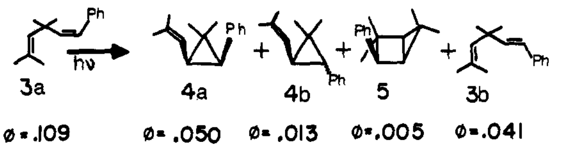
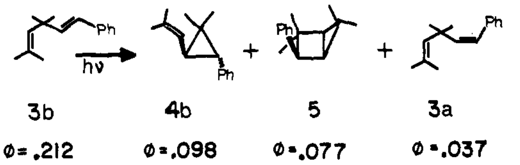


(2a)



(2b)

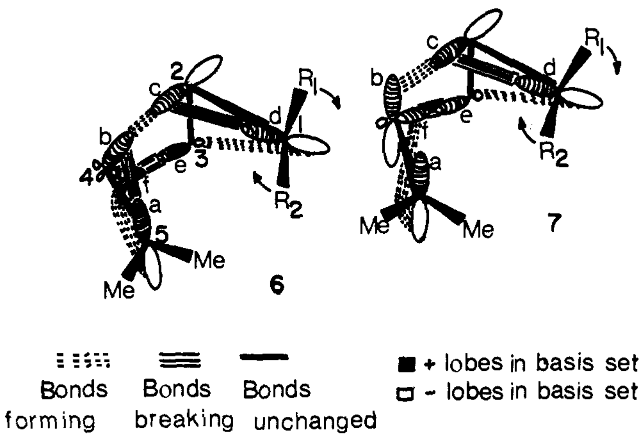


Figure 1. Reaction stereochemistry.

panecarboxylic acids, whose configurations rest on firm nmr evidence,[9] into the corresponding aldehydes and then reaction with isopropylidenetriphenylphosphorane to give **4a** and **4b**, respectively. The structure of housane (**5**) is derived from nmr and comparison with the nmr data of Hammond.[10] The stereochemistry there rested on the H-3 and H-4 nmr coupling constants for syn and anti isomers of 2 and 0 cps, respectively.

In contrast to the direct irradiations, benzophenone sensitized photolyses of the *cis*- and *trans*-phenyl dienes **3a** and **3b** gave no di-π-methane rearrangement and only cis–trans interconversion. The efficiencies were $\phi = 0.087$ for cis → trans and $\phi = 0.12$ for trans → cis.

A most exciting result is that the di-π-methane rearrangement of the phenyl dienes **3a** and **3b** is stereospecific, and the situation at C-1 parallels that at C-5 in that cis reactant leads preferentially to cis product and trans reactant gives trans product.

The lack of specificity in housane (**5**) formation may derive from loss of stereochemistry in a 1,4 biradical formed by 2,4 bonding and then intersystem crossing to triplet, but the evidence that **5** is the kinetic product is less certain due to experimental limitations. The greater housane formation from the *trans*-diene **3b** is reasonable since the syn,syn conformation is more likely for this isomer than for **3a**.

The stereochemistry of the reaction is most readily understood in terms of the drawings in Figure 1. For convenience the syn,syn geometry is drawn, in which the two π bonds and the methane carbon 3 are in the U-shaped conformation. The stereochemical reasoning, however, is independent of which conformation is utilized. In inspecting Figure 1, one should recognize that the two representations **6** and **7** are equivalent. The former differs in showing the isobutenylidene sp^2 hybrid and one π-system p orbital combined into two equivalent sp^5 hybrids at C-4.

It is seen in the reaction that group R_1, which is initially trans with respect to the methane carbon C-3 on π bond 1,2, is twisted trans to the isopropylidene group; and R_1 and $Me_2C{=}CH-$ become trans in the product. This motion is depicted in Figure 1. The new three-ring σ bond must then arise from overlap of the anti lobe at carbon 1. As mentioned, tentative evidence for a preference for inversion of configuration at the methane carbon in the di-π-methane rearrangement has been advanced by us previously,[2b,c] and this overlap is used in Figure 1.[11]

Least motion might be considered as a potential factor in controlling the reaction stereochemistry. However, presently it is seen that an approximately equal twist is required to arrive at either stereochemistry at C-1.

As noted earlier,[2b] this stereochemistry is excited state allowed since the six electron array is of the Möbius variety.[12]

Finally, still another case is available in which the singlet excited state rearranges *via* a concerted process with a cyclic orbital array while the triplet leads to a biradical and subsequent energy dissipation by double bond twisting.[2b]

Acknowledgment. Support of this research by AROD and NSF is gratefully acknowledged.

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Received April 6, 1972

The Use of Shift Reagents in Nuclear Magnetic Resonance Studies of Chemical Exchange

Sir:

A paramagnetic complex shifts the magnetic resonance frequency of nuclei in polar solvents by[1]

$$\Delta\nu_c = C_sK_j/kT \qquad (1)$$

where C_s is the concentration of complex and K_j is a contact shift constant characteristic of each set of nuclei and the applied field. Complexes, such as Eu(thd)$_3$ and Pr(thd)$_3$,[2] produce[3-5] "chemical shifts" be-

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[1] D. R. Eaton and W. D. Phillips, *Advan. Magn. Resonance*, **1**, 103 (1965); H. J. Keller and K. E. Schwarzhaus, *Angew. Chem., Int. Ed. Engl.*, **9**, 196 (1970).

[2] Eu(thd)$_3$ represents tris(2,2,6,6-tetramethyl-3,5-heptanedionato)europium(III), also designated as Eu(DPM)$_3$. Eu(fod)$_3$ represents tris(1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedionato)europium(III). Pr(thd)$_3$ and Pr(fod)$_3$ represent the praseodymium(III) complexes.

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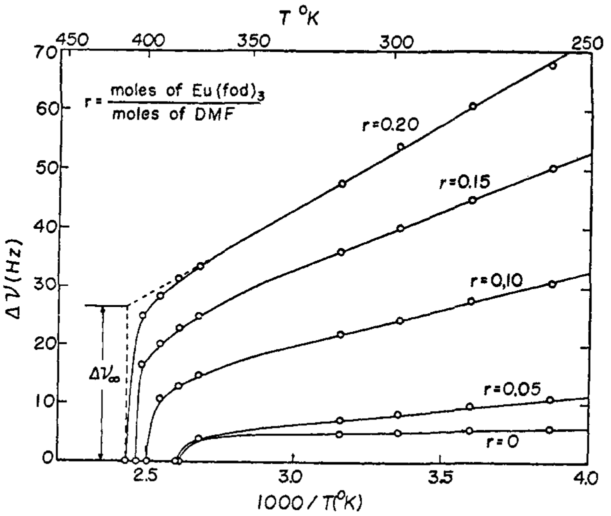

Figure 1. The separation $\Delta\nu$ between the pmr lines of the two α-CH_3 groups in DMF at 60 MHz as a function of $1/T$ and the amount of shift reagent.

tween the nmr frequencies of different nuclei in the solvent by differences in K_j.[1] Such effects are adjustable *via* the concentration or nature of the shift reagent and are useful for analyzing nmr spectra in structural[6] and conformational[7] studies. Similarly, shift reagents should have applications in nmr studies of chemical exchange, where the range of measurable rates and the accuracy both increase with the chemical shift between the exchanging groups.[8] We have investigated several of these possibilities and can report that the prospects, though limited, are promising.

One limitation arises from the temperature dependence of electron relaxation in the shift reagent, which becomes slower at lower temperatures. This produces spin-exchange broadening which can obscure chemical exchange effects. Also, many shift reagents have poor solubility at lower temperatures, producing smaller shifts. However, two new shift reagents, $Eu(fod)_3$ and $Pr(fod)_3$,[2] have smaller line-broadening effects and greater solubility,[5] so we have investigated their use in measuring the internal rotation rates of several amides. The amides were studied as 5 mol % solutions in purified tetrachloroethane (TCE),[9] having various molar ratios of shift reagent to amide. The proton spectra were observed with a Varian A-60A spectrometer and V-6040 variable temperature probe.

In our initial studies, we have confirmed that $Eu(fod)_3$ produces much less line broadening, its effects being displaced about 50° below those for $Eu(thd)_3$, even though it produces comparable shifts. Nonetheless, even $Eu(fod)_3$ causes broadening large enough at temperatures below 275°K to obscure ring inversion processes (*e.g.*, that of cyclohexanol) which we have attempted unsuccessfully to observe. However, at temperatures above 310°K, the broadening is negligible so processes with a higher free energy of activation $\Delta G^{\ddagger}$ such as the internal rotation of amides can be studied to good advantage. Figure 1 presents the combined effects of temperature and $Eu(fod)_3$ upon the separation $\Delta\nu$ between cis and trans α-CH_3 group resonances in DMF.[10] The reagent shifts both proton lines downfield, the shift of cis protons being greatest.[1,11] The $\Delta\nu$ is linear[11] in r at a given $T < T_c$, as is its dependence upon $1/T$ for a given r (eq 1). Moreover, the coalescence temperature increases with the addition of $Eu(fod)_3$ because the latter increases $\Delta\nu_\infty$, the effective shift without chemical exchange.

The chemical exchange broadening is most sensitive to the exchange rate at T_c, for which $k_c = \pi\Delta\nu_\infty/\sqrt{2}$.[8] Therefore we determined T_c and $\Delta\nu_\infty$ as a function of r. Two independent determinations were made of each $\Delta\nu_\infty$, one from the line width at T_c,[8,10] the other by extrapolating the $\Delta\nu$ *vs.* $1/T$ curves to $1/T_c$ (Figure 1). For low concentrations of $Eu(fod)_3$, $r \lesssim 0.3$, the two values agree well within ±0.5 Hz; this, with an uncertainty of ±0.5° in T_c, gives ±0.12 kcal/mol in $\Delta G^{\ddagger}$. However, at higher concentrations, the temperature dependence of $\Delta\nu$ is much steeper and falls below the linear $1/T$ plot at lower temperatures, so the extrapolated value of $\Delta\nu_\infty$ is less accurate. The nonlinearity probably results from equilibria involving the $Eu(fod)_3$ and may be of interest in that connection.

Typical results for $\Delta\nu_\infty$ and T_c are given in Table I along with values of $\Delta G^{\ddagger}$ calculated from them. The results are consistent with earlier work,[10,12–15] except that $\Delta G^{\ddagger}$ increases slightly with increasing T_c, especially for the DMF–$Eu(fod)_3$ solutions in which T_c covers a range of more than 50°.[12] The increase in

Table I. Pmr and Activation Parameters for Internal Rotation of Amides with Various Molar Ratios of $Eu(fod)_3$[a]

r[a]	$\Delta\nu_\infty$, Hz[b]	T_c, °C	$\Delta G^{\ddagger}$[c]	Lit. values, $\Delta G^{\ddagger}$, T_c, Ref
Dimethylformamide (DMF)				
0.00	5.0	114.0	21.00	20.9 in TCE, 113°, 12
0.10	14.0	131.5	21.16	20.9 in TCE, 115°, 13a
0.30	40.5	152.5	21.40	21.7 neat, 116°, 13b
0.50	71.0	164.0	21.52	
0.60	76.0	167.5	21.63	
Dimethylacetamide (DMA)				
0.00	5.3	66.0	18.27	18.5 in TCE, 73°, 12
0.05	6.8	69.5	18.30	18.2 neat, 75°, 14
0.10	15.1	82.0	18.42	
0.15	21.0	88.0	18.50	
Dimethylpropionamide (DMP)				
0.00	4.4	51.0	17.55	18.0 neat, 54°, 15a
0.05	7.8	58.0	17.57	16.6 in CCl_4, 44°, 15b
0.10	16.0	70.0	17.73	
0.15	22.0	74.0	17.73	

[a] The molar ratio $Eu(fod)_3$/amide in TCE solutions with 5 mol % of amide. [b] The width at half-height of the 60-MHz pmr at T_c. [c] In kcal/mol, obtained from the Eyring equation, $k_c = (kT_c/h)\exp(-\Delta G^{\ddagger}/RT_c)$.

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(9) Impurities in the solvent greatly increased the exchange rate and decreased $\Delta G^{\ddagger}$.

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$\Delta G^{\ddagger}$ might be caused by the amide-shift reagent association. But at least part of it should come from the temperature-dependent entropy term in $\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger}$. The $\Delta S^{\ddagger}$ for the amides is about -5 eu,[10] enough to increase $\Delta G^{\ddagger}$ with T_c by nearly the amount observed. The dependence of T_c and $\Delta G^{\ddagger}$ upon resonance frequency as well as upon r and the nature of the shift reagent are being investigated to separate the two contributions. Such approaches could be helpful in obtaining accurate measurement of $\Delta S^{\ddagger}$.

Acknowledgment. This research was supported by ONR and NSF.

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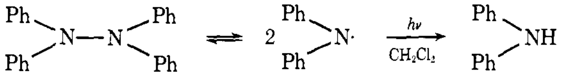
Photochemistry of Organic Cation Radicals. The Photo Benzidine Rearrangement of Tetraphenylhydrazine Cation Radical

Sir:

Aromatic cation radicals generally have absorption maxima in the visible at wavelengths of >500 nm while their parent bases absorb in the uv, usually at <290 nm. The energy of absorption corresponds to <57 and >100 kcal/mol, respectively. This suggests that it may be possible to carry out photochemical transformations in organic cation radicals using low-energy visible light in cases where the precursor undergoes fragmentation by the more energetic uv radiation. We now report an example illustrating this principle, that of the photobenzidine rearrangement of the tetraphenylhydrazine cation radical. There have been a number of recent papers[1-5] concerning the photolytic reactions of organic cations but there do not appear to be any reports of photolytic reactions of cation radicals.

Tetraphenylhydrazine (1) absorbs in the uv at 295 nm. Upon photolysis, the N–N bond undergoes cleavage producing diphenylamino radicals (2).[6] We have observed that photolysis of 1 in dichloromethane is accompanied by the formation of diphenylamine 3. The reaction is inefficient, probably due to the recombination of 2, but goes in high yield. No benzidine rearrangement product could be detected.



1 2 3

Results of quite a different nature are obtained by photolysis of the tetraphenylhydrazine cation radical (4, λ_{max} 465 nm) in either quartz or Pyrex vessels. The reaction results in the equimolar formation of tetraphenylhydrazine (1) and the oxidized form of *N,N'*-diphenylbenzidine (6).

The cation radical (4) fluoroborate was prepared by quantitative coulometric oxidation of 1 in dichloromethane. In the dark, 4 is stable in dichloromethane but when exposed to light, the violet solution of 4 first turns deep blue and then bright green. When a uv cuvette containing a 10^{-4} *M* solution of 4 was placed in front of a desk lamp (100 W), a new absorption band appeared at 580 nm while the band at 465 nm due to 4 was quickly obscured by a new broad band (λ_{max} 460 nm).[7] Both new absorption bands continued to grow for about 2 hr and then the 580-nm band began diminishing while the broad band continued to grow. The 580-nm band was shown to be due to the dication (6)[8] which was prepared independently by anodic oxidation of *N,N'*-diphenylbenzidine in dichloromethane. The new broad band at 460 nm was shown to be due to the monoprotonated quinone imine (8) by incremental addition of trifluoroacetic acid (TFA) to a dichloromethane solution of the quinone imine (λ_{max} 435 nm) and by addition of triethylamine to a solution of the dication (6) in dichloromethane. Both the 435-nm band due to the quinone imine and the 460-nm band due to 8 disappeared on addition of sufficient amounts of TFA to the dichloromethane solutions which was accompanied by the formation of 6 (λ_{max} 580 nm).

The yield of 1 was determined directly on the photolysis solution by the magnitude of the absorption band at 295 nm and the yield of 9 (λ_{max} 330 nm) was determined by the magnitude of absorption at 350 nm after treatment of the photolysis solution with triethylamine. Yields were found to be 70 (1) and 67% (9) based on the stoichiometry of Scheme I. For purposes of isolation, the fluoroborate salt of 4 (from 72 mg of 1 in 1 l. of dichloromethane) was subjected to irradiation through Pyrex using a medium-pressure mercury lamp for 20 min. Evaporation of the solvent followed by basic work-up and recrystallization from dichloromethane gave 1 (15 mg,[9] mp 144–147°, lit.[10] 149°, λ_{max} 295 nm) and 9 (12 mg,[9] mp 239–242,° lit.[11] 240–242°, λ_{max} 330 nm), the H nmr and ir spectra of which were identical with those of the authentic compounds.

The nature of the reduction of 7 on treatment with base is unknown. We have been able to reproduce this reaction with a variety of bases including 2,6-lutidine, triethylamine, sodium methoxide in methanol, and aqueous sodium hydroxide. However, in no case have we been able to find the species which has undergone oxidation.

The initial rearrangement product, presumably the cation radical of *N,N'*-diphenylbenzidine (5), was not detected. This is not surprising since electron transfer with 4 would be expected to be a rapid reaction. An alternative is that 5 disproportionates to the dication (6) and the benzidine (9) and 9 is then oxidized to 6 by the tetraphenylhydrazine cation radical (4). The latter is feasible since cyclic voltammetry of 9 in dichloro-

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