signals (**8e**,**8i**) other peaks in the spectrum were used.

Deuterium Incorporation. Samples were prepared as above, using TFA-*d* as solvent. The samples were heated at 100 °C, and the reaction monitored by ^{1}H NMR. **8h** was heated in TFA-*d*/D_2SO_4 (0.3 mL/1 μL) to an equilibrium mixture (about 3 h). The sample was analyzed by 250 MHz ^{1}H, ^{13}C, and ^{2}H NMR.

Registry No. **8a**, 98587-62-3; **8b**, 98587-64-5; **8c**, 98587-66-7; **8d**, 98587-68-9; **8e**, 98587-70-3; **8f**, 98587-72-5; **8g**, 98587-74-7; **8h**, 98587-76-9; **8i**, 98587-78-1; **9a**, 98587-80-5; **9b**, 98587-82-7; **9c**, 98587-84-9; **9d**, 98587-86-1; **9e**, 98587-88-3; **9f**, 98587-90-7; **9g**, 98587-92-9; **9h**, 98587-94-1; **9i**, 98587-96-3; PhNHMe, 100-61-8; O_2N-*p*-C_6H_4NHMe, 100-15-2; Cl-*p*-C_6H_4NHMe, 932-96-7; Me-*p*-C_6H_4NHMe, 623-08-5; MeO-*p*-C_6H_4NHMe, 5961-59-1; O_2N-*p*-C_6H_4CH=CHCHO-(*E*), 49678-08-2; Cl-*p*-C_6H_4CH=CHCHO-(*E*), 49678-02-6; PhCH=CHCHO-(*E*), 14371-10-9; Me-*p*-C_6H_4CH=CHCHO-(*E*), 56578-35-9; MeO-*p*-C_6H_4CH=CHCHO-(*E*), 24680-50-0.

Photochemical Transformations. 40. Syn and Anti Migration in Photo-Wagner-Meerwein Rearrangements[1,2]

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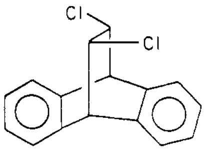
The photochemistry of the trans and cis isomers of 7,8-dichloro-2,3:5,6-dibenzobicyclo[2.2.2]octa-2,5-diene (**1** and **3**) has been explored. The singlet excited states of these compounds are photoactive. In acetonitrile, mixtures of *exo*- and *endo*-4,*anti*-8-dichloro-2,3:6,7-dibenzobicyclo[3.2.1]octa-2,6-diene (**2**-Cl), the *syn*-8-chloro epimers *exo*- and *endo*-**4**-Cl, *N*-(*anti*-8-chloro-2,3:6,7-dibenzobicyclo[3.2.1]octa-2,6-dien-*exo*-4-yl)acetamide (**2**-NHAc) and its *syn*-8-chloro epimer *exo*-**4**-NHAc were produced. In acetic acid, the dichloro compounds and a mixture of the *anti*- and *syn*-8-chloro-2,3:6,7-dibenzobicyclo[3.2.1]octa-2,6-dien-*exo*-4-yl acetates (**2**-OAc and **4**-OAc) were produced. In cyclohexane, irradiation of **2** gave the dichlorides epimeric at C-4 and C-8. All of the photoreactions proceeded with a preponderance of migration with retention at the migration terminus (syn migrations), in contrast to the ground-state reactions which proceed with clean inversion at the migration terminus (anti migration). Failure to see stereospecificity was shown not to be due to C-8 bridge migration. Quantum yields for the various reactions are reported. The results are discussed in terms of several reaction channels following excitation and electron transfer. Radical reductive monodechlorinations of **1** and **3** lead to stereoconvergent radical rearrangements. The syntheses of **2**-NHAc and **4**-NHAc by Ritter reactions from **2**-OAc and **4**-OAc respectively are described.

In the past few years, it has become apparent that the stereochemistry of photo-Wagner–Meerwein rearrangements is quite different from that of ground-state analogues. Ground-state rearrangements proceed, in general, with clean migration of groups anti to the nucleofuge. In the photochemical analogues, except in special cases,[3] syn (suprafacial) migrations are preferred over anti (antarafacial). Thus, for example, treatment of **1** with silver acetate in acetic acid leads cleanly, via anti migration, to **2**-OAc and that of the cis epimer **3** leads cleanly to **4**-OAc.[4]



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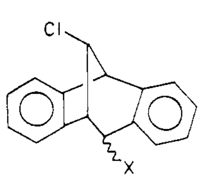

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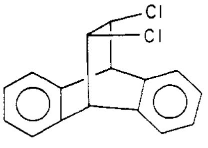

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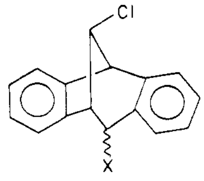

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On the other hand, as described in the preliminary communication[2] and as reported in detail here, direct irradiation of **1** with 254-nm light leads to a mixture containing approximately 75% of **4**-Cl and **4**-OAc (syn migration) products and 25% of the anti migration products **2**-Cl and **2**-OAc. (A simultaneous photolysis of **1** and *endo*-**4**-Cl showed that the solvolysis rearrangement of the nonbenzylic species **1** occurs more rapidly.) Similarly, irradiation of **3** gives about 75% of the syn migration products **2**-Cl and **2**-OAc and 25% of the anti migration products **4**-Cl and **4**-OAc. Data of a similar nature have been reported for cis and trans dichlorides[5] where one of the rings is substituted, that is the 2,3-naphtho–benzo and 2,3-veratro–benzo systems, with systems with nucleofugal groups other than chlorine[1] and for a monobenzobicyclooctadienyl system.[6]

Evidence has been adduced that these reactions proceed via an excited intramolecular electron-transfer state such as **5** or **6**, whose decay may follow either or both of two speculated modes. In the first of these, loss of chloride ion (or other nucleofuge) prior to migration gives the biradical cation **7**, for which stereospecific migration is not demanded (but can be allowed) and which therefore allows for migration of either the electron-deficient ring (denoted by Y) or the "normal" ring. A second process[5] assumes a suprafacial (syn) migration concerted with fragmentation

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[1] Previous paper in series: Cristol, S. J.; Aeling, E. O. *J. Org. Chem.* **1985**, *50*, 2698. A portion of this work was described in a preliminary communication.[2]

[2] Cristol, S. J.; Opitz, R. J.; Bindel, T. H.; Dickenson, W. A. *J. Am. Chem. Soc.* **1980**, *102*, 7977.

[3] Cristol, S. J.; Ali, M. Z. *Tetrahedron Lett.* **1983**, *24*, 5839.

[4] Cristol, S. J.; Parungo, F. P.; Plorde, D. E. *J. Am. Chem. Soc.* **1965**, *87*, 2870.

[5] Cristol, S. J.; Seapy, D. G.; Aeling, E. O. *J. Am. Chem. Soc.* **1983**, *105*, 7337.

[6] Cristol, S. J.; Dickenson, W. A.; Stanko, M. K. *J. Am. Chem. Soc.* **1983**, *105*, 1218.

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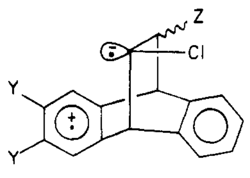

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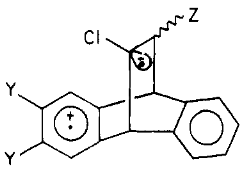

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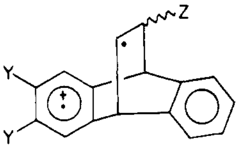
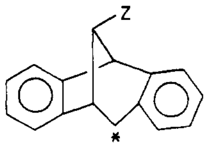


7

of **5** and/or **6**. Combination of these two processes would allow for the partial scrambling of products, that is, for the stereoselectivity rather than stereospecificity observed in these reactions.

While these two decay modes rationalize all the data accumulated in our laboratory, failure to observe stereospecificity may be rationalized in other manners. For example, one may surmise that some later-stage intermediate, such as **8**, intervenes, in which the asterisk denotes



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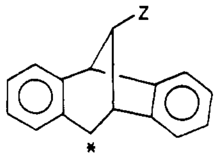


9

the "active" site, i.e., cationic or radical.[7] This might then suffer rearrangement to **9** by a 1,2-migration of the C-8 one-carbon bridge from C-5 to C-4.[8] This assumption is readily testable by use of appropriately labeled species.

This paper reports data (product ratios and quantum yields) on direct irradiations of **1** and **3** in three solvents (acetonitrile, acetic acid, and cyclohexane) and an attempted sensitization in acetone and, in addition, reports results on analogous compounds labeled with deuterium at C-1 and C-4. The labeling experiments show that the **8** $\rightleftharpoons$ **9** interconversion suggested above does not occur. In addition, synthesis of **2**-NHAc and **4**-NHAc by Ritter reactions (ground state) are described, as are the radical monodechlorinations of **1** and **3**.

Results

Direct irradiation of **1** in acetonitrile with 254-nm light led to four dichloride rearrangement products and to two amide products in measurable yield. The quantum yield for the syn rearrangement dichlorides **4**-Cl was 0.105, while that for the anti epimers **2**-Cl was 0.033. Our gas chromatography analytical method did not separate exo and endo epimers nor include analysis of the amide solvolysis products. A large-scale reaction indicated that the **2**-Cl and the **4**-Cl mixtures contained approximately equal amounts of exo and endo epimers and that the rearranged dichloride to amide ratio was 68:32. Of the 32% amide produced, 24% was the syn-8-chloro compound *exo*-**4**-NHAc and 8% was the anti-8-chloro compound *exo*-**2**-NHAc. No endo amides were seen. Thus the quantum yield for **4**-NHAc was approximately 0.049 and that for **2**-NHAc was 0.016. The ratio of syn-8-chloro products (syn migration) to anti-8-chloro products was 3:1 for both the dichloride return product and for the amide solvolysis product. The data are collected in Table I.

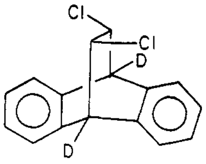
Similar experiments were conducted with the cis dichloride **3** in acetonitrile and with both **1** and **3** in acetic acid. These data are also collected in Table I.

The fraction of reaction leading to solvolysis varies from 0.21 to 0.5, but, as these values are taken from experiments in which most of the starting material had been photoreacted, a portion of the amide or acetate products came from rearranged dichlorides. Thus we are unable to comment in a significant fashion on the values for the fractions of solvolysis reported. However, it is known[11] that photosolvolysis of **2**-Cl gives only **2**-NHAc or **2**-OAc and that of **4**-Cl gives only **4** species, so that the sum of the syn-8-chloro and anti-8-chloro products is meaningful. Thus one notes that **1** gives, in a ratio of 3:1 to 4:1, a preponderance of syn-8-chloro (**4**) products (i.e., syn migration preferred) and **3** gives, in similar ratios, a preponderance of anti-8-chloro (**2**) products (likewise, syn migration preferred).

In cyclohexane, **1** reacted slowly upon irradition to give **4**-Cl ($\phi \simeq 0.03$) and **2**-Cl ($\phi \simeq 0.005$). There was significantly greater loss of starting material, but the side reaction products were not investigated. **3** was too insoluble in cyclohexane to study.

Irradiation of either **1** or **3** in acetone with 300-nm light did not result in reaction, even upon extensive irradiation. When **3** was irradiated in acetonitrile in the presence of 0.1 M *cis*-piperylene, no quenching of rearrangement was observed. These experiments provide evidence that the reactions occur from the excited singlet state rather than from a quenchable triplet state. However, *trans*-piperylene was formed in a quantum yield of 0.04, suggesting[12] that a portion of the energy wastage in this system occurs by intersystem crossing to a nonreactive triplet. As the triplet of piperylene decays almost equally to both *cis*- and *trans*-piperylene,[12] the intersystem crossing quantum yield was about 0.08.

In order to test for the possibility that the lack of stereospecificity in the photoreactions was due to a C-8 bridge migration, that is **8** $\rightleftharpoons$ **9**, we prepared compound **10**, the 1,4-dideuterio analogue of **1**. Dideuterioanthracene was prepared[13] by treatment of 9,10-dilithioanthracene with deuterium oxide. Mass spectral analysis indicated that



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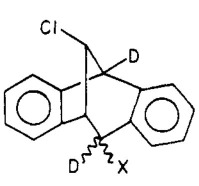

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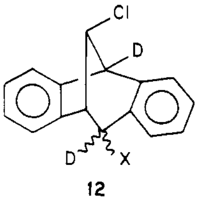

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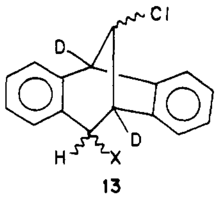

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[7] In the latter case, one of the rings would be a radical cation.

[8] Such a process is known to occur only with considerable rarity in ground-state processes[1,9,10] but presumably could occur with electronically or vibrationally hot species.

[9] Cristol, S. J.; Bopp, R. J. *J. Org. Chem.* **1974**, *39*, 1336.

[10] (a) Cristol, S. J.; Parungo, F. P.; Plorde, D. E.; Schwarzenbach, K. *J. Am. Chem. Soc.* **1965**, *87*, 2879. (b) Cristol, S. J.; Caple, R.; Sequeira, R. M.; Smith, L. O., Jr. *Ibid.* **1965**, *87*, 5679.

[11] Opitz, R. J. Ph.D. Dissertation, University of Colorado, Boulder, 1980.

[12] Lamola, A. A.; Hammond, G. S. *J. Chem. Phys.* **1965**, *43*, 2129.

[13] Pawliczek, J. B.; Gunther, H. *Tetrahedron* **1970**, *26*, 1755.

Table I. Rearrangement and Solvolysis Product Quantum Yields on 254-nm Irradiation of Dichlorides

		quantum yield of product					fraction of solvolysis product
compd irradiated	solv	2-Cl	4-Cl	2-Z[a]	4-Z[a]	ratio of 2:4	
1	CH_3CN	0.033 ± 0.004[b]	0.105 ± 0.006[b]	0.016[c]	0.049[c]	0.32	0.32
3	CH_3CN	0.085 ± 0.002[b]	0.027 ± 0.006[b]	0.98[c]	0.014[c]	4.7	0.50
1	HOAc	0.018[b]	0.088[b]	0.006[d]	0.040[c]	0.19	0.31
3	HOAc	0.054[b]	0.024[b]	0.019[e]	0.002[d]	2.8	0.21
1	cyclohexane	0.005	0.029			0.2	

[a] Z = NHAc when solvent is CH_3CN: Z = OAc when solvent is HOAc. [b] Approximately 50:50 exo–endo. [c] Substantially all exo. [d] Peak too small to see any endo epimers. [e] About 95% exo.

the product contained approximately 75% of 9,10-dideuterioanthracene, 25% of 9-deuterioanthracene, and no undeuterated material; this product was sufficient for our purpose. Treatment with *trans*-1,2-dichloroethene gave **10** (contaminated, of course, with some monodeuterated material). **10** was irradiated in acetic acid, and the product was separated by column chromatography into dichloride and acetate fractions. Proton NMR data on the dichloride fraction indicated that the absorbances at C-1 (back bridgehead) and C-4 (benzylic position) were only about 15% as intense as those for other protons for both the **2**-Cl and the **4**-Cl analogues **11**-Cl and **12**-Cl, respectively, without any perceptible decrease in the absorbances at C-5. Thus most, if not all, of the deuterium in these molecules was as anticipated for a process without **8** → **9** scrambling; that is, there was no evidence for **13**-Cl. The acetate fractions similarly showed an intensity about 15% of that of normal for the protons at C-1 and C-4 for the **2**-OAc and **4**-OAc analogues, without any measurable decrease at C-5. The proton NMR spectra were not accurate enough to rule out a small amount of **8** → **9** scrambling (although they do rule this out as the major process for the formation of the minor isomer), and we therefore subjected the acetate mixture to deuterium NMR analysis.

Unfortunately the H-5 absorbance occurs at about δ 3.7 and that of H-1 at about δ 4.1 in both **2**-OAc and **4**-OAc, so that a small deuteron absorbance at C-5 (that is, for **13**-OAc) would be obscured by the large broad absorbance of the C-1 deuteron. Use of the lanthanide shift reagent $Eu(fod)_3$[14] cleanly separated the resonances due to protons (or deuterons) at C-1, C-4, and C-5. No absorbance ascribable to a deuteron at C-5 was detected. It is thus clear that no **8** ⇌ **9** scrambling to give **13**-OAc occurred in the photochemical reaction.

The azobisisobutyronitrile-promoted reaction of **1** and **3** with tri-*n*-butyltin hydride[15] was carried out to see if radical intermediates could be involved (although they could hardly account for solvolysis products). **1** gave, along with carbon-skeleton unrearranged monochloride, a 40:60 mixture of **2**-H and **4**-H. Similar treatment of **3** gave a 35:65 mixture. These results are identical within our limits of error, demonstrating that radical reactions are stereoconvergent.

Conclusions

Unlike the ground-state solvolysis reactions of **1** and **3**, which proceed via clean anti (antarafacial) Wagner–Meerwein rearrangement,[4] irradiations in acetonitrile and acetic acid lead to photo-Wagner–Meerwein rearrangement and photosolvolyses with rearrangement in which, for each isomer, the principal migration is syn (suprafacial) but in which there is a large component of anti (antarafacial) migration. The reactions involve the excited singlet state; the triplets are unreactive. The minor products (those of anti migration) are not the result of a C-8 bridge migration on the reaction path(s). The results require two reaction paths, one of which involves a 1,2-migration with retention of configuration at the migration terminus and one which allows inversion or a combination of inversion and retention. These results are consistent with ideas proposed previously,[5] in which electron transfer occurs from the π,π^* excited state to give the zwitterion **5** or **6**, which, on the one hand, may lose chloride ion prior to rearrangement to give a biradical cation **7**, which allows both syn and anti migration. The zwitterion, on the other hand, may suffer syn migration concerted with loss of chloride. This process gives the major product in both the solvolysis and the ion pair return processes.

It is of interest that the ion pair return process leads to substantial amounts of exo and endo dichloride, while the solvolyses lead preferentially to exo amide to to exo acetate. The exo acetates are also produced almost exclusively in ground-state reactions,[4] as are the exo amides. One therefore may assume that by the time the solvent-separated ion pair stage is reached in the photoreaction, the cationic portion is similar to (or identical with) the ground-state cation. It may also be inferred that the epimerization reaction occurs at the intimate ion pair stage, and that the rate of interconversion between the epimeric ion pairs and ion recombination is comparable with that of conversion of the intimate ion pair to the solvent-separated ion pair.

The results in cyclohexane deserve some comment. It is of interest that Wagner–Meerwein rearrangement with principal syn migration occurs in this solvent as well, although in lower quantum and chemical yields than in the more polar solvents. That radicals are not involved, even in cyclohexane, may be inferred by a comparison of the photochemical results in cyclohexane with those of the free-radical reduction in benzene. Formation of ionic products, that is, fragmentation into chloride ion and an excited-state cation, even in cyclohexane, is consistent with recent results found by Peters[16] on the photochemistry of triphenylchloromethane in hydrocarbon solvents.

Experimental Section

^1H NMR spectra were determined at 60 or 90 MHz with Me_4Si as internal reference. ^2H NMR spectra were determined on a JEOL PFT-100 NMR spectrometer operating in the Fourier transform mode, with $CDCl_3$ as internal reference and C_6F_6 as internal lock. Mass spectra were obtained with a Varian MAT CH-5 or CH-7 spectrometer.

Large-scale and NMR-scale irradiations were done in a Rayonet Srinivasan-Griffin reactor equipped with either 254- or 300-nm lamps. Quantum-yield irradiations were done in a similar reactor at 254 nm with a merry-go-round apparatus.[17] Irradiations were done in quartz (254 nm) or Pyrex (300 nm) tubes. Quantum-yield

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[14] Jensen, H.; Schaumburg, K. *Acta Chem. Scand.* **1971**, *25*, 663.

[15] Kuivila, H. J. *J. Org. Chem.* **1960**, *25*, 284; *J. Am. Chem. Soc.* **1966**, *88*, 571.

[16] Peters, K. S., private communication.

[17] Cristol, S. J.; Micheli, R. P. *J. Am. Chem. Soc.* **1978**, *100*, 854.

samples were degassed prior to irradiation with four freeze–pump–thaw cycles. Other samples were deoxygenated with N_2 bubbling.

Quantum-yield analyses were done with a Hewlett-Packard 5750 gas chromatograph (GC) with a flame-ionization detector and 3 m × 2 mm glass low-coated Carbowax column. Octadecane was used as a GC reference. For quantum yields in CH_3CN and HOAc, this was added as an aliquot in $CHCl_3$ after irradiation and before any further treatment. All GC analyses were triple replicates. The column used for determination of *trans*-1,3-pentadiene was a β,β'-oxybispropionitrile aluminum column.

Cyclopentanone actinometry[18] samples, run simultaneously with quantum-yield samples, were analyzed on a 2 m × 3 mm 10% UC-W98 stainless steel column, with *n*-nonane as an internal standard.

Acetonitrile was distilled from CaH_2 prior to use. HOAc and cyclohexane were used without purification.

Dry-column chromatography[19] was used for separations in large-scale irradiations. Woelm silica gel was used in a nylon column. Fractions were found by examination with UVS-11 Mineralight, cut, and extracted. Extraction residues after evaporation of solvent were weighed and analyzed by NMR.

Identification of substituted dibenzobicyclo[3.2.1]octa-2,6-dienes (2 and 4) was based upon comparisons of spectral data with similar data on authentic compounds.[20]

***trans*- and *cis*-7,8-dichloro-2,3:5,6-dibenzobicyclo[2.2.2]-octa-2,5-diene (1 and 3)** were prepared as described by Cristol and Hause.[21] The crude products were dissolved in $CHCl_3$ and washed repeatedly with concentrated H_2SO_4, followed by water and saturated $NaHCO_3$ washes. After the $CHCl_3$ was removed by distillation, recrystallization from hexanes (for 1) or from $CHCl_3$/hexanes (for 3) gave products with physical properties identical with those already described.[20,21]

Direct Irradiation of 1 in Acetonitrile. A solution of 785 mg (2.85 mmol) of 1 in 25 mL of CH_3CN was irradiated at 254 nm for 2.3 h. Water was then added, and the solution was extracted several times with ether. The solvents were evaporated from the combined organic layers, and the residue was separated by dry-column chromatography (70-cm column) with 5% ether/hexanes as eluent. One fraction, R_f 0.6, consisted (by NMR analysis) of approximately 60% starting material, 15% *exo*-4-Cl,[20,22] 20% *endo*-4-Cl,[20,22] 5% *exo*-2-Cl,[20,23] and a trace of *endo*-2-Cl. The amount of this fraction was 1.75 mmol. A fraction at the origin contained 0.33 mmol of amides. NMR analysis indicated approximately 75% of *exo*-4-NHAc and 25% of *exo*-2-NHAc.

***endo*-4,*anti*-8-Dichloro-2,3:6,7-dibenzobicyclo[3.2.1]octa-2,6-diene (*endo*-2-Cl)** was prepared from 1.96 g (7.6 mmol) of the corresponding exo alcohol 2-OH[4] in 50 mL of a 1:1 (vol) mixture of CH_3CN and CCl_4 with 4.10 g (15.6 mmol) of Ph_3P. After 5 h, the solvent was removed by evaporation. The resulting oil was separated by dry-column chromatography, using 10% ether in hexanes to develop the column. The fraction having R_f 0.6–0.8 was extracted with ether to give 1.59 g of a mixture of ca. 80% *endo*- and 20% *exo*-2-Cl. Recrystallization from hexane gave 1.13 g (54%) of *endo*-2-Cl: mp 110–112 °C; ^1H NMR ($CDCl_3$) δ 7.1–7.6 (8 H, m, Ar), 5.60 (1 H, d, H-4, $J_{4,5} = 5$ Hz), 4.65 (1 H, s, H-8), 4.15 (1 H, s, H-1), 3.95 (1 H, d, H-5, $J_{5,4} = 5$ Hz). Anal. Calcd for $C_{16}H_{12}Cl_2$: C, 69.84; H, 4.40. Found: C, 69.93; H, 4.43.

In a trial run using tris(dimethylamino)phosphorus[24] in carbon tetrachloride, rather than triphenylphosphine, almost pure *endo*-2-Cl was produced in the displacement reaction.

Preparation of *N*-(*anti*-8-Chloro-2,3:6,7-dibenzobicyclo-[3.2.1]octa-2,6-dien-*exo*-4-yl)acetamide (*exo*-2-NHAc). To a solution of 340 mg (1.1 mmol) of 2-OAc[4] in 10 mL of CH_3CN was added 0.2 mL of concentrated H_2SO_4. The solution was heated at reflux for 91 h. After the solution was cooled, water and $CHCl_3$ were added. The layers were separated, and the aqueous layer was washed with $CHCl_3$ until a cloudy precipitate was no longer visible. The combined chloroform layers were then washed twice with water, once with saturated aqueous $NaHCO_3$, once with saturated aqueous NaCl, and dried ($MgSO_4$). Evaporation of the solvent gave 260 mg (77%) of *exo*-2-NHAc. Recrystallization from acetone gave 100 mg of white solid: mp 298–300 °C; ^1H NMR (Me_2SO-d_6) δ 8.75 (1 H, d, NH, $J_{N,4} = 9$ Hz), 7.1–7.5 (8 H, m, Ar), 5.15 (1 H, s, H-8), 5.05 (1 H, dd, H-4, $J_{4,N} = 9$ Hz, $J_{4,5} = 2$ Hz), 4.35 (1 H, s, H-1), 3.5 (1 H, d, H-5, $J_{5,4} = 2$ Hz), 2.0 (3 H, s, CH_3). Anal. Calcd for $C_{18}H_{16}ClNO$: C, 72.60; H, 5.42. Found: C, 72.54; H, 5.60.

Preparation of *N*-(*syn*-8-Chloro-2,3:6,7-dibenzobicyclo-[3.2.1]octa-2,6-dien-*exo*-4-yl)acetamide (*exo*-4-NHAc). A solution of 1.22 g (4.1 mmol) of 4-OAc,[4] 0.5 mL of water, and 1.1 mL of concentrated H_2SO_4 in 50 mL of CH_3CN was heated at reflux for 20 h. Workup as above (CH_2Cl_2 as solvent) gave 1.15 g (94%) of *exo*-4-NHAc: mp 186.5–193.5 °C. Recrystallization from methylene chloride/hexanes gave 590 mg (48%): mp 199.5–200.5 °C; ^1H NMR (Me_2SO-d_6) δ 8.15 (1 H, d, NH, $J_{N,4} =$ 8 Hz), 7.1–7.4 (8 H, m, Ar), 5.05 (1 H, H-8, t, $J_{8,1} = J_{8,5} = 5$ Hz), 4.90 (1 H, d, H-4, $J_{4,N} = 8$ Hz), 4.25 (1 H, d, H-1, $J_{1,8} = 5$ Hz), 3.55 (1 H, d, H-5, $J_{5,8} = 5$ Hz), 2.0 (3 H, s, CH_3). Anal. Calcd for $C_{18}H_{16}ClNO$: C, 72.60; H, 5.42. Found: C, 72.77; H, 5.60. Additional crops from concentration of the mother liquor gave an additional 350 mg of *exo*-4-NHAc, for a total of 940 mg (77%).

Quantum Yields of the Direct Irradiation of 1 in Acetonitrile. Two determinations were done. In the first, 51.4 mg (0.19 mmol) of 1 was dissolved in 10 mL of CH_3CN. Aliquots of 2 mL were irradiated at 254 nm for 2 h and analyzed by gas chromatography. For the second determination, dichloride 1 (46 mg, 0.17 mmol) was treated identically, with 1.5 h of irradiation. Results are recorded in Table I.

Direct Irradiation of 3 in Acetonitrile. Dichloride 3 (60 mg, 2.18 mmol) was dissolved in acetonitrile (50 mL) and irradiated at 254 nm for 2.2 h. The irradiation solution was worked up as with 1 above. A fraction with $R_f \sim 0.6$ contained 0.80 mmol of various dichlorides. NMR analysis showed 24% *exo*-2-Cl, 24% *endo*-2-Cl, 8% *exo*-4-Cl, and 8% *endo*-4-Cl, with the remainder being starting material. Another fraction, 0.12 mmol, was about two-thirds *exo*-4-Cl. The origin fraction contained 0.59 mmol of amides. NMR analysis showed an 8:1 mixture of *exo*-2-NHAc and *exo*-4-NHAc.

Quantum Yields of the Direct Irradiation of 3 in Acetonitrile. Two determinations were done. For the first, 55.1 mg (0.20 mmol) of 3 was treated as described above for 1, with 1.75 h of irradiation. For the second determination, 43.2 mg (0.16 mmol) of 3 was irradiated for 1.5 h. Results are given in Table I.

Direct Irradiation of 1 in Acetic Acid. A solution of 856 mg (3.11 mmol) of 1 in 25 mL of HOAc was irradiated at 254 nm for 2.7 h. The irradiated solution was dissolved in ether, washed with water, saturated aqueous $NaHCO_3$, and saturated aqueous NaCl, and dried ($MgSO_4$). The products were separated by dry-column chromatography with 10% ether/hexanes. The fraction with R_f 0.8 contained 1.61 mmol of dichlorides and consisted of 70% starting material. The remainder was *exo*-4-Cl, *endo*-4-Cl, and *exo*-2-Cl, in a 3:3:2 ratio. A fraction with R_f 0.4 contained 0.24 mmol of acetate, with about 75% being *exo*-4-OAc[4] and the remainder being equal amounts of *exo*-2-OAc[4] and *endo*-4-OAc.[4] An intermediate fraction contained 0.05 mmol of *exo*-4-Cl and 0.03 mmol of *exo*-2-OAc.

Quantum Yields of the Direct Irradiation of 1 in Acetic Acid. A solution of 51.0 mg (0.19 mmol) of 1 in 10 mL of HOAc was prepared and 2-mL aliquots were irradiated at 254 nm for 1.5 h. After irradiation, a standard octadecane solution (in $CHCl_3$) was added. $CHCl_3$ and water (several milliliters each) were added and the layers separated. The aqueous layer was washed once with chloroform. The combined organic layers were washed with water and saturated aqueous $NaHCO_3$, and dried ($MgSO_4$). The resulting solutions were analyzed by GC. Results are given in Table I.

Direct Irradiation of 3 in Acetic Acid. A solution of 500 mg (1.82 mmol) of 3 in 100 mL of HOAc was irradiated at 254 nm for 2.8 h. This was worked up as described for 1 above. A

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Table II

$Eu(fod)_3$ added, mmol	$Eu(fod)_3$/4-OAc, M/M	chemical shifts, δ					
		CH_3	H-1	H-4	H-5	H-8	H_{ortho}
0	0	2.2	4.1	5.8	3.75	4.85	7.5
0.006	0.09	2.85	4.25	7.05	4.5	5.0	7.65
0.016	0.24	4.05	4.45	9.15	5.7	5.3	8.35
0.029	0.43	5.3	4.7	11.3		5.6	9.1

Table III

$Eu(fod)_3$ added, mmol	$Eu(fod)_3$/2-OAc, M/M	chemical shifts, δ					
		CH_3	H-1	H-4	H-5	H-8	H_{ortho}
0	0	2.15	4.15	6.05	3.7	5.0	7.55
0.005	0.07	2.75	4.25	7.0	4.2	5.25	7.6
0.014	0.21	3.7	4.5	8.55	5.0	5.7	8.2
0.026	0.38	4.9	4.7	10.5	5.95	6.2	8.95

dry-column chromatography fraction with R_f 0.8 was 0.30 mmol of mixed dichlorides, with one-third starting material and two-thirds products. A fraction with R_f 0.7 was 0.33 mmol of a similar mixture, with 40% starting material and 60% products. The products in combined fractions were a mixture of *exo*-**2**-Cl, *endo*-**2**-Cl, *exo*-**4**-Cl, and *endo*-**4**-Cl in a 3:3:1:1 ratio. A fraction with R_f 0.6 was 0.23 mmol pure *exo*-**2**-OAc, while a fraction with R_f 0.4 contained 0.25 mmol of a mixture of 80% *exo*-**2**-OAc and 20% *exo*-**4**-OAc.

Quantum Yields of the Direct Irradiation of 3 in Acetic Acid. A solution of 27.4 mg (0.10 mmol) of **3** in 10 mL of HOAc was treated as compound **1** above, with 1.3 h of irradiation. Only the starting material and **2**-Cl and **4**-Cl could be determined accurately by GC. The quantum yields of the acetates reported in Table I are based on these quantum yields and the ratios observed in the larger irradiation.

Sensitized Irradiation of 1 and 3 in Acetone. A solution of 1.08 g (3.9 mmol) of **1** in 35 mL of acetone was irradiated at 300 nm. Samples were taken after 10, 34, and 104 h and were analyzed by thin-layer chromatography. Only the starting material and, after long irradiation, a brown spot at the origin were seen. No indication of the possible rearranged compounds was seen.

A similar experiment was conducted with a solution of 1.02 g of **3** in 70 mL of acetone, which gave similar results.

Sensitized Irradiation of 1 in Dilute Acetone. A solution of 29 mg (0.11 mmol) of **1** in 1 mL of 5% acetone-d_6 in acetonitrile-d_3 was irradiated at 300 nm. NMR spectra were run at the start and after 22 h and 4 and 11 days. The spectra were all identical (with that of **1**).

Quantum Yields of the Direct Irradiation of 1 in Cyclohexane. Dichloride **1** (51.4 mg, 0.19 mmol) and octadecane (14.2 mg, 0.056 mmol) were dissolved in 10 mL of cyclohexane and 2-mL aliquots were irradiated at 254 nm for 1.9 h. The samples were analyzed by gas chromatography. Results are given in Table I.

Quantum Yields of the Direct Irradiation of 1 in Acetonitrile with Added *cis*-1,3-Pentadiene. An 0.103 M solution of *cis*-1,3-pentadiene was prepared from 176 mg (2.58 mmol) of diene and 25 mL of acetonitrile. A solution of 50.4 mg (0.18 mmol) of **1** in 10 mL of this solution was prepared, and 2-mL aliquots were irradiated at 254 nm for 1.2 h. After irradiation, the samples were analyzed by gas chromatography. The quantum yield for **4**-Cl was 0.110 and that for **2**-Cl was 0.025.

Gas chromatographic analysis of the 1,3-pentadiene showed that 2.31×10^{-6} mol of *trans*-1,3-pentadiene was produced (light flux, 5.77×10^{-5} einstein), for a quantum yield of 0.040.

Simultaneous Direct Irradiation of 1 and *endo*-4-Cl. Solutions of 27.2 mg (0.10 mmol) of **1** and 26.4 mg (0.10 mmol) of *endo*-**4**-Cl in 1 mL of acetic acid-d_4 were prepared and irradiated simultaneously at 254 nm. The reactions were followed by NMR, with spectra taken after 1.3 and 3.0 h. After 1.3 h, the NMR of the sample of **1** indicated that approximately 75–80% of the starting material had reacted. Present were *exo*-**4**-Cl, *endo*-**4**-Cl, and *exo*-**4**-OAc. NMR analysis of the *endo*-**4**-Cl reaction showed that about 85% of starting material remained; some *exo*-**4**-Cl was visible. After 3 h, **1** was almost completely reacted. The other reaction mixture consisted of two-thirds starting material and one-third *exo*-**4**-Cl and solvolysis product *exo*-**4**-OAc combined.

Preparation of 9,10-Dideuterioanthracene from 9,10-Dibromoanthracene. The procedure used was a modification of that of Pawliczek and Gunther.[13] The yield after recrystallization was 39%: mp 214.5–217 °C; ^1H NMR ($CDCl_3$) δ 8.45 (0.26 H, s, H-9, H-10), 8.05 (4 H, dd, J = 7, 3 Hz), 7.5 (4 H, dd, J = 7, 3 Hz); mass spectrum, m/e (relative intensity) 178 (10), 179 (31), 180 (100), 181 (16).

1,4-Dideuterio-*trans*-7,8-dichloro-2,3:5,6-dibenzobicyclo[2.2.2]octa-2,5-diene (10) was prepared from 1.26 g (7.0 mmol) of 9,10-dideuterioanthracene and 5 mL (6.3 g, 65 mmol) of *trans*-1,2-dichloroethene, as described for **1**.[21] This gave 1.0 g of white crystals of **10**: mp 112–114 °C; ^1H NMR ($CDCl_3$) δ 7.5–7.2 (8 H, m, Ar), 4.4 (0.34 H, br s, bridgehead), 4.15 (2 H, s, bridge); mass spectrum, m/e (relative intensity) 275 (2.3), 276 (5.4), 277 (2.9), 278 (3.9). The NMR data indicated that the product contained about 17% hydrogen and 83% deuterium at the bridgehead positions. The mass spectral data indicated that the product was approximately 70% dideuterated and 30% monodeuterated. The absence of a significant peak at m/e 274 indicated that there was essentially no undeuterated material.

Direct Irradiation of 10 in Acetic Acid. A solution of 685 mg (2.47 mmol) of **10** in 25 mL of HOAc was irradiated at 254 nm for 3 h. After irradiation, the product was worked up as described above for **1** to give 608 mg of an oil.

Dry-column chromatography (developed with 10% ether/hexanes) led to several fractions. One fraction, R_f 0.9–1.0, weighed ca. 475 mg and contained **10** as the major component. However, ^1H NMR showed the presence of deuterated *endo*-**4**-Cl and *exo*-**2**-Cl. The H-4 peaks at δ 5.75 and 5.25 and that for H-1 of *endo*-**4**-Cl were only 15% as large as those for undeuterated chlorides. The H-1 peak for *exo*-**2**-Cl was hidden under a starting material peak, so that its presence was not confirmed.

Three acetate fractions were isolated, weighing 23, 28, and 11 mg. The latter two consisted, by NMR analysis, almost entirely of *exo*-**4**-OAc, while the first also contained *exo*-**2**-OAc. For both products, the intensity of the absorbances for H-1 and H-4 were only 15% of those for undeuterated peaks.

^2H NMR spectra were run on these samples. The chloride sample showed four peaks: δ 5.81 (D-4 of *endo*-**4**-Cl), 5.20 (D-4 of *exo*-**2**-Cl), 4.47 (D-1 and D-4 of **10**), and 4.22 (D-1 of *endo*-**4**-Cl and *exo*-**2**-Cl). The combined acetate sample showed two peaks: δ 5.78 (D-4 of *exo*-**2**-OAc and *exo*-**4**-OAc) and 4.09 (D-1 of *exo*-**2**-OAc and *exo*-**4**-OAc). $Eu(fod)_3$ (0.057 mmol) shift reagent[14] was added. Three absorbances were seen: δ 11.09 (D-4 of *exo*-**4**-OAc), 9.88 (D-4 of *exo*-**2**-OAc about 33% as intense as the δ 11.09 absorbance), and 4.70 (D-1 of both compounds). No other peaks were seen.

NMR Shift Reagent Study of *exo*-4-OAc. Increasing amounts of $Eu(fod)_3$ shift reagent[14] were added to a solution of 19.9 mg (0.067 mmol) of *exo*-**4**-OAc in 1 mL of $CDCl_3$, with ^1H NMR spectra taken before and after each addition. The chemical shifts of the protons are shown in Table II.

NMR Shift Reagent Study of *exo*-2-OAc. A solution of 20.2 mg (0.068 mmol) of *exo*-**2**-OAc in 1 mL of $CDCl_3$ was treated as above. The results are shown in Table III.

Tri-*n*-butyltin Hydride Reduction of 1 and 3. A solution of 277 mg (1.01 mmol) of **1**, 379 mg (1.30 mmol) of tri-*n*-butyltin hydride, and 28 mg of azobisisobutyronitrile in 40 mL of benzene was heated at reflux for 16 h. CCl_4 (3 mL) was then added, to quench the reaction. The solvent was evaporated, and the mixture was purified by dry-column chromatography using 3% ether/hexanes as the developer. The fraction with R_f 0.7 was excised and extracted with ether and was found, by NMR analysis, to contain starting material and products. No other fraction contained significant amounts of these materials. Column chromatography did not effect separation of these compounds, but it did remove much of the tri-*n*-butyltin chloride produced. Four compounds were present (in addition to the tin chloride): starting material 1, 7-chloro-2,3:5,6-dibenzobicyclo[2.2.2]octa-2,5-diene, 2-H, and 4-H. The absorbances for the protons at C-8 in 2-H and 4-H (δ 4.75 and 4.65, respectively) were well enough separated to make cut-and-weigh integration possible. This showed a 60:40 ratio of 4-H to 2-H.

A solution of 275 mg (1.00 mmol) of 3, 381 mg (1.30 mmol) of tri-*n*-butyltin hydride and 26 mg of azobisisobutyronitrile in 40 mL of benzene was treated as above, except that the reaction time was 7 h. Workup and analysis as was described for 1 gave a ratio of 65:35 for 4-H to 2-H.

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Remarks on the Chameleon Behavior of an Allyllithium: ^{13}C and ^6Li NMR

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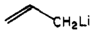
Carbon-13 NMR of 5,5-dimethyl-1-lithio-2-hexene (4) in cyclopentane, in the presence of different ligands at different ligand concentrations, and at different temperatures shows the system to contain a mixture of covalent and ionic delocalized forms in fast dynamic equilibrium with the latter prevailing in the presence of vicinal trans diamines, especially at low temperatures. It is concluded that 1,2-addition in RLi-initiated polymerization of dienes results from ionic allylic live ends and not from covalent secondary allyllithium. The latter are energetically unstable compared to the ionic delocalized forms.

Allylic lithium compounds have been studied extensively and variously described (leaving out aggregation and solvation) as ionic (1), covalent (2), or different species in between (3).[4–6]

1



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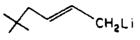
3

In this article we present new conclusions, based on ^{13}C and ^6Li NMR data obtained as a function of temperature and ligand concentration, regarding the structure and dynamic behavior of 1-lithio-5,5-dimethyl-2-hexene (4). Compound 4 was chosen because it is quite soluble in a variety of media,[7] including hydrocarbons. Further, in order to investigate possible ^{13}C,^6Li coupling and increase the signal/noise ratio in ^{13}C NMR, compound 4 has been prepared enriched with both these isotopes, with ^{13}C at C(1) or C(4). Of the two stable isotopes ^7Li and ^6Li, the latter has the lower quadrupole moment and is less likely to bring about decoupling from ^{13}C due to fast quadrupole relaxation.[8] Hence 4 has been prepared enriched in ^6Li.

Results and Discussion

As noted in part elsewhere,[9] the ^{13}C NMR of 4 in a variety of hydrocarbon solvents shows resonances for C(1), C(2), and C(3) around 20, 144 and 100 (vs. Me_4Si) ppm, respectively (see Table I). Two spectra are observed which may be assigned to pseudospecies **4t** (trans) and **4c** (cis), omitting aggregation effects, in agreement with the literature.[7,9] In general carbon shifts in unsolvated organolithium compounds differ little from corresponding hydrocarbon shifts. For instance C(1) of butyllithium at 11 ppm is close to methyl of butane at 13 ppm. Since the shift of C(1) in **4ct** is so similar to C(1) of 5,5-dimethyl-2-hexene, a covalent structure has been assigned.



4t

4c

Table I. ^{13}C NMR Shifts (Me_4Si, ppm) of $(CH_3)_3CCH_2CH{=}CHCH_2Li$ in Different Solvents (1 M, 20 °C)

	$C_6D_5{}^{12}CH_3$	C_6D_6	$(CH_2)_5$
C(1)	21.16	19.96	19.6
	21.49	20.82	21.42
C(2)	140.62	144.49	140.13
	144.51		143.94
C(3)	101.88	102.64	101.14
	102.30	102.96	102.0
C(4)	41.87	42.0	41.73
	48.45	48.79	48.05
C(6)	29.65	29.4	32.3
	31.36	31.34	32.56

The cis/trans ratio of compound 4 in cyclohexane varies with temperature, 193–293 K yielding a ΔH of 2.6 ± 0.3 kcal for the conversion cis $\rightleftharpoons$ trans. On cooling these samples of 4 the line widths for C(1) and C(3) increase significantly compared to the other lines in the spectra; thus for **4ct** in toluene-d_8 while at 301 K all lines are ca. 4 Hz wide, by 258 K the widths for C(1) and C(3) are 56 and 132 Hz, respectively, and yet the C(4) width is still 4 Hz. Coupling between ^{13}C and ^6Li or ^7Li is not observed in the ^{13}C NMR of any of these samples down to 173 K. Strongly irradiating at the ^6Li frequency (^6Li-enriched

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