

the other hand, the (–) enantiomer showed only weak activity. Similar results were obtained by electroantennogram (EAG) studies.⁸ The threshold concentration of the (+) enantiomer was 1×10^{-7} g/ml, which is slightly lower than that of the racemate (1×10^{-6} g/ml), whereas the (–) enantiomer needed a much higher concentration (1×10^{-4} g/ml). Interestingly, difference of the activity between both enantiomers is far stronger than the one expected from the enantiomeric composition of synthetic products. The present data, although still preliminary, implicate a chiral receptor system in the olfactory organ of the male insects, and may suggest possibility that the natural pheromone is the (+) enantiomer. Detailed assays will be conducted next summer.

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References and Notes

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- Analytical and spectrometric data for all synthetic compounds were in agreement with their structures.
- K. Koga, M. Taniguchi, and S. Yamada, *Tetrahedron Lett.*, 263 (1971).
- Assignment of the absolute stereochemistry on **9** and **10** was done as the result of chemical transformation of the former compound into (7*R*,8*S*)-disparlure, and of the latter into (7*R*,8*R*) trans analog, respectively, through the stereospecific reactions as described in this report.
- J. A. Dale, D. L. Dull, and H. S. Mosher, *J. Org. Chem.*, **34**, 2543 (1969).
- The optical purity of **9** was also investigated by converting **9** by oxidation (KMnO₄) followed by lactonization and methylation into a methyl ester of **6**. Its optical rotation, $[\alpha]^{25}_D +13.5^\circ$ (*c* 1.39, MeOH), indicated **9** to be contaminated with 4% of its enantiomer.
- The method of B. C. Block (*J. Econ. Entomol.*, **53**, 172 (1960)) was used with a partial modification.
- EAG potentials were recorded from the antenna of a living moth, as in early investigations by D. Schneider (*Z. Vergl. Physiol.*, **40**, 8 (1957)) and by J. Boeckh, H. Sass, and D. R. A. Wharton (*Science*, **168**, 589 (1970)). A glass rod was dipped into a hexane solution of disparlure prepared in the concentrations as shown in the table. Olfactory stimuli were presented by inserting the glass rod into the airstream passing over the antenna of insects.

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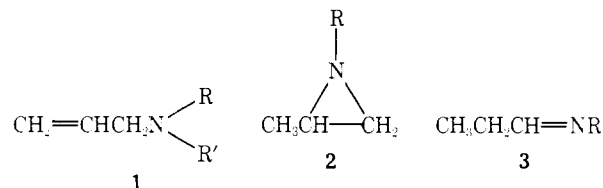
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Photochemical Transformations. X. Photoreactions of Aliphatic Allylamines¹

Sir:

In extending our studies^{2,3} on the photoreactions of allylic compounds containing heteroatoms, we have discovered several new reactions in the irradiation of allylamines of

general formula **1**. These reactions, which include a new general synthesis of aziridines **2**, are not anticipated from the known photochemistry of simple allylic alcohols, ethers, esters, which are either photoinert (except for cis–trans isomerization) or give hydrogenation products,³ of allylic halides,² or of simple olefins or polyenes.



- $R = R' = H$
- $R = n\text{-Bu}$; $R' = H$
- $R = \text{cyclo-C}_6\text{H}_{11}$; $R' = H$
- $R = t\text{-Bu}$; $R' = H$
- $R = R' = n\text{-Bu}$

Following the observation² that ketones sensitize the photoisomerization of allylic halides to cyclopropyl halides, we attempted similar procedures with allylamine (**1a**) in pentane and in acetonitrile.⁴ No isomeric products were formed, but ketone reductions and condensations to give Schiff bases ($R_2C=NCH_2CH=CH_2$) resulted. No photo-reactions occurred with **1a** in benzene, toluene, or pyridine.

On the other hand, direct irradiation of 0.2 *M* **1a** in cyclohexane (7 hr) or in acetonitrile (6 hr) gave 55 and 31% loss of reactant, forming three products in combined yields of 12 and 23%, respectively.⁵ The ratio of the three products was 1:3:3 in both solvents. The minor component was identified as *n*-propylamine (pmr spectrum). The more volatile major product was identified as 2-methylaziridine (**2a**) by nmr and mass spectral comparisons. The third product was not identified, but it was not cyclopropylamine (expected if allylamine behaved analogously to allyl chloride²).

Irradiation of a 0.05 *M* solution of *N*-cyclohexylallylamine (**1c**) in cyclohexane gave four products, in combined 61% yield.⁶ Loss of **1c** remained nearly constant (quantum yield 0.08) over the first hour (40% loss) but declined thereafter. The product yields were 6:29:14:12. Unlike the latter three, the most volatile component (6% yield) was not basic. It was identified as allylcyclohexane. The 29% product was cyclohexylamine. The 14% yield component was identified as *N*-cyclohexyl-2-methylaziridine (**2c**) by comparison of vpc retention time and ir and nmr spectra to those of an authentic sample.⁷ The fourth component was identified as *N*-propylidenecyclohexylamine (**3c**) by comparison of spectral properties (and odor) with those of a sample prepared by condensation of cyclohexylamine and propionaldehyde in anhydrous benzene over 3Å molecular sieves.

Irradiation of **1c** in tetrahydrofuran and acetonitrile gave comparable yields of cyclohexylamine, aziridine **2c**, and Schiff base **3c**. Allylcyclohexane was not produced, but 2-allyltetrahydrofuran was isolated (18% yield) in the THF experiment.

Irradiation of allyl-*n*-butylamine (**1b**) in cyclohexane gave *n*-butylamine, the aziridine **2b**, and the Schiff base **3b**, and that of allyl-*tert*-butylamine (**1d**) in decalin gave *tert*-butylamine, aziridine **2d**, and Schiff base **3d** at rates and with yields comparable to analogous products obtained from **1c**.

When the tertiary amine, *N,N*-di-*n*-butyl-*N*-allylamine (**1e**), which is constitutionally unable to isomerize to aziridine or to Schiff bases by hydrogen migration, was irradiated in cyclohexane (initial $\phi \sim 0.15$), propene,⁸ *N*-butylidene-*n*-butylamine,⁹ and di-*n*-butylamine⁹ were formed in 59, 60, and 40% yields, respectively.

Work has been reported on irradiation of a number of al-

lylic anilines and allylic methylanilines;^{10,11} the reported products, which include neither aziridines nor Schiff bases, may be derived from allylic and amino radicals produced by bond homolysis.^{10,11} It seems plausible that the fragmentation reactions we report here may similarly involve homolysis, although the interesting possibility of a hydrocarbon analog¹² of a Norrish type II cleavage with the tertiary amine **3e** remains to be excluded.¹³ While it is premature to speculate in detail upon the mechanisms of the rearrangements to aziridines and to Schiff bases, appropriate labeling experiments may provide data useful to this end. For the present, we consider the intermediacy of a zwitterion, analogous to the intermolecular exciplexes derived from photoexcited arenes and amines,¹⁴ as highly likely for the aziridine formation. Further analogy may be seen in the additions of primary, secondary, and tertiary amines to olefins and to benzene, where similar exciplexes may be proposed.¹⁵

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- Solutions were prepared under nitrogen from olefin-free deaerated solvents. Amines were freshly distilled under nitrogen from KOH. Direct irradiations were conducted with a type L Hanovia lamp using Vycor filters and sensitized irradiations with Pyrex filters. Quantum yield studies used sealed quartz ampoules degassed at 10^{-5} Torr and 254-nm light.
- Yields and product ratios (a) were determined by vpc analysis on $\frac{1}{8}$ in. 15% Carbowax 20-M + 5% KOH columns using hydrocarbon internal references, (b) are approximate in 1a irradiations since the areas were determined using a TC detector and are uncorrected, and (c) are exact in 1b-e irradiations, determined using flame ionization techniques and appropriate molar response ratios. Products were isolated by distillation under nitrogen through a Vigreux column to yield a product concentrate from which individual components were isolated by vpc collection on a $\frac{1}{4}$ in. Carbowax-KOH column.
- Yields of constituents were determined several times during the reaction and remained constant to 90% loss of **1c** (4 hr).
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- Propene was isolated, identified, and measured as 1,2-dibromopropane by bubbling the nitrogen purge through a $\text{Br}_2\text{-CCl}_4$ gas wash bottle.
- Identified by spectral comparisons.
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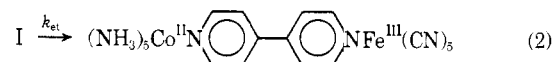
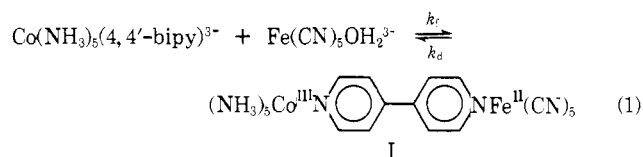
Formation of a Precursor Binuclear Complex and Intramolecular Electron Transfer Mediated by 4,4'-Bipyridine¹

Sir:

Inner sphere redox reactions proceed by a sequence of steps: formation of a precursor complex, intramolecular

electron transfer, and dissociation of the successor complex.² For most systems, the first step is an unfavorable, rapid equilibrium (Q), and electron transfer is rate-determining (k_{et}). The measured rate constants are, therefore, composite quantities (Qk_{et}). Many attempts have been made to measure rates of elementary steps, but only partial success has been achieved.³⁻⁵

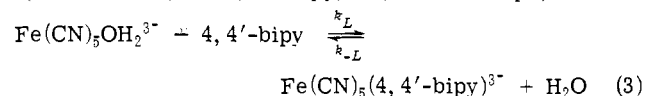
For the reduction of 4,4'-bipyridinepentaamminecobalt(III) by aquopentacyanoferrate(II),⁶ we have measured the rate of formation and dissociation of the precursor complex I (eq 1) and the rate of intramolecular electron transfer (eq 2).



The formation of I was monitored at 480 nm, 25°, pH 8.0 (tris(hydroxymethyl)aminomethane buffer), $\mu = 0.10$ M (LiClO_4), $[\text{Co}] = (0.39\text{--}72) \times 10^{-5}$ M, and $[\text{Fe}] = (0.92\text{--}17.4) \times 10^{-5}$ M and yielded $k_f = (5.5 \pm 0.3) \times 10^3$ $\text{M}^{-1} \text{sec}^{-1}$.

The spectrum of I was obtained by repetitively scanning equimolar mixtures of $\text{Fe}(\text{CN})_5\text{OH}_2^{3-}$ and $\text{Co}(\text{NH}_3)_5(4,4'\text{-bipy})^{3+}$ and extrapolating to the time of mixing.⁸ I exhibits a maximum at ~ 505 nm ($\epsilon \sim 6 \times 10^3$ $\text{M}^{-1} \text{cm}^{-1}$). $\text{Fe}(\text{CN})_5\text{L}^{3-}$ complexes with L = pyridine, 4,4'-bipyridine, and pyrazine exhibit metal to ligand electron transfer bands at 362 ($\epsilon 3.5 \times 10^3$), 432 ($\epsilon 5.6 \times 10^3$), and 452 ($\epsilon 5.0 \times 10^3$) nm, respectively.⁹ The wavelength of maximum absorption of $\text{Fe}(\text{CN})_5(4,4'\text{-bipy})^{3-}$ increases upon coordination of the remote N. Thus, with CH_3^+ and H^+ , the maximum shifts to 520 ($\epsilon 5.6 \times 10^3$)⁹ and 515 ($\epsilon 4.7 \times 10^3$)¹⁰ nm, respectively. Therefore, the 505 nm ($\epsilon \sim 6 \times 10^3$) band observed for I represents strong evidence for the proposed structural assignment.

The measurement of k_{et} posed serious difficulties, even in the presence of EDTA^{2-} (added to sequester the cobalt(II) produced and prevent precipitation) and ascorbic acid (added to reduce the $\text{Fe}(\text{CN})_5(4,4'\text{-bipy})^{2-}$ produced and prevent its rapid reaction with I). In order to drive reaction 1 to more than 98% completion, and because of rapid reduction of I by $\text{Fe}(\text{CN})_5\text{OH}_2^{3-}$, $\text{Co}(\text{NH}_3)_5(4,4'\text{-bipy})^{3+}$ was in excess. Under these circumstances, I is regenerated by reaction of $\text{Fe}(\text{CN})_5\text{OH}_2^{3-}$ produced by aquation of $\text{Fe}(\text{CN})_5(4,4'\text{-bipy})^{3-}$ (reverse of eq 3) with the



excess Co(III), and the kinetics of disappearance of I are quite complicated. Initial rates from a dozen runs, with $[\text{Co}] = (1.0\text{--}29.2) \times 10^{-5}$ M, $[\text{Fe}] = (4.3\text{--}19.1) \times 10^{-6}$ M, $[\text{ascorbic acid}] = (1.0\text{--}2.2) \times 10^{-3}$ M, $[\text{EDTA}^{2-}] = (1.0\text{--}7.0) \times 10^{-4}$ M, pH 8.0 (Tris buffer), and $\mu = 0.10$ M (LiClO_4), yielded values of k_{et} in the range $(2\text{--}4) \times 10^{-3}$ sec^{-1} .

Since the quality of the measurements of k_{et} was unsatisfactory, we sought to obtain k_{et} by a procedure which provided unequivocal evidence for the intramolecular electron transfer pathway. This was achieved by allowing I to be formed by reaction of $\text{Fe}(\text{CN})_5\text{OH}_2^{3-}$ with $\text{Co}(\text{NH}_3)_5(4,4'\text{-bipy})^{3+}$, and then, before much of reaction 2 took place, adding pyridine in excess. Since pyridine reacts rapidly¹¹