**Table I.** Asymmetric Reduction of α-Acetamidoacrylic Acids[a]

| Substrate | Solvent | Temp, °C | Abs press, atm | Reaction time, hr | %[c,d] ee |
|---|---|---|---|---|---|
| 4a | 88% i-PrOH | 25 | 3.5 | 3 | 92.8 |
| 4a | 88% i-PrOH | 50 | 3.5 | 0.8 | 93.6 |
| 4a | 88% i-PrOH | 25 | 27 | 0.8 | 91.8 |
| 4a | 50% MeOH[e] | 25 | 4 | 4 | 95.7 |
| 4a | 50% MeOH[e] | 50 | 4 | 1.3 | 95.2 |
| 4a | 50% MeOH[e] | 25 | 27 | 1.0 | 95.5 |
| 4b | MeOH[b] | 50 | 3.5 | 1 | 89.4 |
| 4b | MeOH | 50 | 3.5 | 1.5 | 89.5 |
| 4b | MeOH | 25 | 3.5 | 4 | 90.9 |
| 4b | 88% i-PrOH | 50 | 3.5 | 0.7 | 94.0 |
| 4c | MeOH | 50 | 4.0 | 0.75 | 93.5 |

[a] All hydrogenations were run with 0.05% metal levels based on substrate and at concentrations of $2 \times 10^{-4}$ M. [b] In this run, an in situ catalyst was employed while, in all other examples, the crystalline complex [Rh(COD) (bisphosphine)]$^+$ BF$_4^-$ was used. [c] Enantiomeric excess. [d] All rotations were measured without isolation by diluting to volume and comparing with a blank, taking for pure 5a {[α]$^{20}$D + 47.5° (c 1.0, 95% EtOH)} , 5b {[α]$^{20}$D + 40.8° (c 1.0, MeOH)} , and 5c {[α]$^{20}$D + 35.1° (c 0.5, MeOH)} . In the case of the basic solutions, an additional 0.55 equiv of NaOH was added before dilution to volume. In no case was the catalyst contribution in the blank more than 2%. [e] Run as sodium carboxylate with 0.95 equiv of NaOH.

**Scheme I**
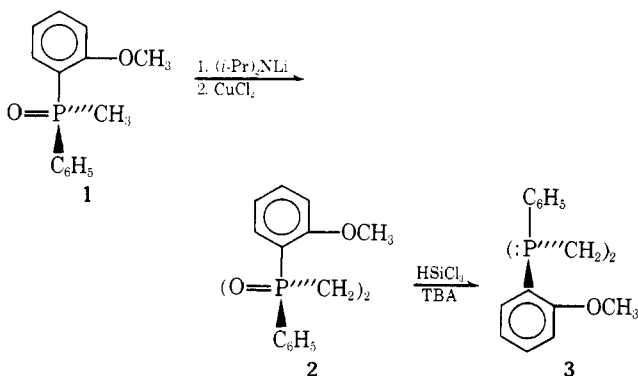
phine oxide (1) {[α]$^{20}$D +25.9° (c 1.0, MeOH)} to 1,2-bis(o-anisylphenylphosphinyl)ethane (2) {[α]$^{20}$D −44.9° (c 1.0, MeOH)} was achieved using a modification of Mislow's procedure.[3] Metallation with lithium diisopropylamide[4] at 5° in place of butyllithium at −70° significantly improved the yields. The bisoxide 2 was reduced to 3 {[α]$^{20}$D −85.0° (c 1.0, CHCl$_3$)}, employing a combination of trichlorosilane and tri-n-butylamine in acetonitrile at 70°.[5] Less meso-3 and higher conversions were obtained with tributylamine than with the more commonly used triethylamine. Oxidation of (−)-3 to (+)-2 with H$_2$O$_2$ established that there was inversion at both asymmetric centers during the silane reduction of 2 to 3. A solid complex[6] of (−)-3, of the type [Rh(1,5-cyclooctadiene)(bisphosphine)]$^+$ BF$_4^-$, was prepared from [Rh(COD)Cl]$_2$ and 3. Hydrogenations were run with either the complex or with an in situ catalyst formed from 3 and [Rh(COD)Cl]$_2$. Table I shows the enantiomeric excess of substituted alanines obtained under a va-
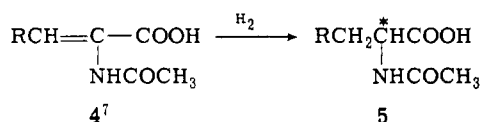
4a, 5a, R = phenyl
4b, 5b, R = 3-methoxy-4-acetoxyphenyl
4c, 5c, R = 3-(1-acetyl-indolyl)-

riety of conditions for the following hydrogenation reaction. In all cases, (−)-3 gives derivatives of L-amino acids. Several points in the table merit discussion. As in our previous experience, the hydrogenation can be run on either the free acid or the carboxylate anion,[1b,c,e] however, with ligand 3, better results are observed with the anion. The high optical yields obtained with the bisphosphine 3 were not sensitive to temperature and pressure,[1e] and excellent results could be obtained without a rate penalty.

This nonsensitivity to variables as well as the superior optical yields may be attributed to the rigid, five-membered ring possible between 3 and the rhodium, which prevents rotation around the metal–phosphorus bonds. The modest results (40% ee) obtained with α-phenylacrylic acid support our contention[1b,e] that the methoxyl group is improving the selectivity by hydrogen bonding with the amide substrate.

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RCH=C—COOH  →(H$_2$)  RCH$_2$ĊHCOOH
|                                |
NHCOCH$_3$                       NHCOCH$_3$

4[7]                             5

## Energy Storage and Release. Direct and Sensitized Photoreactions of Benzvalene. Evidence for a Quantum Chain Process, an Adiabatic Photorearrangement, a Degenerate Photovalence Isomerization, and Two Reactive Triplet States

Sir:

It is remarkable that the valence isomers of benzene, although they store enormous potential energy in their highly strained aromatizable structures, are kinetically stable at room temperature.[1] To identify features controlling the storage and release of chemical energy in simple organic molecules, we studied the response of one of these valence isomers, benzvalene,[2] to the further energy enhancing processes of direct and sensitized excitation by light.

The photochemistry of benzene (1), the prototype aromatic molecule, has been studied extensively.[3] Several isomers (2, 3, 4) are known to result upon irradiation in solution,[3-5] but none of these result from benzene's fluorescent state, the lowest vibrational state of S$_1$. Apparently, 2 is formed from an upper vibrational state of S$_1$ (1) and 3 from
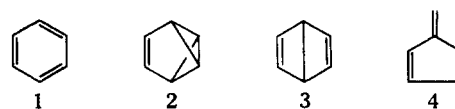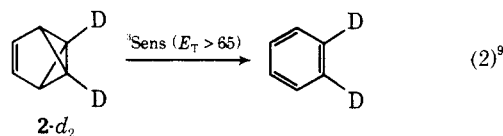
1    2    3    4
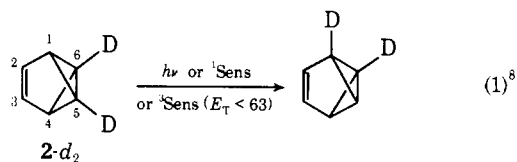
Table I. Photochemical Reactions of Benzvalene

| Sensitizer | Triplet energy | $\phi_1{}^b$ | $\phi_{VI}{}^b$ | $k_q{}^c$ |
|---|---|---|---|---|
| Acetone | 78 | 2.1 | | 30 |
| Acetophenone | 74 | 2.8 | | 4 |
| Xanthone | 74 | 3.0 | <0.1 | |
| Benzophenone | 69 | 1.6 | <0.1 | 30 |
| 4-Bromobiphenyl | 66 | | | 12 |
| 1,4-Dibromonaphthalene | 60 | | | 4 |
| Biacetyl | 56 | | | 10 |
| Benzil | 53 | ~0.1 | ~0.2e | 3 |
| None | | ~0.1 | ~0.2e | |
| Pyrene[a] | 77[a] | ~0.1 | ~0.2e | 30[d] |

[a] Singlet sensitizer. Energy in kilocalories per mole. [b] $\phi_1$ is the quantum yield for benzene formation at ~0.3 $M$ benzvalene. $\phi_{VI}$ is the quantum yield for scrambling (valence isomerization) in the absence of a quantum chain. See text. [c] Phosphorescence quenching constant ($\times 10^{-9} M^{-1}$ sec$^{-1}$). [d] Fluorescence quenching constant ($\times 10^{-9} M^{-1}$ sec$^{-1}$). The formation of benzene excited states is energetically allowed since, in addition to the singlet excitation energy of pyrene, the energy released when benzvalene isomerizes to benzene drives the reaction. [e] The benzene was analyzed[9] after the extent of conversion had been measured by ^{1}H NMR and the sample heated to 100° to convert the remaining benzvalene to benzene. 5,6-Dideuteriobenzvalene upon heating to 100° yields only o-dideuteriobenzene.

$S_2$ (1); **4** seems to be a secondary photoproduct derived from **2**.[6] The quantum yields are very low[3,6,7] and the yields of isolable products seem limited further by secondary photoprocesses.

We report here a number of aspects (Table I) of the photochemistry of **2**: (a) the direct ($\lambda_{ex}$ = 254 nm, 3-methylpentane, room temperature) and singlet (pyrene) sensitized isomerizations to benzene and fulvene are inefficient ($\phi \sim 0.1$); (b) the reaction inefficiency results from *degenerate photovalence isomerization* (eq 1); (c) triplet sensitizers whose energies are less than about 65 kcal/mol but greater than 53 kcal/mol also effect this valence isomerization, while those whose energies are greater sensitize the rearrangement of **2** to **1**; (d) the phosphorescences of all these triplet sensitizers (whose triplet energies vary from 78 to 53 kcal/mol) are quenched by **2** at diffusion rates; (e) at high concentrations **2** undergoes a triplet sensitized chain reaction yielding **1** with quantum yields approaching 4; (f) direct photoexcitation of **2** does not give significant benzene fluorescence (77°K or room temperature) or phosphorescence (77°K); (g) the high energy triplets isomerize 5,6-dideuteriobenzvalene to ortho dideuteriobenzene (eq 2).

$$\text{2-}d_2 \xrightarrow[\text{or }^3\text{Sens }(E_T < 63)]{hv \text{ or }^1\text{Sens}} \quad (1)^8$$

$$\text{2-}d_2 \xrightarrow{^3\text{Sens }(E_T > 65)} \quad (2)^9$$

We interpret the change in benzvalene's reaction mode, from valence isomerization to aromatization, as the energies of triplet sensitizers are increased to indicate that two triplets of benzvalene react and that these do not interconvert appreciably. If we assume the high energy sensitizers excite an upper triplet ($T_2$) of **2** that ring opens to benzene triplet, we can also understand why the quantum yield is greater than unity, for if benzvalene($T_2$) transforms to benzene($T_1$), the latter should be capable of sensitizing the decomposition of another benzvalene molecule. We thus pro-
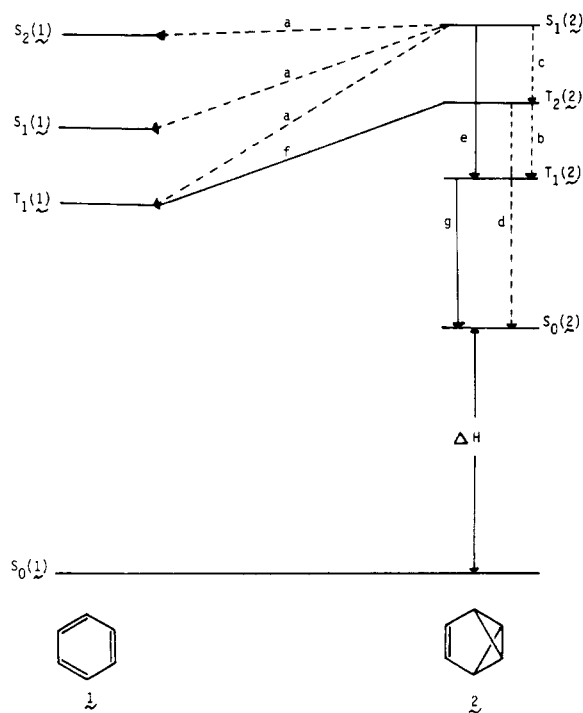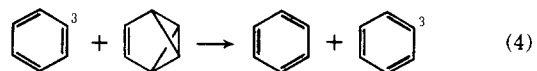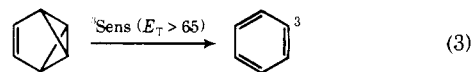


Figure 1. Energy diagram showing the interconnections between the states of benzvalene and benzene.

pose that the limiting quantum yields are greater than unity when high energy sensitizers are employed because the quantum chain process indicated in eq 3 and 4 operates.[10]

$$\quad \xrightarrow{^1\text{Sens }(E_T > 65)} \quad {}^3 \quad (3)$$

$$\quad {}^3 + \quad \rightarrow \quad + \quad {}^3 \quad (4)$$

In agreement with this proposal, the quantum yields for the sensitized conversion do not depend on sensitizer concentration, but do depend strongly on benzvalene concentration. Thus with benzophenone as sensitizer, $\phi$ = 1.0 when [2] = 0.1 $M$, $\phi$ = 2.1 when [2] = 0.77 $M$, and $\phi \sim 4$ when [2] = $\infty$. Further support for a quantum chain process involving benzene triplet is provided by the observation that 1-pentene and cis-2-pentene both decrease the quantum yield for the benzophenone-sensitized reaction **2** → **1** but the limiting quantum yield (approached at 1 $M$ concentrations of these olefins) is 0.8.[11] Upon excitation by low energy sensitizers, we suppose **2** gives a different, lower energy, triplet ($T_1$), which deactivates mainly by a degenerate valence isomerization and yields benzene less efficiently.

Figure 1 is a summary. The following energetically feasible transitions do not occur efficiently: (a) $S_1(2)$ to $S_2(1)$, $S_1(1)$, or $T_1(1)$, as no benzene fluorescence or phosphorescence is observed upon direct excitation of **2**; (b) $T_2(2)$ to $T_1(2)$, as the degree of scrambling observed with high energy triplet sensitizers is low; (c) $S_1(2)$ to $T_2(2)$, as direct photoexcitation of **2** yields benzene inefficiently; (d) $T_2(2)$ to benzvalene, as high energy triplet sensitizers yield benzene efficiently. On the other hand, the following transitions probably do occur efficiently: (e) $S_1(2)$ to $T_1(2)$, as the direct and low energy triplet sensitizers result in similar scrambling; (f) $T_2(2)$ to $T_1(1)$, as the quantum yield of benzene is decreased by pentenes; (g) $T_1(2)$ to benzvalene, as low energy triplet sensitizers give back benzvalene with its nuclei scrambled.

The most remarkable feature of these results is that the

energy-rich benzvalene structure, even after it is excited by the absorption of a >110 kcal photon or by receiving 53 kcal of triplet energy, survives. Three other features—the quantum chain sequence,[10,12] the photosensitized adiabatic valence isomerization,[13] and the two independently reacting triplet states of one molecule—have been observed in other molecules only rarely.

**References and Notes**

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(7) H. Lutz and G. Stein, *J. Phys. Chem.*, **78**, 1909 (1974).
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(9) The benzene-$d_2$ was recovered by GLPC and analyzed by infrared spectroscopy. For quantitative analysis, the three dideuteriobenzenes were synthesized and use was made of their differing absorptions: ortho at 1476 and 1449 cm$^{-1}$, meta at 1445 and 1420 cm$^{-1}$, and para at 1469, 1406, and 595 cm$^{-1}$. After 100% photoconversion the amount of meta isomer was less than 10% and the amount of para isomer was equal to or less than 0.5%.
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(12) With the exception of 1,2-dioxetanes,[10] only one other example of a documented quantum chain sequence is reported: J. Saltiel, D. E. Townsend, and A. Sykes, *J. Am. Chem. Soc.*, **95**, 5968 (1973). A cationic chain sequence involving a Dewar benzene was discovered: T. R. Evans, R. W. Wake, and M. M. Sifain, *Tetrahedron Lett.*, 701 (1973).
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## Stabilization of Low Valent Iron and Alkyl and Hydride Derivatives of Iron(I) by Macrocyclic Ligands Having Nitrogen Donors

*Sir:*

Recent studies on the complexes of macrocyclic ligands have revealed a rich oxidation-reduction chemistry that far exceeds expectation, particularly for transition metal derivatives with rings having the common nitrogen donor atoms.[1-4] We report here a series of derivatives of iron(I) that are stabilized by chelation of the iron atom to the unsaturated tetraaza macrocycle of structure I. The ligand



I
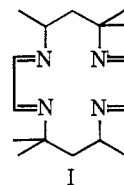
also facilitates the synthesis of hydride and alkyl derivatives of the iron(I) atom, and such species are of potential significance to homogeneous catalysis. These products are all highly reactive but readily subject to handling in the absence of oxygen and moisture.

On the basis of our earlier electrochemical studies,[3,5] the ligand 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene (abbreviated $Me_6[14]1,3,8,10$-tetraeneN$_4$ or more simply tetraeneN$_4$, structure I)[6] was chosen as the member of the family of tetraazamacrocycles that should be most effective in stabilizing both low oxidation state iron complexes and their alkyl and hydride derivatives. In acetonitrile solutions, [Fe(tetraeneN$_4$)(CH$_3$CN)$_2$]$^{2+}$ exhibits three well-defined reduction waves at $-0.80$, $-1.41$, and $-1.83$ V vs. Ag-AgNO$_3^-$ (0.1 $M$) (0.1 $M$ $n$-Bu$_4$NBF$_4$ supporting electrolyte).[3] Controlled potential electrolysis on the first reduction plateau ($-1.2$ V) produces purple [Fe$^I$(tetraeneN$_4$)]$^+$ which was isolated in 80% yield as the CF$_3$SO$_3^-$ salt. Anal. Calcd for C$_{17}$H$_{28}$N$_4$SO$_3$F$_3$Fe: C, 42.42; H, 5.82; N, 11.65; S, 6.67. Found: C, 41.92; H, 6.02; N, 11.47; S, 6.70.

Magnetic susceptibility measurements indicate an effective moment of 2.3 BM.[7] The anisotropic ESR spectrum of a frozen acetonitrile solution of the iron(I) complex is characteristic of a low-spin d$^7$ system subject to a rhombic distortion from octahedral symmetry ($g$ values: 2.516, 2.059, 1.933). The quasi-reversible Fe(I)/Fe(II) couple is observed at $-0.69$ V.

Although all Fe(I) derivatives containing nitrogen and/or oxygen donors must be considered rare, earlier reports include Na[Fe$^I$(salen)], which is reported[8] to contain high-spin Fe(I), and the product of one-electron reduction of [Fe(Me$_6$[14]aneN$_4$)CH$_3$CN)$_2$]$^{2+}$ (see structure II for the ligand Me$_6$[14]aneN$_4$), which exhibited properties inconsistent with those expected for a simply related Fe(I) derivative.[9] Na[Fe$^I$(TTP)], where TPP is tetraphenylporphyrin, has been fairly well characterized.[10]

II
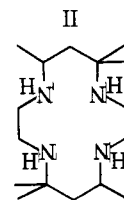


Considerable attention has also been given to the second reduction process that [Fe$^{II}$([14]tetraeneN$_4$)(CH$_3$CN)$_2$]$^{2+}$ undergoes. Controlled potential electrolysis of [Fe$^{II}$(tetraeneN$_4$)(CH$_3$CN)$_2$]$^{2+}$ on the second reduction plateau ($-1.6$ V) produced, in solution, the two-electron reduction product, formally Fe$^0$tetraeneN$_4$. Further reaction of this highly reactive species was followed by repeated scanning of the current-potential curve. It has been found that this process involves abstraction of a hydrogen atom, presumably from the supporting electrolyte $n$-Bu$_4$NBF$_4$, to form an iron(I) hydride derivative, H-Fe$^I$(tetraeneN$_4$)(CH$_3$CN). Anal. Calcd for (C$_{16}$H$_{28}$N$_4$)Fe(H)CH$_3$CN: C, 57.77; H, 8.56; N, 18.73. Found: C, 57.65; H, 8.46; N, 18.64. The purple-black isolated product (10-15% yield) has two quasi-reversible oxidation waves at $-0.73$ and $-0.01$ V. These are assigned to the Fe(I)/Fe(II) and Fe(II)/Fe(III) couples, re-