precipitate of sodium chloride was centrifuged, and solvent was evaporated. The crude product was purified by means of preparative thin-layer chromatography on silica gel: yield 220 mg, oil (62%); $[\alpha]^{20}_D$ −122.1° (c 2.1, benzene); MS m/z 189 (base peak), 92 (60%); ^{1}H NMR (CD_3CN, external Me_4Si): 7.7 (br s), 7.44 (br s), 4.31 (br s), 3.64 (q). ^{1}H NMR spectra were also recorded in CCl_4, C_6D_6, $CDCl_3$, and CD_3COCD_3. In all cases we were unable to observe nonequivalence either of benzylic protons or of 2-methoxy protons in diastereoisomeric benzyl-*1-d*-MPTA thiolo esters.

Acknowledgment. This work was financially assisted by the Polish Academy of Sciences, Grant No. MR-I-12.1.7.10.

Registry No. (*S*)-(−)-**1a**, 1445-91-6; (*R*)-(+)-**1a**, 1517-69-7; (*R*)-(−)-**1b**, 4181-90-2; **2**, 2428-06-0; (*R*)-(+)-**3a**, 71719-69-2; (*R*)-(−)-**3b**, 71719-70-5; (*S*)-(−)-**4a**, 71719-71-6; (*R*)-(+)-**4a**, 71719-72-7; (*S*)-(+)-**4b**, 71719-73-8; (*S*)-(−)-**5a**, 33877-11-1; (*S*)-(+)-**5b**, 71719-74-9; (*R*)-(−)-**6**, 71719-75-0; (*R*)-(−)-**7**, 4181-91-3; (*S*)-(+)-**8**, 71719-76-1; **9**, 4090-55-5; (*R*)-(+)-2-[(1-methylbenzyl)oxy]-5,5-dimethyl-1,3,2-dioxaphosphorinane, 71719-77-2; (−)-2-methoxy-2-(trifluoromethyl)-2-phenylacetyl chloride, 39637-99-5; *S*-(phenylmethyl-*d*) α-methoxy-α-(trifluoromethyl)benzeneethanethioate, 71719-78-3; thiourea, 62-56-6.

Ruthenium-Catalyzed [2 + 2] Cross-Addition of Norbornene Derivatives and Dimethyl Acetylenedicarboxylate

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Bicyclo[2.2.1]hept-2-ene and its derivatives react with dimethyl acetylenedicarboxylate in the presence of ruthenium complex catalysts in benzene at 80–100 °C to give [2 + 2] cross adducts, *exo*-tricyclo[4.2.1.$0^{2,5}$]non-3-ene derivatives. $RuH_2(CO)[P(p\text{-}PhF)_3]_3$, $RuH_2(CO)(PPh_3)_3$, $RuH_2(PPh_3)_4$, and (cyclooctatriene)(cyclooctadiene)ruthenium are effective catalysts. The reaction of 7-oxabicyclo[2.2.1]hept-2-enes affords 9-oxa-*exo*-tricyclo[4.2.1.$0^{2,5}$]non-3-enes. The 1:2 mixture of cyclopentadiene or furan derivatives and dimethyl acetylenedicarboxylate also gives the corresponding tricyclo[4.2.1.$0^{2,5}$]nonene derivatives in the presence of the catalysts. Novel linear hexa- and heptacyclo compounds were prepared by using this reaction.

Two plus two cycloaddition of olefins and/or acetylenes is a valuable route to cyclobutane derivatives. The reaction is formally envisaged as a thermally forbidden process,[1] and the reaction is achieved photochemically[2] or by the use of transition-metal catalysts.[3]

As for the [2 + 2] cross-addition of olefins with acetylenes, inefficient photoaddition of bicyclo[2.2.1]hept-2-ene (norbornene) with dimethyl acetylenedicarboxylate[2e] (yield <10%) and a transition-metal-catalyzed addition of norborna*diene* with acetylenes[3c] have been reported. Thus there have been no reports on the efficient [2 + 2] cross-addition of norbornene with acetylenes.

On the other hand, ruthenium complexes are well-known to be excellent catalysts for hydrogen transfer reactions;[4] however, there have been only a few reports on catalytic carbon–carbon bond formation: e.g., carbonylation of olefins or acetylenes,[5] telomerization of olefins with alkyl halides,[6] polymerization and oligomerization of olefins[7] or acetylenes,[8] and homologation of methyl acetate.[9]

Scheme I

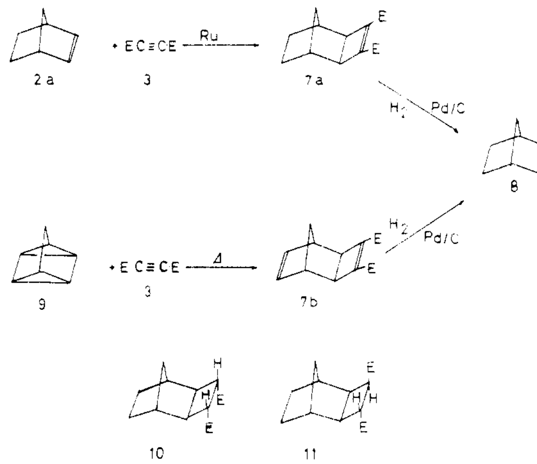

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Table I. [2 + 2] Cross-Addition of Norbornenes with Dimethyl Acetylenedicarboxylate Catalyzed by Ru Complexes[a]

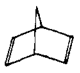
run no.	norbornene deriv (amt, mmol)	catalyst (amt, mmol)	reactn temp, °C	reactn time, h	prod	yield,[b] %
1	2a (10)	1 (0.20)	80	24	7a	52 (65)
2	2a (10)	4 (0.20)	100	6	7a	(78)
3	2a (10)	5 (0.20)	100	6	7a	(56)
4	2a (10)	6 (0.24)	100	6	7a	(87)
5	2a (10)	14 (0.20)	100	6	7a	(10)
					$C_6(CO_2Me)_6$	(18)
6	2b (20)	1 (0.40)	80	48	7b	50
					7b′	2
7	7b (5)	1 (0.10)	80	20	7b′	21
8	2c (10)	1 (0.10)	100	6	7c	39
9[d]	2c (10)	1 (0.20)	100	6	7c	(55)
10	2c (10)	1 (0.20)	100	6	7c	48 (64)
11	2c (10)	6 (0.24)	100	6	7c	(88)
12	2c (10)	13 (0.40)	100	6	7c	40 (52)
13	2c (10)	A[c]	100	6	7c	(29)
14	2c (10)	B[c]	100	6	7c	(5)
15	2d (10)	1 (0.10)	100	20	7d	57
16	2d (10)	13 (0.40)	100	6	7d	(67)
17	2e (10)	1 (0.20)	100	6	7e	68
18	2f (5)	6 (0.24)	100	6	7f	15
					7f′	15
19	2f (5)	6 (0.20)	100	8	7f′	54
20	2g (10)	1 (0.20)	100	6	7g	59
21	2h (10)	1 (0.20)	100	6	7h	21
22	2h (10)	6 (0.10)	100	6	7h	84
23	2i (10)	1 (0.20)	100	8	7i	10

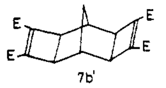
[a] The mole ratio of 2/3 is 1:1 except for run 9. [b] Isolated yields based on the norbornene derivatives. GLC yields are given in parentheses. [c] A, $RuCl_2(PPh_3)_4$ (0.2 mmol)-$NaBH_4$ (0.8 mmol)-diglyme (10 mL); B, $RuCl_3 \cdot 3H_2O$ (0.2 mmol)-$NaBH_4$ (0.4 mmol)-dioxane (10 mL). [d] 2f/3 = 1:2.

These facts prompted us to investigate the carbon-carbon bond formation reaction catalyzed by ruthenium complexes. Recently, it has been briefly reported that $RuH_2(PPh_3)_4$ (1) catalyzes a [2 + 2] cross-addition of norbornene derivatives with dimethyl acetylenedicarboxylate, affording a novel route to the *exo*-tricyclo[4.2.1.$0^{2,5}$]nonene system.[10] In this report, the recent progress of the catalysts and the scope of this reaction will be described.

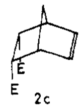
Results and Discussion

Norbornene (**2a**) readily reacted with an equimolar amount of dimethyl acetylenedicarboxylate (**3**) in the presence of a catalytic amount of $RuH_2(PPh_3)_4$ (**1**), $RuH_2(CO)(PPh_3)_3$ (**4**), $RuH_2[P(p\text{-}PhF)_3]_4$ (**5**), or $RuH_2(CO)[P(p\text{-}PhF)]_3$ (**6**) in benzene at 80–100 °C to give the corresponding [2 + 2] cross-adduct dimethyl *exo*-tricyclo[4.2.1.$0^{2,5}$]non-3-ene-3,4-dicarboxylate (**7a**) in yields of 87–56% (Table I). The structure of **7a** was assigned on the basis of the spectral and microanalytical data, and it was confirmed by the following method. The hydrogenation of **7a** catalyzed with 5% Pd/C gave a hydrogenated product **8**, which was also obtained by the hydrogenation of **7b** prepared by the reaction of quadricyclane (**9**) with **3**.[11] The melting point of **8** (63 °C) is different from those of **10** (84 °C) and **11** (78 °C) reported,[2f] and the stereochemistry of **8** shown in Scheme I was deduced on the basis of its ^1H NMR spectrum which is fully consistent with the structure. The exo structure of the adduct **7a** was confirmed by the ^1H NMR spectrum: the signal of the protons of the cyclobutene ring does not couple with that at the bridgehead.[11,12] The reaction was highly selective (>95%), and byproducts such as cyclohexadiene derivatives[13] (1:2 adduct of **2** and **3**) or a homodimer of the olefins[3c] were not detected. To our knowledge this is the first example of [2 + 2] cross-addition of unsubstituted norbornene with acetylenes catalyzed by transition-metal complexes. In the reaction of norbornadiene (**2b**) with **3**, in addition to the

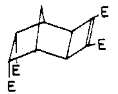

2b



7b′



2c



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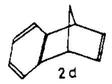
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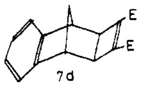

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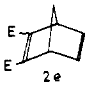
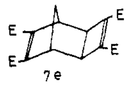
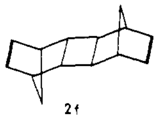
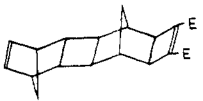


2e

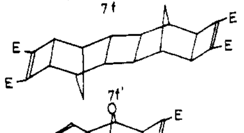


7e

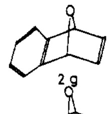

2f

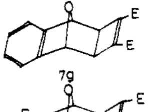


7f

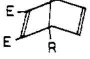


7f′

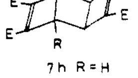

2g



7g



2h R=H
2i R=Me



7h R=H
7i R=Me

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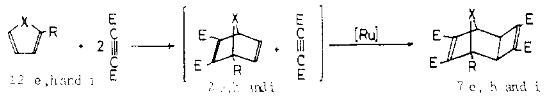
Table II. Reaction of Cyclopentadiene or Furan Derivatives with Dimethyl Acetylenedicarboxylate Catalyzed by Ru Complexes[a]

run no.	substrate	catalyst (amt, mmol)	prod	yield, %[b]
24	cyclopentadiene	1 (0.05)	7e	66
25	cyclopentadiene	6 (0.10)	7e	63
26	furan	1 (0.10)	7h	13
27	furan	4 (0.10)	7h	57
28	furan	5 (0.10)	7h	29
29	furan	6 (0.10)	7h	73
30	2-methylfuran	1 (0.10)	7i	~0
31	2-methylfuran	6 (0.10)	7i	10

[a] Five millimoles of the substrate and 10 mmol of **3** were used in each run; reaction time, 6 h; reaction temperature, 100 °C. [b] Isolated yields based on the substrate.

Scheme II



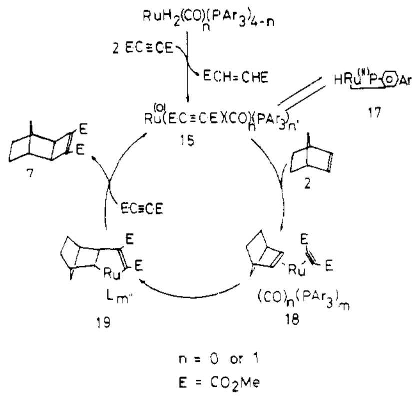
e, X = CH_3; R = H
h, X = O; R = H
i, X = O; R = Me

1:1 [2 + 2] cross-adduct **7b** (yield 50%), a 1:2 adduct **7b′** derived by the double [2 + 2] addition was also obtained (2%). The increase of the mole ratio of **3**/**2b** did not increase the yield of **7b′**; only the oligomer of **3** was formed. The adduct **7b′** was obtained in a moderate yield by the reaction of **7b** with **3** (run 7, Table I). The present [2 + 2] cross-addition is generally successful for norbornene derivatives; **2c–e** also gave the corresponding adducts, **7c–e**, in fairly good yields. The results were summarized in Table I. Using this reaction, we synthesized linear polycyclo compounds. The exo,trans-exo dimer of norbornadiene, **2f**, reacted with 1 mole equiv of **3** to give a 1:1 adduct **7f** (a hexacyclo compound) and 1:2 adduct **7f′** (a heptacyclo compound), both in 15% yields. At the mole ratio **3**/**2f** = 2, **7f′** was obtained in 54% yield, and **7f** could not be isolated. The derivatives of 7-oxabicyclo[2.2.1]hept-2-ene such as **2g–i** also gave the corresponding [2 + 2] cross adducts, **7g–i**.

A 1:2 mixture of cyclopentadiene or a furan derivative (**12e**, **12h**, or **12i**) and **3** also gave **7e**, **7h**, or **7i** in fairly good yields. Results were summarized in Table II. In these reactions, the Diels-Alder adduct **2e**, **2h**, or **2i** is formed in the first step, and then the [2 + 2] cross-addition occurred (Scheme II). Although **7e** and **7h** have been prepared by the reaction of quadricyclane derivatives with dimethyl acetylenedicarboxylate,[14,15] the facile reaction procedure and the high yield of the products in the present reaction afford a novel synthetic route to tricyclo[4.2.1.$0^{2,5}$]non-3-enes.

In these reactions, in addition to $RuH_2(CO)_n(PAr_3)_{4-n}$ (n = 0 or 1), (cyclooctatriene)(cyclooctadiene)ruthenium(0) (**13**) was a considerably effective catalyst. Although $RuCl_3 \cdot 3H_2O$–$NaBH_4$–diglyme or $RuCl_2(PPh_3)_4$–$NaBH_4$–dioxane systems were also effective, only the lower activities were observed. In the case of $Ru(CO)_3(PPh_3)_2$ (**14**), a small amount of the [2 + 2] cross-adduct was obtained, and the major product was hexamethoxycarbonylbenzene. These results were also summarized in Table I. Bis(cyclooctadiene)iron and $RhCl(PPh_3)_3$ were inactive, and only the starting materials were recovered.

Scheme III



As for acetylene derivatives, unfortunately only dimethyl acetylenedicarboxylate was successful. Methyl acetylenecarboxylate reacted, affording an amorphous black compound containing none of the norbornene moiety. In the reaction of diphenylacetylene, phenylacetylene, or 1-octyne, only the starting materials were recovered, or a small amount of product which is supposed to be a dimer of the acetylene was detected by GLC. The optimum reaction temperature was 80–100 °C, and the yield of the [2 + 2] adduct considerably decreased above 120 °C or below 60 °C.

Although the mechanism of the [2 + 2] cross-addition is not clear at the present time, one of the possible reaction routes may be explained by assuming the formation of a zerovalent complex **15** by the reaction of $RuH_2(CO)_n(PAr_3)_{4-n}$ (n = 0 or 1) with **2** or **3** (Scheme III). It has been reported that $RuH_2(PPh_3)_4$ reacts with olefins such as ethylene or styrene to give Ru(R—C=C)$(PPh_3)_3$ (**16**),[16] the structure of which was recently pointed out to be RuH(R—C=C)$(PC_6H_5Ph_2)(PPh_3)_2$ (**17**).[17] In any way, a zerovalent ruthenium complex is reasonably considered to be formed in the early step of the reaction of $RuH_2(CO)_n(PAr_3)_{4-n}$ with **2** or **3**. The successive formation of Ru^0(nor)(acet)$(CO)_n(PAr_3)_m$ (**18**; nor = norbornene and acet = acetylene) and a metallacyclopentene complex **19**, followed by the reductive elimination reaction, could afford the [2 + 2] cross-adduct **7** and a Ru(0) species **15** again (Scheme III). The fact that the zerovalent complex **13** effectively catalyzes the [2 + 2] reaction also supports the Ru(0) ⇄ Ru(II) catalytic cycle.[18] Concerning the metallacyclopentene intermediate, the related reaction intermediates in the homodimerization of norbornadiene with Ir[19] or Ni[20] catalyst have been isolated. The activity of the catalyst increased when one of the phosphine ligands in **1** and **5** is substituted with a carbon monoxide. One plausible explanation for this effect is the prevention of the orthometalation of the triphenylphosphine in the zerovalent intermediate **15**. The enhanced π-acceptor character of carbon monoxide may cause the decrease of the electron density on the ruthenium atom, and the formation of **17**, which may be converted into inactive species, would be partially disturbed.[21]

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(18) The possibility of the Ru(II) ⇄ Ru(IV) catalytic cycle could not be ruled out completely.

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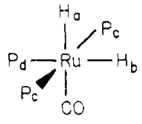
Experimental Section

All melting points and boiling points were uncorrected. Infrared spectra were taken on a Hitachi Model EPI-G2 or 215 spectrometer either as films or in potassium bromide disks. Proton nuclear magnetic resonance spectra were obtained on a JEOL MP-60 or Varian HR-220, HA-100, or JNM-FX-100 spectrometer as 1–10% solutions using tetramethylsilane as an internal reference. Mass spectra were taken on a JMS-O1SG mass spectrometer. Microanalyses were performed by the Laboratory for Organic Elemental Microanalysis at the Faculty of Pharmaceutical Science at Kyoto University. Gas chromatographic analysis (GLC) were carried out on a 1.5 m × 3 mm stainless-steel column packed with 5% SE-30 on 60/80-mesh Shimalite. All the catalytic reactions were carried out in an atmosphere of argon.

Norbornene (**2a**), norbornadiene (**2b**), furan, 2-methylfuran, dimethyl acetylenedicarboxylate, and benzene were commercial samples and were purified by distillation in an atmosphere of argon before use. The norbornene derivatives **2c**,[22] **2d**,[23] **2e**,[24] **2f**,[25] **2g**,[23] **2h** and **2i**,[26] $RuH_2(CO)(PPh_3)_3$ (**4**),[27] and (cyclooctatriene)(cyclooctadiene)ruthenium (**13**)[28] were prepared by the methods described in the literature. $RuH_2(PPh_3)_4$ (**1**) was prepared in two ways: from $RuCl_3{\cdot}3H_2O$[29] and from $RuCl_2(PPh_3)_3$.[30] Although the complex obtained by the former method (mustard yellow) contains a small amount of contaminants, both complexes showed the same catalytic activity, and the complex prepared by the facile former method was used.

Dihydridotetrakis[tris(*p*-fluorophenyl)phosphine]ruthenium (5) was prepared by a method similar to that for **1**.[29] Yellow microcrystals of **5** were obtained in a yield of 60%: mp 157–160 °C dec; $\nu_{\text{Ru-H}}$ 2020 cm^{-1}; ^{1}H NMR (100 MHz, benzene-d_6) τ 20.56 (2 H, m, RuH_2). Anal. Calcd for $C_{72}H_{50}F_{12}P_4Ru$: C, 63.21; H, 3.68. Found: C, 62.11; H, 3.96.

Carbonyldihydridotris[tris(*p*-fluorophenyl)phosphine]ruthenium (6) was prepared by a method similar to that for **4**.[27] Colorless microcrystals of **6** were obtained in 96% yield: mp 202–205 °C dec; $\nu_{\text{Ru-H}}$ 2030, $\nu_{\text{C}\equiv\text{O}}$ 1940 cm^{-1}; ^{1}H NMR (100 MHz, benzene-d_6) τ 16.82 [1 H, $J(H_aP_d)$ = 16.6 Hz, $J(H_aP_c)$ = 30.0 Hz, $J(H_aH_b)$ = 6.2 Hz], 18.61 [1 H, $J(H_bP_d)$ = 75.2 Hz, $J(H_bP_c)$ = 29.0 Hz, $J(H_bH_a)$ = 6.2 Hz], RuH_2.[27] Anal. Calcd for $C_{55}H_{38}OF_9P_3Ru$: C, 61.17; H, 3.55. Found: C, 62.08; H, 3.82.



6

Dimethyl *exo*-Tricyclo[4.2.1.$0^{2,5}$]non-3-ene-3,4-dicarboxylate (7a). A mixture of **1** (0.23 g, 0.20 mmol), benzene (10 mL), **2a** (0.94 g, 10 mmol), and **3** (1.42 g, 10 mmol) was heated in a sealed tube at 80 °C for 24 h. Distillation of the reaction mixture afforded 1.2 g (52%) of **7a**: bp 83–86 °C (0.25 torr); IR (neat) 1720, 1632 cm^{-1}; ^{1}H NMR (CCl_4, 220 MHz) δ 3.72 (s, 6 H, OMe), 2.60 (s, 2 H, *endo*-cyclobutene), 2.25 (s, br, 2 H, bridgehead), 1.61 (d, J = 6.9 Hz, 2 H, endo), 1.34 (d, J = 10.6 Hz, 1 H, bridge), 1.13 (d, J = 6.9 Hz, 2 H, exo), 1.06 (d, J = 10.6 Hz, 1 H, bridge); MS *m/e* 236, 205, 204, 203. Anal. Calcd for $C_{13}H_{16}O_4$: C, 66.09; H, 6.83. Found: C, 65.85; H, 7.05.

Hydrogenation of 7a and 7b. 7a (1.8 g, 7.8 mmol) was hydrogenated under an atmospheric pressure of hydrogen in the presence of 0.5 g of 5% Pd/C in methyl acetate (10 mL). In the course of 24 h, a quantitative amount of hydrogen was absorbed, and distillation of the reaction mixture afforded **8** as a colorless liquid (1.3 g, 73%) which gradually crystallized: bp 95–98 °C (0.08 torr); mp 63–64 °C; IR (KBr) 1738 cm^{-1}; ^{1}H NMR (CCl_4, 220 MHz) δ 3.54 (s, 6 H, OMe), 3.43 (m, 2 H, cyclobutane), 2.46 (s, 2 H, bridgehead), 2.39 (m, 2 H, cyclobutane), 2.00 (d, 1 H, J = 10.5 Hz, bridge), 1.45 (d, br, J = 7.3 Hz, 2 H, endo), 1.17 (d, 1 H, J = 10.5 Hz, bridge), 0.95 (dd, J = 7.3, 2.0 Hz, exo). Anal. Calcd for $C_{13}H_{18}O_4$: C, 65.53; H, 7.61. Found: C, 65.70; H, 7.64. The identical compound was also obtained by a similar hydrogenation of the 1:1 adduct of quadricyclane and dimethyl acetylenedicarboxylate (**7b**)[11] (yield 60%).

Dimethyl *exo*-Tricyclo[4.2.1.$0^{2,5}$]nona-3,7-diene-3,4-dicarboxylate (7b). A mixture of **1** (0.46 g, 0.40 mmol), benzene (20 mL), **2b** (2.0 mL, 20 mmol), and **3** (2.84 g, 20 mmol) was heated in a sealed tube at 80 °C for 48 h. Distillation of the reaction mixture afforded 2.4 g (50%) of **7b**: bp 94–96 °C (0.26 torr); IR (neat) 1710, 1630 cm^{-1}; ^{1}H NMR (CCl_4, 60 MHz) δ 6.17 (m, 2 H, olefinic), 3.75 (s, 6 H, OMe), 2.72 (s, br, 2 H, bridgehead), 2.52 (s, 2 H, endo), 1.40 (s, br, 2 H, bridge); MS *m/e* 234, 203. Anal. Calcd for $C_{13}H_{14}O_4$: C, 66.66; H, 6.02. Found: C, 66.90; H, 5.75. The residue of the distillation was chromatographed (preparative TLC, silica gel); elution with benzene–diethyl ether (2:3) and recrystallization from methanol afforded colorless needles of **7b′** (0.15 g, 2%) (see below for the spectral and analytical data for **7b′**).

Tetramethyl *exo,exo*-Tetracyclo[4.4.1.$0^{2,5}$.$0^{7,10}$]undeca-3,8-diene-3,4,8,9-tetracarboxylate (7b′). A mixture of **1** (0.12 g, 0.10 mmol), benzene (5 mL), **7b** (1.2 g, 5.0 mmol), and **3** (0.71 g, 5.0 mmol) was heated in a sealed tube at 80 °C for 20 h. The reaction mixture was concentrated to ca. 2 mL and cooled at 5 °C overnight. Recrystallization of the formed crystals from methanol gave colorless needles (0.40 g, 21%) of **7b′**: mp 142–143 °C; IR (KBr) 1747, 1702, 1622 cm^{-1}; ^{1}H NMR (CCl_4, 60 MHz) δ 3.70 (s, 12 H, OMe), 2.70 (s, 4 H, endo), 2.37 (s, br, 2 H, bridge), 1.37 (s, br, 2 H, bridgehead); MS *m/e* 376, 345, 311. Anal. Calcd for $C_{19}H_{20}O_8$: C, 60.64; H, 5.36. Found: C, 60.88; H, 5.57.

Tetramethyl *exo*-Tricyclo[4.2.1.$0^{2,5}$]nona-3-ene-3,4-*endo*-7,8-tetracarboxylate (7c). A mixture of **1** (0.23 g, 0.20 mmol), **2c** (2.10 g, 10 mmol), benzene (10 mL), and **3** (1.42 g, 10 mmol) was heated in a sealed tube at 100 °C for 6 h. Distillation of the reaction mixture afforded a colorless liquid which crystallized in several hours to afford 1.68 g (48%) of **7c**: bp 148–150 °C (1.1 torr); mp 98–99 °C; IR (KBr) 1737, 1699, 1626 cm^{-1}; ^{1}H NMR (CCl_4, 60 MHz) δ 3.76 (s, 6 H, OMe), 3.67 (s, 6 H, OMe), 3.38 (s, 2 H, endo), 3.15 (m, 2 H, exo), 2.67 (s, br, 2 H, bridgehead), 1.43 (AB q, J = 11.2 Hz, 2 H, bridge); MS *m/e* 352, 321. Anal. Calcd for $C_{17}H_{20}O_8$: C, 57.95; H, 5.72. Found: C, 57.84; H, 5.93.

Dimethyl 7,8-benzo-*exo*-tricyclo[4.2.1.$0^{2,5}$]non-3-ene-3,4-dicarboxylate (7d) was obtained in a manner similar to that described above as a colorless liquid which crystallized in 1 h: 1.65 g, 57%; bp 134–135 °C (0.45 torr); mp 94–95 °C; IR (KBr) 1728, 1713, 1628 cm^{-1}; ^{1}H NMR (CCl_4, 60 MHz) δ 7.1 (m, 4 H, Ar), 3.80 (s, 6 H, OMe), 3.23 (s, br, 2 H, bridgehead), 2.68 (s, 2 H, endo), 1.77 (s, br, 2 H, bridge); MS *m/e* 283, 252, 224. Anal. Calcd for $C_{17}H_{16}O_4$: C, 71.82; H, 5.67. Found: C, 71.74; H, 5.49.

Tetramethyl *exo*-Tricyclo[4.2.1.$0^{2,5}$]nona-3,7-diene-3,4,7,8-tetracarboxylate (7e). A mixture of **1** (0.23 g, 0.20 mmol), benzene (10 mL), **2e** (2.1 g, 10 mmol), and **3** (1.42 g, 10 mmol) was heated in a sealed tube at 100 °C for 6 h. The reaction mixture was concentrated to ca. 3 mL and cooled at 5 °C for several hours. Recrystallization of the formed precipitates from methanol afforded colorless crystals of **7e**: 2.4 g, 68%; mp 89–90 °C (lit.[14] mp 88 °C); IR and ^{1}H NMR spectra were identical with those reported.[14] Anal. Calcd for $C_{17}H_{18}O_8$: C, 58.28; H, 5.18. Found: C, 58.14; H, 5.18.

Tetramethyl *exo,exo,trans-exo,exo*-Heptacyclo[10.4.1.1.$0^{2,11}$.$0^{3,10}$.$0^{5,8}$.$0^{13,16}$]octadeca-6,14-diene-6,7,14,15-tetracarboxylate (7f′) and Dimethyl *exo,trans-exo,exo*-Hexacyclo[10.2.1.$1^{4,9}$.$0^{2,11}$.$0^{3,10}$.$0^{5,8}$]hexadeca-6,13-diene-6,7-dicarboxylate (7f). A mixture of **6** (0.26 g, 0.24 mmol), benzene (20 mL), **2f** (0.92 g, 5.0 mmol), and **3** (0.71 g, 5.0 mmol) was heated in a sealed tube at 100 °C for 6 h. The reaction mixture was

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concentrated to ca. 3 mL, and then 10 mL of methanol was added. The formed precipitates were collected, and recrystallization from hot methanol–benzene gave colorless crystals of **7f′** (0.35 g, 15%). The solvent of the filtrate was evaporated, and the residual solid was extracted with 10 mL of ether–benzene (1:1) and the extract filtered. The filtrate was concentrated to ca. 1 mL, and the recrystallization of the formed precipitates from methanol gave 0.24 g (15%) of **7f**. The yield of **7f′** increased when the mole ratio of **2f**/**3** was 1:2. A mixture of **6** (0.26 g, 0.24 mmol), **2f** (0.92 g, 5 mmol), benzene (5 mL), and **3** (1.42 g, 10 mmol) was heated in a sealed tube at 100 °C for 8 h. The reaction mixture was allowed to stand at room temperature overnight. Recrystallization of the formed colorless crystals from benzene–methanol (3:2) gave 1.26 g (54%) of **7f′**. From the filtrate, **7f** could not be isolated. **7f**: mp 110–111 °C; IR (KBr) 3065, 1735, 1710, 1625 cm^{-1}; ^{1}H NMR ($CDCl_3$, 100 MHz) δ 5.97 (m, 2 H, olefinic), 3.77 (s, 6 H, OMe), 2.64 (m, 2 H), 2.58 (s, 2 H), 2.15 (s, 2 H), 1.78, 1.22 (AB q, 2 H, J = 8.5 Hz, bridge), 1.70, 1.21 (AB q, 2 H, J = 11.5 Hz, bridge), 1.48 (s, 4 H, cyclobutane). Anal. Calcd for $C_{20}H_{22}O_4$: C, 73.60; H, 6.79. Found: C, 73.03; H, 6.98. **7f′**: mp 259–260 °C; IR (KBr) 1730, 1708, 1630 cm^{-1}; ^{1}H NMR ($CDCl_3$, 60 MHz) δ 3.77 (s, 12 H, OMe), 2.53 (s, 4 H, *endo*-cyclobutene), 2.13 (s, br, 4 H, bridgehead), 1.70 (s, 4 H, cyclobutane), 1.60 (AB q, J = 11.4 Hz, 4 H, bridge); mol wt (cryoscopic in benzene) 420 (468.5). Anal. Calcd for $C_{26}H_{28}O_8$: C, 66.67; H, 6.02. Found: C, 66.46; H, 6.02.

Dimethyl 7,8-benzo-8-oxatricyclo[4.2.1.0^{2,5}]non-3-ene-3,4-dicarboxylate (7g) was prepared from **2g** (10 mmol) and **3** (10 mmol) in the same manner used in the preparation of **7e** (yield 59%). **7g**: mp 151–152 °C; IR (KBr) 1731, 1714, 1638 cm^{-1}; ^{1}H NMR ($CDCl_3$, 60 MHz) δ 7.23 (m, 4 H, Ph), 5.16 (s, 2 H, bridgehead), 3.83 (s, 6 H, OMe), 2.93 (s, 2 H, endo); MS *m/e* 286, 255, 227. Anal. Calcd for $C_{16}H_{14}O_5$: C, 67.13; H, 4.93. Found: C, 66.92; H, 4.95.

Tetramethyl 7-oxa-*exo*-tricyclo[4.2.1.0^{2,5}]nona-3,7-diene-3,4,7,8-tetracarboxylate (7h) was prepared from **2h** (10 mmol) and **3** (10 mmol) in the same manner used in the preparation of **7e** (yield 21%). **7h**: mp 160–161 °C (lit.[30] mp 157–158 °C); IR and ^{1}H NMR spectra were identical with those reported.[30] Anal. Calcd for $C_{16}H_{16}O_9$: C, 54.55; H, 4.58. Found: C, 54.53; H, 4.38.

Tetramethyl 1-methyl-7-oxa-*exo*-tricyclo[4.2.1.0^{2,5}]nona-3,7-diene-3,4,7,8-tetracarboxylate (7i) was prepared in the same manner described above: yield 10%; mp 102–103 °C; IR (KBr) 1730, 1715, 1633 cm^{-1}; ^{1}H NMR ($CDCl_3$, 60 MHz) δ 5.03 (s, 1 H, bridgehead), 3.87 (s, 3 H, OMe), 3.80 (s, 3 H, OMe), 3.10 (s, 2 H, endo), 1.63 (s, 3 H, Me); MS *m/e* 366, 335. Anal. Calcd for $C_{17}H_{18}O_9$: C, 55.74; H, 4.95. Found: C, 55.91; H, 4.92.

Reaction of Furan Derivatives or Cyclopentadiene with 3. The reaction of furan is representative. A mixture of **6** (0.11 g, 0.10 mmol), benzene (5 mL), furan (0.36 mL, 5 mmol), and **3** (1.42 g, 10 mmol) was heated in a sealed tube at 100 °C for 6 h. The solvent of the reaction mixture was evaporated, and the formed precipitates were collected on a glass filter and washed with a small amount of methanol. Recrystallization from methanol gave colorless crystals of **7h** (yield 1.29 g, 73%). The reaction of 2-methylfuran or cyclopentadiene with **3** was carried out similarly. Yields of the products were summarized in Table II.

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Registry No. **1**, 19529-00-1; **2a**, 498-66-8; **2b**, 121-46-0; **2c**, 39589-98-5; **2d**, 4453-90-1; **2e**, 947-57-9; **2f**, 1624-12-0; **2g**, 573-57-9; **2h**, 1829-60-3; **2i**, 18064-04-5; **3**, 762-42-5; **4**, 25360-32-1; **5**, 71901-90-1; **6**, 71901-91-2; **7a**, 5063-02-5; **7b**, 13155-83-4; **7b′**, 71928-61-5; **7c**, 61697-17-4; **7d**, 61697-16-3; **7e**, 20180-47-6; **7f**, 71901-86-5; **7f′**, 71901-87-6; **7g**, 71928-62-6; **7h**, 17732-05-7; **7i**, 71901-88-7; **12e**, 542-92-7; **12h**, 110-00-9; **12i**, 534-22-5; dimethyl dihydro-*cyo*-tricyclo-[4.2.1.0^{2,5}]non-3-en-3,4-dicarboxylate, 71901-89-8; $C_6(CO_2Me)_6$, 6237-59-8.

Rates and Equilibria for the Addition of Methoxide Ion to 2,6-Diphenyl- and 4-Methoxy-2,6-diphenylpyrylium Cations

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The reactions of addition of MeO^- to the title cations, **1** and **2**, respectively, have been studied spectrophotometrically in MeOH. Owing to the high reactivity of these cations, buffers have been used for the kinetic measurements. The system Et_3N/Et_3NH^+ has been found suitable because of the low reactivity of Et_3N toward the substrates. Rate and equilibrium constants for the addition to position 4 of **1** and to positions 2 and 4 of **2** have been determined or estimated at 25 °C. The equilibria are well shifted toward the adducts, much more than in the additions of MeO^- to N-substituted pyridinium cations. The lower rate of addition to the methoxy-bearing position of **2** with respect to that of addition to the hydrogen-bearing position of **1** is discussed in terms of electronic and other structural effects and also in comparison with related data for the addition to the trinitrobenzene and dinitrothiophene systems.

The formation of anionic σ adducts (Meisenheimer adducts) from neutral, suitably substituted aromatic molecules and negatively charged nucleophiles has been intensively investigated in physical organic studies.[1] Quantitative work has also been carried out in more recent years with similar adducts from heteroaromatic six- and five-membered ring substrates.[2-4]

Adduct formation may also occur in reactions of a different charge type, such as the ones involving cationic substrates, and negatively charged nucleophiles to give

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