83.4; H, 6.0%); IR ν_{max} 1750, 1730, 1595 cm^{-1}. NMR δ_H 7.2-6.55(20H), 6.55-6.4(2H), 3.55(6H, s), 3.15-3.0(2H), 3.0-2.7(6H); δ_C 173.0 (ester C=O), 141.8, 140.3, 135.4, 134.3, 131.7, 131.2, 128.9, 127.6, 126.7, 126.0, 125.1 (11 >C= resolved), 51.6, 48.5, 46.2, 40.1, 36.9, (5 saturated C) ppm.

From the mother liquors there was obtained, by fractional crystallisation from Me_2CO-light petroleum, the dihydrosemibullvalene derivative 16 (0.22 g), identical with an authentic specimen.[1] Examination of the material remaining in the mother liquors by tlc failed to show the presence of any products other than 15 and 16.

Thermal rearrangement of the cyclohexa-1,3-diene 15. A solution of 15 (100 mg) in xylene (20 ml) was heated under reflux for 24 hr. Removal of the solvent, followed by recrystallisation of the residue from C_6H_6-light petroleum, gave the dihydrosemibullvalene derivative 16 (80 mg), identical with an authentic sample.[1]

exo-1,6,7,8-Tetraphenyltricyclo[4.2.1.$0^{2,5}$]nona-3,7-dien-9-one 12. The tetracyclone adduct 3b (10.5 g) was heated in refluxing xylene (100 ml) for 12 hr. The solvent was removed under reduced pressure, and the oily residue was crystallised from EtOH at 0°. Recrystallisation from the same solvent then afforded 12 (2.6 g, 36%), m.p. 194-195° (dec) (lit. 191°); IR ν_{max} 1780, 1600 cm^{-1}; NMR δ_H 7.5-7.1(10H), 7.1-6.65(10H), 6.60(2H, s), 3.90(2H, s) ppm.

exo-1,6,7,8-Tetraphenyltricyclo[4.2.1.$0^{2,5}$]nonan-9-one 22b. The cyclobutene 12 (1.4 g) in C_6H_6 (25 ml) and EtOH (10 ml) absorbed 1 equiv of H_2 at room temp and atmos pressure in the presence of 10% Pd-on-C. The catalyst was removed by filtration, and the filtrate was evaporated under reduced pressure. Crystallisation of the residue from EtOH gave 22b (1.15 g, 82%), m.p. 191-192° (dec) (Found: C, 90.2; H, 5.85. $C_{33}H_{26}O$ requires: C, 90.4; H, 6.0%); IR ν_{max} 1780, 1600 cm^{-1}; NMR δ_H 7.45-7.1(10H), 7.1-6.65(10H), 3.55-3.3(2H), 2.6-2.25(2H); 1.9-1.55(2H) ppm.

2,3,4,5-Tetraphenylcyclo-octa-1,3,5-triene 19. The cyclobutane 21b (1.1 g) in tetralin (10 ml) was kept at 180-190° for 45 min, and then the solution was chromatographed on silica. Elution with toluene gave an oily fraction which crystallised from MeOH to yield 19 (0.42 g, 41%), m.p. 137-138° (Found: C, 93.4; H, 6.6 $C_{32}H_{26}$ requires: C, 93.6; H, 6.4%); IR ν_{max} 1600 cm^{-1}; NMR δ_H 7.55-6.8(20H), 6.3-6.1(2H), 3.25-2.85(2H), 2.65-2.25(2H); δ_C 143.6, 141.4, 140.5, 139.5, 130.2, 128.5, 128.2, 127.6, 127.3, 126.8, 126.4 (11 >C= resolved), 27.9 (saturated C) ppm.

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†† Correct elemental analytical figures could not be obtained, and the molecular ion was not observed in the mass spectrum (loss of CO).

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