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ADDITION REACTIONS OF CYCLOOCTATETRAENE WITH 1,3-DIPHENYLISOBENZOFURAN THE BENZENE RING AS DIENOPHILE IN A [4+2] CYCLOADDITION REACTION

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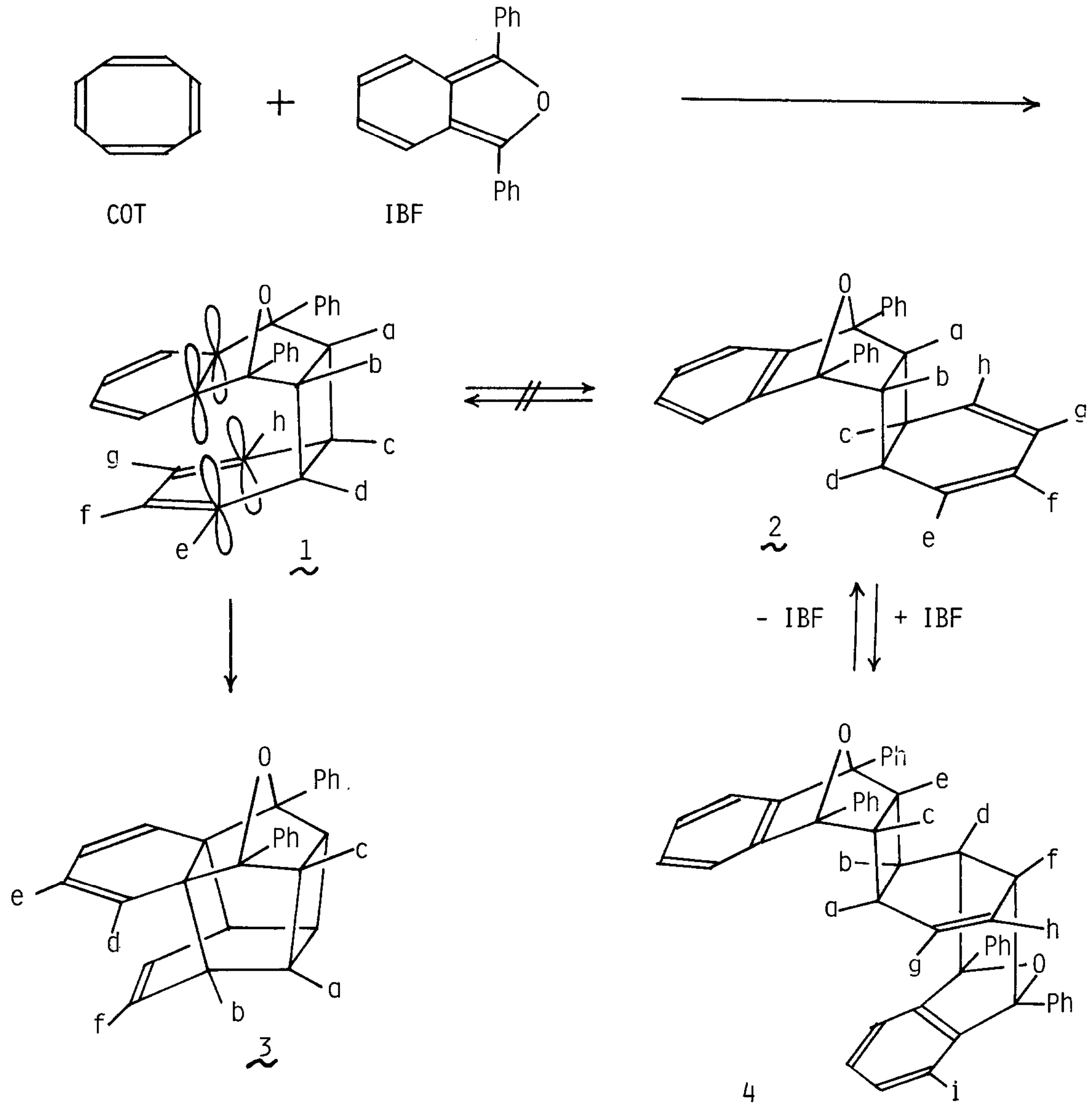
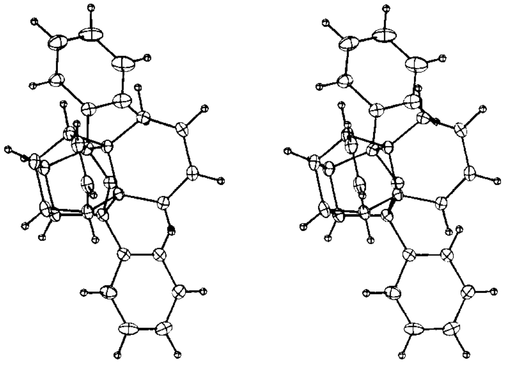
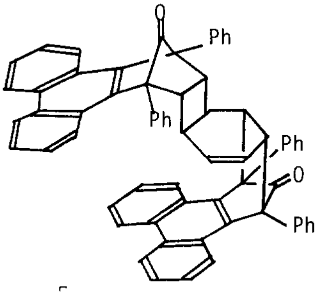
Summary: Addition reactions of cyclooctatetraene with 1,3-diphenylisobenzofuran resulted in the formation of three 1:1 cycloadducts, 1, 2, and 3, and a 1:2 cycloadduct, 4. Single crystal X-ray analysis established 3 to be a cage compound formed by an unprecedented [4+2] cycloaddition reaction of 1 in which the double bond of the benzene moiety acted as the dienophile.

While it has been well established that cyclooctatetraene (COT) can participate in Diels-Alder reactions as either a 2π component (dienophile)[2] or as a 4π component (diene),[3] detailed reports of the former are relatively few in number. Similarly, while numerous reports of cycloaddition reactions of the benzene system exist in the literature,[4] we are unaware of any thermal [4+2] cycloadditions in which the benzene moiety is the dienophile. We now wish to report on the reaction of COT with 1,3-diphenylisobenzofuran (IBF) which provides as its major product, a cage compound formed by a sequential process which involves an initial reaction where COT is the dienophile followed by a second step in which a isolated benzene ring is the dienophile. We believe this to be the first example of a dialkyl substituted benzene moiety acting as a 2π component.

When a benzene solution containing eqivalent amounts of COT and IBF was heated at 100°C for 26 h and the reaction mixture was purified by chromatography on silica gel, 1, 2, 3, and 4 were obtained in 2.6, 5.7, 31 and 1.3% yields, respectively. Elemental analyses and mass spectral molecular ion peaks identified 1, 2, and 3, as 1:1 adducts of COT with IBF while 4 was found to result from addition of two equivalents of IBF to one equivalent of COT.







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The structure of 4 was shown to be that illustrated, primarily on the basis of ^{1}H NMR spectral data obtained using double resonance techniques.[5] Comparison of the NMR data for 4 with those for the analogous adduct, 5,[6] strongly supported this structural assignment. The structure of 3 was initially assigned on the basis of its NMR spectral properties. This assignment was unequivocally confirmed by a syngle crystal X-ray analysi of 3.[7-9] The structures of 1 and 2 were assigned on the basis of their NMR spectral properties and their chemical reactivity. When 2 was heated to 110°C in benzene with 2.5 equivalents of IBF for 3 h, 4 was formed quantitatively. The reversible nature of this second cycloaddition was demonstrated when 4 was maintained at 140°C for 24 h in benzene. At the end of this period, the reaction mixture contained 2 (32%), IBF (33%), and 4 (66%).

When 1 was maintained at 130°C in benzene for 30 H, a mixture of 3 (23%) IBF (20%), and 1 (30%) was produced. This indicated that 1 underwent two different reactions, to produce 3 by a cycloaddition path, and IBF through a retro-Diels-Alder reaction. The absence of 2 and 4 from this reaction mixture indicated that 1 and 2 were not readily interconverted under the reaction conditions.

The isomerization of 1 to 3 is the result of an intramolecular [4+2] cycloaddition (Diels-Alder reaction) in which the benzene moiety of 1 acts as the dienophile. Although the benzene ring is known to participate in several types of cycloaddition reactions such as: thermal [4+2] cycloaddition with acetylene or ethylene to give barrelene or dihydrobarrelene in which benzene reacts as the 4π component,[4a] photoinduced [2+2] cycloaddition with acetylene to give COT,[4b] and photoinduced [4+4] cycloaddition with conjugated dienes to give bicyclo[4.2.2]decatriene,[4c] we believe that the formation of 3, as described above, constitutes the first example of a thermal [4+2] cycloaddition in which benzene is the 2π component in a Diels-Alder reaction which produces a tetrahydronaphthalene. We believe that the intramolecular cycloaddition reaction which converts 1 into 3 is a result of the proximity of the edge of the benzene ring to the ends of the 1,3-butadiene moiety.

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5. All new compounds gave satisfactory elemental analuses and molecular ion peaks in their mass spectra. The melting points and spectral properties of the individual compounds are as follows:

1: Mp 174°C; UV (EtOH): 266 nm (log ε, 3.70), 273 nm (log ε, 3.72); IR (KBr): 3030, 2910, 1605 cm^{-1}; NMR ($CDCl_3$) δ: 2.67 (m, 2H, H_a, H_b), 3.03 (m, 2H, H_c, H_d), 5.48 (m, 4H, H_e-H_h), 6.9-7.7 (m, 14H, Ph).

2: Mp 177°C; UV (EtOH): 266 nm (log ε, 3.66), 273 nm (log ε, 3.43); IR (KBr): 3030, 2910, 1605 cm^{-1}; NMR ($CDCl_3$) δ: 2.08 (m, 2H, H_a, H_b), 3.31 (m, 2H, H_v, H_d), 5.71 (m, 4H, H_e-H_h), 6.9-7.6 (m, 14H, Ph).

3: Mp 218°C; UV (EtOH): 275 nm (log ε, 3.51), IR (KBr): 3050, 2910, 1600 cm^{-1}; NMR ($CDCl_3$) δ: 2.57 (m, 2H, H_a),3.01 (m, 2H, H_b), 3.20 (m, 2H, H_c), 4.59 (m, 2H, H_d), 5.50 (m, 2H, H_e), 6.27 (m, 2H, H_f), 7.2-7.5 (10H, Ph).

4: Mp 204°C; UV (EtOH): 265 nm (log ε, 3.73), 272 nm (log ε, 3.50); IR (KBr): 3030, 2910, 1605 cm^{-1}; NMR ($CDCl_3$) δ: 0.77 (m, H_a), 1.37 (m, H_b), 2.66 (m, H_c), 3.04 (d, H_d), 3.20 (m, H_e), 3.53 (m, H_f), 5.48 (m, H_g), 5.80 (m, H_h), 6.48 (m, H_i), 6.8-7.7 (m, 27H, Ph). Coupling constants (Hz), $J_{ab}=9$, $J_{ac}=4$, $J_{ag}=3$, $J_{ah}=2$, $J_{ce}=10$, $J_{be}=6$, $J_{df}=10$, $J_{fh}=4$, $J_{gh}=11$.

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7. An ORTEP generated stereoview of **3** is present directly below structure **3**.

8. The white crystals of $C_{28}H_{22}O$ belonged to the monoclinic space group $P2_1/n$ (non-standard setting of $P2_1/c$). The measured cell constants, a=7.634(4), b=22.184(3), c=11.719(2) A and β=104.07(2) A, gave a calculated density of 1.292 g/cc for four moleculed in the unit cell at ambient temperatures. Data were collected on a fully automated Enraf-Nonius CAD4 Diffractometer by using a variable rate ω-2θ scan technique and graphite monochromatized Mo Kα radiation (λ=0.71073 A). After Lorentz-polarization corrections, 2099of 3749 unique reflections (56%) with 2θ=0-50° were observed for $[F_0 > 2\sigma(F_0)^2]$. A combination of direct methods and difference Fourier synthesis was used to locate all non-hydrogen atoms. The no-hudrogen atoms were refined with anisotropic thermal parameters using full-matrix least squares analysis. The hydrogen atoms were included at idealized positions with fixed isotropic thermal parameters. The final weighted R factor for the structure was 0.042. All calculations were carried out on a PDP 11/34 computer using the Enraf-Nonius SPD programs. This crystallographic computing package is described by Frentz, B. A. in "Computing in Crystallography"; Schenck, H.; Olthof-Hazekamp, R.; van Konigweld, H.; Bassie, G. S., Eds.,; Delft University Press; Delft, Holland, 1978; pp64-71.

9. The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Center, University Chemical Laboratory, Lensfield Road, Cambridge CB2 iEW, U. K. Any request should be accompanied by the full literature citation for this communication.

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