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NOVEL [4+6]π CYCLOADDUCT FROM FRONTIER-CONTROLLED PERICYCLIC REACTION OF 2,5-DI-METHOXYCARBONYL-3,4-DIPHENYLCYCLOPENTADIENONE WITH CYCLOOCTATETRAENE

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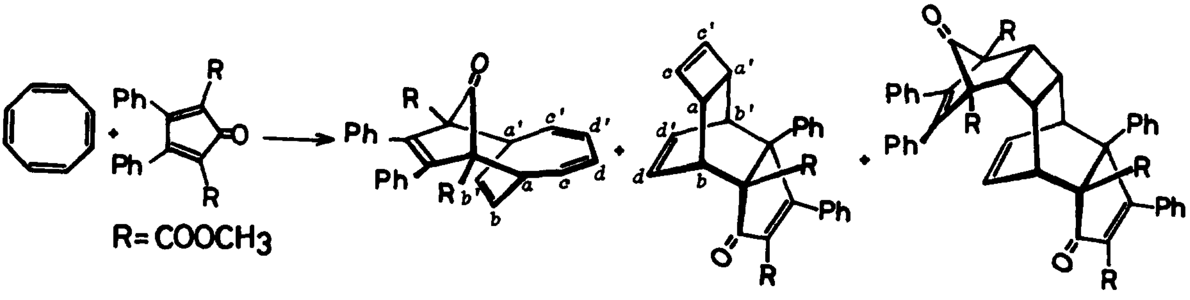
Summary: Treatment of 2,5-dimethoxycarbonyl-3,4-diphenylcyclopentadienone with an excess of cyclooctatetraene gives the novel exo[4+6]π cycloadduct together with the endo[2+4]π and bis-Diels-Alder cycloadducts. The CNDO/2 MO calculation indicates that HOMO(COT)-LUMO(cyclopentadienone) interaction will be more important than the other.

The chemistry of cyclooctatetraene (COT) has received considerable attention in the past decade and several reviews have appeared.[1] Cycloaddition reaction of COT with electron-deficient 2π-components, wherein COT plays the role of 4π donor based on the dynamic properties with isomerization to bicyclo[4.2.0]octa-2,4,7-triene are extensively studied. By contrast, it is known that COT dimerizes more rapidly than it undergoes cycloaddition to 4π-components such as 2,5-dimethyl-3,4-diphenylcyclopentadienone (MPC).[2]

The finding that the potent electron-deficient diene, 2,5-dimethoxycarbonyl-3,4-diphenylcyclopentadienone (CPC) reacts with N-ethoxycarbonylazepine (NEA) to give novel exo[4+6]π and endo[2+4]π cycloadducts in high yields[3] prompted us to examine the additivity of CPC to COT.

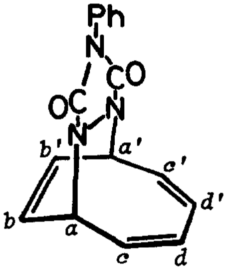
We now report a first example, so far as we know, of novel exo[4+6]π cycloadduct (1) which could not be originally supposed by taking into consideration of the nonplanar conformation (tub structure) only.[4]

CPC reacts with COT under refluxing benzene for 8 hr to give two types of 1:1 cycloadduct (1) [m.p. 189-198 °C(decomp.), 46 %] and (2) [m.p. 225-228 °C, 9 %]



1 2 3

together with 2:1 adduct (3) [m.p. 257-258 °C, 35 %]. The 1:1 and 2:1 nature were shown by mass spectrometry and elemental analyses. The structure of 1 is mainly assigned on the basis of the PMR data of double resonance technique,[5] in which bridgehead protons at δ 3.88 (2H, m, Ha and Ha', Jab = 5, Jab' = 3) strongly coupled with adjacent vinyl protons at δ 5.74 (2H, dd, Hb and Hb'), and particularly four olefinic protons appeared at δ 6.04 (4H, m, Hc and Hc', Hd and Hd', Jac = 5, Jcd ≃ 3) excluding the possibility of other structure such as 4. Comparison of the PMR spectral patterns of the adduct (1) is grossly similar to the adduct (5) derived from COT and 4-phenyl-1,2,4-triazoline-3,5-dione[5] indicating the skeletal resemblance to each other. The exo nature of the adduct (1) was apparently deduced from the chemical shift of Hc (Hc') and Hd (Hd') characteristic of exo diene protons observed in 6[6] and 7[3] and the fact that Hb (Hb') at δ 5.74 has suffered an upfield shift relative to that at δ 5.96 of the adduct (5), which might be shielded by phenyl ring current. The IR spectrum of 1 also supports this assignment showing a characteristic carbonyl band at 1768 cm^{-1} to suggest the presence of a bridged carbonyl group of exo[4+6]π cycloadduct which absorbs at lower frequency[3] than that of bicyclo[2.2.1]hepta-7-one moiety in 3 (1806 cm^{-1}). On the other hand, the CMR spectrum of 1 displayed the bridgehead carbons [δc 71.54 and 40.72] suggesting the symmetrical structure. The minor compound (2) is easily assigned the endo[2+4]π adduct, which showed an enone carbonyl absorption at 1710 cm^{-1}, and four olefinic protons at δ 5.76, 5.86 (2H, d, Hc and Hc') and 6.34 (2H, dd, Hd and Hd'), and four bridgehead protons at δ 3.52 (2H, m, Hb and Hb') and 2.28 (2H, m, Ha and Ha'). On the other hand, the configuration of the cyclobutane moiety in the adduct (3) was determined by the crystallographic data of the analogous 2:1 cycloadduct[7] from phencyclone and COT.



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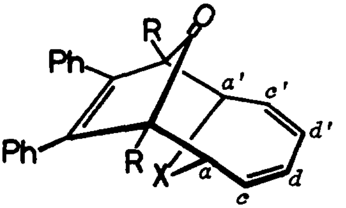
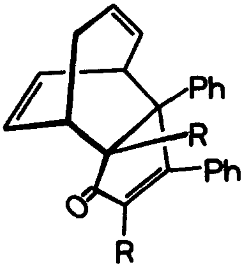


6: R=CH_3, X=CH_2

7: R=$COOCH_3$, X=$NCOOC_2H_5$



8: R=CH_3

The lack of dependence of rate[8] on change in solvent polarity rules out a dipolar intermediate suggested in cycloaddition reaction of COT with tetracyanoethylene.[4] For the formation of the [4+6]π cycloadduct (1) in thermal condition, two different pathways shown in Figure are possible, one involving sigmatropic rearrangements ([3,3] or [1,5]) of the adducts (4 and 9) and the other direct cycloaddition of CPC (4π) to COT (6π). The former pathway may be excluded by consideration of the orientation of interacting orbitals in compound (9) as depicted in Figure and the thermal stability[6] of the analogous compound such as 8. This assumption is also supported by the observation that tlc monitoring[9] of the reaction did not reveal initial formation of the adduct even under mild condition.

In general, addition of dienophiles to COT eventuates in Diels-Alder ([4+2]π) reaction with the valence tautomer. On the contrary, CPC shows high reactivity to COT in comparison with other cyclopentadienones such as tetracyclone or MPC which have often been used as trapping reagent, usually without success.

From these facts, it could be explained satisfactory in terms of the frontier orbital control[10] with predominant donor-acceptor interaction between the HOMO (COT) and the LUMO (CPC) assisted by narrow frontier molecular orbital (FMO) separation. Indeed, the CNDO/2 MO calculation[11] indicates a 0.7 eV lowering of LUMO for CPC as compared to MPC and a comparable donor property for COT to N-ethoxycarbonylazepine (See Figure). In light of the very low LUMO energy, CPC should be more readily trapped by electron-rich COT as 6π donor.

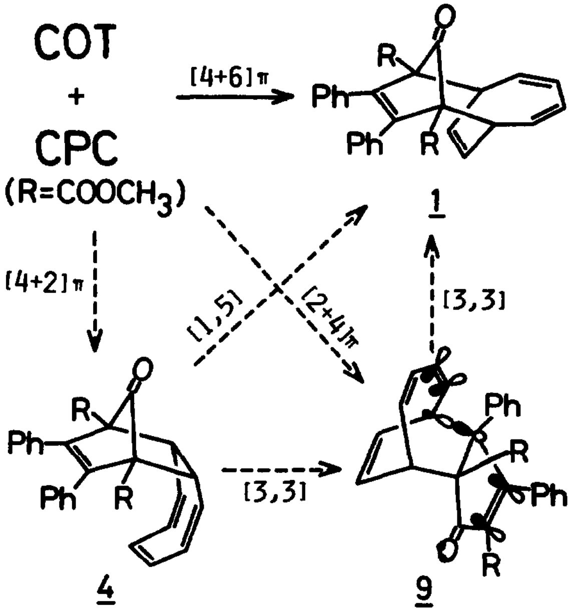


Chart Reaction Pathway

We are currently examining the cycloadditivity of COT to other cyclopentadienones.[14]

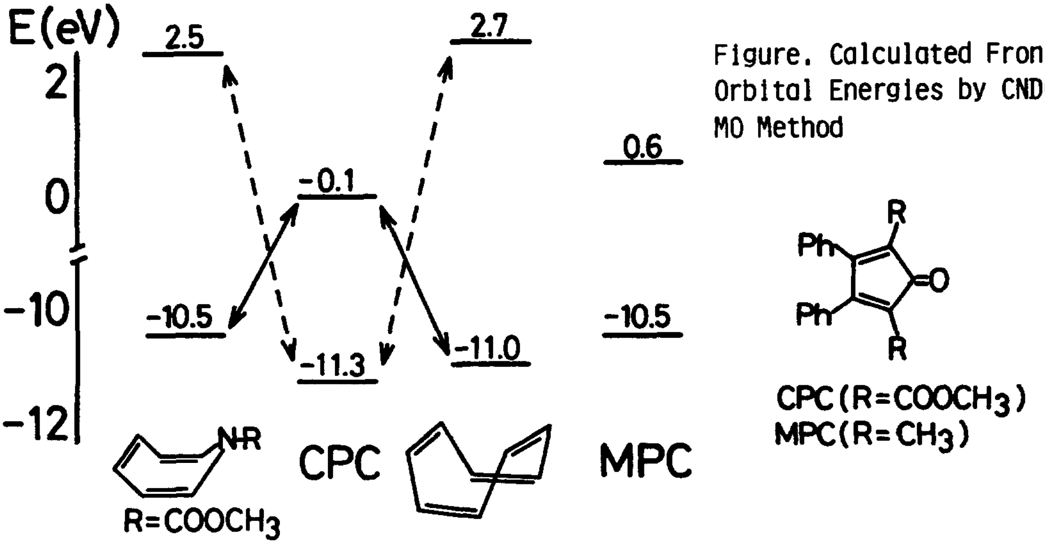


Figure. Calculated Frontier Orbital Energies by CNDO/2 MO Method

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References and Notes:

1) For reviews see a) G. Schröder, 'Cyclooctatetraene', Verlag Chemie, GmbH, Weinheim/Bergstr, 1965. b) G. I. Fray, R. G. Saxton, 'The Chemistry of Cyclooctateraene and its Derivatives', Cambridge University Press, 1978.
2) K. N. Houk and L. J. Luskus, J. Org. Chem., 42, 4151 (1977).
3) K. Harano, T. Ban, M. Yasuda, and K. Kanematsu, Tetrahedron Letters, 1979, 1599.
4) L. A. Paquette, Tetrahedron, 31, 2855 (1975), and references cited therein.
5) Irradiation of the aliphatic proton multiplet at δ 3.88 led to collapse of the two proton quartet at δ 5.74 into a sharp singlet indicating the absence of coupling between the protons at δ 5.74 and the other four olefinic protons centered at δ 6.04 [see, for example, A. B. Evnin, R. D. Miller, and G. R. Evanega, Tetrahedron Letters, 1968, 5863].
6) K. N. Houk and R. B. Woodward, J. Am. Chem. Soc., 93, 4143 (1970).
7) K. Harano, M. Yasuda, and K. Kanematsu, manuscript in preparation.
8) The half-lives of CPC at 47.8 °C are as follows: 3.2 hr in acetonitrile; 3.1 hr in chlorobenzene.
9) Thin layer chromatographic analyses were performed with a Iatroscan TH-10 tlc analyser with a flame ionization detector.
10) H. Fujimoto, S. Inagaki, and K. Fukui, J. Am. Chem. Soc., 98, 2670 (1976), and references cited therein.
11) In CNDO/2 MO calculation, geometry and bond angles and lengths for COT were taken from the X-ray results.[12] Three dimensional coordinates of N-methoxycarbonylazepine (NMA) are composed using X-ray results of N-brosylazepine and iron tricarbonyl complex of NMA.[13] The optimum geometries of the cyclopentadienones were determined from X-ray results[3] in which substituents were rotated by 60° out of cyclopentadienone.

All the calculations were performed on the FACOM M-200 computer in the center of Kyushu University.
12) J. Border, R. G. Parker, and R. H. Stanford, Acta Cryst., B28, 1069 (1972).
13) I. C. Paul, S. M. Johnson, L. A. Paquette, J. H. Barrett, and R. J. Haluska, J. Am. Chem. Soc., 90, 5023 (1968).
14) A definitive assignment of configuration of [4+6]π cycloadduct (1) by X-ray analysis cannot be made at present since well formed crystals are not available (twinning).

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