active intermediate in the action of coenzyme A dependent bacterial aldehyde dehydrogenase.[20] In this scheme, intermediate IV then undergoes two-equivalent oxidation at the activated carbon, analogous to the latter stages of the oxidation of I, to give a coordinated thioacid which is finally hydrolyzed to carboxylate and regenerated catalyst.

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(21) ANL-AUA-AEC Laboratory Graduate Participant, 1972–1973.

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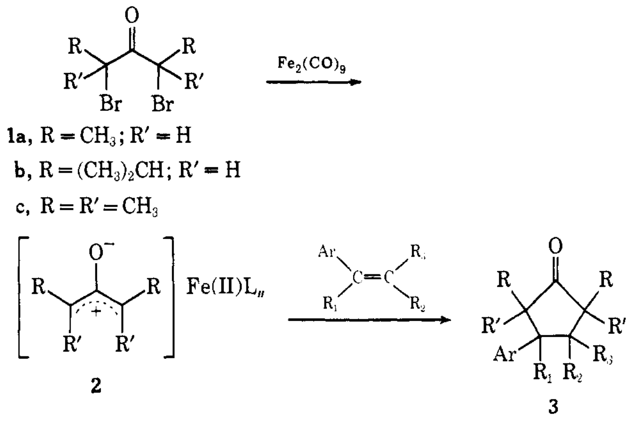
Reaction of α,α'-Dibromo Ketones and Aromatic Olefins Promoted by Iron Carbonyl. A Cationic 3 + 2 → 5 Cycloaddition[1]

Sir:

The cycloaddition reaction of allylic moieties at the C-1 and C-3 termini is currently of interest.[2–4] According to the principle of conservation of orbital symmetry,[5] the cycloaddition of allyl anions to olefins in a 3 + 2 → 5 fashion ($[_\pi 4_s + {}_\pi 2_s]$ process) is thermally allowed, whereas the coupling between allyl cations and olefins ($[_\pi 2_s + {}_\pi 2_s]$ process) is a thermally forbidden reaction. Recent publications on the reaction of allyl anions and aromatic olefins forming cyclopentyl anions[3c,d,6] prompted us to describe the formally corresponding cycloaddition of allyl cations.

Scheme I



1a, R = CH_3; R' = H
b, R = $(CH_3)_2CH$; R' = H
c, R = R' = CH_3

Treatment of α,α'-dibromo ketones **1** with $Fe_2(CO)_9$ is known to generate the oxyallyl-iron(II) intermediates of type **2** (L = Br^-, CO, and solvent, etc.), which behave as an allyl cation since the negative charge is masked by complexing with the Fe(II) ion.[7] As shown in Scheme I, the reactive species can be trapped by aryl-substituted olefins to produce the cyclopentanones (**3**). For instance, when a mixture of the dibromide **1a** (10 mmol), 1,1-diphenylethylene (40 mmol), and $Fe_2(CO)_9$ (12 mmol) in dry benzene (20 ml) was heated at 60° for 14 hr under nitrogen, *cis*- and *trans*-2,5-dimethyl-3,3-diphenylcyclopentanones (ir (CCl_4) 1741 cm^{-1}) were obtained in 70% combined yield;[8] the isomeric ratio was dependent on the work-up conditions. In addition, an open-chain 1:1 adduct, 4-methyl-6,6-diphenylhex-5-en-3-one (**4**), was produced in 7% yield: ir (CCl_4) 1713 (C=O) and 1664 cm^{-1} (C=C); nmr (CCl_4) δ 5.95 (d, J = 10.5 Hz, =CH); uv (C_2H_5OH) 224 (log ϵ 4.12) and 255 nm (4.10). Several examples of the coupling reaction are given in Table I. Simple aliphatic olefins such as isobutylene could not be used as an olefinic receptor. α,α'-Dibromoacetone failed to yield the cyclic adduct.

Table I. Iron Carbonyl Promoted Reaction of α,α'-Dibromo Ketones and Aromatic Olefins[a]

Dibromide	Olefin	Yield of **3**,[b] %
1a	Styrene[c]	65
1a	1,1-Diphenylethylene	70
1a	α-Methylstyrene[c]	70
1a	α-Cyclopropylstyrene	95
1a	*trans*-Stilbene	30
1a	Indene	45
1a	Ferrocenylethylene[c,d]	30
1b	1,1-Diphenylethylene	27
1c	*trans*-Anethole	55[e]

[a] Unless otherwise stated, reaction was carried out in benzene at 50–60° for 12–14 hr using dibromide, olefin, and $Fe_2(CO)_9$ in a mole ratio of 1:4:1.2. Reaction conditions were not optimized. Usually, a mixture of diastereomers was obtained. The formation of acyclic adducts of type **4** as by-product was observed. [b] Isolated yield based on the starting dibromo ketone. [c] Considerable polymerization of the olefin was observed. [d] Dibromide and olefin were used in a mole ratio of 1:2. [e] A single isomer. The *p*-methoxyphenyl and methyl at C-4 are trans to each other.

Thus, the allylic cations (**2**) were revealed to cycloadd readily to aryl-substituted olefins, although constraints are imposed by orbital symmetry factors.[5] The cycloaddition could be best explained by assuming a stepwise mechanism with the ionic intermediates of type **5**; cyclization therefrom leads to the cyclopentanones **3**, while prototropy from **5** (R_2 or R_3 = H) gives rise to the electrophilic *olefinic* substitution products of type **4**. Most of the olefins listed in Table I are known to form the iron-tetracarbonyl complexes by interacting with

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(1) Carbon–Carbon Bond Formations Promoted by Transition Metal Carbonyls. VII. Part VI: R. Noyori, S. Makino, and H. Takaya, *Tetrahedron Lett.*, in press.

(2) Allyl cations: (a) R. Noyori, Y. Baba, S. Makino, and H. Takaya, *ibid.*, in press; (b) H. M. R. Hoffmann, K. E. Clemens, and R. H. Smithers, *J. Amer. Chem. Soc.*, **94**, 3940 (1972), and references cited therein.

(3) Allyl anions: (a) W. T. Ford, R. Radue, and J. A. Walker, *Chem. Commun.*, 966 (1970); (b) R. Huisgen and P. Eberhard, *J. Amer. Chem. Soc.*, **94**, 1346 (1972); (c) R. Eidenschink and T. Kauffmann, *Angew. Chem.*, **84**, 292 (1972); (d) G. Boche and D. Martens, *ibid.*, **84**, 768 (1972).

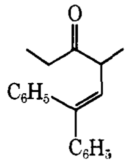
(4) Cycloreversion of cyclopentyl radicals to allyl radicals and olefins: W. R. Dolbier, Jr., I. Nishiguchi, and J. M. Riemann, *J. Amer. Chem. Soc.*, **94**, 3642 (1972).

(5) R. B. Woodward and R. Hoffmann, *Angew. Chem.*, **81**, 797 (1969).

(6) Stereochemistry of the cycloaddition has not been investigated.

(7) R. Noyori, Y. Hayakawa, M. Funakura, H. Takaya, S. Murai, R. Kobayashi, and S. Tsutsumi, *J. Amer. Chem. Soc.*, **94**, 7202 (1972).

(8) All new compounds gave correct elemental analyses and consistent spectral data (ir, nmr, uv, and mass spectra).



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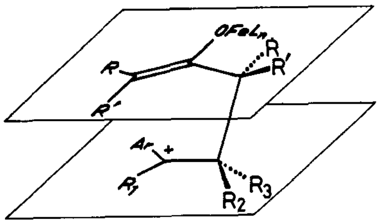
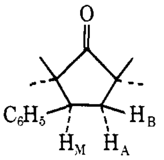


5

$Fe_2(CO)_9$.[9] Although the complex formation would assist the reaction by bringing the reactants in close proximity, the yield of the adducts does not necessarily correlate to the ease of the complex formation but appears to depend on the substituents affecting the stability of the carbocations. The reaction between α-cyclopropylstyrene and **1a**, which proceeds *via* the cationic species **5** stabilized by both phenyl and cyclopropyl groups, is remarkably smooth (95% yield). Competition experiments revealed that the reaction of α-methylstyrene with **1a** (benzene, 60°, <10 min) takes place approximately five times faster than that of unsubstituted styrene. The reaction using a 1:1 mixture of styrene and *trans*-β-methylstyrene as an olefinic substrate afforded only the styrene adduct. These results imply that the reaction rate is also sensitive to steric environment around the carbon–carbon double bond.

Particularly noteworthy is the fact that aryl-substituted olefins enter into the cycloaddition in a *stereospecific* manner and with retention of configuration. The dibromide **1c** (2 mmol) was mixed with a stirred suspension of $Fe_2(CO)_9$ (1 mmol) in benzene at 50° under nitrogen. After a 15-min reaction, *cis*-β-deuteriostyrene (2 mmol, prepared from deuteriophenylacetylene and disiamylborane) was added, and the resulting mixture was maintained at the same temperature for an additional 1 hr. Usual work-up followed by glpc purification gave the cyclopentanone **6**-*d*, mp 43–45°, in 10% yield.[10] The structure was firmly established by nmr analysis. The spectrum of the undeuterated adduct **6** (CCl_4, 100 MHz) exhibited a typical ABM multiplet centered at δ 1.9 (H_A), 2.2 (H_B), and 3.1 (H_M) ($J_{AB} = J_{BM} = 9.9$ Hz and $J_{AM} = 7.2$ Hz), while the spectrum of **6**-*d* displayed two broad doublets at δ 1.89 and 3.10 due to H_A and H_M ($J_{AM} = 7.2$ Hz), respectively.[11] Although stereospecificity of cycloaddition reaction has been used as a criterion of the concertedness,[12] the observed stereochemical result could be attributed to the rapid ring closure of the intermediate **5** or else its conformational integrity resulting from a charge-transfer interaction.[13]



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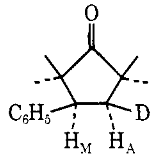

6-*d*

Acknowledgment. Financial support from the Matsunaga Science Foundation is acknowledged.

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(9) R. Victor, R. Ben-Shoshan, and S. Sarel, *J. Org. Chem.*, 37, 1930 (1972).

(10) When the styrene was present in the reaction system from the beginning of the reduction, its cis-trans isomerization induced by $Fe_2(CO)_9$ occurred, though the cyclopentanone adduct was obtained in much improved yield.

(11) The dideuteriocyclopentanone 6-*3,4-cis-d*$_2$ (prepared by (1) aldol cyclization of 3,3,5-trimethyl-1-phenylhexane-1,4-dione with 10% CH_3ONa-CH_3OH (25°, 12 hr), (2) dehydration with 85% H_3PO_4 (120°, 20 min), and (3) catalytic deuteration over 10% Pd–C in *n*-hexane (atmospheric pressure, 25°, 4 hr)) gave a broad signal at δ 2.20 due to H_B.

(12) However, see N. D. Epiotis, *J. Amer. Chem. Soc.*, **94**, 1941 (1972), and papers in this series.

(13) Certain transition metals are known to remove the orbital-symmetry restrictions in pericyclic reactions [review: F. D. Mango and J. H. Schachtschneider, "Transition Metals in Homogeneous Catalysis," G. N. Schrauzer, Ed., Marcel Dekker, New York, N. Y., 1971, p 223]. The exact role of Fe atom or ion in the dibromo ketone–$Fe_2(CO)_9$ reactions is not yet known, but no apparent perturbations on the reaction mode have been observed.[7] For the reaction of **2** with 1,3-dienes forming 4-cycloheptenones, see R. Noyori, S. Makino, and H. Takaya, *J. Amer. Chem. Soc.*, **93**, 1272 (1971).

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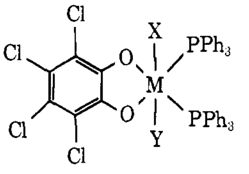
Oxidation of *o*-Quinone Adducts of Transition Metal Complexes

Sir:

Oxidative addition of *o*-quinones to a variety of low-valent metal complexes has attracted recent attention. Quinone additions to metals with formal d^{10},[1-5] d^8,[1,2,6] d^6,[6,7] d^4,[8] and d^2[9] electronic configurations have been reported. However, it has not been previously recognized that these complexes undergo a number of well defined, one-electron transfer reactions.

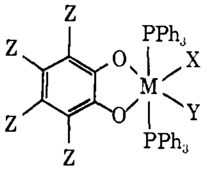
In particular complexes obtained from tetrahalobenzoquinones undergo one-electron oxidation to give complexes whose properties are indicative of the presence of coordinated semiquinone radicals. These oxidations have been detected by cyclic voltammetry which reveals that electron transfer in each case is reversible. Oxidative peak potentials (E_p^{ox}) for complexes **1–6** are set out in Table I. In addition the ruthenium complexes **5** and **6** undergo a second reversible one-electron oxidation at +1.7 V.



1, M = Pd; X,Y = nothing

2, M = Pt; X,Y = nothing

3, M = Ir; X = Cl; Y = CO



4, M = Rh; X = Cl; Y = CO; Z = Cl

5, M = Ru; X,Y = CO; Z = Cl

6, M = Ru; X,Y = CO; Z = Br

These oxidations may also be effected chemically with either of the oxidants—$NiS_4C_4(CF_3)_4$[10] or silver

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