J. Org. Chem. 1981, 46, 526-531

High Periselectivity of 2-Oxyallyl Cations: Kinetic Evidence of the Cyclocoupling Reaction and Its Mechanistic Aspects

Takashi Ishizu, Masato Mori, and Ken Kanematsu*

Institute of Synthetic Organic Chemistry, Faculty of Pharmaceutical Sciences, Kyushu University 62, Maidashi, Higashi-ku, Fukuoka 812, Japan

Received May 27, 1980

The 2-oxyallyl cation prepared from 7 and $Fe_2(CO)_9$ shows high periselectivity in reactions with tropones and 6-(dimethylamino)fulvene, losing dimethylamine, to give the formally $[2_\pi(3C) + 8_\pi]$ and $[2_\pi(3C) + 6_\pi]$ adducts **8** and **24**, respectively. These reactions have second-order rate constants that are quite sensitive to the ionizing power of the reaction medium, indicating that they proceed by a stepwise mechanism that involves high polarization in charge separation between the ground state and the transition state. The 2-oxyallyl cation also reacts with cycloheptatriene to give the $[2_\pi(3C) + 6_\pi + 2_\sigma]$ adduct **18** and with cyclopentadienones to give the $[2_\pi(3C) + 4_\pi]$ adduct **20**. The rate constants of these latter reactions are also second order but have low sensitivity to the ionizing power of the reaction medium, suggesting that they proceed by a concerted mechanism.

One of the novel features of the chemistry of 2-oxyallyl cations is their ability to undergo cyclocoupling reactions.[1-4] With general interest, the cycloadditions of reactive 2-oxyallyl-Fe(II) cations (**1**) with certain olefins and 1,3-dienes have been known to be good synthetic routes for the preparation of five- (**2**) and seven-membered carbonyl compounds (**3**) (Scheme I).

To account for the regioselectivity of the cyclocouplings with olefins, Noyori et al.[3,4] showed that the $[2_\pi(3C) + 2_\pi]$ cycloaddition involving 2-oxyallyl-Fe(II) cation (**1**) proceeds in a stepwise manner through the ionic intermediate **4**. On the other hand, the reaction of the $[2_\pi(3C) + 4_\pi]$ cycloaddition with dienes proceeds by a concerted mechanism through the cyclic transition state **5**.

Quantitative studies seem to be necessary for a more precise description of the reactions of 2-oxyallyl cations with a variety of cyclic olefins.

We here describe kinetic data on the reactions of 2-oxyallyl-Fe(II) cation (**1**) with seven-membered-ring unsaturated polyenes (tropones and cycloheptatriene), cyclopentadienones and 6-(dimethylamino)fulvene, which were chosen as model compounds for the examination of periselectivity of 2π, 4π, 6π, and 8π reactants.

Results

Cycloaddition of 2-Oxyallyl-Fe(II) Cation (1) with Tropones. Cycloadditions of **1**, generated from 2,4-dibromo-2,4-dimethylpentan-3-one (**7**) and $Fe_2(CO)_9$, with tropone (**6a**), 2-chlorotropone (**6b**), and 2-phenyltropone (**6c**) in dry benzene afforded the corresponding $[2_\pi(3C) + 8_\pi]$ adducts (**8a–c**) in good yields. The structures of the adducts were assigned on the basis of spectroscopic data and some chemical conversions. The elemental composition of **8a** was established by high-resolution mass spectroscopy. The IR and ^1H NMR spectra of **8a** (Table I) support the structure. The ^1H NMR spectral patterns of the olefinic protons are generally similar to those of the cycloheptatriene moiety. In a decoupling experiment of the olefinic H_β, the methine proton H_α appeared as a singlet. In the ^{13}C NMR spectrum of **8a**, only one signal in the carbonyl region appeared at 216.5 ppm. Therefore, the alternative structures such as **9**, **10**, and **11** could be ruled out (Scheme II).

Scheme I

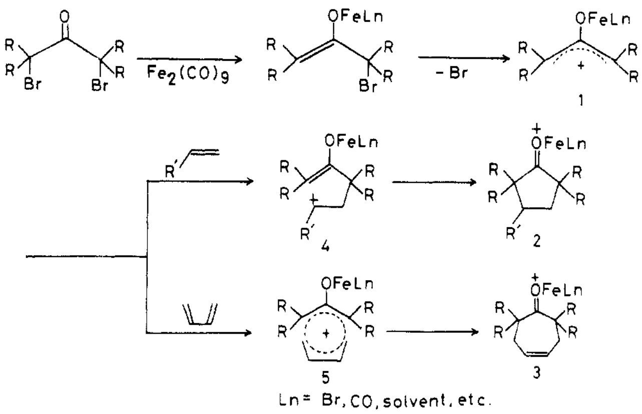


Table I. ^1H NMR and IR Spectral Data of Adducts **8a–c**

adduct	NMR chemical shift, δ^a $(J)^b$	IR ν_{max},^{c} cm^{-1} (C=O)
8a	1.26 (s, 3 H, Me), 1.32 (s, 3 H, Me), 1.40 (s, 3 H, Me), 1.48 (s, 3 H, Me), 1.98 (d, 1 H, CH, J = 5.6), 4.96 (dd, 1 H, olefinic H, J = 9.0, 5.6), 5.80–5.96 (m, 1 H, olefinic H), 6.08–6.32 (m, 1 H, olefinic H), 6.48–6.53 (m, 2 H, olefinic H)	1722
8b	1.24 (s, 3 H, Me), 1.35 (s, 3 H, Me), 1.40 (s, 3 H, Me), 1.56 (s, 3 H, Me), 2.14 (d, 1 H, CH, J = 6.0), 5.12 (dd, 1 H, olefinic H, J = 8.4, 6.0), 6.12–6.30 (m, 1 H, olefinic H, J = 8.4, 6.0), 6.48–6.53 (m, 2 H, olefinic H)	1719
8c	1.23 (s, 6 H, Me), 1.44 (s, 3 H, Me), 1.52 (s, 3 H, Me), 2.11 (d, 1 H, CH, J = 6.4), 5.10 (dd, 1 H, olefinic H, J = 8.5, 6.4), 6.16–6.36 (m, 1 H, olefinic H), 6.48–6.76 (m, 2 H, olefinic H), 7.24–7.48 (m, 5 H, aromatic H)	1718

[a] Solvent $CDCl_3$. [b] J values are given in hertz. [c] In Nujol.

Similarly, 2-chlorotropone (**6b**) and 2-phenyltropone (**6c**) were treated with **7** in the presence of $Fe_2(CO)_9$ to give the adducts **8b** and **8c**, respectively. The ^1H NMR spectra of these adducts are grossly similar to that of **8a**, indicating a skeletal similarity. Furthermore, the structure of **8a** is supported by chemical conversion as shown in Scheme III.

---

(1) Turro, N. J.; Edelson, S. S.; Williams, J. R.; Darling, T. R.; Hammond, W. B. *J. Am. Chem. Soc.* **1969**, *91*, 2283.

(2) Cookson, R. C.; Nye, M. J. *J. Chem. Soc.* **1965**, 2009.

(3) Noyori, R.; Yokoyama, K.; Hayakawa, Y. *J. Am. Chem. Soc.* **1973**, *95*, 2722.

(4) Takaya, H.; Makino, S.; Hayakawa, Y.; Noyori, R. *J. Am. Chem. Soc.* **1978**, *100*, 1765.

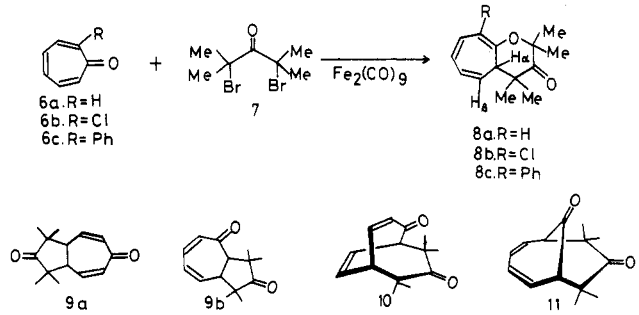
0022-3263/81/1946-0526$01.00/0

Table II. ^{1}H NMR, IR, and Mass Spectral Data of Adducts 20a-d

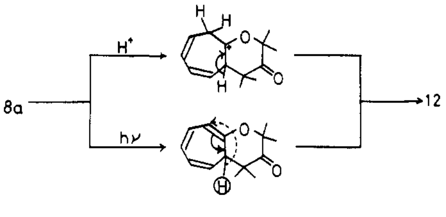
adduct	NMR chemical shift, δ^a $(J)^b$	IR ν_{max},^{c} cm^{-1} (C=O)	mass spectrum, m/e (%)
20a	1.13 (s, 6 H, Me), 1.20 (s, 12 H, Me), 7.05 (s, 10 H, aromatic H)	1705, 1748	372 (100)
20b	0.79 (t, 6 H, Me, J = 7.5), 1.14 (s, 6 H, Me), 1.18 (s, 6 H, Me), 1.78 (q, 2 H, CH$_2$, J = 7.5), 2.14 (q, 2 H, CH$_2$, J = 7.5), 7.13 (s, 10 H, aromatic H)	1702, 1748	400 (100)
20c	0.87 (t, 6 H, Me, J = 3.4), 1.15 (s, 6 H, Me), 1.18 (s, 6 H, Me), 1.32-2.19 (m, 8 H, CH$_2$), 7.10 (s, 10 H, aromatic H)	1702, 1742	428 (100)
20d	0.80 (t, 6 H, Me, J = 6.8), 1.14 (s, 6 H, Me), 1.17 (s, 6 H, Me), 1.25-2.25 (m, 12 H, CH$_2$), 7.11 (s, 10 H, aromatic H)	1708, 1742	456 (100)

[a] Solvent CDCl$_3$. [b] J values are given in hertz. [c] In Nujol.

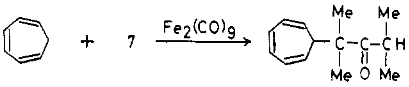
Scheme II



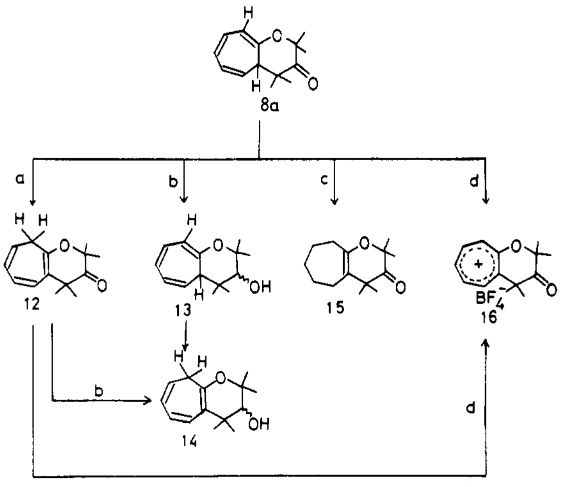
Scheme IV



Scheme V



Scheme III



a: H$^+$ (TsOH) or hν, b: LiAlH$_4$, c: H$_2$/Pd-C in H$^+$, d: Ph$_3$C$^+$BF$_4^-$

A solution of **8a** in chloroform was heated with p-toluenesulfonic acid (TsOH) at 55 °C to give a rearrangement product **12** in 86% yield. The ^{1}H NMR spectrum of **12** exhibited signals of four methyl groups as singlets at δ 1.31 and 1.32, a methylene group as a doublet at δ 2.46 (J = 7.1 Hz), four olefinic protons as multiplets at δ 5.20–5.48 (1 H), 6.08–6.28 (1 H), and 6.40–6.52 (2 H). In a decoupling experiment of the olefinic protons at δ 5.20–5.48, the methylene group appeared as a singlet. Thus, the structure was assigned as the rearrangement product **12** (Scheme III). The rearrangement of **8a** by an acid catalyst could proceed via a carbonium ion intermediate. Interestingly, **12** was also obtained by irradiation of **8a** with a high-pressure 100-W mercury lamp in a Pyrex vessel at room temperature. In this case, **12** could be formed via the photoinduced 1,3-sigmatropic shift of **8a** as shown in Scheme IV.

Reduction of **8a** with lithium aluminum hydride (LAH) gave the corresponding alcohol **13** in 62% yield. Further treatment of **13** in the presence of TsOH or by photolysis gave **14**, which was also obtained by the LAH reduction of **12**. The stereochemistry of the alcohols **13** and **14** is uncertain at this stage. Hydrogenation of **8a** over 5% Pd–C in ethanol afforded **15** in 80% yield. The ^{1}H NMR spectrum showed olefinic protons. The ^{13}C NMR spectrum exhibited two signals due to the vinylic carbons, at 116.25 and 149.77 ppm, and one due to the carbonyl carbon at 215.70 ppm. On the other hand, treatment of **8a** or **12** with triphenylmethyl fluoroborate afforded **16**, which showed characteristic tropylium protons as multiplets at δ 8.44–9.16 (5 H) by ^{1}H NMR and a carbonyl group at 1736 cm^{-1} by IR. Thus, the generation of **16** suggests that both **8a** and **12** contain a 6π-electron system.

Reaction of 2-Oxyallyl-Fe(II) Cation (1) with Cycloheptatriene. The reaction of **1** with cycloheptatriene (**17**) in dry benzene at 70 °C gave an ene-type ([2_π(3C) + 6_π + 2_σ]) product (**18**) in 65% yield (see Scheme V).

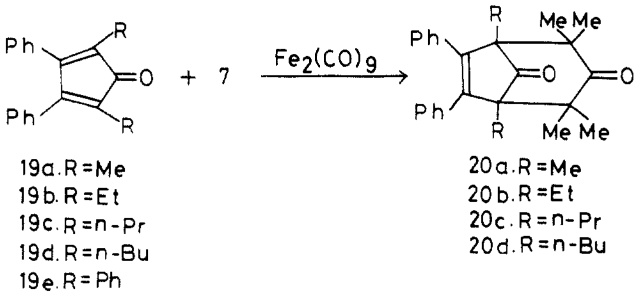
The ^{1}H NMR spectrum of **18** exhibited characteristic signals of two isopropyl methyl groups at δ 1.00 (6 H, d, J = 7.1 Hz) and 1.30 (s, 6 H), an allylic methine proton coupled by vinylic protons at δ 2.16 (d, J = 6.6 Hz), an isopropyl methine proton at δ 3.02 (heptet, 7.1 Hz), olefinic protons at δ 5.08–5.28 (2 H, m), 6.12–6.32 (2 H, m), and 6.52–6.72 (2 H, m).

Cycloadditions of 2-Oxyallyl-Fe(II) Cation (1) with Cyclopentadienones. Cycloadditions of the cyclopentadienones **19a–d** with **7** in the presence of Fe$_2$(CO)$_9$ in dry benzene gave the corresponding [2_π(3C) + 4_π] cycloadducts **20a–d** in moderate yields. However, a similar cycloaddition reaction of **1** with tetracyclone (**19e**) could not be effected even under more drastic conditions, presumably because of steric hindrance of the two phenyl groups at the 2,5-positions in the cyclopentadienone moiety (Scheme VI).

The structures assigned to **20** are in accord with the spectral data summarized in Table II. Each methylene proton was coupled because of hindered rotation by the methyl groups.

Conformational Analysis of the [2_π(3C) + 4_π] Adducts 20. The conformation of carbobicyclic systems has

Scheme VI



Scheme VII

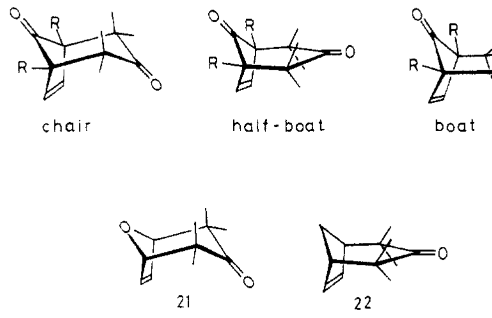


Table III. Chemical Shift Differences of Axial and Equatorial Methyl Protons for 20a-d

compd	chemical shift differences,[a] Δ, ppm
20a	0.00
20b	0.04
20c	0.03
20d	0.03
21[b]	0.42
22[b]	0.21

[a] Δ = δ(axial methyl protons) − δ(equatorial methyl protons). [b] See ref 5 and 6.

been deduced from the chemical shift difference of axial and equatorial methyl protons.[5] In general, the axial proton and methyl group which are α to the carbonyl moiety of a cyclohexanone chair were found to appear downfield from the equatorial proton and methyl group.

From the data in Table II, it is evident that the chemical shift difference of two methyl groups is consistently small for the adduct **20b**, in accord with the postulated greater deformation of the cyclohexanone chair form.[6] Each of the ^{1}H NMR spectral patterns of the other adducts **20a**, **20c**, and **20d** are similar to that of **20b**, indicating a similar conformation. Thus, the conformation of these adducts is probably that of the half-boat form (Scheme VII). The chemical shift differences of the two methyl groups are summarized in Table III.

Reaction of 2-Oxyallyl-Fe(II) Cation (1) with 6-(Dimethylamino)fulvene. Reaction of 2-oxyallyl-Fe(II) cation (1) with 6-(dimethylamino)fulvene (**23**) afforded **24** in 17% yield. The ^{1}H NMR spectrum of **24** exhibited signals of four methyl groups as singlets at δ 1.33 (6 H) and 1.39 (6 H) and four olefinic protons as multiplets at δ 6.0–7.0. Since compound **24** was unstable at room temperature, it was converted to a hydrogenated compound **25**. The mass spectrum of **25** showed a molecular ion peak at *m/e* 192. The ^{1}H NMR spectrum of **25** exhibited signals of four methyls as singlets at δ 1.13 (6 H) and 1.15 (6 H) and the methylene groups as multiplets at δ 1.71–2.55 (8 H). Apparently, the resonance due to the olefinic protons was absent. While the UV spectrum of **24** was very similar to that of 6,6-dimethylfulvene, the structure **24** was assigned as the [2_π(3C) + 6_π] adduct (Scheme VIII).

Scheme VIII

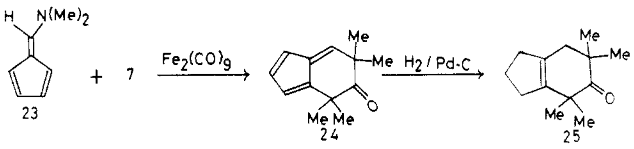


Table IV. Solvent Effect on Cycloaddition of 7 with Tropone in the Presence of $Fe_2(CO)_9$

solvent	E_T, kcal mol^{-1}	rate constants, *k*, L mol^{-1} s^{-1}
toluene	33.9	1.35×10^{-2}
benzene	34.5	1.82×10^{-2}
ethylene glycol dimethyl ether	38.2	2.58×10^{-1}

Table V. Solvent Effect on Reaction of 7 with Cycloheptatriene in the Presence of $Fe_2(CO)_9$

solvent	E_T, kcal mol^{-1}	rate constants, *k*, L mol^{-1} s^{-1}
toluene	33.9	2.18×10^{-4}
benzene	34.5	2.49×10^{-4}
tetrahydrofuran	37.4	2.21×10^{-4}
ethylene glycol dimethyl ether	38.2	2.26×10^{-4}

Table VI. Solvent Effect on Cycloaddition of 7 with 2,5-Diethyl-3,4-diphenylcyclopentadienone (19b) in the Presence of $Fe_2(CO)_9$

solvent	E_T, kcal mol^{-1}	rate constants, *k*, L mol^{-1} s^{-1}
n-hexane	30.9	1.33×10^{-2}
toluene	33.9	1.09×10^{-2}
benzene	34.5	9.31×10^{-3}

Table VII. Solvent Effect on Reaction of 7 with 6-(Dimethylamino)fulvene in the Prescence of $Fe_2(CO)_9$

solvent	E_T, kcal mol^{-1}	rate constants, *k*, L mol^{-1} s^{-1}
toluene	33.9	5.17×10^{-5}
benzene	34.5	9.51×10^{-5}
tetrahydrofuran	37.4	2.09×10^{-3}
ethylene glycol dimethyl ether	38.2	3.64×10^{-3}

Discussion

The cycloaddition reaction of 2-oxyallyl-Fe(II) cation species (1) with 1,3-dienes is classified as a [2_π(3C) + 4_π] process. This cationic cycloaddition of a symmetry-allowed type proceeds in a concerted manner via the cyclic transition state, and the regioselectivity would be controlled by FMOs of the cycloaddends. Indeed, the experimental findings by Noyori et al.[3,4] are not consistent with the stepwise mechanism via the zwitterions but agree with the concerted process via the cyclic transition state **5** as described above.

We have attempted to elucidate the mechanism of the reactions of **1** with **6a**, **17**, **19b**, and **23** by measuring their reaction rates.

---

(5) Rawson, D. I.; Carpenter, B. K.; Hoffmann, H. M. R. *J. Am. Chem. Soc.* **1979**, *101*, 1786.

(6) Hoffmann, H. M. R. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 819.

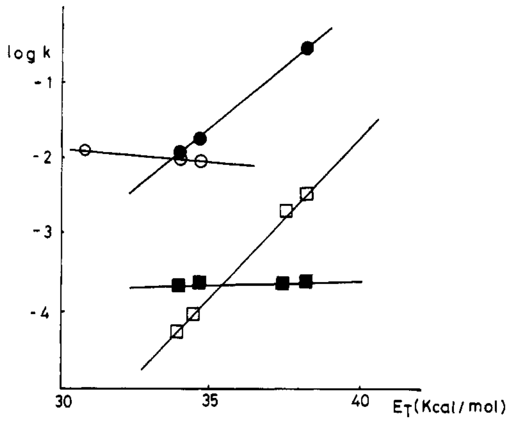


Figure 1. Plot of log k vs. E_T for the reactions of 7 with various polyenes [(●) tropone **6a**, (○) 2,5-diethyl-3,4-diphenylcyclopentadienone (**19b**), (□) 6-(dimethylamino)fulvene (**23**), (■) cycloheptatriene (**17**)] in the presence of $Fe_2(CO)_9$.

Table VIII. Sensitivity of Reactions of 7 with Various Polyolefins in the Presence of $Fe_2(CO)_9$ to Solvent Ionizing Power (E_T Value)

polyolefins	solvent sensitivity parameter, A^a
tropone	30.2
cycloheptatriene	0.743
2,5-diethyl-3,4-diphenylcyclopentadienone	−3.68
6-(dimethylamino)fulvene	44.1

^{a} $A = s \times 10^2$.

The kinetic data were obtained by monitoring the formation of the adducts by thin-layer chromatography (TLC). The second-order rate constants were calculated according to usual method. The rates of reactions were also determined by measuring the disappearance of the substrates in same way, and satisfactory second-order behaviors were observed. The E_T values of Dimroth[7] were used as the scale of solvent ionizing power in studying the effect of solvent on the reaction rate constants (Tables IV–VII). Plots of log k vs. E_T values for each solvent show a linear relationship (log $k = aE_T + b$), as shown in Figure 1.

Values of the least-squares slope(s) for each of the reactions are summarized in Table VIII.

In the cases of the cycloadditions of 2-oxyallyl cation (**1**) with tropone (**6a**) and 6-(dimethylamino)fulvene (**23**), A values are large, indicating that the cycloadditions proceed through highly polarized transition states such as intermediates **26** and **27**, which are consistent with a stepwise mechanism. Since the 2-oxyallyl cations are electron-deficient species, tropone is attacked on negatively charged oxygen by the electrophilic 2-oxyallyl cations.[8] Thus, the electrophilic attack of the cation on oxygen is easier than on other sites, which would have led to other adducts such as **9**, **10**, or **11**.

The cation LUMO and electron-donating fulvene HOMO interactions are expected for the $[2_\pi(3C) + 6_\pi]$ cycloaddition as depicted in Figure 2. However, this reaction is a symmetry-forbidden process and may arise in the stepwise fashion through initial Michael addition to the fulvene at C-1 by the electrophilic cation. From these results, we conclude that both two-step cycloadditions can be induced by suitably polarized polyenes and allyl cation pairs.

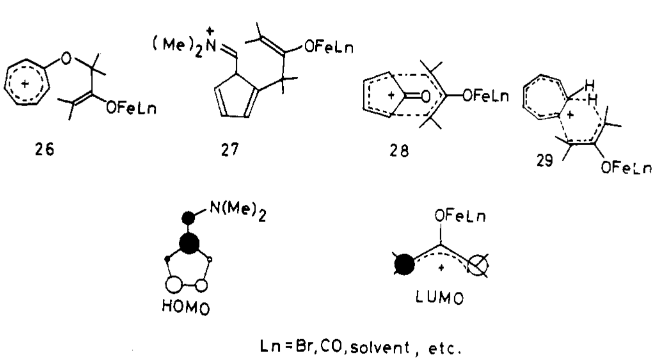


Figure 2.

On the other hand, both $[2_\pi(3C) + 6_\pi + 2_\sigma]$ and $[2_\pi(3C) + 4_\pi]$ cycloaddition reactions are symmetry-allowed processes. Indeed, in the cases of the reactions of **1** with **17** and **19b**, A values are very small. These results may be explained by a mechanism which involves very little change in charge separation between their ground states and the transition states, by a concerted mechanism through the cyclic intermediates **28** and **29**.

Experimental Section

Melting points were measured with a Yanagimoto micro melting point apparatus and are uncorrected. UV spectra were determined with a Hitachi EPS-3T spectrophotometer. ^1H NMR spectra were taken with a JEOL PS-100 spectrometer with Me_4Si as an internal standard; chemical shifts are expressed in δ values. ^{13}C NMR spectra were recorded on a JEOL FX-100 with Me_4Si as internal standard. IR spectra were taken with a JASCO DS-701G infrared spectrophotometer. Mass spectra were obtained with a JEOL JMS-01SG double-focusing spectrometer operating at an ionization potential of 75 eV. The solid samples were ionized by electron bombardment after sublimation directly into the electron beam at 150–200 °C. The reaction rates were measured with a Iatroscan TH-10 TLC analyzer.

9,9,11,11-Tetramethyl-8-oxabicyclo[5.4.0]undeca-2,4,6-trien-10-one. A mixture of $Fe_2(CO)_9$ (1.72 g), **7** (1.28 g), and **6a**[9] (0.5 g) in 30 mL of dry benzene was stirred at 50 °C for 30 h. The mixture was filtered and washed with water. The organic layer was dried ($MgSO_4$) and evaporated under reduced pressure. The residue was chromatographed on silica gel, using benzene, to give **8a** (0.51 g, 50%) as a colorless oil: n^{25}_D 1.514; ^{13}C NMR ($CDCl_3$) 20.55 (q), 23.90 (q), 25.25 (q), 26.36 (q), 44.15 (s), 46.85 (d), 84.54 (s), 107.32, 118.89 and 126.70 (each d, 4 C, one of these signals is overlapping), 126.93 (d), 145.13 (s), 216.53 (s); exact mass 218.1292 (calcd 218.1306).

6-Chloro-9,9,11,11-tetramethyl-8-oxabicyclo[5.4.0]undeca-2,4,6-trien-10-one. A mixture of $Fe_2(CO)_9$ (1.3 g), **7** (0.98 g), and 2-chlorotropone[10] (**6b**; 0.5 g) in 30 mL of dry benzene was stirred at 40 °C for 70 h. The same workup gave **8b** (0.25 g, 28%) as a pale yellow oil: n^{25}_D 1.508; exact mass 252.0910 (calcd 252.0918).

6-Phenyl-9,9,11,11-tetramethyl-8-oxabicyclo[5.4.0]undeca-2,4,6-trien-10-one. A mixture of $Fe_2(CO)_9$ (1.2 g), **7** (0.90 g), and 2-phenyltropone[11] (0.5 g) in 30 mL of dry benzene was stirred at 45 °C for 30 h. After the same workup the crude product was recrystallized from n-hexane to give **8c** (0.52 g, 65%) as colorless prisms, mp 131–134 °C. Anal. Calcd for $C_{20}H_{22}O_2$: C, 81.60; H,

---

[7] (a) Dimroth, K.; Reichardt, C.; Siepmann, T.; Bohlmann, F. *Justus Liebigs Ann. Chem.* **1963**, *661*, 1. (b) Dimroth, K.; Reichardt, C.; Schweig, A. *Ibid.* **1963**, *669*, 95. (c) For a kinetic study of cycloadditions that proceed via zwitterionic intermediates and the effect of solvent polarity on rate, see Huisgen, R. *Acc. Chem. Res.* **1977**, *10*, 117.

[8] A thermally allowed $[8 + 2]\pi$ cycloaddition would also account for the high stereoselectivity: Truce, W. E.; Lin, Cheng-I. M. *J. Am. Chem. Soc.* **1973**, *95*, 4426 and references cited therein.

[9] Radlick, P. *J. Org. Chem.* **1964**, *29*, 960.

[10] Abadir, B. J.; Cook, J. W.; Loudon, J. D.; Steel, D. K. V. *J. Chem. Soc.* **1952**, 2350.

[11] Nozoe, T.; Mukai, T.; Minegishi, J.; Fujisawa, T. *Sci. Rep. Tohoku Univ., Ser. 1* **1953**, *37*, 388.

7.53. Found: C, 81.47; H, 7.51.

Chemical Conversion of 8a. (a) In Acid. A solution of **8a** (0.5 g) in $CHCl_3$ (10 mL) in the presence of *p*-TsOH (10 mg) was heated at 55 °C for 24 h. The solution was evaporated under reduced pressure, and the residue was chromatographed on silica gel, using benzene, to give **12** (0.43 g, 86%) as a colorless oil.

(b) Photochemical. A solution of **8a** (0.5 g) in $CHCl_3$ (10 mL) was irradiated for 4 h with a high-pressure 100-W mercury lamp in a Pyrex vessel at room temperature. The solvent was removed under reduced pressure and the residue chromatographed on silica gel, using benzene, to give **12** (0.25 g, 49%): bp 90 °C (2 mm); $n^{25}{}_D$ 1.512; IR (neat) 1723 cm^{-1} (C=O); ^1H NMR ($CDCl_3$, Me_4Si) 1.31 (6 H, s), 1.32 (6 H, s), 2.46 (2 H, d, *J* = 7.1 Hz), 5.20–5.48 (1 H, m), 6.08–6.28 (1 H, m), 6.40–6.52 (2 H, m); ^{13}C NMR ($CDCl_3$) 25.13 (q), 25.48 (q), 32.88 (s), 43.86 (t), 81.08 (s), 115.43 (s), 117.13 (d), 125.93 (d), 126.93 (d), 127.17 (d), 139.20 (s), 214.88 (s); exact mass 218.1291 (calcd 218.1306).

Reduction of 8a with $LiAlH_4$. A suspension of $LiAlH_4$ (0.2 g) in 30 mL of dry ether was cooled to 0 °C and to this was added dropwise a solution of **8a** (1.0 g) in 5 mL of dry ether. The mixture was stirred at room temperature for 20 min. The excess $LiAlH_4$ was decomposed by cautious addition of saturated NH_4Cl solution (5 mL) and water (5 mL). The organic layer was dried over $MgSO_4$. The solvent was removed and the residue ws chromatographed on silica gel, using ethyl acetate, to give **13** (0.63 g, 62%) as a colorless oil: $n^{25}{}_D$ 1.526; IR (neat) 3448 cm^{-1} (OH); ^1H NMR ($CDCl_3$) 1.08 (3 H, s), 1.18 (3 H, s), 1.39 (6 H, s), 2.05 (1 H, s, OH), 2.08 (1 H, d, *J* = 5.3 Hz), 3.32 (1 H, s), 5.24 (1 H, dd, *J* = 9.0 and 5.3 Hz), 5.48–5.72 (1 H, m), 6.16–6.28 (1 H, m), 6.36–6.52 (2 H, m); mass spectrum, *m/e* 220 (M^+).

Reduction of 12 with $LiAlH_4$. A suspension of $LiAlH_4$ (0.15 g) in 20 mL of dry ether was cooled to 0 °C and to this was added dropwise a solution of **12** (0.6 g) in 3 mL of dry ether. Workup as described above gave 14 (0.41 g, 67%) as a colorless oil.

Chemical Conversion of 13. (a) In Acid. A solution of **13** (0.5 g) in $CHCl_3$ (10 mL) in the presence of *p*-TsOH (10 mg) was heated at 55 °C for 24 h. The solution was evaporated under reduced pressure, and the residue was chromatographed on silica gel using ethyl acetate to give **14** (0.45 g, 90%).

(b) Photochemical. A solution of 13 (0.5 g) in $CHCl_3$ (10 mL) was irradiated for 4 h with a high-pressure 100-W mercury lamp in a Pyrex vessel at room temperature. The product was worked up as usual to give 14 (0.25 g, 49%): $n^{25}{}_D$ 1.534; IR (neat) 3440 cm^{-1} (OH); ^1H NMR 1.07 (3 H, s), 1.15 (3 H, s), 1.25 (3 H, s), 1.32 (3 H, s), 1.98 (1 H, s, OH), 2.08 (1 H, q, *J* = 7.7 Hz), 2.70 (1 H, q, *J* = 7.7 Hz), 3.45 (1 H, s), 5.20–5.48 (1 H, m), 6.08–6.28 (1 H, m), 6.36–6.60 (2 H, m); mass spectrum, *m/e* 220 (M^+).

Hydrogenation of 8a. Catalytic hydrogenation of **8a** (1.0 g) was carried out in ethanol (40 mL) over 5% Pd–C (0.2 g) at atmospheric pressure. The mixture was filtered and the solvent was removed under reduced pressure. The residue was chromatographed on silica gel, using benzene, to give **15** (0.81 g, 80%) as a colorless oil: $n^{25}{}_D$ 1.481; IR (neat) 1718 cm^{-1} (C=O); ^1H NMR 1.16 (6 H, s), 1.36 (6 H, s), 1.50–2.40 (10 H, m); ^{13}C NMR 24.19 (q), 24.48 (q), 25.07, 27.89, 31.94, and 33.58 (each t, 5 C), 43.92 (s), 76.44 (s), 116.25 (s), 149.77 (s), 215.70 (s); mass spectrum, *m/e* 222 (M^+).

Treatment of 8a or 12 with Triphenylmethyl Fluoroborate. To a solution of triphenylmethyl fluoroborate (0.45 g) in dry CH_2Cl_2 (5 mL) was added a solution of **8a** (0.3 g) or **12** (0.3 g) in dry CH_2Cl_2 (5 mL) at 0 °C. The solution was stirred for 5 min and then evaporated under reduced pressure. The residue was poured into water and extracted with ether. The ether solution was dried over $MgSO_4$ and evaporated in vacuo. The solid was recrystallized from $CHCl_3$–ether (1:1). **16** (0.4 g, 98%) from **8a** and **16** (0.4 g, 96%) from **12**: mp 121–122 °C; IR (Nujol) 1736 cm^{-1} (C=O); ^1H NMR 1.64 (6 H, s), 1.69 (6 H, s), 8.44–9.16 (5 H, m, tropylium cation). Anal. Calcd for $C_{14}H_{17}O_2BF_4$: C, 55.30; H, 5.64. Found: C, 55.17; H, 5.65.

2-(Cyclohepta-2,4,6-trien-1-yl)-2,4-dimethylpentan-3-one. A mixture of $Fe_2(CO)_9$ (2.52 g), **7** (2.72 g), and cycloheptatriene (3.0 g) in dry benzene (50 mL) was stirred at 70 °C for 6 h. The mixture was filtered, washed with water, and dried over $MgSO_4$. The solvent was evaporated under reduced pressure and the residue was chromatographed on silica gel, using benzene, to give 18 (1.32 g, 65%) as a colorless oil: $n^{25}{}_D$ 1.444; IR (neat) 1716 cm^{-1} (C=O); ^1H NMR 1.00 (6 H, d, *J* = 7.1 Hz), 1.30 (6 H, s), 2.16 (1 H, d, *J* = 6.5 Hz), 3.02 (1 H, h, *J* = 7.1 Hz), 5.08–5.28 (2 H, m), 6.12–6.32 (2 H, m), 6.52–6.72 (2 H, m); mass spectrum, *m/e* 204 (M^+). Anal. Calcd for $C_{14}H_{20}O$: C, 82.30; H, 9.87. Found: C, 82.10; H, 9.67.

6,7-Diphenyl-1,2,2,4,4,5-hexamethylbicyclo[3.2.1]oct-6-ene-3,8-dione. A solution of $Fe_2(CO)_9$ (1.4 g), **7** (1.04 g), and 2,5-dimethyl-3,4-diphenylcyclopentadienone dimer (0.5 g) in dry benzene (30 mL) was stirred at 50 °C for 35 h. The mixture was filtered and washed with water and dried over $MgSO_4$. The solvent was removed under reduced pressure to give crude product, which was recrystallized from benzene/*n*-hexane (1:1) to give **20a** (0.25 g, 35%) as colorless crystals, mp 253–255 °C. Anal. Calcd for $C_{26}H_{28}O_2$: C, 83.83; H, 7.58. Found: C, 83.82; H, 7.60.

1,5-Diethyl-6,7-diphenyl-2,2,4,4-tetramethylbicyclo[3.2.1]oct-6-ene-3,8-dione. A solution of $Fe_2(CO)_9$ (1.26 g), **7** (0.94 g), and 2,5-diethyl-3,4-diphenylcyclopentadienone (0.5 g) in dry benzene (30 mL) was stirred at 60 °C for 16 h. Workup as described above gave **20b** (0.2 g, 29%): mp 163–164 °C; ^{13}C NMR 9.92 (q), 16.79 (t), 23.01 (q), 24.25 (q), 58.42 (s), 64.46 (s), 127.11 (s), 128.11 (s), 130.81 (s), 137.21 (s), 146.07 (s), 213.35 (s), 216.11 (s). Anal. Calcd for $C_{28}H_{32}O_2$: C, 83.96; H, 8.05. Found: C, 83.80; H, 8.09.

6,7-Diphenyl-1,5-di-*n*-propyl-2,2,4,4-tetramethylbicyclo[3.2.1]oct-6-ene-3,8-dione. A solution of $Fe_2(CO)_9$ (1.16 g), **7** (0.86 g), and 2,5-di-*n*-propyl-3,4-diphenylcyclopentadienone (0.5 g) in dry benzene (30 mL) was stirred at 50 °C for 34 h. Workup as described above gave **20c** (0.17 g, 26%) as a colorless crystals, mp 139–140 °C. Anal. Calcd for $C_{30}H_{36}O_2$: C, 84.07; H, 8.47. Found: C, 84.01; H, 8.37.

1,5-Di-*n*-butyl-6,7-diphenyl-2,2,4,4-tetramethylbicyclo[3.2.1]oct-6-ene-3,8-dione. A solution of $Fe_2(CO)_9$ (1.06 g), **7** (0.8 g), and 2,5-di-*n*-butyl-3,4-diphenylcyclopentadienone (0.5 g) in dry benzene (30 mL) was stirred at 60 °C for 32 h. Workup as described above afforded **20d** (0.15 g, 22%) as colorless crystals, mp 157–158 °C. Anal. Calcd for $C_{32}H_{40}O_2$: C, 84.16; H, 8.83. Found: C, 84.16; H, 8.79.

3,3,5,5-Tetramethylbicyclo[4.3.0]nona-1,6,8-trien-4-one. A solution of $Fe_2(CO)_9$ (1.5 g), **7** (1.12 g), and 6-(dimethylamino)fulvene[12] (0.5 g) in dry benzene (30 mL) was stirred at 45 °C for 6 h. The mixture was filtered off, washed with water, and dried over $MgSO_4$. The solvent was removed under reduced pressure. The residue was chromatographed on silica gel, using benzene, to give **24** (0.13 g, 17%) as a yellow liquid: IR (neat) 1710 cm^{-1} (C=O); UV λ_{max} (EtOH) 378 nm (ϵ 188); ^1H NMR 1.12 (6 H, s), 1.19 (6 H, s), 6.13–6.38 (2 H, m), 6.50–6.69 (2 H, m); mass spectrum, *m/e* 188 (M^+). Anal. Calcd for $C_{13}H_{16}O$: C, 82.93; H, 8.57. Found: C, 82.88; H, 8.63.

Hydrogenation of 24. Catalytic hydrogenation of **24** (0.33 g) was carried out in ethanol (20 mL) over 5% Pd–C (0.06 g) under a reduced atmospheric pressure of hydrogen. The mixture was filtered and the solvent was removed under reduced pressure. The residue was chromatographed on silica gel, using benzene, to give **25** (0.15 g, 33%) as a colorless oil: $n^{25}{}_D$ 1.461; IR (neat) 1708 cm^{-1} (C=O); ^1H NMR 1.13 (6 H, s), 1.15 (6 H, s), 1.71–2.55 (8 H, m); mass spectrum, *m/e* 192 (M^+). Anal. Calcd for $C_{13}H_{20}O$: C, 81.20; H, 10.48. Found: C, 81.28; H, 10.55.

Kinetics. Measurements of Rates of Reactions of 2-Oxyallyl Cations and Various Polyenes. The mixture of $Fe_2(CO)_9$, **7**, the polyenes, and 2-methoxynaphthalene (as an internal standard) in a solvent was stirred at 50.8 ± 0.1 °C. The reaction was followed by withdrawing 1-mL aliquots at intervals of appropriate time. The aliquots were cooled to 0 °C followed by filtering of the insoluble ferric bromide. The concentration of forming product was measured by the internal standard method with a thin-layer chromatograph analyzer (Iatroscan TH-10 TLC analyzer, Iatron Laboratories, Inc., Tokyo). The rate constants were calculated from the slope of plots of log $[(a - x)/(b - x)]$ vs. time by the least-squares method. The rates of reactions were also determined by measuring the decrease of the substrates in the same way, and the same satisfactory second-order constants were calculated.

---

[12] Hafner K.; Vöpel, K. H.; Ploss, G.; König, C. *Justus Liebigs Ann. Chem.* **1963**, *661*, 52.

The kinetic data are listed in Tables III-VII.

Acknowledgment. We are grateful to Miss Takako Ishibashi for helpful discussions and experimental assistance.

Registry No. **6a**, 539-80-0; **6b**, 3839-48-3; **7**, 17346-16-6; **8a**, 75918-92-2; **8b**, 75933-25-4; **8c**, 75918-93-3; **12**, 75918-94-4; **13**, 75918-95-5; **14**, 75918-96-6; **15**, 75933-26-5; **16**, 75933-32-3; **18**, 75918-97-7; **19b**, 51932-77-5; **20a**, 75918-98-8; **20b**, 75918-99-9; **20c**, 75919-00-5; **20d**, 75919-01-6; **24**, 75919-02-7; **25**, 75919-03-8; 2-phenyltropone, 14562-09-5; cycloheptatriene, 544-25-2; 2,5-dimethyl-3,4-diphenylcyclopentadienone dimer, 38883-84-0; 2,5-dipropyl-3,4-diphenylcyclopentadienone, 61202-93-5; 2,5-dibutyl-3,4-diphenylcyclopentadienone, 75919-04-9; 6-(dimethylamino)fulvene, 696-68-4.

Solvomercuration–Demercuration. 8. Oxymercuration–Demercuration of Methoxy-, Hydroxy-, and Acetoxy-Substituted Alkenes[1]

Herbert C. Brown* and Gary J. Lynch[2]

Richard B. Wetherill Laboratory, Purdue University, West Lafayette, Indiana 47907

Received August 25, 1980

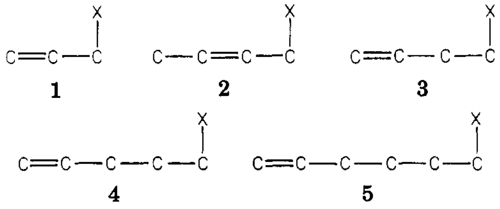
The oxymercuration–demercuration (OM–DM) of a series of methoxy-, hydroxy-, and acetoxy-substituted alkenes was examined. The systems examined were the allyl, crotyl, 3-buten-1-yl, 4-penten-1-yl, and 5-hexen-1-yl. The methoxyalkenes undergo hydration with very high regioselectivity and almost quantitative yield in all cases. However, a small –I effect is observed in the case of the allylalkene (97.1% Markovnikov vs. 99.5% in 1-hexene). Moreover, in the crotyl case, a major directing effect is observed: 97.7% 3-ol, 2.3% 2-ol. The other three alkenes undergo the OM reaction with no effect from the methoxy group (99.5% Markovnikov isomer). In contrast, only allyl-, crotyl-, and 3-buten-1-yl alcohols produce major amounts of hydrated products, the diols. While no hydroxyl group directing effect is observed in the allyl system, a major one is again seen in the case of the crotyl: 93.5% 1,3-diol and 6.5% 1,2-diol. The major products from the 4-penten-1-yl and 5-hexen-1-yl alcohols are 2-methyltetrahydrofuran and 2-methyltetrahydropyran, respectively, resulting from OH-5 and OH-6 neighboring group participation in the OM stage. The acetoxy alkenes undergo hydration to give diols in ca. 80% yield with ca. 20% unreacted starting material. This is the result of a competitive deoxymercuration reaction which is occurring in the DM stage. However, the yield of hydrated products can be increased by varying the amount of base used in the DM. Neighboring-group participation, AcO-5, is observed in the allyl system only, resulting in a 65% yield of the Markovnikov oxymercurial, by ^{1}H NMR analysis, and a 35% yield of the acetoxy-exchanged mercurial. Again, a major –I-directing effect of the acetoxy group was observed in the crotyl system but not in the others. In addition to the expected 1,2- and 1,3-diols, the OM–DM of crotyl acetate also resulted in small amounts of the unexpected 2,3-diol under kinetic conditions. Finally, a modified DM procedure has been developed which is compatible with the acetoxy group.

The oxymercuration–demercuration (OM–DM) of olefins is an extraordinarily valuable method for the Markovnikov hydration of olefins and dienes with remarkably high regioselectivity.[1,3] For example, 1-hexene undergoes reaction to give a 94% yield of alcohols, a 99.5% yield of 2-hexanol and a 0.5% yield of 1-hexanol (eq 1).

$$CH_3(CH_2)_3CH{=}CH_2 \xrightarrow[THF,\ H_2O]{Hg(OAc)_2} \xrightarrow[2.\ NaBH_4]{1.\ NaOH} CH_3(CH_2)_3C(OH)HCH_3 \quad (1)$$

While there are numerous examples in the literature on the OM–DM of functionally substituted alkenes, there are but a few detailed, systematic studies.[4-10] Consequently, we undertook such a study on representative functionally substituted acyclic alkenes. The results are detailed and discussed in this as well as the following paper in this series.

Chart I[a]



[a] X = OCH_3, OH, OAc.

Results and Discussion

The alkene systems examined were the allyl (**1**), crotyl (**2**; 2-buten-1-yl), 3-buten-1-yl (**3**), 4-penten-1-yl (**4**), and 5-hexen-1-yl (**5**) with the methoxy, hydroxy, and acetoxy functional groups (Chart I).

---

(1) The oxymercuration–demercuration of unsaturated alcohols was discussed earlier in connection with a study of the reaction of dienes: H. C. Brown, P. J. Geoghegan, Jr., J. T. Kurek, and G. J. Lynch, *Organomet. Chem. Synth.*, 1, 7 (1970).

(2) Texaco research fellow at Purdue University, 1972–1973. Graduate research assistant, 1969–1972, on a study supported by a grant from the Esso Research and Engineering Co.

(3) H. C. Brown and P. J. Geoghegan, Jr., *J. Org. Chem.*, **35**, 1844 (1970).

(4) J. L. Jernow, D. Gray, and W. D. Closson, *J. Org. Chem.* **36**, 3511 (1971).

(5) M. Barelle and M. Apparu, *Bull. Soc. Chim. Fr.*, 2016 (1972).

(6) H. Christol, F. Plénat, and J. Revel, *Bull. Soc. Chim. Fr.*, 4537 (1971).

(7) J. A. Soderquist and K. L. Thompson, *J. Organomet. Chem.*, **159**, 237 (1978).

(8) F. D. Gunstone and P. R. Inglis, *Chem. Phys. Lipids*, **10**, 73, 89, 105 (1973).

(9) Much of the earlier work on the oxymercuration stage has been reviewed; see ref 10.

(10) W. Kitching, *Organomet. Chem. Rev.*, **3**, 61 (1968).

0022-3263/81/1946-0531$01.00/0