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CYCLOADDITION REACTION OF METHYL 2-PYRONECARBOXYLATES WITH 1,3-DIENES

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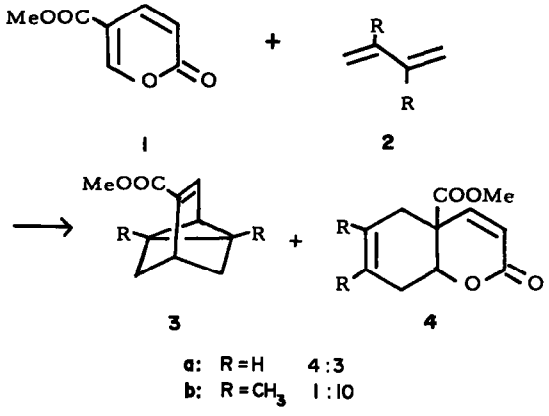
Abstract—The experimental results of thermal cycloaddition reactions of methyl 2-pyrone-3-, 4-, 5- and 6-carboxylates with 1,3-dienes and the theoretical approach by a second order perturbation MO method are described. The sequential introduction of a methoxycarbonyl group onto a 2-pyrone ring caused a variety of selectivities in the cycloaddition reactions with 1,3-butadienes. PMO treatment based only on the frontier molecular orbitals failed to account adequately for this selectivity phenomena because the relative magnitudes of the coefficients in the HO and LU orbitals of 2-pyrones were little affected by the introduction of a substituent. PMO treatment including superjacent and subjacent orbitals along with frontier orbitals rationalized excellently the observed selectivity phenomena.

The Woodward–Hoffmann rule[1] has made a great contribution to the study of cycloaddition reactions. When, however, there are many symmetry-allowed cycloaddition pathways, the orbital symmetry principle cannot give the most favoured pathway (periselectivity),[2] predict the preferred orientation (regioselectivity),[3] nor define their relative reaction rates (reactivity). Recently, several methods applicable to the present problem for predicting the reaction path have been proposed including PMO treatment.[4]

We reported[5] that the thermal cycloaddition reactions of methyl 2-pyrone-5-carboxylate **1** with 1,3-butadienes **2** afforded the tricyclo[3.2.1.$0^{2,7}$]oct-3-enes **3** and tetrahydrocoumarins **4**. In the reactions to afford **3**, the 2-pyrone **1** behaved as a 4π-addend; in the cases to give the latter **4**, **1** acted as a 2π-addend.



Scheme 1.

A priori, there are several modes of [4+2]-addition path in the thermal cycloaddition reaction of a 2-pyrone derivative with a 1,3-diene. Consequently, we think that the 2-pyrone-carboxylates are appropriate model compounds for the purpose of the investigation of the above-mentioned selectivity of the cycloaddition reaction, because each of four substitutions by a methoxycarbonyl group onto 2-pyrone ring causes significant perturbation in charge densities[6] but only has a minimum effect on steric interaction.

Now we wish to describe the product analyses of the thermal cycloaddition reactions of methyl 2-pyrone-3-, 4-, 5- and 6-carboxylates with 1,3-butadienes and to give a rationalization of their selectivities by a second order perturbation molecular orbital (PMO) treatment.[7]

RESULTS AND DISCUSSION

All thermal reactions with 1,3-dienes were continued until no 2-pyrone could be detected by GLC and/or TLC except in the case of the 6-carboxylate.

Reaction with 1,3-*butadiene* **1a**. Reaction of methyl 2-pyrone-3- carboxylate **5** with **2a** in benzene at 150° for 18 h in a pressure bottle afforded two products, **6** (33%) and **7** (2%). The structure of **6**, methyl tricyclo[3.2.1.$0^{2,7}$]oct - 3 - ene - 2 - carboxylate, may be readily deduced by comparison of the ^{1}H-NMR spectrum with that of **3a** (see Table 1). A signal of $H_1(H_7)$ appeared as a singlet at lower field (δ 2.07) than those of other tricyclic compounds. The two olefinic proton resonances which coupled with each other (8.4 Hz) are further split by the coupling with the bridgehead proton H_5. This fact indicates that the methoxycarbonyl group is attached to C_2 of the tricyclic framework.

The minor product **7** is found to be methyl *m*-methoxycarbonyl-cinnamate, identified by comparison with an authentic sample.[8]

Heating of **5** in benzene at 150° for 24 h also gave **7** in a similar yield. Consequently, **7** is thought to originate from the dimer of **5** by consecutive decarboxylation, ring opening, and decarboxylation.[9]

To examine the Cope rearrangement of the kinetically controlled product described later, the reaction of **5** with **2a** was tried at 70° for 8 days. PLC separation gave only the precursors of **6**, **8** and **9**, in the ratio of 4.5 : 1. Under these conditions it is thought that the usual Cope rearrangement does not occur.

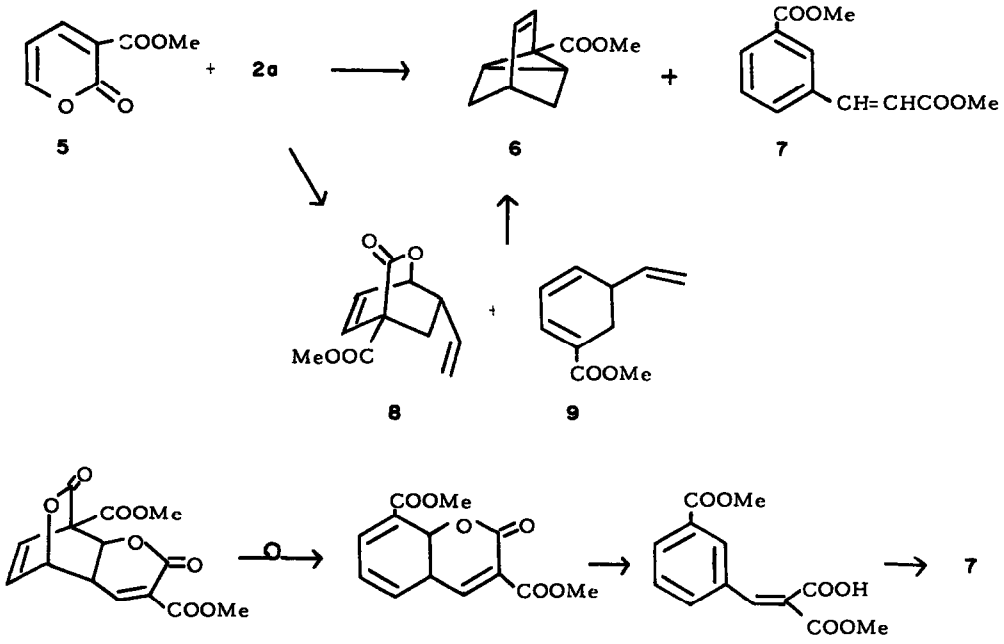
A similar reaction of methyl 2-pyrone-4-carboxylate **10** with **2a** at 150° for 24 h gave two tricyclic compounds, **11** and **3a**, in the ratio of 1.7 : 1 as revealed by ^{1}H NMR assay based on the ester-methyl signals. This ester mixture could not be separated by the ordinary methods (TLC or GLC). In order to effect the separation, this mixture was converted into an aldehydic mixture composed of **12** and **13** by LAH reduction, followed by MnO_2 oxidation. After preparative GLC separation, **12**

Table 1. ^{1}H NMR data for the tricyclic compounds. (Chemical shifts in δ (ppm); coupling constants in Hz)

Compound	H_1	H_2	H_3	H_4	H_5	H_{8X}	H_{8N}	CH_3	COOMe
6	2.07	—	6.27	5.84	2.55	0.80	1.62	—	3.68
11	2.1	2.1	—	6.98	2.66	0.73	1.61	—	3.76
3a	1.57	1.6	6.93	—	3.12	0.72	1.59	—	3.64
15	1.51	1.5	5.84	6.05	—	0.84	1.91	—	3.67
19	—	—	6.24	5.87	2.39	0.97	1.56	1.36	3.66
16	—	1.79	—	6.91	2.58	0.79	1.56	1.26	3.75
3b	—	1.2	6.99	—	3.08	0.79	1.57	1.28	3.64
20	—	1.3[a]	6.05[a]	6.05[a]	—	1.00	1.80	1.21	3.77

	$J_{1,2}$	$J_{2,3}$	$J_{2,4}$	$J_{3,4}$	$J_{3,5}$	$J_{4,5}$	$J_{5,8X}$	$J_{5,8N}$
6	—	—	—	8.4	1.2	6.9	4.8	11.8
11	8.4	—	2.7	—	—	7.6	5.0	11.6
3a	[b]	5.6	—	—	1.8	—	4.8	11.7
15	[b]	5.0	1.9	8.9	—	—	—	11.3
19	—	—	—	8.4	1.4	6.5	5.0	12.0
16	—	—	2.5	—	—	7.4	4.5	11.8
3b	—	6.3	—	—	2.1	—	5.1	11.7
20	—	[a]	[a]	[a]	—	—	—	11.2

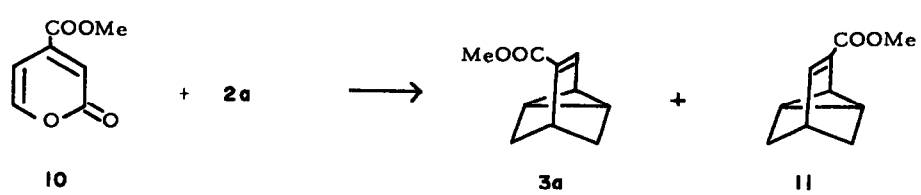
[a] Deceptively simple ABX spectra; two lines (6 Hz spacing).
[b] Obscured.



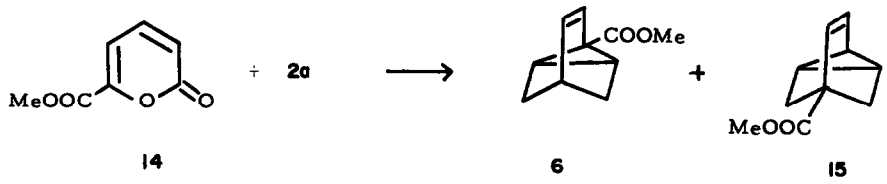
Scheme 2.

was reconverted to the methyl ester **11** by Corey's method,[10] whose ^{1}H NMR spectrum showed only one olefinic proton signal and the H_2 proton signal due to the methoxycarbonyl at C-4 at lower field (0.6 ppm) than that of **3a**. The minor one **13** was identical with the aldehyde derived from **3a** which was obtained in the reaction of **1** and **2a**.

Reaction of **1** with **2a** at 150° for 40 h gave only **3a** and no tetrahydrocoumarin derivative **4a** was obtained under these conditions.



Scheme 3.



Scheme 4.

Heating methyl 2-pyrone-6-carboxylate **14** and **2a** at 150° for 13 days gave two tricyclic compounds, **6** and **15**, in the ratio of 3.3:1 by GLC analysis, but the reactivity of **14** toward **2a** was very poor and much of **14** was recovered unchanged (64%). The location of the methoxycarbonyl group in **15** was assigned by the downfield shift of the *endo*-H_8 by about 0.3 ppm in its ^1H NMR spectrum (Table 1).

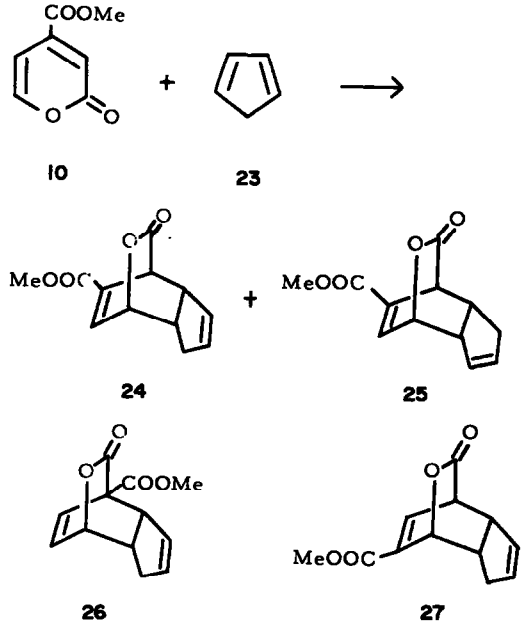
Reaction with 2,3-dimethylbutadiene **2b**. Reaction of **10** with excess of **2b** in benzene at 150° for 36 h gave a major product **18** in 75% yield and three minor products **16**, **3b** and **17**. The structure of the major product **18**, 6,7 - dimethyl - 4a - methoxycarbonyl - 4a,5,8,8a - tetrahydroisocoumarin, and minor product **17**, 6,7 - dimethyl - 4 - methoxycarbonyl - 4a,5,8,8a - tetrahydrocoumarin, were inferred from their elemental analyses, IR and NMR spectra. The ^1H NMR spectra of **18** shows two olefinic protons constituting an AB quartet ($J = 6.0$ Hz) and **17** showed only one olefinic proton as a singlet (δ 6.68). The structure of **16** was inferred by comparison with the ^1H NMR of **11**.

In order to examine the possibility of Cope rearrangement, the thermal treatment of **18** at 180° for 24 h in a sealed tube was carried out and only **18** was recovered (GLC and ^1H NMR analysis).

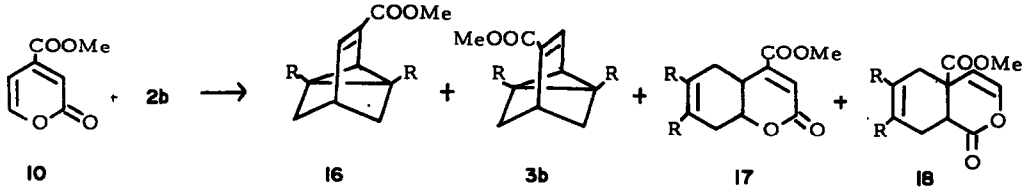
Similar reaction of **14** with **2b** for 6 days gave four products, **19**, **20**, **21** and **22** in 7, 12, 17 and 12% yield, respectively, based on the recovered starting material **14**. Therefore there was no significant selectivity in this reaction. Thermal treatment of **21** at 180° for 24 h also did not induce any appreciable change.

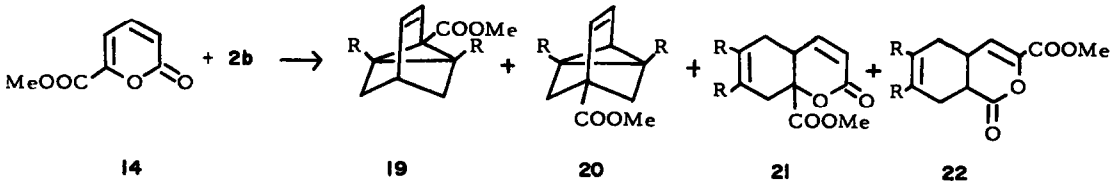
Reaction of **5** with **2b** gave an oily mixture, in which no 1:1 adduct was detected by GLC and ^1H NMR but the adducts between one molecule of **5** and two molecules of **2b** was obtained as evidenced by mass spectrum (M^+, 318) and NMR spectrum. But they were not further investigated because of difficulty in separation.

Reaction of **10** *with cyclopentadiene.* Reaction of **10** with cyclopentadiene **23** in boiling benzene solution for 3 h yielded a crystalline mixture, **24** and **25**, in the ratio of 2:1, which was confirmed by ^{13}C NMR spectrum using Cr(III)-acetylacetonate as a relaxation reagent with use of gated decoupling (without NOE with ^1H-decoupling).[11] This crystalline mixture was composed of two 1:1 adducts of **10** and **23** as judged from its elemental analysis, and ^1H and ^{13}C NMR spectra indicated that the molecular framework of these adducts were very similar to those of **26** and **27**.[5] The major adduct **24**, obtained by



Scheme 6.

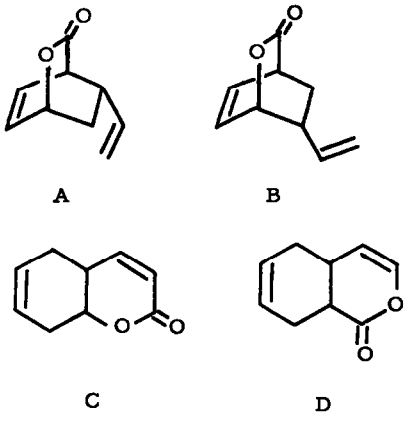




Scheme 5.

fractional recrystallization, was 5 - methoxycarbonyl - r - 3a,4,7,c - 7a - tetrahydroindene - c - 4,c - 7 - carbolactone. The position of the double bond in the cyclopentene moiety of **24** was determined using ^{1}H NMR decoupling technique. The minor adduct **25** was not isolated but its structure was deduced by ^{1}H and mainly ^{13}C NMR spectra of the mother liquor enriched with **25**.

Perturbation MO treatment. There are four possible symmetry allowed adducts resulting from the first cycloaddition reaction between the 2-pyrone and a 1,3-diene; type A, B, C and D. Type A and B adducts are regioisomers when the 2-pyrone reacts as a diene, and collapse into tricyclic derivatives by intramolecular cycloadditions. When the 2-pyrone reacts as a dienophile, type C adduct (a tetrahydrocoumarin) or type D adduct (a tetrahydroisocoumarin) is formed.



In the reaction reported here the change of position of the methoxycarbonyl group in the 2-pyrone ring caused the different modes of addition. We now describe a PMO treatment of this problem which leads to an understanding of the different selectivities.

The perturbation method has become an increasingly powerful tool for the understanding of diverse fields including cycloaddition reactions.[12] From well-known formulas of a second order perturbation theory[7] we can write an equation for the stabilization energy (SE) of the interaction of two molecules M and N where the union of M and N occurs at atoms r and s, and t and u.

$$SE = 2\left(\sum_{M}^{occ}\sum_{N}^{vac} - \sum_{M}^{vac}\sum_{N}^{occ}\right)\frac{(C_r^M C_s^N \gamma_{rs} + C_t^M C_u^N \gamma_{tu})^2}{E_M - E_N}.$$

In the expression above, γ stands for the resonance integral between the two interacting atomic orbitals at the union sites, and E_M and C_r^M are the energy and the coefficient of atom r of the corresponding MO of molecule M, respectively.

Most perturbation treatment of cycloaddition reactions has only focused on the interactions between the frontier orbitals (highest occupied (HO) and lowest unoccupied (LU)) of both reactants, since the inverse dependence of SE on the orbital energy differences (ΔE) ensures that the terms involving the frontier orbitals will be larger than those of the others.

In this report we retained the standpoints involving (i) computation of both HO–LU without choosing the term of minimum ΔE (the frontier orbital method) and (ii) evaluation of orbital energy by experimental values rather than calculation since the latter values are fairly dependent on the method of calculation.

The relative magnitudes of orbital coefficients (such as C_r^M) were determined by the result of CNDO/2 calculation.[6]

The HO orbital energies of 2-pyrones and 1,3-dienes[15] were approximated from ionization potential data obtained from the photoelectron spectra, assuming Koopmans' theorem.

The LU orbital energy may be set equal to the negative of the electron affinity of the molecule; the values have, however, not been obtained for 2-pyrones and 1,3-dienes. The relative energies of the LU orbitals in a similar series of molecules can be approximated from electron transition data, and the estimation by the following relationship is described in detail in Houk's report.[13]

$$E_{LU} - E_{HO} = \pi\pi^* \text{ transition energy} + \Delta.$$

We have chosen the Δ values for the 2-pyrone (4.6 eV) and for the 1,3-dienes (4.3 eV) as estimated by Houk.[13,14] Then the LU orbitals of 2-pyronecarboxylates and 1,3-dienes are calculated from the UV spectral maxima of each using the above relationship.

Figure 1 shows that the energy gap (ΔE) between LU(pyrone)–HO(diene) is the smallest and this frontier orbital interaction is much more important in all cases.

In the LU orbitals of 2-pyrones, the coefficients at C-4 are very large and those of C-5 are smallest. Due to the larger differences between the coefficients at C-4 and C-5, LU(pyrone)–HO(diene) interaction preferentially stabilizes the transition states leading to type D adducts. But another frontier interaction, HO(pyrone)–LU(diene) contributes to the type C adducts. The relative magnitudes of the coefficients in HO and LU orbitals of 2-pyrones are little affected by the introduction of a methoxycarbonyl group.

The summations of two terms of frontier orbital interactions predict only the type D adduct except for the

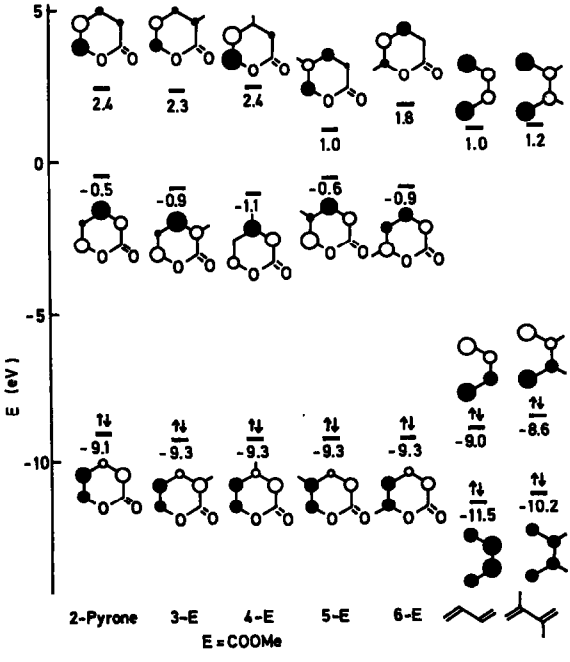


Fig. 1. Estimated orbital energies and coefficients for 2-pyrones and 1,3-butadienes.

cases of 6-carboxylate with 1,3-dienes predicting the type C, and consequently cannot explain the observed results.

Recently it was suggested that the subjacent and superjacent orbitals (next HO (NHO) and next LU (NLU)) played important roles along with the frontier orbitals in the understanding of the reactivities.[16] In the field of cycloaddition, the periselectivity in the reaction of fulvene is discussed in terms of a crossover of LU and NLU[17] and the superjacent orbital effects.[18] Therefore, in order to rationalize the observed selectivity, the interactions including NHO and NLU were taken into consideration, but the terms related to NHO(pyrone) and NLU(diene) are not considered because energy gaps of the corresponding interactions were far larger than those of the frontier orbital interactions and consequently the contributions was exceedingly small.

The NHO orbital energies of 1,3-dienes are determined directly from the photoelectron spectra as 11.46 eV for 1,3-butadiene and 10.18 eV for 2,3-dimethylbutadiene.[15] The NLU energies of 2-pyrones are estimated directly from the differences of the corresponding orbital energies (ΔE_{NLU-LU}) calculated by CNDO/2 by summing up to the estimated LU energies. The values thus obtained are shown in Fig. 1.

As Fig. 1 shows, the introduction of a methoxycarbonyl group perturbed the NLU orbitals very much, in which the coefficient at C-6 was much larger in 4-carboxylate, and much smaller in the 6-derivative. The separations of NLU(pyrone)–HO(diene) are 9.6–11.4 eV and are comparable to those of HO(pyrone)–LU(diene) (10.2–10.5 eV).

LU(pyrone)–NHO(diene) separations were 10.5–10.9 eV for 1,3-butadiene and 9.2–9.6 eV for 2,3-dimethylbutadiene, and rather smaller than those of NLU(pyrone)–HO(diene). This interaction term contributes to the SE of type A and type B modes. Because the NHO of 1,3-dienes are symmetric in nodal property, the contribution of type C or type D is small from the orbital symmetry criteria.

The total SE summed up four terms (Table 2) indicates reasonable predictions except for the cases of the adducts of 4-carboxylate.

The type C adduct **4a** from the reaction of 5-carboxylate with 1,3-butadiene was easily transformed into the tricyclic compound **3a** when heated at 150°. This transformation is considered to be the [3,3]-sigmatropic reaction (Cope rearrangement).[5] In the reactions with 1,3-butadiene the [3,3]-sigmatropic reaction of type C adduct into the type A adduct is probably possible in all cases at the reaction temperature of 150°. Similarly, type D adduct can be converted into the type B product by this rearrangement. Then two different paths (path i and path ii in Scheme 7) are possible for the formation of the tricyclic compounds. However, in the reactions with 2,3-dimethylbutadiene none of the Cope rearrangement occurred at 150°.

In our PMO treatment the type C adduct is predicted in the case of 4-carboxylate with 1,3-butadiene. Accordingly it may be argued that the observed type A adduct could be formed from type C aduct by [3,3]-sigmatropic reaction.

Evidently the thermal reaction should be studied at reaction temperatures lower than those causing [3,3]-sigmatropic reaction. However 2-pyrone-4- and 6-carboxylates (**10** and **14**) reacted with 1,3-butadiene at 100° to give complicated results, because of the formation of many labile intermediate adducts such as type **8** and **9**, and of low reactivity.

In the reaction of 4-carboxylate with 2,3-dimethylbutadiene, the type D adduct was the major product experimentally but PMO treatment predicts the type C adduct as the most favourable one. The driving force of the prediction of type C is mainly the very large magnitudes of the coefficients of C-5 and C-6 in the NLU of 4-carboxylate. This result is reminiscent of the difficulty in estimating the energy level of superjacent orbitals, which was beyond our experimental method until now.[19]

CONCLUSIONS

(1) The sequential introduction of a methoxycarbonyl group onto a 2-pyrone ring causes a variety of selectivities in the cycloaddition reaction with 1,3-dienes.

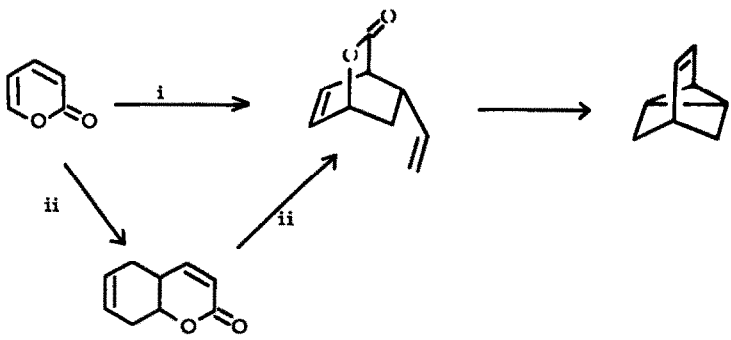
(2) PMO treatment based only on the frontier molecular orbitals failed to account adequately for this selectivity phenomena.

(3) PMO treatment including superjacent and subjacent orbitals along with frontier orbitals rationalized fairly well the observed selectivity.

EXPERIMENTAL

All m.ps were determined on a hot-stage microscope and are uncorrected as are b.ps. IR spectra were recorded as neat film, unless otherwise specified, on a Shimadzu IR-27C spectrometer. Mass spectra (MS) were obtained with a Hitachi RMS-4 spectrometer at 70 eV. ^{1}H NMR spectra were measured on a Varian EM-360 spectrometer, unless otherwise specified, in CCl_4 solution using TMS as an internal standard. Decoupling experiments were conducted on a Varian HA-100 spectrometer (frequency sweep). ^{13}C NMR spectra were obtained using a Varian CFT-20 spectrometer in $CDCl_3$ solution, using TMS as an internal standard. Microanalyses were performed by Mrs. K. Fujimoto using a Yanagimoto C.H.N. Corder MT-1.

Compounds **1**, **5**, **10** and **14** were prepared according to reported methods.[20]



Scheme 7.

Table 2. The interaction energies[a] of various terms together with corresponding ΔE values (eV), total SE,[a] and experimental results

Type	LU_P–HO_B	HO_P–LU_B		NLU_P–HO_B	LU_P–NHO_B	Total SE	Exp (ratio)
3-COOMe + 1,3-*butadiene*							
A	2.24	1.32	3.6	0.54	1.62	5.7	100
B	2.10	1.44	3.5	0.36	1.72	5.6	0
C	1.46	1.67	3.1	1.62	0.19	4.9	0
D	3.75	1.40	5.2	0.01	0.06	5.2	0
ΔE	8.1	10.3		11.3	10.6		
4-COOMe + 1,3-*butadiene*							
A	1.87	1.36	4.2	1.45	1.57	6.2	63[b]
B	2.06	1.47	3.5	0.93	1.45	5.9	37[b]
C	0.65	1.76	2.4	4.01	0.14	6.6	0
D	3.72	1.43	5.1	0.03	0.00	5.2	0
ΔE	8.0	10.3		11.5	10.5		
5-COOMe + 1,3-*butadiene*							
A	2.68	1.30	4.0	0.44	1.90	6.3	43
B	2.44	1.38	3.8	0.18	2.07	6.1	0
C	2.10	1.78	3.9	1.82	0.20	5.9	57
D	3.13	1.27	4.4	0.52	0.01	4.9	0
ΔE	8.4	10.3		10.0	10.9		
6-COOMe + 1,3-*butadiene*							
A	2.35	1.36	3.7	0.18	1.74	5.6	23[b]
B	2.26	1.45	3.7	0.12	1.80	5.6	77[b]
C	2.41	1.81	4.2	1.27	0.04	5.5	0
D	2.84	1.35	4.2	0.64	0.00	4.8	0
ΔE	8.1	10.3		10.8	10.6		
3-COOMe + 2,3-*dimethylbutadiene*							
A	2.24	1.21	3.5	0.52	0.98	5.0	—
B	1.97	1.32	3.3	0.32	0.98	4.6	—
C	1.49	1.54	3.0	1.63	0.15	4.8	—
D	3.83	1.29	5.1	0.19	0.05	5.4	—
ΔE	7.7	10.5		10.9	9.3		
4-COOMe + 2,3-*dimethylbutadiene*							
A	1.75	1.25	3.0	1.43	0.88	5.3	5
B	1.98	1.35	3.3	0.81	0.88	5.0	2
C	0.67	1.62	2.3	4.04	0.11	6.4	6
D	3.81	1.31	5.1	0.03	0.00	5.2	86
ΔE	7.6	10.5		11.1	9.2		
5-COOMe + 2,3-*dimethylbutadiene*							
A	2.57	1.12	3.7	0.45	1.16	5.3	9
B	2.27	1.27	3.5	0.14	1.16	4.8	0
C	2.13	1.64	3.8	1.85	0.16	5.8	91
D	3.19	1.17	4.4	0.53	0.01	4.9	0
ΔE	8.0	10.5		9.6	9.6		
6-COOMe + 2,3-*dimethylbutadiene*							
A	2.23	1.25	3.5	0.08	1.04	4.6	25
B	2.12	1.35	3.5	0.01	1.04	4.5	15
C	2.46	1.66	4.1	1.28	0.03	5.4	35
D	2.91	1.24	4.1	0.65	0.00	4.8	25
ΔE	7.7	10.5		10.4	9.3		

[a] All SE are presented by the unit of $2 \times 10^{-2} \times \gamma^2$/eV.
[b] May not be formed via kinetic control (see Text).

Reaction of **5** *with* **2a**. (a) A mixture of **5** (311 mg) and **2a**, which was prepared from 3-sulfolene (709 mg) *in-situ*, was heated at 150° for 18 h in benzene in a pressure bottle with a trace of hydroquinone (N_2 atmosphere). After evaporation, Kugelrohr distillation gave two fractions. First fraction (132 mg; 80–140°/3 mm) purified by preparative TLC gave 110 mg (33%) of methyl tricyclo[3.2.1.$0^{2,7}$] - oct - 3 - ene - 2 - carboxylate **6**; b.p. 82°/3 mm; IR: 1735, 1620 cm^{-1}; MS: *m/e* 164 (M^+, 39), 133 (12), 105 (100), 104 (14), 103 (12), 79 (15), 77 (19%). (Found: C, 73.01; H, 7.39. Calc. for $C_{10}H_{12}O_2$: C, 73.14; H, 7.37%). Separation by preparative TLC of the second fraction (32 mg; 140–180°/3 mm) gave 11 mg (2%) of pure methyl *m*-methoxycarbonylcinnamate **7**; m.p. 79–80° (lit.[8] 79–80°); IR: 1725, 1640, 750, 710 cm^{-1}; MS: *m/e* 221 ($M^+ + 1$, 14), 220 (M^+, 69), 189 (100), 157 (71), 149 (30%); ^1H NMR: δ 7.3–8.3 (m, 4H, Ph-), 7.72 (d, 1H, 16.4 Hz), 6.48 (d, 1H, 16.4 Hz), 3.93 (s, 3H), 3.81 (s, 3H).

Heating **5** (154 mg) in PhH at 150° for 24 h gave **7** (5 mg; 2%) after purification.

(b) A solution of **5** (312 mg) and a trace of hydroquinone in 10 ml of PhH and 3 ml of **2a** was heated at 70° in a pressure bottle for 8 days. After evaporation of the solvent, preparative TLC separation gave 282 mg (68%) of **8** and 51 mg (15%) of **9**.

1 - Methoxycarbonyl - 6 - vinyl - 2 - cyclohexene - 1,4 - carbolactone **8**: IR: 1740, 1760 cm^{-1}; ^1H NMR($CDCl_3$): δ 6.79 (ddd, $J_{2,3}$ = 7.9, $J_{2,4}$ = 1.9, $J_{2,6}$ = 1.0 Hz, H_6), 6.57 (dd, $J_{2,3}$ = 7.9, $J_{3,4}$ = 5.0 Hz, H_3), 4.9–5.6 (m, 3H, –CH=CH_2), 3.90 (s, 3H, OCH_3), 3.22 (ddd, $J_{5X,6}$ = 9.3, $J_{6,7}$ = 7.6, $J_{5N,6}$ = 3.6 Hz, H_6), 2.58 (ddd, $J_{5N,5X}$ = 13.7, $J_{5X,6}$ = 9.3, $J_{4,5X}$ = 4.1 Hz, H_{5X}), 1.52 (ddd, $J_{5N,5X}$ = 13.7, $J_{5N,6}$ = 3.6, $J_{4,5N}$ = 1.5 Hz, H_{5N}); ^{13}C NMR: δ 169.9 (s, lactone C=O), 167.8 (s, ester C=O), 136.5 (d, C_2), 131.7 (d, C_3), 130.1 (d, vinyl CH), 118.2 (t, vinyl CH_2), 74.4 (d, C_4), 59.3 (s, C_1), 52.8 (q, OCH_3), 39.0 (d, C_6), 32.8 (t, C_5).

Methyl 6 - vinyl - 1,3 - cyclohexadienecarboxylate **9**: IR: 1708 cm^{-1}; ^1H NMR($CDCl_3$): δ 7.06 (m, 1H, H_2), 6.06 (m, 2H, H_3 and H_4), 5.70, 5.10 and 4.87 (each 1H m, vinyl), 3.77 (s, 3H, OCH_3), 3.40 (m, 1H, H_6), 2.5 (m, 2H, CH_2); ^{13}C NMR: δ 176.0 (s, C=O), 137.4 (d, C_4), 133.1 (d, C_2), 131.7 (d, C_3), 123.5 (d, vinyl CH), 114.3 (t, vinyl CH_2), 65.2 (s, C_1), 51.6 (q, OCH_3), 33.4 (d, C_6), 28.9 (t, C_5).

A solution of **8** (52.5 mg) in 5 ml PhH was heated at 70° for 7 days giving 40 mg of recovered **8** and 5 mg of **9** after preparative TLC. At 110° both **8** and **9** were converted into **6** in good yield.

Reaction of **10** *with* **2a**. A similar reaction of **10** (308 mg), 3-sulfolene (700 mg) and a trace of hydroquinone at 150° for 24 h gave an oily mixture (158 mg; 80–140°/3 mm). Column chromatographic separation (Al_2O_3; PhH) gave one fraction (124 mg; 38%), of which ^1H NMR analysis of methyl protons of methoxycarbonyl showed that **11** and **4** existed in the ratio of 1.7:1. $LiAlH_4$ reduction of this mixture (124 mg), followed by active MnO_2 oxidation in hexane, gave a mixture of two aldehydes **12** and **13** (71 mg; 70%), which were converted gradually by atmospheric O_2 into the corresponding acids. (Found: C, 71.84; H, 6.93. Calc. for $C_9H_{10}O_2$: C, 71.98; H, 6.71%). The aldehydic mixture were separated by preparative GLC (10% PEG 20 M; 17°) to give pure **12** (23 mg) and **13** (11 mg).

3-Formyltricyclo[3.2.1.$0^{2,7}$]oct-3-ene **12**; MS: *m/e* 134 (M^+, 34), 105 (100), 91 (34), 79 (41%); NMR: δ 9.49 (s, CHO), 6.87 (dd, H_4, 7.0 and 2.6 Hz), 2.78 (dt, H_5, 7.0 and 4.5 Hz), 2.29 (dt, H_2, 2.6 and 6.7 Hz), 1.68 (dd, H_{8X}, 11.6 and 4.5 Hz), 1.59 (d, H_1, 6.7 Hz), 0.80 (d, H_{8N}, 11.6 Hz).

4-Formyltricyclo[3.2.1.$0^{2,7}$]oct-3-ene **13**; MS: *m/e* 134 (M^+, 42), 133 (55), 105 (100), 91 (43), 79 (49), 77 (38%); NMR: δ 9.26 (s, CHO), 6.97 (dd, H_3, 3.5 and 1.8 Hz), 3.28 (m, H_5), 1.8 (m, 2xH_1 and H_2), 1.69 (dd, 11.8 and 4.8 Hz), 0.69 (d, H_{8N}, 11.8 Hz).

Conversion of **12** *to methyl ester* **11**. A mixture of **12** (23 mg), NaCN (44 mg), AcOH (16 mg), active MnO_2 (305 mg), and MeOH was stirred for 24 h (N_2) at room temp. After removal of MeOH, partioning between CH_2Cl_2 and water, and concentration of CH_2Cl_2 extract gave 15 mg (53%) of methyl tricyclo[3.2.1.$0^{2,7}$]oct - 3 - ene - 3 - carboxylate **11**; b.p. 85°/4 mm; IR: 1715, 1620 cm^{-1}; MS: *m/e* 164 (M^+, 27), 105 (100), 104 (18), 79 (16), 77 (17%). (Found: C, 73.24; H, 7.64. Calc. for $C_{10}H_{12}O_2$: C, 73.14; H, 7.37%).

Unequivocal synthesis of **13**. $LiAlH_4$ reduction of **3a**[5] (162 mg), followed by active MnO_2 oxidation in hexane, gave **13** (70 mg; 70%). MS and NMR spectra of this material were identical with the above-mentioned product.

Reaction of **14** *with* **2a**. A similar reaction of **14** (351 mg) and 3-sulfolene (1.063 g) at 150° for 13 days gave, after preparative TLC, an oily mixture (47 mg; 35% based on the recovered starting material) consisted of **6** and **15** in the ratio of 3.3:1 by GLC analysis, in addition to recovered **14** (125 mg; 64%). Preparative GLC separation (Apiezon Grease L, 120°) of this mixture gave **6** and a pure sample of methyl tricyclo[3.2.1.$0^{2,7}$]oct - 3 - ene - 5 - carboxylate **15**; b.p. 82°/3 mm; IR: 1730, 1620 cm^{-1}; MS: *m/e* 164 (M^+, 31), 105 (100), 104 (25), 103 (21), 79 (22), 77 (27%). (Found: C, 73.01; H, 7.21. Calc. for $C_{10}H_{12}O_2$: C, 73.14; H, 7.37%).

Reaction of **10** *with* **2b**. A soln of **10** (1.00 g) and **2b** (3 ml) in PhH was heated at 150° for 36 h. After removal of the solvent, column chromatographic separation (SiO_2; PhH–AcOEt) gave four products; methyl 1,7 - dimethyltricyclo[3.2.1.$0^{2,7}$]oct - 3 - ene - 3 - carboxylate **16** (62 mg; 64%); b.p. 108°/3 mm; IR: 1715, 1620 cm^{-1}; MS: *m/e* 192 (M^+, 45), 133 (100), 105 (48), 91 (32%); ^{13}C NMR: δ 167.3 (s), 137.6 (d), 128.6 (s), 51.3 (q), 34.9 (t), 32.3 (d), 29.1 (d), 25.2 (s), 14.9 (q). (Found: C, 74.84; H, 8.49. Calc. for $C_{12}H_{16}O_2$: C, 74.97; H, 8.37%).

3b (15 mg; 2%), identified with an authentic sample.[5]

17 (85 mg; 6%); m.p. 110–11.5°; IR: 1730, 1240, 1225, 960, 895, 775 cm^{-1}; MS: *m/e* 236 (M^+, 22), 190 (22), 155 (17), 82 (100), 77 (38%); ^1H NMR: δ 6.68 (s, 1H), 4.60 (pseudo q, 1H), 3.85 (s, 3H), 2.8 (m, 1H), 1.8–2.5 (m, 4H), 1.64 (s, 6H); ^{13}C NMR: δ 164.9 (s), 164.4 (s), 151.3 (s), 125.2 (d), 124.6 (s), 121.2 (s), 76.2 (d), 52.7 (q), 35.8 (t), 32.9 (t), 32.5 (d), 18.9 (q), 18.5 (q). (Found: C, 65.87; H, 7.10. Calc. for $C_{13}H_{16}O_4$: C, 66.08; H, 6.83%).

18 (1.153 g; 75%); b.p. 120°/3 mm; IR: 1774, 1740, 1250, 1216, 1195 cm^{-1}; MS: *m/e* 236 (M^+, 20), 177 (100), 149 (32), 82 (95), 67 (47%); ^1H NMR: δ 6.50 (d, 1H, 6.0 Hz), 5.18 (d, 1H, 6.0 Hz), 3.73 (s, 3H, 3.19 (t, 1H, 6.0 Hz), 2.4 (m, 4H), 1.63 (s, 6H); ^{13}C NMR: δ 169.2 (s), 165.6 (s), 141.7 (d), 123.6 (s), 110.2 (d), 52.6 (q), 44.4 (s), 40.3 (d), 37.2 (t), 29.6 (t), 18.9 (q), 18.4 (q). (Found: C, 66.08; H, 6.88. Calc. for $C_{13}H_{16}O_4$: C, 66.08; H, 6.38%).

Heating of neat **18** in a sealed tube at 180° for 24 h did not afford any change by ^1H NMR and GLC analysis.

A similar reaction of **17** did not give any tricyclic compound.

Reaction of **14** *with* **2b**. A soln of **14** (474 mg) and **2b** (460 mg) in PhH was heated at 150° for 6 days. After removal of the solvent, preparative TLC separation gave four products and recovered **14** (88 mg; 19%).

Methyl 1,7 - dimethyltricyclo[3.2.1.$0^{2,7}$]oct - 3 - ene - 2 - carboxylate **19** (33 mg; 7%); b.p. 108°/3 mm; IR: 1735, 1620 cm^{-1}; MS: *m/e* 192 (M^+, 43), 177 (27), 133 (100), 117 (22), 105 (46), 91 (35%). (Found: C, 75.08; H, 8.68. Calc. for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39%).

Methyl 1,7 - dimethyltricyclo[3.2.1.$0^{2,7}$]oct - 3 - ene - 5 - carboxylate **20** (56 mg; 12%); b.p. 108°/3 mm; IR: 1730, 1620 cm^{-1}; MS: *m/e* 192 (M^+, 39), 133 (100), 132 (20), 117 (25), 105 (60), 91 (35%). (Found: C, 74.93; H, 8.63. Calc. for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39%).

6,7 - Dimethyl - 4a - methoxycarbonyl - 4a,5,8,8a - tetrahydrocoumarin **21** (162 mg; 27%); m.p. 89.5–92°; IR: 1730, 1715, 1650 cm^{-1}; MS: *m/e* 236 (M^+, 6), 190 (52), 177 (95), 176 (69), 159 (95), 158 (67), 105 (50), 95 (55), 82 (71%); ^1H NMR: δ 7.05 (dd, 1H, 10.2 and 6.1 Hz), 5.99 (d, 1H, 10.2 Hz), 3.79 (s, 3H), 2.0–3.0 (m, 5H). (Found: C, 65.91; H, 6.70. Calc. for $C_{13}H_{16}O_4$: C, 66.08; H, 6.83%).

6,7 - Dimethyl - 3 - methoxycarbonyl - 4a,5,8,8a - tetrahydrocoumarin **22** (103 mg; 17%); b.p. 125°/3 mm; IR: 1761, 1734, 1655 cm^{-1}; MS: *m/e* 236 (M^+, 39), 155 (52), 149 (33), 106 (23), 91 (23), 82 (100), 67 (54%); ^1H NMR: δ 6.41 (d, 1H, 5.7 Hz), 3.78 (s, 3H), 2.7 (m, 1H), 2.0 (m, 4H), 1.30 (m, 1H, 5.7 Hz). (Found: C, 65.92; H, 7.12. Calc. for $C_{13}H_{16}O_4$: C, 66.08; H, 6.83%).

Reaction of **6** *with* **2b**. A soln of **6** (306 mg) and 2b (250 mg) in PhH was heated at 150° for 6 h. Distillation gave an oily mixture (111 mg; 180–230°/3 mm), which contained 1:2 adducts of **6** and **20** from the basis of MS spectral analysis (*m/e* 318 (M^+)). The adducts could not be separated by any method until now.

Reaction of **10** *with* **23**. A soln of **10** (154 mg) and freshly distilled **23** (1 ml) in PhH was refluxed for 3 h. Column chromatographic separation gave a crystalline mixture (196 mg; 89%); m.p. 116–122°; MS: *m/e* 176 ($M^+ - 44$, 5), 161 ($M^+ - 59$, 5), 155 (86), 66 (100%). (Found: C, 65.59; H, 5.53. Calc. for $C_{12}H_{12}O_4$: C, 65.44; H, 5.49%). Fractional recrystallizations (seven times) of this mixture from MeOH gave 5 - methoxycarbonyl - r - 3a,4,7,c - 7a - tetrahydroindene - c - 4,c - 7 - carbolactone **24** (59 mg); m.p. 129–130°; ^1H NMR ($CDCl_3$): δ 2.53 (H_{1N}), 1.84 (H_{1X}), 5.5 (H_2 and H_3), 3.4 (H_{3a}), 4.09 (H_4), 7.19 (H_6), 5.27 (H_7), 3.13 (H_{7a}), 3.76 (OMe): $J_{1N,1X}$ = 17.8, $J_{1N,7a}$ = 10.0, $J_{1X,7a}$ = 4.6, $J_{1N,2}$ = 4.8, $J_{1X,2}$ = 3.6, $J_{2,3}$ = 5.6, $J_{3,3a}$ not determined, $J_{3a,7a}$ = 10.0, $J_{3a,4}$ = 3.8, $J_{4,6}$ = 3.7, $J_{6,7}$ = 5.6, $J_{7,7a}$ = 4.8 Hz; ^{13}C NMR: δ 172.1 (s), 163.4 (s), 136.9 (d), 135.7 (s), 133.1 (d), 129.3 (d), 76.2 (d), 52.3 (q), 47.1 (d), 44.5 (d), 40.0 (d), 34.5 (t). The regiosomer, 6 - methoxycarbonyl - r - 3a,4,7,c - 7a - tetrahydroindene - c - 7,c - 4 - carbolactone **25**, was not isolated but its ^{13}C NMR spectrum was obtained with

use of the **25** enriched mother liquid: δ 172.1 (s), 164.0 (s), 140.1 (d), 136.1 (d), 135.7 (s), 127.1 (d), 75.6 (d), 52.6 (d), 52.3 (q), 45.3 (d), 36.8 (d), 34.5 (t). The original reaction mixture was shown to be composed of **24** and **25** in the ratio of 2:1 by ^{13}C NMR analysis by the aid of relaxation reagent (Cr(II)-acetylacetonate; 0.1 M) with use of gated decoupling method (without NOE with ^{1}H-decoupling).

UV and photoelectron spectra of methyl 2-pyronecarboxylates. UV spectra were obtained in MeOH soln; **1** λ_{max} 291 nm (ϵ 4770); **5**, 301 nm (ϵ 15,810); **10**, 317 nm (ϵ 4580); **14**, 301 nm (ϵ 10,550). The lowest vertical ionization potentials are as follows; **1**, 9.31 eV; **5**, 9.28 eV; **10**, 9.25 eV; **14**, 9.30 eV.

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