

Cycloaddition Reaction of Methyl Coumalate with Fulvenes

By

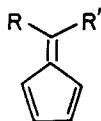
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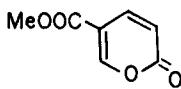
Abstract

Cycloaddition reaction of methyl 2-pyrone-5-carboxylate to dimethyl- and phenyl-fulvene gave peri-, regio-, and stereoselectively 1-isopropylidene- and 1-benzylidene-6-methoxycarbonyl-*r*-3a,4,7,*c*-7a-tetrahydroindene-*c*-4,*c*-7-carbolactone, respectively.

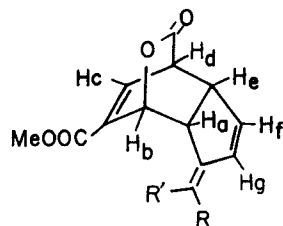
Periselectivity, found in many symmetry-allowed cycloaddition reactions, has received considerable attention.¹⁾ The fulvenes (1) were known to behave as 4π -electron cycloaddend.²⁾ More recently, it has been reported that these act as 6π -cycloaddend^{3a,d)} as well as 2π -addend.^{1e)} On the other hand, we have found that methyl coumalate (2-pyrone-5-carboxylate) (2), a 2-pyrone, behaves as 2π - as well



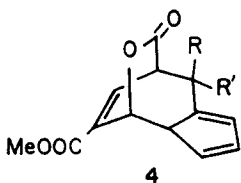
1 a, R = Ph, R' = H
b, R = R' = Me



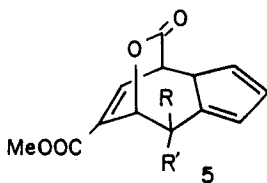
2



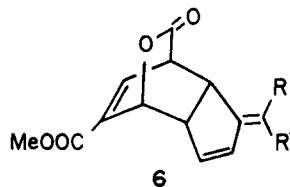
3 a, R = Ph, R' = H_h
b, R = H_h, R' = Ph
c, R = R' = Me



4



5



6

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as 4π -cycloaddend.³⁾ *A priori*, there can be many symmetry-allowed cycloadditions, such as [6+4] and [4+2] fashions, in the thermal reaction between **1** and **2**. The present work was initiated with the hope of demonstrating the actual mode of the cycloaddition reaction.

Results and Discussion

The reaction of **2** with phenylfulvene (**1a**) in benzene solution at 120°C for 4 h gave a crystalline mixture of the 1:1 adducts in an 85% yield. Fractional recrystallizations from ethanol gave **3a** (13%) and **3b** (37%). In solution, these adducts were so unstable as to give intractable materials.

A similar reaction of **2** with dimethylfulvene (**1b**) at 100°C for 30 h gave a single 1:1 adduct **3c** in a 44% yield.

Elemental analyses revealed **3a-c** to be undecarboxylated 1:1 adducts. The NMR spectral data are shown in Table 1. Only in the case of the adduct **3a** can almost all coupling constants be determined, and the assignments are firmly established by decoupling techniques. The signal of H_a appeared as a doublet of doublets of doublets; the coupling constants (6.8 Hz) between H_a and another ring-junction proton (H_b) indicates that the adduct **3a** is not a [6+4] adduct (**4** or **5**), but a [4+2] adduct (**3** or **6**). The absence of a coupling between H_a and any endocyclic olefinic proton (H_e , H_f , or H_g) is indicative of the structure **3a**, excluding the alternative [4+2] adduct **6**. The values of $J_{a,b}$ (4.5 Hz) and $J_{a,e}$ (3.1 Hz) verified the *endo*-configuration of the adduct.

Table 1. NMR Spectral Data for **3**

H	Chemical shifts (δ)			Coupling constants (Hz)			
	3a	3b	3c	J	3a	3b	3c
a	4.16 (ddd)	3.65 (m)	3.45 (m)	a,b	4.5	4.8	4.3
b	5.68 (dd)	5.79 (dd)	5.77 (dd)	b,c	2.3	2.3	2.3
c	7.05 (dd)	7.02 (dd)	6.97 (dd)	c,d	6.5	6.6	6.5
d	3.72 (dd)	3.73 (dd)	3.66 (dd)	d,e	3.1	3.2	(3.0)*
e	3.55 (m)	3.40 (m)	3.45 (m)	a,e	6.8	**	**
f	5.76 (m)	6.57 (m)	6.18 (m)	e,f	2.7	1.7	1.5
g	6.13 (m)	5.89 (m)	5.50 (bd)	f,g	5.4	5.7	5.7
h	6.27 (bd)	6.37 (bs)	—	a,h	2.4	**	—
OMe	3.47 (s)	3.62 (s)	3.63 (s)	e,g	1.7	**	**
Me	—	—	1.59 (bs)	g,h	1	1.7	—
Ph	7.30 (m)	7.15 (m)	—	f,h	**	1.0	—

* Determined with use of a shift reagent.

** Not determined.

It can be safely stated that the adducts **3b** and **3c** have the same ring system as **3a**, in view of the similarity in the NMR parameters, especially with regard to the values of $J_{a,b}$ and $J_{a,c}$ (*endo*-configuration) and to the chemical shifts of H_c and H_d (regiospecificity).

The difference between **3a** and **3b** is ascribed to the location of the phenyl group in the benzylidene moiety. The proton H_b in the structure **3b** is supposed to be deshielded by the endocyclic double bond to appear at a lower field.⁴⁾ Hence the *trans*-configuration was assigned to the isomer **3b** since the signal of H_b of **3b** is located at a lower field than that of **3a**.

The UV absorption maxima in ethanol are at 285 nm (ϵ 4,690) for **3a** and 283 nm (ϵ 23,300) for **3b**. The wavelengths of the maxima attributable to the 1-phenylbutadiene chromophore⁵⁾ indicate clearly that these are not the [6+4] adduct (**4** or **5**) but the [4+2] adduct (**3** or **6**). The diminished absorption intensity suggests the *cis*-configuration to **3a** since the *cis*-1-phenylbutadiene will experience difficulty in attaining coplanarity.⁵⁾

Thus, it has been firmly established that the reaction of **1** with **2** leads to *endo*-[4+2] cycloadducts.

The periselectivity observed in these reactions was unexpected at the onset of the work. However, in the meantime it was reported⁶⁾ that 2-pyrone itself and fulvenes reacted to give only [4+2] adducts with fulvenes as dienophile. The reaction proceeded with a regiospecificity similar to our results. More recently, Ebine and his coworkers⁷⁾ reported that the thermal cycloaddition reactions of 6-aminofulvenes with **2** gave azulene derivatives originating from the decarboxylation of the adduct of type **4**, thus differing in periselectivity from ours.

Houk's discussion⁸⁾ about peri- and regioselectivity that the reaction course results from a narrower fulvene HO-pyrone LU separation may be applied straightforwardly to our reaction, since the electron-withdrawing substituent (methoxy-carbonyl group) lowers both frontier orbital energies.⁸⁾ The difference between the results of Ebine and ours may be explained by the substitution of an amino group (electron-donating group) at fulvene C-6 causing a crossover of its HO orbitals⁸⁾ and the coefficient factor of superjacent (NLU) orbital.⁸⁾ An analogous example has been found in the reaction of a nitrile oxide.¹⁰⁾ The reported low yield in Ebine's reaction might be attributed to the accompaniment of another type of pericyclic reaction such as described in the present work.

Experimental

Reaction of **2** with Phenylfulvene (**1a**).

A solution of 450 mg of **2** and 450 mg of **1a** in 15 ml of benzene was heated in

a pressure bottle at 120°C until the red color of 1a disappeared (4 h). The residue after vacuum evaporation was crystallized from EtOH to give 768 mg of a crystalline mixture (mp 141–143°C). Fractional recrystallizations from EtOH afforded 117 mg (13%) of 3a and 328 mg (37%) of 3b.

The less soluble product, (*Z*)-1-benzylidene-6-methoxycarbonyl-*r*-3a,4,7,*c*-7a-tetrahydroindene-*c*-4, *c*-7-carbolactone (3a), had mp 183–184°C (dec); IR (nujol): 1764, 1708, 1625 cm⁻¹; UV (EtOH): λ_{max} 285 nm (ε 4,690). Found: C, 73.92; H, 5.36. Calcd for C₁₉H₁₆O₄: C, 74.01; H, 5.23%.

The predominant product, (*E*)-1-benzylidene-6-methoxycarbonyl-*r*-3a,4,7,*c*-7a-tetrahydroindene-*c*-4,*c*-7-carbolactone (3b), had mp 154–155°C (dec); IR (nujol): 1772, 1722, 1632 cm⁻¹; UV (EtOH): λ_{max} 283 nm (ε 23,300). Found: C, 74.27; H, 5.33. Calcd for C₁₉H₁₆O₄: C, 74.01; H, 5.23%.

Reaction of 2 with Dimethylfulvene (1b).

A solution of 100 mg of 2 and 120 mg of 1b in 10 ml of benzene was heated in a pressure bottle at 100°C for 30 h. Solvent removal in vacuo and recrystallization from MeOH gave 92 mg (44%) of 1-isopropylidene-6-methoxycarbonyl-*r*-3a,4,7,*c*-7a-tetrahydroindene-*c*-4,*c*-7-carbolactone (3c), mp 140–141°C; IR (nujol): 1762, 1720, 1620 cm⁻¹. Found: C, 69.25; H, 6.41. Calcd for C₁₅H₁₆O₄: C, 69.21; H, 6.20%.

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- 10) All melting points were determined on a hot stage microscope and are uncorrected. NMR spectra were determined on a JEOL C-60HL instrument. Decoupling experiments were achieved on a Varian HA-100 spectrometer (frequency sweep).