diazonium benzoate ion pair (k_N) is indeed considerably more rapid than its dissociation[4] (k_d).

The comparison of the fractions of ion-pair return (R) from the DDM and solvolytic routes is rendered somewhat inexact for two reasons. One has to do with side reactions of DDM, so that total observed yields of ester and ether (or alcohol) from the DDM reactions are only 91–98%, leaving some ambiguity as to the best way to treat the data in deriving R (Table II). The other has to do with the fact that R values from the DDM reaction must be extrapolated to the higher temperatures at which it is necessary to study the solvolyses, and this extrapolation may introduce some error. The available data suggest that ion-pair return may, in fact, be slightly more important in the DDM reactions than in the solvolyses. This may be a slight indication of lack of equivalence of both oxygen atoms in the solvolytic $R^{+-}OBz$ ion pairs, thus making k_{eq} too low a measure of ion-pair return.[5]

It is interesting to compare the present situation regarding ion-pair return with its counterpart in free-radical chemistry, namely, cage recombination of radicals.[6] Pertinent radical pairs are those from 1,1'-azocyanocyclohexane[5] (RN_2R) and from the corresponding "mixed dimer," N-(1-cyanocyclohexyl)pentamethyleneketenimine (RR') in C_6H_5Cl at 80°. If one corrects the decomposition of mixed dimer[6] for recombination to RR', it is evident that the nitrogen-evolving generation of radical pairs gives only *ca.* half as much cage recombination as does the alternate route from mixed dimer. Thus radical pairs are disrupted by nitrogen evolution much more than are the $R^{+-}OBz$ ion pairs.

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(4) Estimates of *ca.* 10^{-2} for a dissociation K_d and 10^{10} l. mole^{-1} sec^{-1} for a diffusion-controlled k_{-d} in EtOH lead to a value of 10^8 sec^{-1} for k_d. Thus, $k_N \geqslant 10^{10}$ sec^{-1}, making heterolysis of $RN_2^{+-}OBz$ more than 10^{12} times as fast as that of RBr.[2b] This fits with other information on deamination. See D. Y. Curtin and M. Wilhelm, *Helv. Chim. Acta*, 40, 2129 (1957).

(5) There is also a slight indication of lack of equivalence of both oxygen atoms in deamination of N-nitroso-N-benzhydrylbenzamide: E. H. White, M. J. Billig, and J. M. Bakke, Abstracts, 149th National Meeting of the American Chemical Society, Detroit, Mich., April 5–9, 1965, p 37P.

(6) *E.g.*, G. S. Hammond, *et al.*, *J. Am. Chem. Soc.*, **82**, 5386, 4394 (1960). Ion pairs, with their additional electrostatic attractive forces, give rise in favorable solvents[2] to much greater proportions of cage recombination than do radicals.

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Novel Reactions of Olefin–Metal Carbonyl Complexes[1]

Sir:

Interconversions are known between π- and σ-allylic transition metal complexes which are accompanied by gain or loss of CO or other ligand on the metal.[2] We now report some facile interconversions between π-bonded olefin and carbonium ion complexes in which the number of the available C=C sites in the organic moiety engaged with the metal varies depending on the number of CO ligands on the same metal.

The recently reported cyclooctatetraenemolybdenum tricarbonyl[3] (I), $C_8H_8Mo(CO)_3$, and the previously known 1,3,5-cyclooctatrienemolybdenum tricarbonyl[4] (II), 1,3,5-$C_8H_{10}Mo(CO)_3$, will each readily add 1 mole of CO at room temperature and *at 1 atm or less* to give the new and hitherto inaccessible complexes, $C_8H_8Mo(CO)_4$ (III) and 1,3,5-$C_8H_{10}Mo(CO)_4$ (IV). The nmr spectra of III and IV indicate a tub conformation for the C_8H_8 or C_8H_{10} moieties, these being complexed to molybdenum by 1,5-olefinic groups. This should be compared with the 1,3-diene bonding of the olefin to the metal in $C_8H_8Fe(CO)_3$[5] and in C_8H_{10}-$Fe(CO)_3$.[6] This contrast further illustrates the different geometrical preferences[7] of the $Mo(CO)_4$ and $Fe(CO)_3$ groups which otherwise have identical electronic requirements for four π electrons on four carbon atoms (4π–4C).

The new complexes III and IV are moderately stable as solids, tending to lose some CO after several weeks storage. Under certain circumstances[8] the loss of CO may be extremely rapid.

The cyclooctatetraenemolybdenum tetracarbonyl complex (III) was protonated to see whether the $C_8H_9^+$ group would serve as a 4π–5C donor to the $Mo(CO)_4$ group and possibly give rise to the classical structure V akin to $C_8H_9^+Fe(CO)_3$ (Va)[10] from protonation of $C_8H_8Fe(CO)_3$. However, solution of III in H_2SO_4 was accompanied by immediate evolution of CO, with formation of the homoaromatic monohomotropyliummolybdenum tricarbonyl species[3] (VI), identical in all respects with the product from protonation of cycloctatetraenemolybdenum tricarbonyl I. Because of the relatively high stability of the monohomotropylium structure[3] and other factors related to the transition metal, CO evolution accompanies protonation so that a 6π–7C arrangement on a $Mo(CO)_3$ group is achieved. A striking stereochemical feature of the protonation of III is its high stereospecificity. Solution of III in D_2SO_4 shows that the deuterium added to the complex becomes exclusively the "outside" C-8

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(1) Research sponsored by the U. S. Army Research Office (Durham) and the National Science Foundation(GP-4175).

(2) *E.g.*, R. F. Heck and D. S. Breslow, *J. Am. Chem. Soc.*, **82**, 4438 (1960); J. C. W. Chien and H. C. Dehm, *Chem. Ind.* (London), 745 (1961); see also M. L. H. Green and P. L. I. Nagy, *Advan. Organometal. Chem.*, **2**, 325 (1964).

(3) S. Winstein, H. D. Kaesz, C. G. Kreiter, and E. C. Friedrich, *J. Am. Chem. Soc.*, **87**, 3267 (1965).

(4) E. O. Fischer, C. Palm, and H. P. Fritz, *Chem. Ber.*, **92**, 2645 (1959).

(5) B. Dickens and W. N. Lipscomb, *J. Chem. Phys.*, **37**, 2084 (1962).

(6) The nmr and infrared spectra of this complex show conclusively that the olefin is the bicyclo[4.2.0]octadiene-2,4 tautomer: R. Burton, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 594 (1961); T.A. Manuel and F. G. A. Stone, *J. Am. Chem. Soc.*, **82**, 366 (1960).

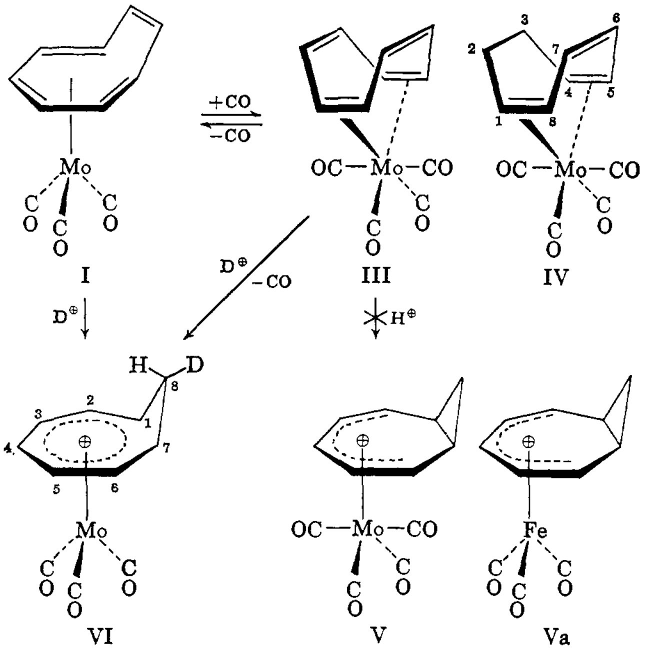
(7) This contrast was previously evidenced by the ability of molybdenum to form the 1,5-cyclooctadiene complex, 1,5-$C_8H_{12}Mo(CO)_4$: E. O. Fischer and W. Froelich, *Chem. Ber.*, **92**, 2995 (1959); M. A. Bennett and G. Wilkinson, *Chem. Ind.* (London), 1516 (1959). This same olefin with iron carbonyl was quantitatively isomerized to 1,3-C_8H_{12}, although no stable organometallic product was isolated: J. E. Arnet and R. Pettit, *J. Am. Chem. Soc.*, **83**, 2955 (1961).

(8) In solution, III disproportionates to give free C_8H_8 and insoluble $C_8H_8[Mo(CO)_4]_2$, a new derivative. *Anal.* Calcd for $C_{16}H_8Mo_2O_8$: C, 36.93; H, 1.55; Mo, 36.90. Found: C, 37.05; H, 1.70; Mo, 36.78. Due to insolubility of this complex, its nmr spectrum may be obtained only for supersaturated solutions resulting immediately after completion of the disproportionation reaction; a single sharp line at τ 5.99 is thus observed for the complex, in agreement with the similar single line observed for the C_8H_8 ring in $C_8H_8[Co(C_5H_5)]_2$.[9]

(9) H. P. Fritz and H. Keller, *Chem. Ber.*, **95**, 158 (1962).

(10) (a) G. N. Schrauzer, *J. Am. Chem. Soc.*, **83**, 2966 (1961); (b) A. Davison, W. McFarlane, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 4821 (1962).

deuterium, the only C-8 proton visible in the nmr spectrum being the high-field "inside" one at τ 10.20. This is the identical stereospecificity previously observed[3] in protonation of I.



A deep red solution of $C_8H_8Mo(CO)_3$[3] (1.8 g) in hexane (180 ml) is subjected to CO at atmospheric pressure, with shaking, for 4 min;[11] the color changes to bright orange and the excess CO is swept away with nitrogen. Fine yellow needles of $C_8H_8Mo(CO)_4$ (III), obtained by slow cooling, are washed onto a fritted filter and sucked dry under nitrogen; yield, 1.3 g, or 65% based on starting complex. The compound may be recrystallized in hexane, but as rapidly as possible due to disproportionation which occurs in solution.

Anal. Calcd for $C_{12}H_8MoO_4$: C, 46.15; H, 2.58; Mo, 30.75. Found: C, 46.39; H, 2.73; Mo, 30.88.

Fresh solutions of III show two sharp lines in the nmr, τ 4.46 and 5.80, characteristic of the tub conformation of this olefin in its complexes.[9] III shows four medium to strong bands in the carbonyl stretching region as may be expected for a *cis*-disubstituted octahedral metal carbonyl: 2049 (m), 1969 (m), 1959 (m), and 1902 (s) cm^{-1} (Beckman IR 4, LiF prism, cyclohexane solution).

Yellow crystals of 1,3,5-$C_8H_{10}Mo(CO)_4$ (IV) are prepared in a manner entirely analogous to III from 1,3,5-$C_8H_{10}Mo(CO)_3$[12] (infrared ν_{CO} 2044 (m), 1962 (s), 1950 (m), and 1907 (s) cm^{-1}).

Anal. Calcd for $C_{12}H_{10}MoO_4$: C, 45.86; H, 3.21; Mo, 30.55. Found: C, 45.61; H, 3.33; Mo, 30.43.

The nmr spectrum of IV consists of three singlets, relative intensities 2:4:4, at τ 4.05 ($H_{6,7}$), 5.06 ($H_{1,4,5,8}$), and 7.16 (methylene $H_{2,3}$), respectively. This can be accounted for only by the structure shown for IV.[13]

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[11] Further CO insertion, which occurs readily, leads to complete displacement of olefin and formation of hexacarbonyl.

[12] Prepared in 16% yield by the method of Fischer, *et al.*,[4] or in higher yield (41%) by reaction of the olefin with the diglyme complex of $Mo(CO)_3$ analogous to the preparation of I.[3] The nmr spectrum was identical with the one reported by R. B. King, *Inorg. Chem.*, **2**, 807 (1963).

[13] Bonding of the metal to 1,3-olefinic sites of either the cyclooctatriene or the tautomeric bicyclo[4.2.0]octadiene-2,4 may be excluded with certainty. In the first of these two possibilities a very complex spectrum would be expected since all the protons are different. In the second case, five separate proton signals are expected, as found[6] for this group in $C_8H_{10}Fe(CO)_3$.

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exo–endo Rate Ratios in the Solvolysis of Tertiary 2-Benznorbornenyl *p*-Nitrobenzoates. Evidence for the Absence of Significant Carbon Participation as a Factor in the *exo–endo* Rate Ratios

Sir:

The high *exo–endo* rate ratio exhibited by norbornyl brosylate, 350,[1a] and the high stereospecificity exhibited by the product, >99.9% *exo*,[1b,2] have been attributed to carbon participation in the transition state followed by the formation of a bridged norbornyl cation which substitutes almost exclusively *exo*. The two phenomena have previously been considered to provide independent confirmatory evidence for carbon participation. However, a careful examination of the energy diagram published by Goering and Schewene[2] makes it clear that these two characteristics are not independent, but are closely related. It follows from the principle of microscopic reversibility that in the symmetrical system which was the subject of their study the norbornyl intermediate, in reacting with the solvent, must pass over the same two transition states that are involved in the solvolysis of the reactants (Figure 1).

It follows that the factor responsible for the difference in energy between the exo and endo transition states must likewise be responsible for the stereoselectivity leading to the almost exclusive formation of the exo product. The amount of bridging that may or may not be present in the free ion is not directly involved in the stereoselectivity of the substitution. It is the amount of bridging in the exo transition state, or whatever the factor responsible for the difference in stability of the two transition states, that will control the distribution of the norbornyl cation between exo and endo products.

The authors discussed their results in terms of stabilization of the *exo* transition state by carbon bridging.[2] However, the diagram is equally compatible with the alternative proposal that the *endo* transition state is destabilized by steric interactions between the departing group and the projecting ethylene bridge[3,4] (Figure 1). It follows that an understanding of the factors involved in the high *exo–endo* rate ratios exhibited by norbornyl derivatives should help resolve the problem of the structure of the norbornyl cation.

The 2-benznorbornenyl derivatives[5] appear to offer

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[1] (a) S. Winstein, *et al.*, *J. Am. Chem. Soc.*, **74**, 1127 (1952); (b) *ibid.*, **87**, 376 (1965).

[2] H. L. Goering and C. B. Schewene, *ibid.*, **87**, 3516 (1965).

[3] H. C. Brown, F. J. Chloupek, and M.-H. Rei, *ibid.*, **86**, 1248 (1964).

[4] It is important to recognize that up to the present time no experimental data have been reported to provide independent confirmation for the postulated presence of participation and accompanying charge delocalization in a norbornyl system not undergoing rearrangement to a more stable structure.

[5] (a) P. D. Bartlett and W. P. Giddings, *J. Am. Chem. Soc.*, **82**, 1240 (1960); (b) W. P. Giddings and J. Dirlam, *ibid.*, **85**, 3900 (1963).