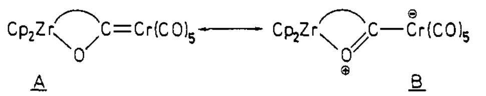
ambient temperature).[11] (^{1}H NMR δ 1.49, 1.50 (H8s/a), 4.91 (H7), 4.53 (H6), 4.20, 2.66 (H5/5′); $^{2}J_{HH}$ (Hz) = 4.0 (H8s/a), −17.4 (H5/5′); $^{3}J_{HH}$ (Hz) = 8.4 (H8s/7), 13.5 (H8a/7), 15.9 (H7/6), 4.7, 9.8 (H6/5,5′); ^{13}C NMR ($^{1}J_{CH}$, Hz) δ 44.4 (149) C8, 129.3 (146) C7, 112.3 (149) C6, 68.3 (129) C5.) This causes the zirconocene Cp ligands to be diastereotopic (^{1}H NMR δ 5.23, 5.26; ^{13}C NMR δ 108.87, 109.02). A typical ^{13}C chemical shift difference[12] is found between CO ligands trans (δ 225.0) and cis (δ 219.7) to the carbene unit. The observed ^{13}C absorption of the carbene carbon atom itself (δ 363.7) is close to the low-field limit of the range characteristic of Fischer-type carbene complexes.[12]

The molecular structure of the metallacyclic zirconoxycarbene complex **9a** was determined by X-ray crystallography (Figure 1).[13] The bent metallocene unit (Zr–$\bar{C}$(Cp) = 2.486 (5) Å, Cp(C)–Zr–Cp′(C) = 129.2 (4)°) is connected to the chromium carbene moiety by a rigid framework, incorporating a substituted η^3-allyl unit[13] and the "carbene oxygen" O4. Structural features around chromium are in the expected range for a Fischer-type carbene complex[1] (Cr–C1 = 1.887(3), Cr–C2 = 1.882 (4), Cr–C3 = 1.879 (5), Cr–C4 = 2.063 (4) Å; C3–Cr–C4 = 177.0 (2)°). Quite remarkable is the short O4—C4 bond, with 1.254 (5) Å clearly among the shortest values so far observed for a Cr═C—OR moiety.[1,14] In connection with the observed rather long Zr—O4 bond[6] of 2.188 (3) Å this is an indication for a pronounced metal acyl character, emphasizing on the relative importance of resonance form B for describing the metal carbene moiety in **9a**.



A B

This might well be the primary reason that a substantially decreased Zr–O4–C4 angle (136.1 (3)°) and a π-allyl ligand is favored around zirconium for **9a** as opposed to **6**.[6]

Reactions of butadiene zirconocene (**1** ⇄ **3**) with molybdenum and tungsten hexacarbonyl proceed exactly analogously. We obtained the bimetallic carbene complexes **9b** (M = Mo) and **9c** (W) in 61% and 72% isolated yield. Spectroscopic properties of these compounds are almost identical with those observed for the chromium complex **9a**.[15]

Unfortunately, the reaction of the M(CO)$_6$ complexes **7a–c** with the rapidly equilibrating (butadiene)ZrCp$_2$ isomer system is too slow for an experimental observation of differences in reaction rates between **1** and **3**. The much higher isomerization activation barrier of the (*s-trans-/s-cis*-butadiene)hafnocene system ($\Delta G^{\ddagger}_{60\,°C}$(**1′** → **3′**) = 24.7 kcal/mol; equilibrium at 60 °C, **1′**/**3′** < 1/99)[4b] compared to the zirconium analogue ($\Delta G^{\ddagger}_{10.5\,°C}$(**1** → **3**) = 22.7 kcal/mol; equilibrium 25 °C, **1**/**3** = 45/55)[4] allows a clear mechanistic differentiation,[6,7b] however. Reaction of a 80/20 mixture of the hafnium complexes **1′**/**3′** with 0.7 equiv of Cr(CO)$_6$ (**7a**) in benzene at room temperature results exclusively in the consumption of the (*s-trans*-η^4-butadiene)HfCp$_2$ isomer **1′** to yield the Hf/Cr–carbene complex **9a′**.[15] Under these conditions (*s-cis*-butadiene)hafnocene remains unaffected by the added metal carbonyl. Treatment of a **1′**/**3′** mixture with W(CO)$_6$ at ambient temperature furnishes a similar result. This is a strong indication that the reactions of the diene zirconocene and hafnocene systems with coordinated carbon monoxide indeed represent examples of a principally new synthetic entry to the class of Fischer-type carbene complexes, which is characterized by an electrocyclic ring-closure reaction of a (η^2-olefin)(η^2-carbonyl)metallocene-type intermediate (**8**).[6,7] There is a good chance that a rapid expansion of the already extremely well-studied chemistry of Fischer-type carbene complexes will result from the discovery of this new reaction type.[16]

Acknowledgment. Financial aid from the Thyssen-Stiftung and the Fonds der Chemischen Industrie (grants to G.E.) is gratefully acknowledged.

Supplementary Material Available: Detailed description of the structural analysis of **9a**; includes tables of positional parameters and temperature factors, interatomic distances and bond angles for hydrogen and non-hydrogen atoms, least-squares planes, and calculated and observed structure factors (15 pages). Ordering information is given on any current masthead page.

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(11) Atom numbering scheme as given in Figure 1.

(12) Kreiter, C. G.; Formacek, V. *Angew. Chem.* **1972**, *84*, 155. Fischer, E. O.; Hollfelder, H.; Friedrich, P.; Kreissl, F. R.; Huttner, G. *Chem. Ber.* **1977**, *110*, 3467.

(13) **9a** crystallizes in the orthorhombic space group *Pnam*; lattice parameters a = 22.398 (5) Å, b = 7.283 (2) Å, c = 12.302 (2) Å; V = 2006.7 (8) Å^3; Z = 4; 1857 unique data; $R(F_o)$ = 0.036, $R(F_o)^2$ = 0.048, $R_w(F_o)^2$ = 0.069. Since the molecule lies on a crystallographic mirror plane (passing through Zr, Cr, C3, O3, C4, and O4), the four carbon atoms originating from the butadiene unit occupy twofold disorder positions on either side of the plane. The perpendicular displacements of these atoms from the plane are +0.24 (2), −0.36 (2), +0.49 (2), and +0.30 (2) Å for C5, C6, C7, and C8, respectively. Details of the X-ray data collection and structural analysis are given in the supplementary material.

(14) Manojlovič-Muir, L.; Muir, K. W. *J. Chem. Soc., Dalton Trans.* **1974**, 2427. Webb, M. J.; Bennett, M. J.; Chan, L. Y. Y.; Graham, W. A. G. *J. Am. Chem. Soc.* **1974**, *96*, 5931. Beck, W.; Raab, K.; Nagel, U.; Steinmann, M. *Angew. Chem.* **1982**, *94*, 556.

(15) **9b** (M = Mo): Anal. Calcd for $C_{20}H_{16}O_6MoZr$: C, 44.53; H, 2.99. Found: C, 43.97; H, 2.74. IR (C_6D_6) 2057, 1986, 1924 cm^{-1}. ^{1}H NMR δ 5.22, 5.26 (Cp), 1.49, 1.50, 4.94, 4.63, 4.08, 2.54 (H8–H5); $^{2}J_{HH}$ (Hz) = 4.0 (H8s/a), −17.7 (H5/5′); $^{3}J_{HH}$ (Hz) = 8.7 (H8s/7), 13.1 (H8a/7), 16.0 (H7/6), 4.8, 9.9 (H6/5,5′); ^{13}C NMR: 108.91, 108.76 (Cp), 44.3, 129.3, 113.7, 70.0 (C8–C5), 359.7 (C4), 215.6 (C3), 208.8 (C2,C1). **9c** (M = W): Anal. Calcd for $C_{20}H_{16}O_6WZr$: C, 38.29; H, 2.57. Found: C, 38.29; H, 2.60. IR 2058, 1979, 1922 cm^{-1}; ^{1}H NMR: 5.20, 5.24, 1.48, 1.51, 4.94, 4.56, 4.01, 2.42; $^{2}J_{HH}$ (Hz) = 4.0 (H8s/a), −17.7 (H5/5′); $^{3}J_{HH}$ (Hz) = 8.0 (H8s/7), 14.0 (H8a/7), 16.0 (H7/6), 4.8, 9.9 (H6/5,5′); ^{13}C NMR: 108.81, 108.93, 44.5, 129.3, 113.2, 71.7, 342.2, 205.7, 200.7. **9a′** (Hf, Cr): IR 2052, 1981, 1929 cm^{-1}; ^{1}H NMR: 5.196, 5.198 (Cp), 1.27, 1.31, 4.92, 4.50, 4.18, 2.63 (H8–H5); $^{2}J_{HH}$ (Hz) = 4.9 (H8s/a), −17.5 (H5/5′); $^{3}J_{HH}$ (Hz) = 7.7 (H8s/7), 14.1 (H8a/7), 16.1 (H7/6), 4.9, 9.6 (H6/5,5′).

(16) Coupling of *two* coordinated CO molecules at zirconium could possibly represent another example of this reaction type: Berry, D. H.; Bercaw, J. E.; Jircitano, A. J.; Mertes, K. B. *J. Am. Chem. Soc.* **1982**, *104*, 4712. Casey, C. P.; Jordan, R. F.; Rheingold, A. L. *Organometallics* **1984**, *3*, 504.

Catalytic Methanol Synthesis from Carbon Monoxide and Water

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The chemistry of formate ion is an active area of current interest due to its importance in the catalysis of the water gas shift reaction[1] (WGS) in eq 1. The hydrogen produced by WGS is typically

$$CO + H_2O \rightarrow H_2 + CO_2 \qquad (1)$$

used for catalytic methanol or Fischer–Tropsch synthesis in a second process. We report here the first catalytic reaction of formate ion to yield an organic product, methanol. This new formate ion chemistry is generally applicable to a range of metal oxide catalysts and allows the direct synthesis of methanol from carbon monoxide and water in a single process.

Addition of metal oxide catalysts to the molten lithium/potassium formate salts listed in Table I results in the smooth evolution of gaseous products containing hydrogen, methanol, and carbon monoxide as described by the limiting stoichiometries given in eq 2 and 3, respectively.[2] Significantly, only the lead-based

$$2HCO_2^- \rightarrow H_2 + CO + CO_3^{2-} \qquad (2)$$

$$4HCO_2^- \rightarrow CH_3OH + CO + 2CO_3^{2-} \qquad (3)$$

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(1) (a) Thomas, C. L. "Catalytic Processes and Proven Catalysts"; Academic Press: New York, 1970; p 104. (b) Yoshida, T.; Veda, Y.; Otsuka, S. *J. Am. Chem. Soc.* **1978**, *100*, 3941. (c) Paonessa, R. S.; Trogler, W. C. *Ibid.* **1982**, *104*, 3529. (d) King, A. D., Jr.; King, R. B.; Yang, D. B. *Ibid.* **1981**, *103*, 2699. (e) Immirzi, A.; Musco, A. *Inorg. Chim. Acta* **1977**, *22*, L35. (f) Ford, P. C. *Acc. Chem. Res.* **1981**, *14*, 31.

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Table I. Formate Ion Disproportionation with Metal Oxide Catalysts[a]

catalyst		melt		conditions		products					
type	amt, mmol	HCO_2K, mmol	HCO_2Li, mmol	temp	time, h	CH_3OH, mmol	HCO_2CH_3, mmol	H_2, mmol	CO, mmol	CO_2, mmol	CO_3^{2-}, mmol
PbO	0.06	160	375	230	3	0.51	0.15	0.03	0.38	0.15	1.2
PbO	0.26	180	430	230	21	1.4	0.34	0.05	0.94	0.62	*b*
PbO	0.31	160	375	230	7	1.1	0.22	0.03	0.59	0.51	2.7
PbO	25.0	720	0	250	40	14.0	0.0	19.0	9.0	28.0	53
$ZnO{\cdot}Cr_2O_3$	0.34	160	375	230	41	0.62	0.19	1.1	1.8	0.30	3.2
$NaVO_3$	2.6	3	10	220	18	0.0	0.0	0.04	0.04	0.9	*b*
$2CuO{\cdot}Cr_2O_3$	5.0	6	18	220	20	0.01	0.02	2.7	1.3	6.5	*b*

[a] Reactions were performed in vacuo. Liquid products were collected at −198 °C and analyzed on a 6-ft porapak Q column. Noncondensable gases were collected with a Toepler pump and analyzed on a 3.5-ft spherocarb column at 80 °C. [b] Not determined.

Table II. Methanol Synthesis from Carbon Monoxide and Water

cat.	temp	H_2,[a] mm	CH_3OH,[b] mm	H_2O,[b] mm	CO_2,[a] mm	CO,[a] mm	log (Q/K)[c]	
							eq 13[d]	eq 14[e]
$PbMoO_4$[f]	250	173	110	59	130.0	278	−0.3	3.5
$PbTiO_3$[g]	315	10	29	180	0.5	530	−5.5	6.0
$PbTiO_3$[g]	350	123	20	63	0.5	544	−4.0	4.0
PbV_2O_6[h]	180	104	11	88	10.0	537	−7.4	1.0

[a] Analyzed by gas chromatography, see Table I. [b] Determined from the isolated liquid yield and measured gas flow rate over a 24-h period. [c] Ratio of the observed reaction quotient to the theoretical equilibrium constant. [d] Equilibrium constant calculated on the basis of $\Delta H°_{298} = -41.36$ kcal, $\Delta S°_{298} = -73.18$ eu. [e] Equilibrium constant calculated on the basis of $\Delta H°_{298} = -21.68$ kcal, $\Delta S°_{298} = -52.90$ eu. [f] $PbMoO_4$, 0.5 mol; HCO_2Li, 0.25 mol; HCO_2Na, 1.47 mol; HCO_2K, 1.35 mol; H_2O, 57 μL/h; CO, 15 mL/min. [g] $PbTiO_3$, 0.1 mol; HCO_2Li, 0.75 mol; HCO_2K, 2.25 mol; H_2O, 40 μL/h; CO, 35 mL/min. [h] PbV_2O_6, 0.07 mol; HCO_2Li, 1.0 mol, HCO_2K, 2.25 mol; H_2O, 84 μL/h; CO, 15 mL/min.

catalysts exhibit a high selectivity for methanol production while the transition metal oxides tend to favor hydrogen. In addition to methanol, the lead catalysts yield small quantities of methyl formate and traces of formaldehyde. Both are believed to be organic intermediates in the formate ion disproportionation reaction in eq 3 as indicated by the mechanism in Scheme I.

Scheme I

$$2HCO_2^- \rightarrow CH_2{=}O + CO_3^{2-} \qquad (4)$$

$$2CH_2{=}O \rightarrow HCO_2CH_3 \qquad (5)$$

$$HCO_2CH_3 \xrightarrow{\text{base}} CH_3OH + CO \qquad (6)$$

Evidence for formaldehyde as an intermediate formed by ketonic decarboxylation, eq 4, is provided by its direct observation and by the observation that the corresponding cross reaction between acetate and formate ions yields acetaldehyde as the major organic product with lead dioxide catalyst under similar conditions.[3] Condensation of the formaldehyde from eq 4 according to the Tischenko reaction[4] in eq 5 followed by the base-induced decarbonylation[5] of eq 6 would yield the observed organic products of methyl formate and methanol, respectively.

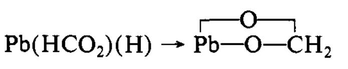
A mechanism that invokes standard hydride addition–elimination steps is presented in Scheme II for the ketonic decarboxylation reaction in eq 4. Lead(II) hydrides have been described as transient intermediates[6] and precedents exist for lead hydroxide formate synthesis eq 7,[2,7] formate decarboxylation eq 8,[8] and hydroplumbation of carbonyl moieties eq 10.[9] Indeed, Stuve and Madix have recently reported reactions analogous to the microscopic reverse for both the important steps in eq 10 and 11.[10]

Scheme II

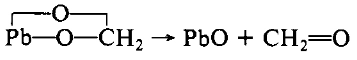
$$PbO + HCO_2^- + HCO_3^- \rightarrow Pb(OH)(HCO_2) + CO_3^{2-} \qquad (7)$$

$$Pb(OH)(HCO_2) \rightarrow [Pb(OH)(H) + CO_2] \rightarrow Pb(HCO_3)(H) \qquad (8)$$

$$Pb(HCO_3)(H) + HCO_2^- \rightarrow Pb(HCO_2)(H) + HCO_3^- \qquad (9)$$



$$Pb(HCO_2)(H) \rightarrow \overset{\ulcorner\!-\!O\!-\!\urcorner}{Pb{-}O{-}CH_2} \qquad (10)$$



$$\overset{\ulcorner\!-\!O\!-\!\urcorner}{Pb{-}O{-}CH_2} \rightarrow PbO + CH_2{=}O \qquad (11)$$

The carbonate ion coproduct from formate ion disproportionation in eq 3 may be recycled according to eq 12. This process

$$CO_3^{2-} + 2CO + H_2O \rightarrow 2HCO_2^- + CO_2 \qquad (12)$$

is thermodynamically favorable, $\Delta G°_{298} = -5.7$ kcal, and is independently observed to proceed to 99.9% conversion within 1 h at 800 psi of carbon monoxide and 200 °C. Combination of the formate disproportionation in eq 3 with the carbonate recycle in eq 12 yields the net methanol synthesis reaction in eq 13. In

$$3CO + 2H_2O \rightarrow CH_3OH + 2CO_2 \qquad (13)$$

practice, this combination is complicated by the concurrent reduction of lead oxide in the presence of water. However, this problem is overcome by the use of an appropriate oxy anion to stabilize the lead. Thus, addition of carbon monoxide and water to a stirred suspension of the catalyst in molten alkali metal formates at 1 atm pressure yields the exit gas composition listed in Table II. Only $PbMoO_4$ is a sufficiently reactive catalyst to bring the methanol synthesis reaction in eq 13 close to equilibrium as indicated by comparison of the experimental reaction quotient with the equilibrium constant in column 8. In contrast, the experimental reaction quotient for eq 14 exceeds the equilibrium

$$2H_2 + CO \rightarrow CH_3OH \qquad (14)$$

constant, in column 9, and therefore rules out on the basis of thermodynamics the prior water gas shift in eq 1 followed by carbon monoxide hydrogenation according to eq 14 as the mechanism by which methanol is produced.

Acknowledgment. We thank Professor J. Halpern for helpful discussions at crucial stages of research. Support for this work

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[2] Experimental details are given in the supplementary material.

[3] Table III in the supplementary material.

[4] (a) March, J. In "Advanced Organic Chemistry: Reactions, Mechanisms and Structure"; McGraw-Hill: New York, 1968; p 910. (b) Goeden, G. V.; Caulton, K. G. *J. Am. Chem. Soc.* **1981**, *103*, 7354. (c) Horino, H.; Yamamoto, A. *Chem. Lett.* **1978**, *17*. (d) Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Am. Chem. Soc.* **1982**, *104*, 2019.

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was provided by the Office of Basic Energy Sciences, Division of Chemical Sciences, US Department of Energy.

Supplementary Material Available: Experimental details and a table of ketonic decarboxylations with lead dioxide catalysts (2 pages). Ordering information is given on any current masthead page.

Diastereoselectivity in Radical Pair Recombination in Lipid Bilayers

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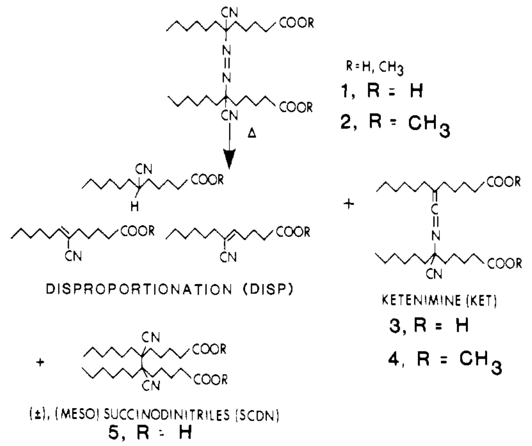
The reactions of free radicals or radical pairs in solution frequently occurs with loss of stereochemistry. Thus, while many radical reactions proceed in high yield, the lack of stereochemical control inherent in these processes has made radical routes unattractive for use in many conversions.[1] One potential solution to the control of stereochemistry in free radical processes is to utilize intermolecular forces to orient radicals or radical pairs. Thus one might anticipate that molecular aggregates such as micelles or the lipid bilayer could exert a stereochemical influence on the course of free radical processes. In this communication, we report on the stereochemical course of diazene decomposition in multilamellar lipid vesicles (MLV) prepared from dipalmitoylphosphatidylchloline (DPPC). We have chosen radical pairs from diazenes as our initial probe of stereochemistry since the behavior of these species is well understood in solution[2] and in the crystal[3] and we have chosen MLVs from DPPC since these molecular aggregates have been thoroughly studied.[4]

The major products of thermal or photochemical decomposition of **1** in DPPC vesicles in water or its methyl ester **2** in chlorobenzene are shown in Scheme I. The ketenimine product **3** is unstable in water and gives a mixture of hydrolysis products although the corresponding methyl ester **4** can be completely characterized. A mild lithium hydroxide hydrolysis of **4** provides the free acid **3** along with substantial amounts of ketenimine hydrolysis products.

The two diastereomers (meso and *dl*) of the succinodinitrile (SCDN) coupling product(s) **5** can be readily separated by HPLC. Stereochemical assignment of the diastereomers of **5** was made by photolysis[3,5] of the known (±)-**2** in a methylcyclohexane/diethyl ether glass at -196 °C. Only one product diastereomer was observed after 5.5 h of photolysis and this product was assigned the (±) stereochemistry.[3]

Diazene decomposition in DPPC vesicles were carried out under degassed conditions and were run to complete diazene decomposition.[6] Product analyisis was performed by reverse-phase HPLC on a C-18 column with solvent methanol/water/acetic acid (750/250/2). Mass balance for decompositions in aqueous emulsions (DPPC vesicles) was low (∼50%) and the hydrolytic instability of product ketenimine in the aqueous media is the major cause of this low product balance. Aliquots taken during the thermolysis of **1** in DPPC emulsions indicate that the amount of ketenimine reaches a maximum during the first half-life of diazene decomposition and then steadily decreases to zero while, in contrast, the disproportionation and coupling products steadily increase over time.[7]

Scheme I



Diastereoselectivity of radical pair coupling in lipid vesicles was studied over the temperature range 29–80 °C. The results for diazene decomposition are summarized in Table I. Diastereoselectivity is expressed as the product ratio (±)-**5**/*meso*-**5** and as diastereomeric excess, % de, in Table I. The results suggest that the mode of decomposition (60 °C thermolysis or 59 °C photolysis) does not influence product stereochemistry and we thus conclude that diazene photoisomerization does not play an important role in determining the stereochemical outcome of the reaction. One striking feature of the results presented in Table I and Figure 1 is the magnitude of stereochemical preservation in the coupling products and the differential degree of diastereoselectivity observed from (±)-**1** as compared to *meso*-**1**. Thus, the diastereomeric excess for decomposition of the (±)-diazene is as high as 72% and the meso diastereomer gives a maximum diastereomeric excess of 50%. These results in lipid bilayer are to be compared with decomposition of the diazene methyl esters **2** (2 mM) in chlorobenzene at 60 °C. Under these conditions, (±)-**2** gives a SCDN coupling product ratio of (±)/meso = 1.16 ± 0.02 (% de = 7.4) while meso **2** gives (±)/meso = 0.95 ± 0.1 (% de = 2.6). These results are typical of radical pair reactions in solution and illustrate the low stereochemical preservation generally observed in isotropic fluid.[2]

It should also be noted that significantly enhanced diastereoselectivity is observed for decomposition of **1** alone in pH 7 buffer. Thus (±)-**1** (1 mM in pH 7 phosphate buffer with 0.1 mM EDTA) at 60 °C gives a (±)/meso SCDN ratio of 2.13 ± 0.1 (36% de) while *meso*-**1** yields SCDN in a (±)/meso ratio of 0.52 ± 0.1 (32% de).[8] While this enhanced diastereoselectivity in aqueous buffer is itself surprising, there are aspects unique to diazene chemistry in DPPC bilayers that deserve emphasis. Namely, the bilayer exerts a differential influence on the diazene diastereomers which manifests itself in the kinetics (see ref 5) and the radical coupling.

The high diastereoselectivity of radical pair coupling observed in lipid bilayers has no counterpart in fluid media. It seems likely, based on analogous work carried out in crystals and glasses,[3] that the enhanced stereoselectivity has its roots in the reduced mobility of the radicals in this medium of high microviscosity.[9,10] In this

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[1] An exception to this general statement are free-radical cyclizations that lead to a predictable stereochemical outcome. See: Beckwith, A. L. J.; Ingold, K. U. In "Rearrangements in Ground and Excited States"; deMayo, P., Ed.; Academic Press: New York, 1980.

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[3] (a) Bartlett, P. D.; McBride, J. M. *Pure Appl. Chem.* **1967**, *15*, 89–107. (b) Jaffe, A. B.; Skinner, K. J.; McBride, J. M. *J. Am. Chem. Soc.* **1972**, *94*, 8510.

[4] Fendler, J. H. "Membrane Mimetic Chemistry"; Wiley: New York, 1982.

[5] The stereochemistry of the diazenes was established by resolution of the (±)-diazene quinine salt. See: Petter, R. C.; Mitchell, J. C.; Brittain, W. J.; McIntosh, T. J.; Porter, N. A. *J. Am. Chem. Soc.* **1983**, *105*, 5700.

[6] 10% diazene in 10 mg of DPPC was vortexted in 1 mL of phosphate buffer to form vesicles. Photolysis was with a 900-W xenon source.

[7] We have purified ketenimine **3**, formed by hydrolysis of **4**, and have carried out thermal decomposition of this unstable compound in DPPC liposomes at 60 °C. Small amounts (<10%) of the SCDN products result from this decomposition but the primary products formed appear to be ketenimine hydrolysis products. We thus believe that this secondary decomposition does not contribute significantly to the product stereochemistry.

[8] A complete study of diazene decomposition in water (pH 7 and 10) will be published at a later date.

[9] We thank Professor J. M. McBride for helpful discussions.

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