ratios are expected to be less sensitive to the presence of multiple species than the shift ratios.[19] Although shifts can be measured more accurately than line widths, the $\langle r^{-6} \rangle$ dependence of the relaxation allows significant error in the measured line width without sacrificing acceptable accuracy in the determination of relative values for r.

The potential for this technique is reflected in the data for substituted pyridine in the presence of Eu(fod)$_3$ and Gd(fod)$_3$. The proton line widths, δ_i were obtained by frequency-swept spin decoupling and corrected for second coordination sphere effects.[23] The quantitative comparison of the observed $(\delta_i/\delta_j)^{-1/6}$ with the estimated r_i/r_j, is illustrated in Table I. The results

Table I. The Effect of Eu(fod)$_3$ and Gd(fod)$_3$ on the Pmr Spectrum of Some Pyridines

	3-H/2-H	4-H/2-H	3-Me/2-H	4-Me/2-H
$\Delta H_i/\Delta H_j$ py[a]	0.31	0.31		
$\Delta H_i/\Delta H_j$ 4-pic[b]	0.32			0.30
$\Delta H_i/\Delta H_j$ 3,5-lu		0.33	0.21	
$\langle (3\cos^2\theta - 1)/r^3 \rangle$	0.38	0.32	0.23	0.21
$(\delta_i/\delta_j)^{1/6}$ 4-pic	0.64			0.54
$(\delta_i/\delta_j)^{1/6}$ 3,5-lu		0.60	0.58	
$\langle 1/r^6 \rangle^{1/6}$ [c]	0.60	0.53	0.54	0.46

[a] Obtained in 100 MHz for a deuteriochloroform solution 0.20 M in pyridine, 0.05 M in Eu(fod)$_3$, and 0.002 M in Gd(fod)$_3$ at 30°; py = pyridine, pic = picoline, lu = lutidine. [b] ΔH(2-H) = 8.24 ppm; the uncorrected δ = 380 Hz. Using Eu(dpm)$_3$, ratios of 0.36 and 0.26 were obtained. [c] Assuming Eu–N and Gd–N bond lengths of 2.65 and 2.60 Å, respectively.

are comparable in accuracy to those obtained by analyzing the relative shifts, $\Delta H_i/\Delta H_j$, in terms of the estimated geometric factors, which are also included in the table for comparison. We stress here that the proposed analysis of the line widths due to a relaxation reagent in the presence of a shift reagent is not intended so much as an alternative to the analysis of the assumed dipolar shifts as a complementary technique by which solution structures may be more critically examined. An important feature of our proposed technique is that it may provide an experimental test for the generally accepted $(3\cos^2\theta - 1)r^{-3}$ dependence of the observed isotropic shift in model lanthanide complexes. A simultaneous fit to both shift and line width data would significantly increase the confidence level of any structure determination. Analysis of line width data may also be at an advantage in cases where $(3\cos^2\theta - 1) \sim 0$, for ^{13}C spectra exhibiting contact shifts and in aqueous systems. A detailed evaluation of the method for solution structural deter-

(19) The line width ratios will be independent of the nature of the species in solution as long as the Gd-donor atom bond distance remains invariant; the dipolar shift ratios will be independent of the species only if the effective magnetic axis[20] coincides with the Eu-donor atom axis in all species.

(20) Caveats have been forwarded regarding the absence of static axial symmetry;[3,21,22] however, these objections may have been overemphasized.[5]

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(23) The natural line widths (4-pic, 2-H, 6.1 Hz; 3-H, 1.7 Hz; 4-Me, 1.2 Hz) were determined by extrapolation of the observed line width with added Eu(fod)$_3$ to the slightly altered position in the presence of Gd(fod)$_3$ and Eu(fod)$_3$. Corrections of 1 Hz for the second coordination sphere relaxations were made using benzene.

mination and the factors contributing to the line widths is in progress.[24]

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Evidence for a Norcaradiene–Bisnorcaradiene Rearrangement in a Di-π-methane System

Sir:

In a series of papers it has been shown that photolyses of diazocyclopentadiene (1) in benzene and its derivatives give spironorcaradienes (2)[1-5] (in equilibrium with their valence isomers 3) which can be isolated if the photolysis is carried out with a long-wavelength filter (λ >360 nm) and if careful work-up procedures are applied.[1-3] With Pyrex filters (λ >290 nm) 2 ⇌ 3 rearrange to benzocycloheptatrienes 4 and their 5-H isomers (5).[6] Two possible mechanisms have been proposed for this rearrangement: (1) a mechanism that is tantamount to a symmetry-allowed[7] [1,7]-sigmatropic shift (to 9) or (2) a di-π-methane rearrangement[8] (to 8). In this communication we report the successful isolation and identification of 6, a product which provides strong evidence for the intermediacy of the novel bisnorcaradiene 8.

A reinvestigation of the irradiation of 1 in benzene[6] using a more powerful Hg high-pressure lamp (Hanovia 450 W, Pyrex filter) showed that in addition to the products 4 and 5 isolated before, another benzocycloheptatriene 6 could also be obtained. The new product was isolated by chromatography of the photolysate on silica gel (petroleum ether–benzene, 7–25%:93–75%). The total yield of 6a + 4a was 65%. Separation could also be achieved by recrystallization from ethanol in which 4a is sparingly soluble.[9] The new benzocycloheptatriene 6a has the following physical properties: mp 102°; uv λ_{max} (CH$_3$CN) 275 nm (ϵ 34,000); ir (KBr) 2930, 1600, 1495, 1450, 765, and 698 cm^{-1}; ^{1}H nmr (CDCl$_3$) τ 2.5–3.3 (m, 25 H), 4.63 (s, 1 H); mass spectrum m/e 446 (M$^+$, base peak). On the basis of the chemical shift of the saturated proton (heptaphenylcycloheptatriene shows a one-hydrogen resonance at τ 4.73[10]) 6a appeared to be the most likely

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Scheme I
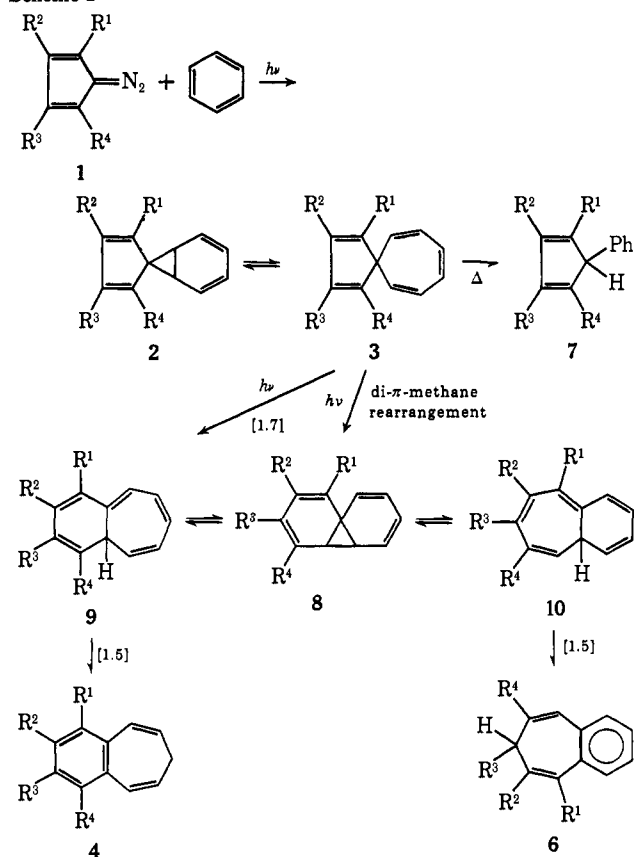
structure although **6a′** could not be rigorously excluded. Unambiguous distinction between these two possibilities was afforded by the nmr of the corresponding adduct **6b** from the reaction of 2,4-diphenylcyclopentadienylidene with benzene. **6b** has the following physical properties: mp 112–114°; ^{1}H nmr (CDCl₃) τ 2.3–2.9 (m, 14 aromatic H's), 3.03 (s, 1 H at C-5), 3.87 (t, $J = 7.5$ Hz, 1 H at C-8), and 7.18 (d, $J = 7.45$ Hz, 2 H at C-7); mass spectrum m/e 294 (M⁺, base peak). Both **6a** and **6b** gave satisfactory analyses.

6′
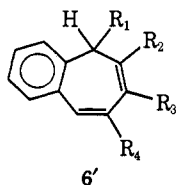
The results from photolyses of a number of diazocyclopentadienes (**1a–d**) in benzene are collected in Table I. The reported products are essentially stable to the photolysis conditions.

From Table I it can be seen that both temperature and substituents affect product formation with lower temperature favoring **4** relative to **6** and higher temperature introducing **7**, a product that has been found[11] to result from pyrolysis of **2** ⇌ **3**.

Thus, in the photoreaction at the higher temperature, **2** ⇌ **3** are apparently generated first photochemically and undergo competitive thermal rearrangement to **7** and photochemical rearrangement to ultimately give **4** and **6**. At lower temperatures only the photochemical rearrangement is observed. Products **4** and **6** from **2** ⇌ **3** are suggested to arise from [1.5] hydrogen migration in **9** and **10** with **9** and **10** interconverting *via*

(11) H. Dürr and H. Kober, *Tetrahedron Lett.*, 1255 (1972).

Table I. Temperature Dependence of Product Distribution in the Photolysis of **1** in Benzene

	R¹	R²	R³	R⁴	Temp, °C	Yield, % 4	6	7
a	Ph	Ph	Ph	Ph	2.5	82	18	a
					7	77	23	a
					37	69	31	a
					100	10	43	47 b
b	Ph	H	H	Ph	40	69	31	c
c	o-Phenylene		o-Phenylene		40	38^d	Trace	a
d	Cl	Cl	Cl	Cl	40	7^e	f	c

^{a} Obtained by nmr. ^{b} Reaction run at 1/100th standard scale; ratio obtained by glc. ^{c} Isolated products. ^{d} Mixture of **4c** and **5c**. ^{e} Predominantly **5d**. ^{f} Trichlorobenzotropylium chloride, **6d**, may have escaped detection due to possible instability to workup conditions.

the bisnorcaradiene **8**.[12] Substituent effects are accommodated by this scheme since chlorine as well as *o*-phenylene substituents (**1c** and **1d**) would be expected to shift an **8–9–10** equilibrium toward **9**.

The point of entry into the **8–9–10** manifold cannot be ascertained from the available data since both the di-π-methane and the [1,7]-sigmatropic rearrangements give the same products if **8**, **9**, and **10** equilibrate prior to hydrogen shift. However, whatever the point of entry, the successful isolation of **6** as well as **4** leaves little question but that photolysis of **2** ⇌ **3** is an effective entry into the bisnorcaradiene system **8**. This is an intriguing molecule not only because of its participation in the degenerate rearrangement of **9** and **10** but also because it might undergo an alternative degenerate
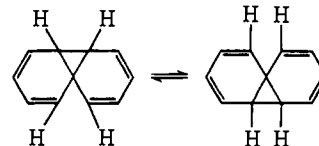
concerted antara–antara [5.5]-sigmatropic rearrangement, a mechanism that may be further encouraged by the destabilization predicted for the [5.5]spirarene formed by a diradical mechanism.[13]

Work on both degenerate rearrangements and substituent effects on these rearrangements is currently in progress.

(12) Although there are at least two other possible mechanisms that might be envisaged for interconversion of **9** and **10** which bypass **8**, neither would be expected to be competitive with either hydrogen migration or the norcaradiene rearrangement. Thus, a concerted [1,11]-sigmatropic rearrangement is thermally forbidden (interconversion of **9** and **10** occurs in the absence of light⁹) and reversible ring opening to the severely crowded *all-cis*-cycloundecahexaene (either by a concerted or a diradical mechanism) that could re-close to the rearranged product would hardly be expected to occur at temperatures as low as 3°.
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(14) National Science Foundation Science Faculty Fellow.
(15) On temporary leave from Tokyo University.

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