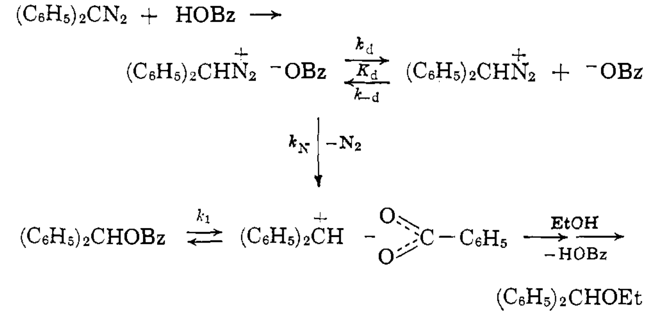
Communications to the Editor

Benzhydryl Benzoate Ion Pairs from Diphenyldiazomethane[1]

Sir:

Solvolysis of various benzhydryl derivatives,[2] such as RCl,[2a] RBr,[2b] $ROCOC_6H_4NO_2$-*p*,[2c] and RSCN,[2d] has been shown to involve benzhydryl carbonium ion pairs which give rise to ion-pair return in competition with dissociation and solvolysis.

The reaction between diphenyldiazomethane (DDM) and molecular benzoic acid (HOBz) in ethanol is most plausibly accounted for in terms of a rate-determining formation of the diazonium benzoate ion pair; the loss of nitrogen without ion-pair dissociation (k_N) gives rise to benzhydryl benzoate ion pairs ($R^+{}^-OBz$) which are responsible for formation of ROBz and ROEt as products.[3] It is of considerable interest and importance[3a,c] to compare the behavior of $R^+{}^-OBz$ ion pairs in this reaction with that of their counterparts in solvolysis under conditions of identical counteranion, solvent, and temperature, and we now report such a comparison.



To assess ion-pair return during ethanolysis of ROBz, we have determined both the titrimetric solvolysis rate constant, k_t, and the rate constant, k_{eq}, for ^{18}O-equilibration[2c] of carbonyl-^{18}O-labeled ROBz. If we assume[2c] equivalence of both oxygen atoms in the $R^+{}^-OBz$ ion pairs, the ionization rate constant of ROBz, k_1, becomes ($k_{eq} + k_t$). Ethanolysis of ROBz proceeds with first-order kinetics at a convenient rate at 100°, almost exclusively with R–O fission and resultant formation of ROEt (99.4%). The first-order ^{18}O-equilibration accompanying alcoholysis does not involve dissociated carbonium ions, since only negligible exchange is observed with added unlabeled HOBz (Table I).

$$RОC\overset{*}{O}C_6H_5 \xrightarrow{k_{eq}} R\overset{*}{O}C\overset{*}{O}C_6H_5$$

Table I. Rates and Ion-Pair Return in Solvolysis of Benzhydryl Esters

	ROBz EtOH, 100°	ROPNB 90 % acetone, 118.6°
10^4k_{eq} (hr^{-1})	6.84 ± 0.50	187[a]
10^4k_t (hr^{-1})	7.78 ± 0.21[f]	64[a]
Solvolysis R[b]	0.47	0.745
DDM R[c]	0.528[d]	0.754[d]
	0.558[e]	0.822[e]

[a] Ref 2c. [b] $[k_{eq}/(k_{eq} + k_t)]$. [c] Extrapolated values. [d] Ester/DDM_0. [e] Ester/[ester + ROEt (or ROH)]. [f] After 15% ethanolysis of 0.0214 *M* ROBz containing 2.307 ± 0.038 atom % excess ^{18}O in the presence of 0.00460 *M* initially added ordinary HOBz, the recovered ROBz analyzed for 2.303 ± 0.033 atom % excess ^{18}O.

The reaction between DDM, mp 29–30°, λ_{max} 525 mμ (EtOH,ε 94.8),[3b] and excess HOBz was performed in a darkened flask at concentrations of HOBz (0.00813–0.0151 *M*) favoring reaction of DDM (0.00590–0.0140 *M*) exclusively with monomeric molecular acid.[3] Listed in Table II are the fractions *R* of ROBz formed in the reactions as evaluated by titrimetric determination of HOBz consumption. The ROEt and some other observed products were determined by vapor phase chromatography.

Table II. Products from Reaction of DDM with HOBz or HOPNB

		Product, %[a]				*R*	
Solvent	Temp, °C	Ester	ROEt ROH	Sum	Ph_2CO	*b*	*c*
EtOH + HOBz							
EtOH	25.0	59.3	37.9	97.2		0.593	0.609
EtOH	73.0	55.4	41.2	96.6	0.81[d]	0.554	0.573
EtOH	100.0[e]					0.528	0.558
% Aq acetone + HOPNB							
80	25.0	68.2	22.5	90.7	1.73	0.682[f]	0.751
90	25.0	74.5	16.4	90.9	1.91	0.745	0.820
90	50.0	74.8	16.3	91.1	1.71	0.748	0.821
90	118.6[e]					0.754	0.822
95	25.0	87.1	11.0	98.1	2.07	0.871	0.888

[a] Product/DDM_0. [b] Ester/DDM_0. [c] Ester/[ester + ROEt (or ROH)]. [d] 0.37% Ph_2CH_2 also observed. [e] Extrapolated value from a plot of log $[R/(1 - R]$ *vs.* $(1/T)$. [f] 0.694 with HOBz.

The reaction of DDM with *p*-nitrobenzoic acid (HOPNB) in aqueous acetone solvents was also examined for comparison with the published data on k_t and k_{eq} for ROPNB in 90% aqueous acetone.[2c]

As is evident from Table I, the fractions of ion-pair return [*R*] from the DDM reaction agree fairly closely with those from solvolysis. Thus, for the benzhydryl system under the present conditions, the diazoalkane route for generating ion pairs leads to essentially the same ion pairs or spectrum of ion pairs as in solvolysis. The present data confirm that nitrogen evolution from a

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[1] Research was supported by the National Science Foundation.

[2] (a) S. Winstein, J. S. Gall, N. Hojo, and S. Smith, *J. Am. Chem. Soc.*, **82**, 1010 (1960); S. Winstein, M. Hojo, and S. Smith, *Tetrahedron Letters*, No. **22**, 12 (1960); S. Winstein, B. Appel, R. Baker, and A. Diaz in "Organic Reaction Mechanisms," Special Publication No. 19, The Chemical Society, London, 1965, pp 109–130; (b) A. Diaz, unpublished work; (c) H. L. Goering and J. F. Levy, *J. Am. Chem. Soc.*, **84**, 3853 (1962); (d) A. Fava, *Acta Cientifica Venezolana*, **15**, 223 (1965).

[3] (a) R. A. M. O'Ferrall, W. K. Kwok, and S. I. Miller, *J. Am. Chem. Soc.*, **86**, 5553 (1964); (b) J. D. Roberts, W. Watanabe, and R. E. McMahon, *ibid.*, **73**, 2521 (1951); (c) S. Winstein, International Symposium on Organic Reaction Mechanisms, Cork, Ireland, July 20–25, 1964.

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.

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).