Journal of Organometallic Chemistry, 282 (1985) 369–381
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

REACTIONS OF COORDINATED CYCLIC POLYOLEFINS *. A NOVEL PERISPECIFIC DIELS–ALDER REACTION OF TRICARBONYL(η^4-CYCLOHEPTATRIENE)IRON AND (CARBOMETHOXY)MALEIC ANHYDRIDE CONTROLLED BY SECONDARY ORBITAL OVERLAP

ZEEV GOLDSCHMIDT *, SHLOMO ANTEBI, HUGO E. GOTTLIEB, DRORA COHEN
Department of Chemistry, Bar-Ilan University, Ramat Gan 52100 (Israel)

URI SHMUELI and ZAFRA STEIN
Department of Chemistry, Tel-Aviv University, Ramat Aviv 69978 (Israel)

(Received September 25th, 1984)

Summary

The cycloaddition reactions of (carbomethoxy)maleic anhydride (CMA) with (η^4-cycloheptatriene)Fe(CO)$_3$ and with uncoordinated cycloheptatriene were investigated. Both reactions are highly stereospecific and give single Diels–Alder adducts. The structure of the metal-bonded adduct X was determined by single-crystal X-ray diffraction. A full analysis of the ^{1}H and ^{13}C NMR spectra of X is described. The corresponding uncomplexed adduct XI was obtained by Diels–Alder reaction of CMA with norcaradiene. The unusual Diels–Alder periselectivity and the stereochemical consequences of the 4 + 2 cycloaddition to X are best rationalized in terms of a concerted reaction controlled by secondary orbital interactions in the transition state.

Introduction

The Diels–Alder reaction is widely recognized as a highly stereospecific cycloaddition [2]. Consequently, it has become a subject of numerous fundamental studies of the control of steric and electronic effects on the reactivity, stereoselectivity and regioselectivity of pericyclic reactions [3].

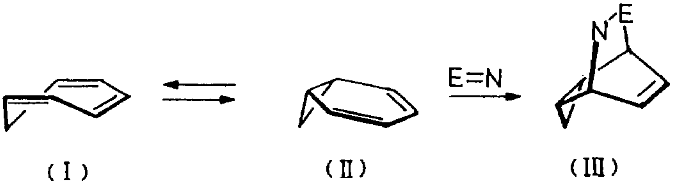
Cycloheptatriene (I) participates in Diels–Alder reactions with a wide variety of

---

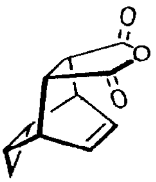
* For previous paper in this series see ref. 1.

0022-328X/85/$03.30

dienophiles (E = N, where E denotes the electrophilic site and N the nucleophilic site of the dienophile), via its equilibrium valence-isomer norcaradiene (II), to give essentially the *anti*-tricyclic adducts of general structure III (eq. 1) [4]. This selectivity has been attributed to the considerably greater reactivity of the planar diene in norcaradiene compared with that of the weakly reactive twisted diene moiety in the boat shape cycloheptatriene [2]. In reactions where geometrical isomers may be distinguished, e.g., in the reaction of cycloheptatriene with maleic anhydride, formation of the *anti-endo* adduct IV prevails (Alder rule) [5], presumably as a result of stabilization of the *endo* Diels–Alder transition state by secondary orbital interactions [6].

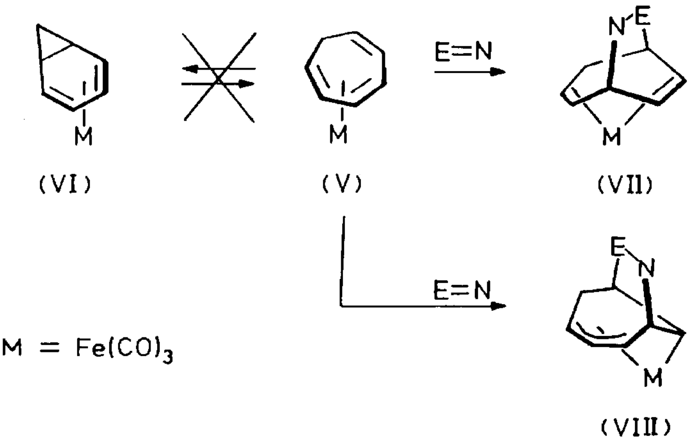


(1)



(IV)

(Cycloheptatriene)Fe(CO)$_3$ (V), which does not isomerize to the corresponding norcaradiene valence-isomer complex VI [7,8], is expected to undergo a normal Diels–Alder reaction to the bicyclic complex VII (eq. 2), but this 4 + 2 cycloaddition [9] has not previously been observed. Instead, the reaction of V and its derivatives with highly reactive dienophiles leads periselectivly to the stable 3 + 2 metal-σ,π-allylic adducts VIII (eq. 3) [10–12].



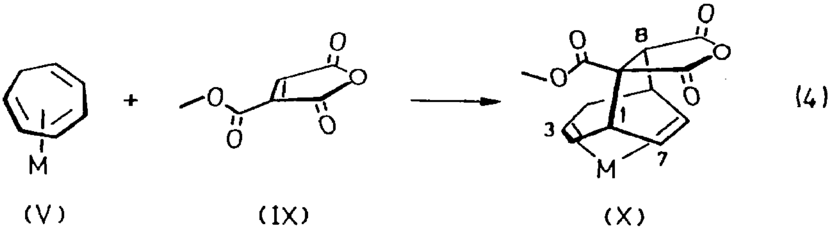
(2)

(3)

Recently Hall et al. [13] introduced the new powerful dienophile (carbomethoxy)maleic anhydride (IX) (CMA), and noted that it is far more reactive than tetracyanoethylene (TCNE) in Diels–Alder reactions. Being a reactive unsymmetrical cycloaddend, this anhydride appeared an excellent reactant for use in studying the mechanistic details and stereochemistry of pericyclic reactions, particularly with unreactive metal-bonded polyene systems. We describe below the first example of a 4 + 2 Diels–Alder reaction, between (cycloheptatriene)$Fe(CO)_3$ (V) and CMA (IX). We also describe the Diels–Alder reaction of CMA (IX) with the uncoordinated cycloheptatriene (I), and discuss possible reasons for the unusual perispecific behavior of CMA toward the cycloheptatriene complex V.

Results

(Carbomethoxy)maleic anhydride (CMA) (IX) (prepared according to Hall et al. [13]) readily reacts with cycloheptatriene-$Fe(CO)_3$ at room temperature to give, after recrystallization, a single 1 : 1 adduct in 62% yield. The IR spectrum in KBr exhibited three characteristic strong absorptions of the ligand carbonyls at 2028, 1978 and 1948 cm^{-1}, and three additional carbonyl absorptions of the anhydride and ester at 1843, 1772 and 1733 cm^{-1}.



The ^1H NMR spectrum shows characteristic signals at 3.90 (3H, s) due to the methyl ester and at 3.79 (d, J 2.5 Hz) due to the anhydride ring proton. There is a single low field resonance which appears as a split triplet at 4.28, ascribed to a bis-allylic bridgehead proton, and one high field signal at 2.21 arising from methylene H(*exo*), which exhibits a broad doublet (J 16 Hz) due to geminal coupling. The remaining six protons resonate in the narrow range between 2.8–3.4 ppm. This spectrum pattern rules out structures containing metal-bonded σ,π-allylic and butadiene moeities. There remains the tempting alternative structure X in which the metal is coordinated to two nonconjugated double bonds. While there is no precedent for cycloaddition reactions of butadiene complexes leading to the less stable nonconjugated counterparts, such a group of 1,4-diene complexes is well known. Their olefinic protons are reported to resonate at ca. δ 3.0 ppm [14]. We therefore carried out a full analysis of the ^1H spectrum by careful decoupling experiments. The geminal and vicinal proton–proton couplings established the connectivity between signals of neighboring hydrogens and allowed the unambiguous spectral assignment illustrated in Fig. 1a.

The structure assigned to X was confirmed by the ^{13}C NMR spectrum [15], which, except for the carbonyl absorptions of δ 166.0, 167.5 (anhydride), 170.0 (ester) and 214.0 (coordinated CO), displayed only high field peaks at $\delta < 71.6$ ppm. Gated decoupling revealed that the four carbon resonances at δ 24.1, 45.4, 59.8 and 71.6 have large ^1J(CH) coupling constants of 160–176 Hz, which corrrespond to two coordinated double bonds. There remain then a methyl (δ 54.1), a methylene (δ

40.8), a quaternary carbon (δ 63.3), and three bridgehead methine carbons at δ 33.8, 37.9 and 51.2 ppm.

To complete the analysis and secure the specific assignments of each proton and carbon in the complex X, we correlated the chemical shifts of the two nuclei in each C–H group through a series of off-resonance decoupled spectra ("Birdsall plots") [16]. The full carbon assignment is shown in Fig. 1b.

The signals of the four olefinic protons appear within a very narrow range (ca. 0.5 ppm). This suggests that they are approximately symmetrically positioned around the metal atom, and are therefore shielded to similar extents. The differences in the high field olefinic carbon shifts are however much more pronounced. Notably, C(2) and C(7) possess considerably higher field signals relative to C(3), and C(6). It also seems that there is a correlation between δ(C) and the corresponding ^1J(CH) so that higher field carbons have larger coupling constants. Since these coupling constants are all in the range observed for sp^2 carbons, and since electron donation is expected to cause upfield shift of such carbon resonances [17], it is reasonable to suggest that the back-bonding orbital interaction of the metal fragment HOMO with the LUMO of the 1,4-diene system is stronger at the inner sites (C(2) and C(7)) than at the outer sites (C(3) and C(6)) [18].

Although the ^{1}H and ^{13}C NMR spectral analyses have unambiguously revealed the structure of the complex adduct as a bicyclo[3.2.2]nona-2,6-diene system, the specific orientation of the anhydride and ester moeities shown in X was not established. In order to verify the stereochemistry of the 4 + 2 cycloadduct, a single-crystal X-ray analysis of X was undertaken, and this unequivocally confirmed that the anhydride ring is *endo*-oriented and that the quaternary carbon is bonded to the bis-allylic bridgehead carbon.

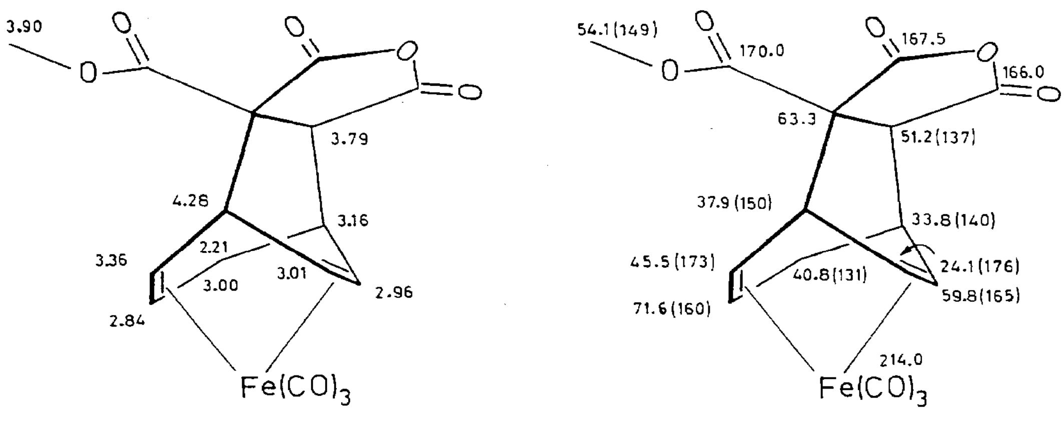


Fig. 1. ^{1}H and ^{13}C NMR signals of X. (a) δ(H) (ppm); coupling constants: $J(1,2) = J(2,3) = J(4n,5) = J(5,6) = J(6,7) = 8.0$ Hz, $J(3,4e) = 6.5$ Hz, $J(1,7) = 4.0$ Hz, $J(5,8) = 2.5$ Hz, $J(1,6) = J(3,4x) = 1.5$ Hz $J(2,4x) = 1.0$ Hz, $J(1,3) = 0.5$ Hz. (b) δ(C) ppm; coupling constants (^1J(CH) Hz) are given in parenthesis.

Crystal structure analysis of compound X *

Unit-cell and intensity data were collected with a CAD4F single-crystal diffractometer (Enraf-Nonius), using graphite-monochromatized Mo-K_α radiation (λ 0.71069 Å). The unit-cell dimensions are based on 2θ measurements of 25 (triply recentered) reflections and their refinement by least squares. Intensity data were collected in the $\omega/2\theta$ mode, with a crystal scan width of $1.1 + 0.3 \tan\theta$, out to $2\theta = 54°$. The fastest and slowest scan rates in this experiment were 5 and 1.3 degrees per minute respectively.

The intensity data were corrected for background counts, variable scanning rates and absorption [19], but not for secondary extinction.

Crystal data. $C_{16}H_{12}FeO_8$, $M = 388.1$, triclinic, a 6.648(1), b 10.289(3), c 12.814(4) Å, α 71.55(3), β 88.29(2), γ 72.83(2)°, V 792.3 Å^3, $Z = 2$, μ 10.24 cm^{-1}, d_c 1.626 g cm^{-3}, $F(000)$ 396, space group $P\bar{1}$.

Part of the structure was obtained by direct methods, using MULTAN 80, and the missing non-H atoms were located in weighted-Fourier and difference syntheses. The least-squares refinement of the complete molecule converged smoothly to $R = 0.041$ for 2552 observations with $I > 3\sigma(I)$, where I is the net intensity of a reflection. In this calculation, the positional parameters of all the atoms, and the (anisotropic) thermal parameters of all the non-H atoms were conventionally refined, while fixed isotropic thermal parameters were assigned to the hydrogens. The initial positions of the latter were obtained from a difference map. The difference map computed after the final cycle was featureless and revealed no indications of misplaced atoms.

The refined atomic parameters, except the anisotropic vibration tensors **, are given in Table 1. In Table 2 we present the bond distances and angles, not involving hydrogen atoms, and the dihedral angles defining the conformation of the seven-membered ring. An ORTEP drawing of the molecule is displayed in Fig. 2. There are no unacceptably short non-bonded interatomic distances in this structure.

Several structural features of the complex adduct X deserve comment. As in butadiene-Fe(CO)$_3$ complexes, the coordination about the iron atom of X is very nearly square pyramidal. The two double bonds and the pair of ligand carbonyls C(2)O(3) and C(4)O(5) define the basal plane of the pyramid, and carbonyl C(6)O(7) holds the apex [20,14d,i]. The Fe(CO)$_3$ group is in a staggered conformation [21] so that the apex carbonyl points away from the bis-allylic bridgehead C(10). This conformation is apparently more stable than the alternative conformation, obtained by a 60° rotation of the Fe(CO)$_3$ group, because a better bonding interaction between orbitals of the Fe(CO)$_3$ fragment [21] and those of the 1,4-diene system [22] is expected at the C(9) and C(11) inner sites, where a better through-space interaction [22] of the π-bonds occurs. Consistently, we also find that the inner C(9)–C(11) distance (2.313 Å) is considerably shorter than the outer C(8)–C(12) distance (2.733 Å).

The distances of the olefinic carbons from the iron atom (2.095–2.156 Å) are all in the range of the Fe–C outer distances in butadiene complexes (2.10–2.16 Å),

---

* The atom numbering in this section is as shown in Fig. 2.

** Table of anisotropic thermal parameters can be obtained from the authors upon request.

whereas the coordinated C–C bond lengths are somewhat shorter than in the conjugated complexes [20]. This is consistent with a weaker bonding between the metal and the organic ligand, and therefore a lower stability of 1,4-diene complexes relative to their 1,3-diene counterparts [14d,18a].

Finally, we note that both coordinated double bonds are slightly twisted. The calculated dihedral angles given in Table 2, indicate an out-of-plane twist of ca. 17° for each of the two double bonds, in such a way that the outer *syn* hydrogens H(8) and H(12) are directed towards the metal. Here again, the resemblance to the conjugated 1,3-diene complexes is striking [20].

When cycloheptatriene (I) was allowed to react with CMA (IX) at room temper-

TABLE 1

POSITIONAL AND ISOTROPIC THERMAL PARAMETERS OF COMPOUND X [a]

Atom	x	y	z	$U_{eq.}/U$ (Å^2)
Fe(1)	0.71661(6)	0.29724(4)	0.36230(3)	0.0419
C(2)	0.5189(6)	0.4585(3)	0.3571(3)	0.0575
O(3)	0.3917(5)	0.5619(3)	0.3541(2)	0.0876
C(4)	0.6137(6)	0.2106(4)	0.4843(3)	0.0629
O(5)	0.5464(5)	0.1525(3)	0.5628(2)	0.1003
C(6)	0.9302(6)	0.3392(5)	0.4107(3)	0.0760
O(7)	1.0645(6)	0.3677(5)	0.4415(3)	0.1272
C(8)	0.9601(5)	0.1133(3)	0.3470(2)	0.0508
C(9)	0.7648(5)	0.0992(3)	0.3277(2)	0.0465
C(10)	0.6407(4)	0.1677(3)	0.2187(2)	0.0412
C(11)	0.5962(4)	0.3240(3)	0.2052(2)	0.0432
C(12)	0.7712(5)	0.3731(3)	0.1920(2)	0.0426
C(13)	0.9718(4)	0.2802(3)	0.1589(2)	0.0415
C(14)	1.0988(5)	0.1643(3)	0.2593(2)	0.0502
C(15)	0.7546(4)	0.1298(3)	0.1189(2)	0.0382
C(16)	0.9123(4)	0.2122(3)	0.0780(2)	0.0373
C(17)	0.8084(5)	0.3243(3)	−0.0279(2)	0.0492
O(18)	0.6240(4)	0.3036(2)	−0.0554(2)	0.0574
C(19)	0.5863(5)	0.1879(3)	0.0246(3)	0.0527
O(20)	0.4331(4)	0.1545(3)	0.0175(2)	0.0780
O(21)	0.8613(4)	0.4219(2)	−0.0853(2)	0.0656
C(22)	0.8497(5)	−0.0330(3)	0.1493(2)	0.0423
O(23)	1.0181(4)	−0.0912(2)	0.1260(2)	0.0593
O(24)	0.7204(4)	−0.0992(2)	0.2057(2)	0.0661
C(25)	0.7911(7)	−0.2545(3)	0.2429(3)	0.0782
H(8)	1.026(5)	0.061(3)	0.419(2)	0.060
H(9)	0.709(5)	0.031(3)	0.383(2)	0.060
H(10)	0.514(5)	0.140(3)	0.227(3)	0.060
H(11)	0.461(5)	0.387(3)	0.191(2)	0.060
H(12)	0.750(5)	0.467(3)	0.169(2)	0.060
H(13)	1.057(5)	0.341(3)	0.116(2)	0.060
H(14A)	1.192(5)	0.073(3)	0.242(2)	0.060
H(14B)	1.194(5)	0.198(3)	0.291(2)	0.060
H(16)	1.047(5)	0.150(3)	0.060(2)	0.060
H(25A)	0.820(5)	−0.283(3)	0.170(2)	0.060
H(25B)	0.916(5)	−0.275(3)	0.290(2)	0.060
H(25C)	0.686(5)	−0.278(3)	0.289(2)	0.060

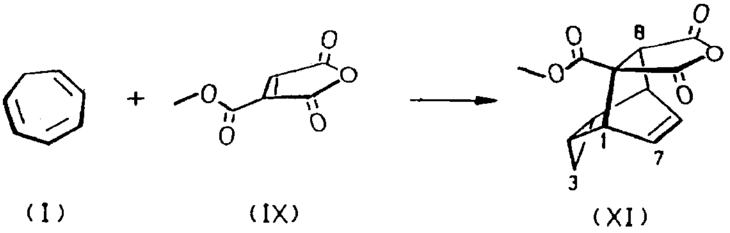
[a] For non-hydrogen atoms $U_{eq.}$ represents the equivalent value of the anisotropic Debye–Waller factor.

ature, in CH_2Cl_2 solution, a single 1 : 1 adduct was isolated in 65% yield (eq. 5). The IR spectrum (in KBr) shows the expected carbonyl bands of the anhydride-ester moiety at 1860, 1785 and 1735 cm^{-1}. The structural assignment as the *anti-endo* adduct XI was based on the ^1H NMR spectrum, which closely resembles that obtained by Ishitobi et al. [5b] for the adduct of cycloheptatriene with maleic anhydride IV. The cyclopropane ring protons appear as three high-field signals at

TABLE 2

BOND DISTANCES (Å), BOND ANGLES (°) AND SOME DIHEDRAL ANGLES (°) IN COMPOUND X

Fe(1)–C(2)	1.769(3)	C(13)–C(14)	1.513(4)
Fe(1)–C(4)	1.766(3)	C(14)–C(8)	1.497(4)
Fe(1)–C(6)	1.781(3)	C(13)–C(16)	1.538(5)
Fe(1)–C(8)	2.156(3)	C(16)–C(15)	1.517(4)
Fe(1)–C(9)	2.152(3)	C(15)–C(10)	1.563(4)
Fe(1)–C(11)	2.095(3)	C(16)–C(17)	1.497(3)
Fe(1)–C(12)	2.131(3)	C(17)–O(18)	1.378(5)
C(2)–O(3)	1.137(4)	O(18)–C(19)	1.386(4)
C(4)–O(5)	1.149(5)	C(19)–C(15)	1.516(4)
C(6)–O(7)	1.135(7)	C(17)–O(21)	1.183(4)
C(8)–C(9)	1.386(5)	C(19)–O(20)	1.181(5)
C(9)–C(10)	1.494(4)	C(15)–C(22)	1.528(4)
C(10)–C(11)	1.500(4)	C(22)–O(23)	1.183(4)
C(11)–C(12)	1.385(5)	C(22)–O(24)	1.312(4)
C(12)–C(13)	1.530(3)	O(24)–C(25)	1.445(4)
C(2)–Fe(1)–C(4)	88.0(2)	C(10)–C(15)–C(19)	105.9(2)
C(4)–Fe(1)–C(6)	103.9(2)	C(10)–C(15)–C(22)	109.6(2)
C(6)–Fe(1)–C(2)	96.8(2)	C(16)–C(15)–C(19)	104.4(2)
C(8)–Fe(1)–C(9)	37.5(1)	C(16)–C(15)–C(22)	113.8(2)
C(11)–Fe(1)–C(12)	38.2(1)	C(19)–C(15)–C(22)	111.1(3)
Fe(1)–C(2)–O(3)	179.8(3)	C(13)–C(16)–C(15)	114.5(2)
Fe(1)–C(4)–O(5)	178.8(4)	C(13)–C(16)–C(17)	111.4(2)
Fe(1)–C(6)–O(7)	179.1(4)	C(15)–C(16)–C(17)	104.3(2)
C(14)–C(8)–C(9)	124.9(3)	C(16)–C(17)–O(18)	110.6(3)
C(8)–C(9)–C(10)	123.7(3)	C(16)–C(17)–O(21)	129.6(3)
C(9)–C(10)–C(11)	101.2(3)	O(18)–C(17)–O(21)	119.8(3)
C(9)–C(10)–C(15)	116.1(2)	C(17)–O(18)–C(19)	110.7(2)
C(11)–C(10)–C(15)	111.4(2)	C(15)–C(19)–O(20)	129.3(3)
C(10)–C(11)–C(12)	115.3(2)	O(18)–C(19)–C(15)	109.4(3)
C(11)–C(12)–C(13)	117.3(3)	O(18)–C(19)–O(20)	121.1(3)
C(12)–C(13)–C(14)	110.8(2)	C(15)–C(22)–O(23)	124.4(3)
C(12)–C(13)–C(16)	109.6(2)	C(15)–C(22)–O(24)	110.8(2)
C(14)–C(13)–C(16)	110.2(2)	O(23)–C(22)–O(24)	124.8(3)
C(8)–C(14)–C(13)	111.8(2)	C(22)–O(24)–C(25)	117.3(3)
C(10)–C(15)–C(16)	111.6(3)		
C(8)–C(9)–C(10)–C(11)	−64.0(4)		
C(9)–C(10)–C(11)–C(12)	66.7(3)		
C(10)–C(11)–C(12)–C(13)	17.6(4)		
C(11)–C(12)–C(13)–C(14)	−85.0(3)		
C(12)–C(13)–C(14)–C(8)	32.9(4)		
C(13)–C(14)–C(8)–C(9)	36.1(5)		
C(14)–C(8)–C(9)–C(10)	−16.6(5)		



(5)

0.27 (H(3)*endo*), 0.38 (H(3)*exo*) and 1.20 (H(2) and H(4)); the bridgehead methine protons resonate at 3.50 (H(5)), 3.68 (H(8)) and 3.82 (H(1)); the two olefinic protons exhibit a signal at 5.92, and the three methyl protons at 3.86 ppm.

Discussion

(Carbomethoxy)maleic anhydride (CMA) joins a large number of dienophiles which stereospecifically react with cycloheptatriene (I) via the norcaradiene valence-isomer (II) to give the *anti-endo* Diels–Alder adduct XI [2,4]. This appears to be consistent with previous results which indicate that the reaction is a symmetry-allowed $\pi 4s + \pi 2s$ concerted cycloaddition [23,2,3]. Our finding that cycloheptatriene-$Fe(CO)_3$ (V) also undergoes an analogous Diels–Alder reaction with CMA (IX) is, however, surprising in the light of numerous earlier reports which show that cycloheptatriene complexes selectively react with strong dienophiles such as tetracyanoethylene (TCNE) and other uniparticulate electrophiles [24] by 3 + 2 cycloaddition [10–12] (eq. 3). Moreover, in the few examples where more than one adduct is formed or when further rearrangements of primary products take place, only 2 + 2

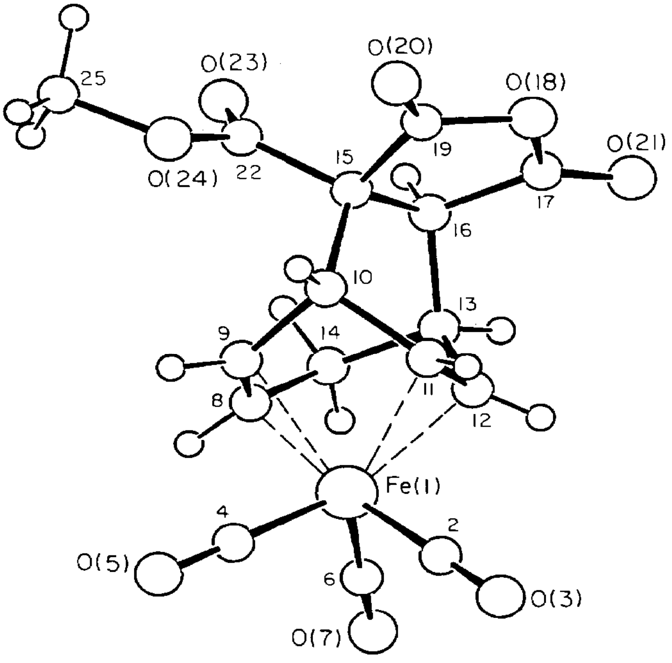
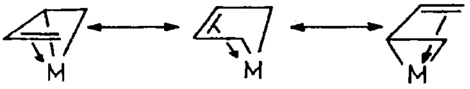


Fig. 2. ORTEP drawing of adduct complex X.

[12d], 5 + 2 [11,12a,b] and 6 + 2 [11,12g] adducts were observed, and none of the 4 + 2 adducts.

The reluctance of V to participate in the Diels–Alder reaction has been implicitly noted previously by Mingos [11] in a comprehensive study of the mechanism of $n + 2$ cycloaddition reactions ($n = 2$–6) of cycloheptatriene-complex with olefins. On the basis of the generalized Woodward–Hoffmann topological rule for pericyclic reactions [23a], and the use of resonance structures (eq. 6) [25] to describe the



(6)

metal–diene bonding, Mingos proposed classification of the 3 + 2 cycloadditions as symmetry allowed [$(\pi 2a + \sigma 2a) + \pi 2s$] reactions (Fig. 3a), whereas the 4 + 2 cycloadditions as symmetry forbidden [$(\pi 2a + \sigma 2s + \pi 2a) + \pi 2s$] reactions (Fig. 3b). However, this analysis can not be supported by the present study, which manifested a highly regio- and stereo-specific Diels–Alder 4 + 2 cycloaddition. We therefore propose classification of the 4 + 2 cycloadditions of cycloheptatriene complexes as symmetry-allowed [$(\pi 2a + \sigma 2a) + \pi 2s$] reactions (Fig. 3c) topologically identical to the 3 + 2 reactions. Both reactions are seen to involve a cyclic six electron array with only two electrons coming from the metal–diene moeity, as opposed to the four electrons required in the forbidden, eight electrons 4 + 2 cycloaddition.

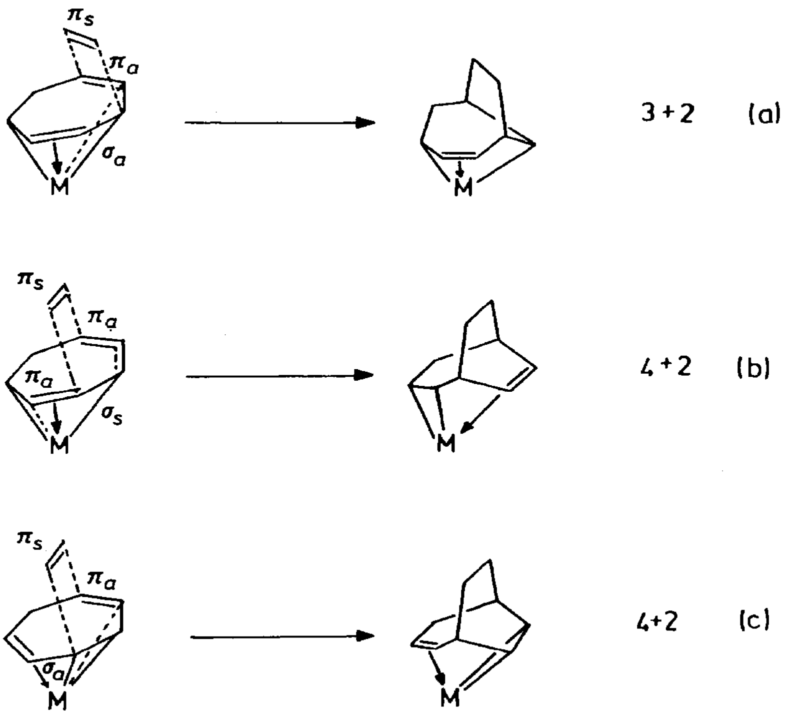


Fig. 3. Cycloaddition reactions of (cycloheptatriene)Fe(CO)$_3$ (V) with uniparticulate electrophiles. (a) [$(\pi 2a + \sigma 2a) + \pi 2s$], allowed 3+2 cycloaddition. (b) [$(\pi 2a + \sigma 2s + \pi 2a) + \pi 2s$], forbidden 4+2 cycloaddition. (c) [$(\pi 2a + \sigma 2a) + \pi 2s$)], allowed 4+2 cycloaddition.

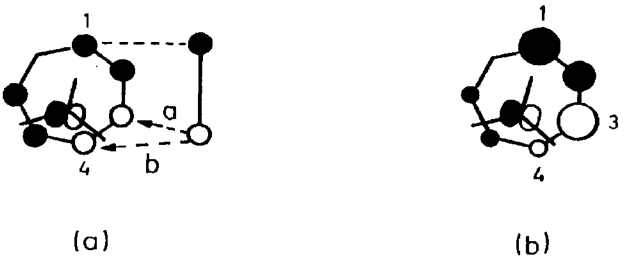


Fig. 4. (a) Frontier molecular orbital interactions of (cycloheptatriene)Fe(CO)$_3$ (HOMO) and olefin (LUMO) in 3 + 2 (route a) and 4 + 2 (route b) cycloadditions. (b) Relative magnitudes of the π coefficients in HOMO complex V.

That the Diels–Alder reaction of V may be regarded as a symmetry-allowed process receives further support from simple frontier molecular orbital (FMO) considerations [3]. Inspection of the first order orbital interaction of cycloheptatriene complex HOMO [7] and the dienophile LUMO, shown in Fig. 4a, reveals that the pair of frontier orbitals are in the expedient in-phase relationship for both the 3 + 2 (route a) and 4 + 2 (route b) cycloadditions. It therefore appears that there is no symmetry-imposed barrier to the 4 + 2 reaction.

Two questions regarding the periselectivity of the cycloadditions now arise. Firstly, why do most uniparticulate electrophiles prefer the 3 + 2 over the 4 + 2 cycloaddition, and secondly, why then does the Diels–Alder reaction with CMA prevail over the 3 + 2 cycloaddition? A further point deserves analysis namely, what are the controlling factors which direct the two unsymmetrical addends to produce specifically one isomer, X, out of the four stereoisomeric 4 + 2 adducts expected upon CMA attack *anti* to the metal-bonded face.

We propose a qualitative solution for these queries by invoking an interplay between first- and second-order orbital interactions. Let us first examine the highly

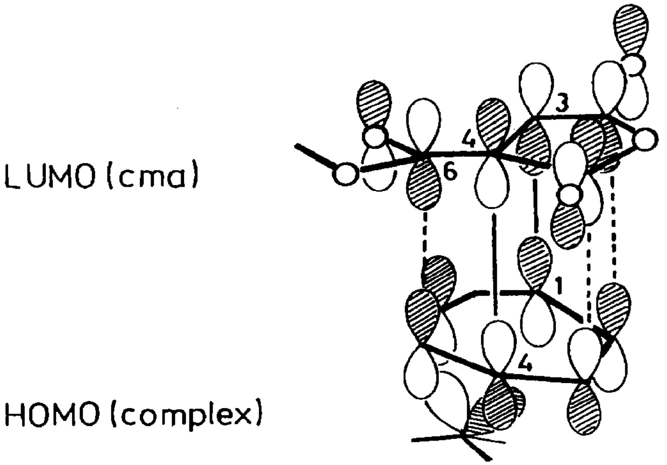


Fig. 5. Primary (full lines) and secondary (broken lines) orbital interactions stabilizing the *endo* transition state of the Diels–Alder reaction of complex V with CMA.

stereospecific Diels–Alder reaction. Figure 5 illustrates the pair of interacting frontier orbitals aligned in a maximum orbital overlap situation. Evidently there is a full correspondence of the coefficient phases, at both the active centers and the active frame regions [26], and so maximum stabilization of the Diels–Alder transition state is provided. Thus, in addition to the bonding (full lines) primary interaction at the active centers of the HOMO (C(1) and C(4)) and the LUMO (C(3)–C(4)) there are two stabilizing secondary interactions which are nonbonding (broken lines). The major one, at the *endo* side of the transition complex, which dictates the *endo*-stereoselectivity, is commonly observed in many Diels–Alder reactions (Alder rule) [2]. The minor secondary interaction occurs at the *exo* side of the transition complex between C(5) in the HOMO and C(6) in the LUMO active frames. It governs the regiochemistry of the reaction, giving preference to the isomer X in which the quaternary C(9) carbon is bonded to the bridgehead C(1) (eq. 4).

The significance of secondary orbital interactions as controlling factors in the regioselectivity of the Diels–Alder reaction has been extensively discussed by Alston [27]. In general, if in an unsymmetrical diene the difference between the coefficients at the active centers is small compared to the difference at the active frame, the regioselectivity will be principally determined by secondary orbital interactions. We can use similar arguments to explain the periselectivity observed in the cycloaddition reactions of V. A closer look at the coefficients of cycloheptatriene-Fe(CO)$_3$ HOMO (Fig. 4b) as calculated by extended Hückel methods [7,28], revealed that, although having the same sign, the coefficient on C(3) is considerably larger than that on C(4). Therefore, uniparticulate electrophiles such as TCNE and hexafluoroacetone (HFA), which have only active centers available for orbital interaction, are expected to follow the usual 3 + 2 cycloaddition. However, this difference between the primary orbital coefficients is not large enough to control the 3 + 2 periselectivity when strong secondary orbital interactions are available. Hence, with CMA the 3 + 2 reaction pathway is not followed. Rather, a favorable transition state for a 4 + 2 cycloaddition is attained which involves maximum orbital overlap at both the active and frame centers and which, as can readily be seen from Fig. 5 is dominated by two secondary orbital interactions. We are thus left with the conclusion that the unusual 4 + 2 periselectivity of the reaction between V and CMA, as well as the regio- and stereospecificity observed in the reaction, are all controlled by the interaction of secondary orbitals in the transition state leading to a symmetry-allowed Diels–Alder reaction.

There is a final point regarding reactions periselectivity which deserves comment. The ability to predict the selectivity of reactions obviously has important implications for stereospecific syntheses. There are however many factors which may effect selectivity. A recent attempt to provide a general treatment of periselectivity was handicapped by the vast number of variations [29]. What is possibly a more promising approach, aimed at establishing rules for periselectivity of cycloadditions by classification of uniparticulate electrophiles according to their reaction mode with specific polyolefin systems, has also recently been attempted [30]. The success of this approach depends on the ability to find polyfunctional systems which have the capability to enter into versatile pericyclic reactions. Cycloheptatriene-Fe(CO)$_3$ (V) appears to represent a good example of a simple organometallic polyene complex which possesses this versatility [1,10–12], and as such deserves further study.

Experimental

General. ^1H and ^{13}C NMR spectra were recorded on a Bruker-AM300 spectrometer equipped with an ASPECT 3000 data system, in $CDCl_3$ and TMS as internal standard. IR spectra were measured on a Perkin–Elmer Model 257 spectrometer. Mass spectra were determined with a GC/MS Finnigan Model 4021 spectrometer. Elemental analysis were carried out in the analytical laboratories of the Hebrew University, Jerusalem. All reactions were conducted under nitrogen.

Tricarbonyl[(η-6,7,9,10)-3aβ-methoxycarbonyl-4,5,8,8aβ-tetrahydro-4,8-etheno-1H-cyclohepta[c]furan-1,3(3aH)-dione]iron (X)

A solution of cycloheptatriene complex V [31] (365 mg, 1.57 mmol) and CMA (IX) [13] (165 mg, 1.06 mmol) in dry CH_2Cl_2 (5 ml) was kept at room temperature for 12 h. The solvent was removed in vacuum and the residue was crystallized from CH_2Cl_2/hexane to give orange prisms (255 mg, 62% yield), m.p. 116°C. IR (KBr) 2028, 1978, 1948 (ligand CO), 1843, 1772 (anhydride carbonyl), and 1733 (ester carbonyl) cm^{-1}; m/e 360 ($M-$CO), 332, 304, Anal. Found: C, 49.80; H, 3.31. $C_{16}H_{12}FeO_8$ calcd.: C, 49.52; H, 3.09%. For ^1H and ^{13}C NMR spectra see text.

3aβ-Methoxycarbonyl-4,4aβ,5,5aβ,6,6aβ-hexahydro-4,6-etheno-1H-cycloprop[f]isobenzofuran-1,3(3aH)-dione (XI)

This was similarly obtained by reaction of cycloheptatriene (I) (100 mg, 1.09 mmol) and CMA (168 mg, 1.08 mmol), in 65% yield, m.p. 126°C (ether/hexane). IR (KBr) 1860, 1785 and 1735 cm^{-1}. Anal. Found: C, 63.08; H, 4.84. $C_{13}H_{12}O_5$ calcd.: C, 62.92; H, 4.84%. For the ^1H NMR spectrum see text.

Acknowledgement

We thank Mrs. Sima Alfi for her assistance in the experimental work. Support by the Planning and Grant Committee of the Council for Higher Education for the purchase of the Bruker AM300 NMR spectrometer, and financial assistance from the André Narboni and Leon Recanati Scholarship Funds (to S.A.) are gratefully acknowledged.

References

1 Z. Goldschmidt, S. Antebi, D. Cohen and I. Goldberg, J. Organomet. Chem., 273 (1984) 347.

2 J. Sauer and R. Sustmann, Angew. Chem. Int. Ed. Engl., 19 (1980) 779 and references cited therein; H. Wollweber in E. Müller (Ed.), Methoden der Organischen Chemie (Houben-Weyl), George Thieme Verlag, Stuttgart, 1970, Vol. V/1c, p. 976; A.S. Onischenko, Diene Synthesis, Israel Program for Scientific Translation, Jerusalem, 1964.

3 I. Fleming, Frontier Orbitals and Organic Chemical Reactions, Wiley, New York, 1976; K.N. Houk in A.P. Marchand and R.E. Lehr (Eds.), Pericyclic Reactions, Academic Press, New York, 1977, Vol. II, p. 181.

4 H. Kessler in H. Müller (Ed.), Methoden der Organischen Chemie (Houben-Weyl), George Thieme Verlag, Stuttgart, 1972 Vol. V/1d, p. 301.

5 (a) K. Alder and G. Jacobs, Chem. Ber., 86 (1953) 1528; (b) H. Ishitobi, H. Tanida, K. Tori and T. Tsuji, Bull. Chem. Soc. Japan, 44 (1971) 2993.

6 (a) R. Hoffmann and R.B. Woodward, J. Am. Chem. Soc., 87 (1965) 4388; (b) W.C. Herndon and L.H. Hall, Theor. Chem. Acta, 7 (1967) 4; (c) M.J.S. Dewar, Tetrahedron Suppl., 8 (1967) 75; (d) L. Salem, J. Am. Chem. Soc., 90 (1968) 553.

7 K.J. Karel, T.A. Albright and M. Brookhart, Organometallics, 1 (1982) 419, and references therein.

8 W. Grimme and H.G. Köser, J. Am. Chem. Soc., 103 (1981) 5919.

9 R. Huisgen, Angew. Chem. Int. Ed. Engl. 7 (1968) 321.

10 (a) M. Green, S. Heathcock and D.C. Wood, J. Chem. Soc., Dalton Trans., (1973) 1564; (b) D.J. Entholt and R. Kerber, J. Organomet. Chem., 38 (1972) 139.

11 M. Green, S. Heathcock, T.W. Turney and D.M.P. Mingos, J. Chem. Soc., Dalton Trans., (1977) 204.

12 (a) Z. Goldschmidt and Y. Bakal, Tetrahedron Lett., (1976) 1229; (b) idem, ibid. (1977) 955; (c) D. Cunningham, P. McArdle, H. Sherlock, B.F.G. Johnson and J. Lewis, J. Chem. Soc., Dalton Trans., (1977) 2340; (d) Z. Goldschmidt and S. Antebi, Tetrahedron Lett., (1978) 271; (e) S.K. Chopra, M.J. Hynes and P. McArdle, J. Chem. Soc., Dalton Trans., (1981) 586; (f) S.K. Chopra, M.J. Hynes, G. Moran, J. Simmie and P. McArdle, Inorg. Chim. Acta, 63 (1982) 177; (g) Z. Goldschmidt and S. Antebi, J. Organomet. Chem., 259 (1983) 119.

13 H.K. Hall, Jr., P. Nogues, J.W. Rhoades, R.C. Sentman and M. Detar, J. Org. Chem., 47 (1982) 1451.

14 For example: (a) M.L.H. Green, L. Pratt and G. Wilkinson, J. Chem. Soc., (1959) 3753; (b) T.N. Margulis, L. Schiff and M. Rosenblum, J. Am. Chem. Soc., 87 (1965) 3269; (c) D.F. Hunt, C.P. Lillya and M.D. Rausch, J. Am. Chem. Soc., 90 (1968) 2561; (d) G.N. Schrauzer, P. Glockner, K.I.G. Ried and I.C. Paul, J. Am. Chem. Soc., 92 (1970) 4479; (e) R. Aumann, Angew. Chem. Int. Ed. Engl., 19 (1971) 188; Chem. Ber., 108 (1975) 1974; (f) A. Eisenstadt, J. Organomet. Chem., 38 (1972) C32; (g) R. Aumann, Chem. Ber., 110 (1977) 1432; (h) J.C. Barborak, S.L. Watson, A.T. McPhail and R.W. Miller, J. Organomet. Chem., 185 (1980) C29; (i) Ph. Narbel, A.A. Pinkerton, E. Tagliaferri, J. Wenger, R. Roulet, R. Garioud, P. Vogel and D. Schwarzenbach, J. Organomet. Chem., 208 (1981) 335.

15 B.E. Mann, Adv. Organomet. Chem., 12 (1974) 135.

16 B. Birdsall, M.J.M. Birdsall and J. Feeney, J. Chem. Soc., Chem. Commun., (1972) 316.

17 J.B. Stothers, ^{13}C NMR Spectroscopy, Academic Press, 1972, p. 183.

18 (a) M. Elian and R. Hoffmann, Inorg. Chem., 14 (1975) 1058; (b) T.A. Albright, Tetrahedron, 38 (1982) 1339.

19 N. Walker and D. Stuart, Acta Cryst., A39 (1983) 158.

20 A.J. Deeming in G. Wilkinson (Ed.), Comprehensive Organometallic Chemistry, Pergamon Press, Oxford, 1982, Vol. 4, p. 337; see also: M.B. Hursthouse, A.G. Massey, A.J. Tomlinson and D.S. Urch, J. Organomet. Chem., 21 (1970) P51; G. Huttner and D. Regler, Chem. Ber., 105 (1972) 3936; M. Bottrill, R. Goddard, M. Green, R.P. Hughes, M.K. Lloyd, B. Lewis and P. Woodward, J. Chem. Soc., Chem. Commun., (1975) 253.

21 T.A. Albright, P. Hofmann and R. Hoffmann, J. Am. Chem. Soc., 99 (1977) 7546; T.A. Albright, R. Hoffmann and P. Hofmann, Chem. Ber., 11 (1978) 1591.

22 R. Hoffmann, Acc. Chem. Res., 4 (1971) 1.

23 (a) R.B. Woodward and R. Hoffmann, The Conservation of Orbital Symmetry, Verlag Chemie, Weinheim, 1970; (b) M.J.S. Dewar and A.B. Pierini, J. Am. Chem. Soc., 106 (1984) 203.

24 L.A. Paquette, G.R. Allen, Jr., and M.J. Broadhurst, J. Am. Chem. Soc., 93 (1971) 4503.

25 F.A. Cotton and G. Wilkinson, Advanced Inorganic Chemistry, 3rd Edition, Wiley-Interscience, 1972, p. 731; M.R. Churchill and R. Mason, Adv. Organomet. Chem., 5 (1967) 93; D.M.P. Mingos, J. Chem. Soc., Dalton Trans., (1977) 20, 26, 31; W.C. Herndon, J. Am. Chem. Soc., 102 (1980) 1538.

26 R. Gleiter and L.A. Paquette, Acc. Chem. Res., 16 (1983) 328.

27 P.V. Alston and R.M. Ottenbrite, J. Org. Chem., 40 (1975) 1111; P.V. Alston, R.M. Ottenbrite and T. Cohen, ibid., 43 (1978) 1864; T. Cohen, R.J. Ruffner, D.W. Shull, W.M. Daniewski, R.M. Ottenbrite and P.V. Alston, ibid., 43 (1978) 4052; P.V. Alston, M.O. Gordon, R.M. Ottenbrite and T. Cohen, ibid., 48 (1983) 5051. See also: I. Fleming and J.P. Michael, Tetrahedron Lett., (1978) 1313; R. Gleiter and D. Ginsburg, Pure Appl. Chem., 51 (1979) 1301; C. Mahaim, P.-A. Carrupt, J.-P. Hagenbuch, A. Florey and P. Vogel, Helv. Chim. Acta, 63 (1980) 1149; R. Gabioud and P. Vogel, Helv. Chim Acta, 66 (1983) 1134; M.E. Garst, V.A. Roberts, K.N. Houk and N.G. Rondan, J. Am. Chem. Soc., 106 (1984) 3882.

28 S.K. Chopra, G. Moran and P. McArdle, J. Organomet. Chem., 214 (1981) C36.

29 J.S. Burnier and W.L. Jorgensen, J. Org. Chem., 49 (1984) 3001.

30 L.T. Scott, I. Erden, W.R. Brunsvold, T.H. Schultz, K.N. Houk and M.N. Paddon-Row, J. Am. Chem. Soc., 104 (1982) 3659 and references therein.

31 H.A. Bockmeulen and A.W. Parkins, J. Chem. Soc., Dalton Trans., (1981) 262; M. Brookhart, K. Karel and L.E. Nance, J. Organomet. Chem., 140 (1977) 203.