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Molecular Orbital Considerations for Kinetically-Controlled Cycloaddition Reactions of Cyclohepta[b]furan-2-ones to 2,3-Bis(methoxycarbonyl)-7-oxabicyclo[2.2.1]heptadiene, Enamines, and Alkoxyethenes

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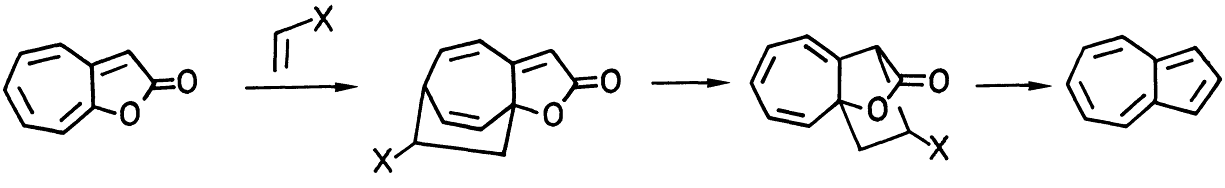
2,3-Bis(methoxycarbonyl)-7-oxabicyclo[2.2.1]heptadiene gave the [4+2] cycloadducts with 8,8-dicyanoheptafulvene and cyclohepta[b]furan-2-ones. This mode is different from the [8+2] cycloadduct formations with the previously studied enamines and alkoxyethenes. The results from MNDO calculations were in accord to the observed modes of the cycloadditions. Thermolysis of the cycloadducts gave the methylidene derivatives of "homobarrelenes".

Currently, formal [8+2] cycloadditions of heptafulvene derivatives attracted attentions: i.e., Takase et al. employed the reaction for preparation of various azulene derivatives from cyclohepta[b]furan-2-ones (**1**) and enamines.1) Furthermore, Nozoe et al. showed that the reaction was applicable to the combination of **1** and alkoxyethenes.2) An MO calculation has predicted the favorite product in the cycloaddition of 3-(methoxycarbonyl)cyclohepta[b]furan-2-one (**1**a) to be [4+2] cycloadduct, and [8+2] cycloadducts, azulene precursors, were explained to be the thermodynamically-controlled products.3)



The cycloadditions of **1** to 2,3-bis(methoxycarbonyl)-7-oxabicyclo[2.2.1]heptadiene (**2**),4) however, gave the [4+2] cycloadducts exclusively. By further heating, these Diels-Alder adducts did not rearrange to [8+2] cycloadducts, but gave unprecedented tricyclic lactones, 2-oxatricyclo[6.2.2.$0^{1,5}$]dodeca-4,6,9,11-tetraen-3-ones (**3**). In this paper, we will describe our experimental findings and the MO considerations on the cycloaddition modes of **1** to olefins.

The thermal reaction of **1**a5) with **2** in chlorobenzene (CB) at 130 °C for 36 h gave three products (**3**a, mp 149–150 °C, **4**a, mp 138–139 °C, and **5**a, mp 189–190

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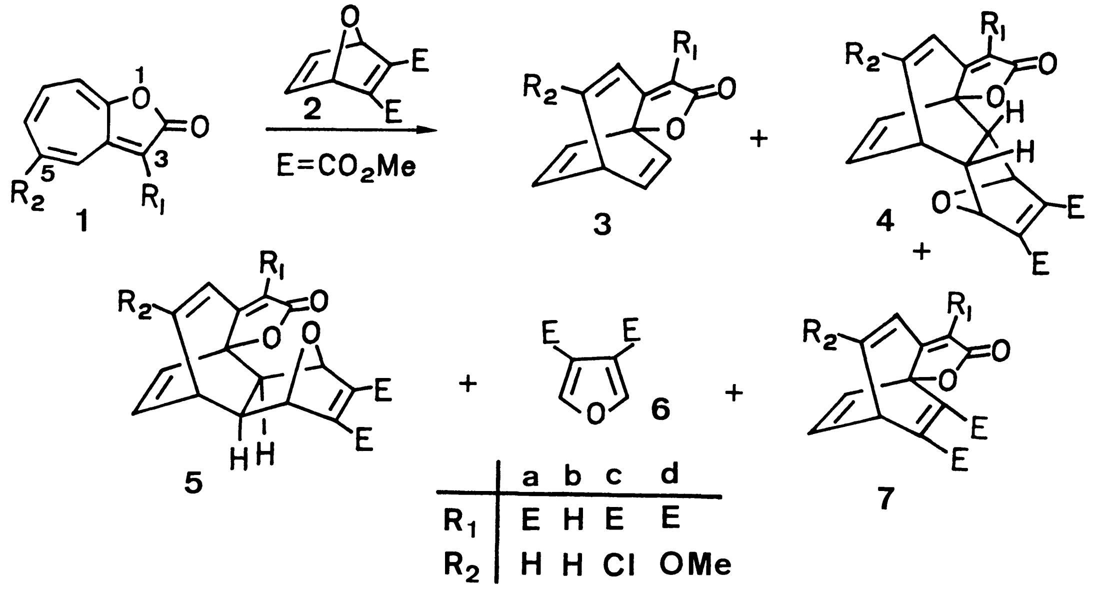
°C)6) together with 3,4-bis(methoxycarbonyl)furan (**6**). The yields are shown in Table 1. The ^{1}H NMR coupling constants of the methine protons deduced the stereochemistries of **4**a and **5**a as depicted. And, **3**a was identified as 4-methoxycarbonyl-2-oxatricyclo[6.2.2.$0^{1,5}$]dodeca-4,6,9,11-tetraen-3-one from the NMR spectrum revealing an element of symmetry. No [8+2] cycloadduct was detectable.

Secondly, the reaction of cyclohepta[b]furan-2-one (**1**b) with **2** gave a 1:1-cycloadduct (**4**b, mp 137–139 °C), cycloreversed **3**b (mp 116.5–117.5 °C) and a Diels-Alder adduct of **1**b to dimethyl butynedioate (**7**b, mp 121–123 °C).

The reactions of **2** with 5-chloro-3-methoxycarbonyl (**1**c)7) and 5-methoxy-3-methoxycarbonyl (**1**d)7) derivatives were similar. The reaction under high-pressure conditions improved the yields of **4**; i.e., at 130 °C under 3000 bar for 36 h, **1**a and **2** afforded **4**a, **3**a, and **6** in 70, 11, and 12% yields, respectively. The pyrolysis of **4** at 130 °C gave **3** and **6** as summarized in Table 2.



	a	b	c	d
R1	E	H	E	E
R2	H	H	Cl	OMe

Table 1. Product Distributions (Yield/%) of the Reaction of **1** and **2** at 130 °C

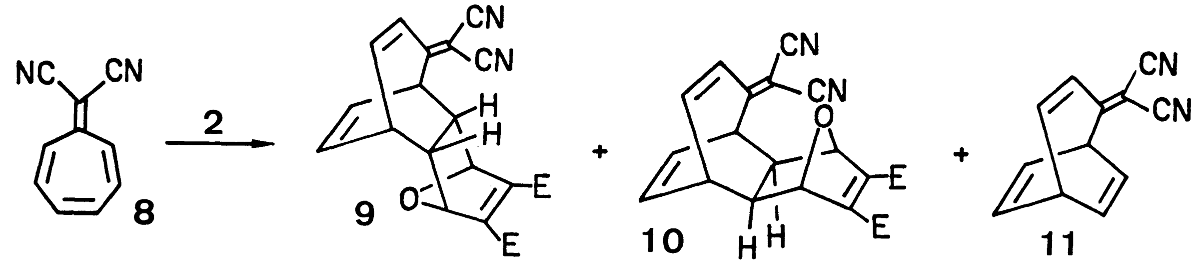
	3	**4**	**5**	**7**	**6**
1a+**2** ⟶	40	43	11	0	41
1b+**2** ⟶	35	26	0	7	35
1c+**2** ⟶	33	14	6	2	33
1d+**2** ⟶	50	34	12	4	50

Table 2. Pyrolysis of **4** to **3** at 130 °C (Yield/%)

	3	**6**
4a ⟶	57	57
4b ⟶	54	54
4c ⟶	70	70
4d ⟶	55	55

Moreover, the reaction of **2** with 8,8-dicyanoheptafulvene (**8**)8) similarly gave the [4+2] cycloadducts (**9**, mp 164–165 °C, 43%, **10**, mp 183–184 °C, 10%) along with the cycloreversed 2-(dicyanomethylidene)homobarrelene (**11**, mp 71–73 °C), in 42% yield. Under 3000 bar, yields of **9** and **10** increased to 76% and 13%, but that of **11** was 2.5%. Thermolysis of **9** in CB at 130 °C for 48 h also gave **11** in 95% yield.

No occurrence of [8+2] cycloadducts even under 1 bar being different from the mode of the reaction between **1** and enamines or alkoxyethenes should be mentioned. The frontier orbitals of **1**b and **2** were calculated by MNDO method together with dimethylaminoethene (**A**) and methoxyethene (**B**).



From the energy separation between frontier orbitals, the [8+2] adducts are preferably formed in the reactions between **1** and **2**, while formation of the [4+2] adducts was favorable in the reactions of **1** with **A** or **B**.

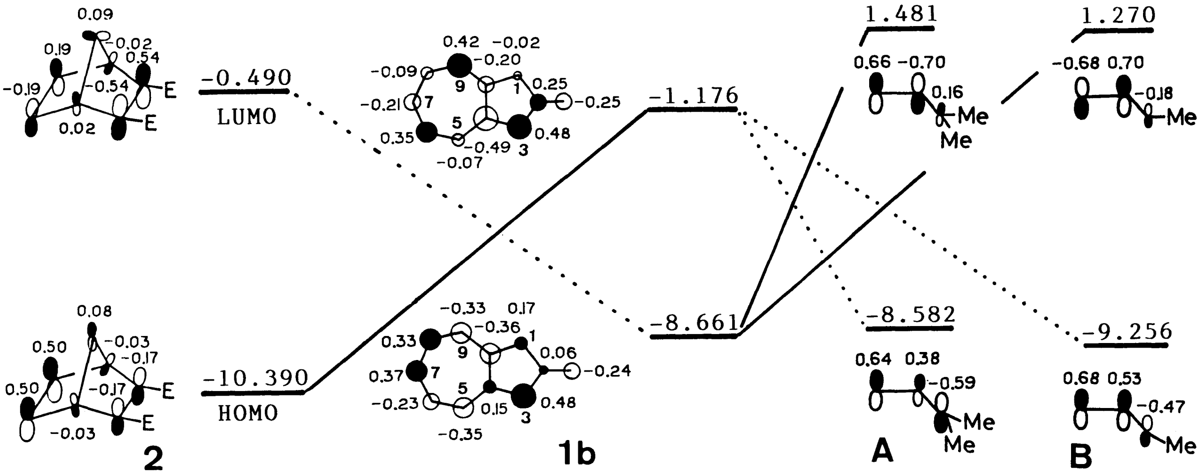


Fig. 1. HOMO-LUMO Correlation Diagrams of **1**b and Olefins.

The exclusive formation of [4+2] adducts from **1** and **2** and [8+2] adducts from **1** and **A** or **B** can be explained in terms of the squares of the coefficients of the frontier orbitals: the energy difference is more favorable for HOMO(**2**)-LUMO(**1**b) interaction ($\Sigma(CrCs)^2/9.21$ eV = 0.005) which expects the [4+2] adduct, than the [8+2]-adduct-forming HOMO(**1**b)-LUMO(**2**) interaction ($\Sigma(CrCs)^2/8.17$ eV = 0.003). In the same time, the antibonding interaction disfavored a formation of the [8+2] adduct (from HOMO(**2**)-LUMO(**1**b) interaction). By analogy, the HOMO(**1**b)-LUMO(**A** or **B**) interactions (0.032 for [8+2] adduct of **A**, 0.034 for **B**) became more favorable than the alternative interactions (0.006 for [4+2] adduct of **A**, 0.008 for **B**).

Consequently, the MO considerations were fully in accord to the results between **1** and olefins. It is highly probable that [8+2] adducts from **1** and **A** or **B** are kinetically-controlled products, although Takase et al. have suggested to be the thermodynamic products on the experimental basis of **1** and 6,6-dimethylfulvene.$^{9)}$

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6) All the products were fully characterized, including following ^{1}H and ^{13}C NMR of key compounds.

3b: δ(H)=3.96(1H, dtt, J=7.7, 6.6, 1.1 Hz), 5.70(1H, s), 6.00(1H, d, J=10.6 Hz), 6.35(2H, dd, J=7.7, 1.1 Hz), 6.52(2H, dd, J=7.7, 6.6 Hz), and 6.57(1H, dd, J=10.6, 7.7 Hz). δ(C)=40.1, 87.8, 111.6, 118.7, 132.1(2C), 133.0(2C), 139.8, 158.2, and 173.5.

4b: δ(H)=2.29(1H, dd, J=8.1, 1.1 Hz), 2.53(1H, dd, J=8.1, 1.1 Hz), 3.48(1H, dd, J=8.8, 7.7 Hz), 3.81(6H, s), 4.92(1H, d, J=1.1 Hz), 5.47(1H, d, J=1.1 Hz), 5.66 (1H, s), 6.09(1H, s, J=8.4 Hz), 6.21(1H, dd, J=8.4, 7.7 Hz), 6.33(1H, d, J=10.6 Hz), and 6.67(1H, dd, J=10.6, 8.8 Hz). δ(C)=39.4, 44.2, 49.3, 52.7, 52.8, 83.6, 85.5, 88.1, 111.4, 121.7, 130.0, 131.0, 144.2, 145.4, 145.5, 162.7, 162.9, 164.0, and 172.8.

5a: δ(H)=2.58(1H, dd, J=8.8, 5.9 Hz), 3.02(1H, d, J=8.8 Hz), 3.73(1H, ddd, J=8.4, 7.0, 5.9 Hz), 3.80(3H, s), 3.81(3H, s), 3.89(3H, s), 4.74(1H, d, J=1.1 Hz), 4.87(1H, d, J=1.1 Hz), 6.22(1H, dd, J=8.4, 0.7 Hz), 6.44(1H, dd, J=8.4, 7.0 Hz), 6.73(1H, dd, J=10.6, 8.4 Hz), and 7.41(1H, d, J=10.6 Hz). δ(C)=38.3, 41.8, 52.1, 52.4, 52.5, 52.6, 79.1, 83.2, 87.4, 113.3, 125.9, 133.1, 135.1, 144.5, 145.4, 146.1, 161.5, 161.8, 162.5, 167.2, and 167.9.

7b: δ(H)=3.78(3H, s), 3.83(3H, s), 4.51(1H, dd, J=7.7, 7.0 Hz), 5.83(1H, s), 6.15(1H, d, J=10.6 Hz), 6.39(1H, dd, J=7.7, 1.5 Hz), and 6.6(2H, m). δ(C)=39.5, 52.8, 52.9, 86.4, 113.3, 119.9, 131.9, 132.7, 133.6, 138.2, 145.0, 155.6, 163.1, 163.9, and 171.7.

9: δ(H)=2.38(1H, dm, J=7.7 Hz), 2.65(1H, dd, J=7.7, 1.1 Hz), 3.51(1H, ddm, J=8.1, 7.7 Hz), 3.82(3H, s), 3.83(3H, s), 4.17(1H, dm, J=7.0 Hz), 4.93(1H, d, J=1.1 Hz), 5.10(1H, d, J=1.1 Hz), 6.09(1H, dd, J=7.7, 7.0 Hz), 6.46(1H, t, J=7.7 Hz), 6.52(1H, dd, J=10.6, 2.2 Hz), and 7.02(1H, dd, J=10.6, 8.1 Hz). δ(C)=40.0, 44.0, 46.1, 48.2, 52.5, 52.6, 81.1, 85.5, 84.6, 111.7, 112.8, 125.4, 126.3, 136.6, 144.9, 145.6, 152.0, 162.3, 162.7, and 169.4.

10: δ(H)=2.63(1H, dd, J=8.4, 5.8 Hz), 2.78(1H, dd, J=8.4, 5.5 Hz), 3.64(1H, td, J=8.0, 5.8 Hz), 3.81(3H, s), 3.83(3H, s), 4.27(1H, t, J=7.0, 5.5 Hz), 4.82(2H, s), 6.16(1H, dd, J=7.3, 7.0 Hz), 6.62(1H, dd, J=8.0, 7.3 Hz), and 6.7–6.8(2H, m). δ(C)=38.8, 44.9, 47.3, 48.0, 52.5, 52.6, 81.7, 82.6, 83.2, 111.8, 113.2, 129.2, 129.9, 140.4, 145.3, 146.0, 147.3, 162.4, 162.5, and 169.5.

11: δ(H)=3.98(1H, dtm, J=8.4, 6.6 Hz), 4.68(1H, tdd, J=6.6, 2.2, 1.5 Hz), 6.06 (1H, dd, J=10.6, 2.2 Hz), 6.36(2H, td, J=6.6, 1.5 Hz), 6.84(2H, td, J=6.6, 1.5 Hz), and 6.95(1H, dd, J=10.6, 8.4 Hz). δ(C)=41.8, 46.8, 81.8, 111.6, 113.1, 122.3, 128.3(2C), 140.2(2C), 149.2, and 164.1.

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