timum charge distribution in these ions, compared to a C–C triple bond. The ability of the electronegative nitrogen atom to accomodate a favorable lone pair of electrons in sp^2, sp^3, and p orbitals adds to the structural versatility of these ions compared to the isoelectronic series of C_3H_4 compounds. The allenic structures 1 and 7 are ca. 20 kcal/mol higher in energy being still interesting targets for experimental realization. Higher total energies were found for the ethynylammonium ion 8 and for the cyclic ions 12 and 13. The other ions considered in this study have high relative energies; thus they are expected to be highly reactive intermediates (9, 10, 11, 15, 16, and 17), which should allow, via in situ generation, valuable synthetic transformations.

A more detailed study of the $H_2C-N-CH_2^+$ hyperface has shown, that in this series of ions only ion 1 corresponds to a minimum, whereas 2, 3, 4, and 14 are indicated to be high energy transition states. The racemization process of chiral derivatives of 1 is predicted to proceed via ion 2; the barrier for 1 was calculated to be ca. 40 kcal/mol. Some of the energy rich isomers have competitive triplet states: 9, 10, 11, 14, and 16, which may contribute to ground-state reactivity. The semiempirical MNDO method performs remarkably well: trends and relative energies are in good agreement with the ab initio data (even for singlet–triplet comparisons).

# Solid- and Liquid-Phase Photodimerizations of 5H-Indolo[1,7-ab][1]benzazepine

Robert B. Bates,[†] Kenner A. Christensen,[†] Anders Hallberg,[‡] Robert E. Klenck,[†] and Arnold R. Martin*[,‡]

Departments of Chemistry and Pharmaceutical Sciences, University of Arizona, Tucson, Arizona 87521

Received January 18, 1984

Unlike other dibenzazepines which give only anti photodimers, 5H-indolo[1,7-ab][1]benzazepine (1) gives a 3:1 ratio of "mirror plane" syn dimer 4 to "twofold axis" syn dimer 5 in the solid state and a 1:3 ratio of 4 to 5 in solution. Eximers are probably responsible for these syn dimers being formed. 4 and 5 crystallize isomorphously, the latter with spontaneous resolution. Unlike the anti dimers, which have planar cyclobutane rings in the crystal, the syn dimers have strongly twisted cyclobutane rings.

The 2 + 2 photodimerization of alkenes to cyclobutanes is a long-known reaction of current importance in applications such as solar to chemical energy conversions and the photocrosslinking of polymers.[1] We have found 1,
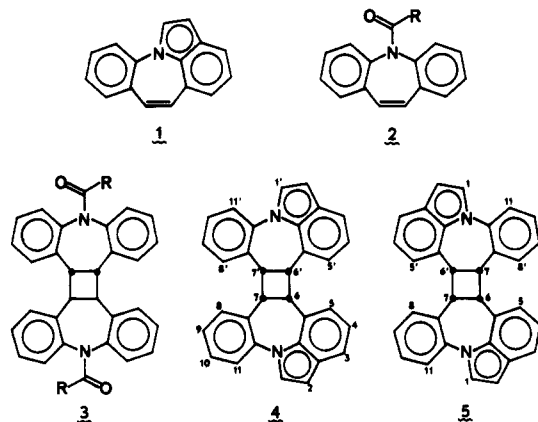
prepared in a study of imipramine and promazine analogues,[2] to be so prone to photochemical dimerization that it is difficult to keep in the monomeric form. Even indirect sunlight rapidly converts 1 (mp 113–114 °C) into a 3:1 mixture of two dimers, and solutions of 1 into the same two dimers but in the reverse ratio. Other dibenz[b,f]-azepines 2 have recently been shown to give exclusively anti dimers 3.[3] We wish to present evidence that 1 gives only syn dimers 4 and 5, with 4 favored in the solid-phase dimerization and 5 predominating in solution, and to give possible reasons for the differing stereo- and regiochemistry in these dimerizations.

The two dimers obtained from 1 were separated by fractional crystallization. While their characteristic ^1H NMR spectral patterns served well as fingerprints, we could not safely use them to make stereochemical assignments, and thus carried out an X-ray study on each dimer.

Experimental Section

A 450-W Hanovia medium-pressure mercury lamp (Pyrex filter) was used for the photolyses. ^1H NMR spectra were recorded on a Bruker WM-250 spectrometer at 250 MHz. Mass spectra were recorded on a Varian MAR 311A double focussing mass spectrometer. Melting points are uncorrected and were determined on a Thomas-Hoover capillary melting point apparatus. Microanalyses were performed by the University Analytical Center, Tucson, AZ.

Dimerization in the Solid State. A 1-mm thick layer of 217 mg (1.0 mmol) of pulverized 1 was irradiated for 16 h to give a

(1) Kricka, L. J.; Ledwith, A. Chem. Rev. 1974, 74, 101 and references therein. Alimoglu, A. K.; Bamford, C. H.; Ledwith, A.; Mullik, S. M. Macromolecules 1977, 10, 1081. Lewis, F. D.; Howard, D. K.; Oxman, J. D. J. Am. Chem. Soc. 1983, 105, 3344.

(2) Hallberg, A.; Deardorff, D. R.; Martin, A. R. Heterocycles 1982, 19, 75.

(3) Harding, M. M. Acta Crystallogr., Sect. C 1983, C39, 397. We have also solved the crystal structure of 3, R = Me, and noted considerable extraneous electron density in the channels along the c axis. Our crystals came out of an acetone solution (open to the air) during the irradiation, but we think this electron density is due to disordered water rather than acetone since the ^1H NMR spectrum of such crystals shows a significant water peak but no acetone peak.

white solid shown by ^{1}H NMR to be a 3:1 mixture of **4** and **5**, respectively. Only traces of starting material were detected by ^{1}H NMR. Repeated recrystallizations from toluene gave **4**: mp 217–222 °C; MS, m/e 434; ^{1}H NMR (CDCl$_3$) δ 4.51 and 4.59 (H6, H7), 6.30 (H2), 6.49 (H5), 6.64 (H4), 6.82 (H9), 6.96 (H11), 7.02 (H8), 7.03 (H1, H10), 7.14 (H3), $J_{1,2}$ = 3.7, $J_{3,4}$ = 7.6, $J_{3,5}$ = 1.2, $J_{4,5}$ = 7.4, $J_{6,6'}$ = $J_{6,7}$ = $J_{7,7'}$ = 8.6, $J_{6,7'}$ = 1.6, $J_{8,9}$ = 6.8, $J_{8,10}$ = 1.7, $J_{9,10}$ = 6.8, $J_{9,11}$ = 1.3, $J_{10,11}$ = 9.0 Hz.

Anal. Calcd for C$_{32}$H$_{22}$N$_2$: C, 88.43; H, 5.10; N, 6.45. Found: C, 88.62; H, 5.30; N, 6.37.

Dimerization in Solution. A solution of 217 mg (1.0 mmol) of **1** in 1.0 mL of toluene was prepared, degassed, and irradiated for 16 h. Evaporation of the solvent gave a white solid, shown to be a 3:1 mixture of **5** and **4**, respectively, by ^{1}H NMR. No starting material was observed. Irradiation of a solution which was not degassed produced the same dimer ratio but the conversion of starting material to dimers was only 50%, indicating that triplet-state intermediates are involved. Repeated recrystallizations from toluene gave **5**: mp 225–228 °C; MS, m/e 434; ^{1}H NMR (CDCl$_3$) δ 4.47 and 4.57 (H6, H7), 6.08 (H2), 6.23 (H5), 6.60 (H4), 6.70 (H1), 6.94 (H11), 7.03 (H3), 7.08 (H9), 7.20 (H10), 7.45 (H8), $J_{1,2}$ = 3.5, $J_{3,4}$ = 7.4, $J_{3,5}$ = 1.2, $J_{4,5}$ = 7.4, $J_{6,7}$ = $J_{6,7'}$ = 8.6, $J_{8,9}$ = 7.5, $J_{8,10}$ = 1.7, $J_{9,10}$ = 6.6, $J_{9,11}$ = 0.9, $J_{10,11}$ = 8.1 Hz.

Anal. Calcd for C$_{32}$H$_{22}$N$_2$: C, 88.43; H, 5.10; N, 6.45. Found: C, 88.53; H, 5.26; N, 6.34.

X-ray Crystallography. Pale yellow crystals of **4** and **5** were obtained by slow evaporation from hexane solutions. Dimensions, 0.3 × 0.4 × 0.4 mm for **4**, and 0.3 × 0.3 × 0.5 mm for **5**; space group, $P2_12_12_1$; a = 8.808 (2) Å, b = 12.197 (6) Å, c = 20.26 (1) Å for **4** and a = 8.542 (2) Å, b = 14.404 (6) Å, c = 18.05 (1) Å for **5**; V = 2177 (1) Å^3 for **4** and 2221 (1) Å^3 for **5**; Z = 4; d_{calcd} = 1.33 g/cm^3 for **4** and 1.30 for **5**. 1415 reflections with 2Θ 4–50° and $I \geq 3\sigma(I)$ were observed for **4** and 1425 for **5**, using a Syntex P2$_1$ diffractometer; no crystal decay was observed and no absorption corrections were made.

The structures were solved using MULTAN 80[4] with benzenes and indole groupings as fixed contributors. Non-hydrogens were refined with anisotropic temperature factors and hydrogens were included in calculated positions with isotropic temperature factors, giving convergence at R = 0.051 for both **4** and **5**.

Results and Discussion

As can be seen in Figures 1 and 2, the major dimer from the solid phase irradiation is "mirror plane" syn dimer **4**, and the major solution dimer is "twofold axis" syn dimer **5**. These substances unexpectedly crystallize isomorphously, as can be seen from the similarity in their atomic coordinates (Table I); only C2' is very different. All the molecules in each crystal are of the same chirality; for mirror plane dimer **4**, this merely requires a twist of each achiral molecule in the same direction as it is added, but for twofold axis dimer **5**, it means spontaneous resolution is occurring.[5] The packing pattern used (Figure 3) is fortunately sufficiently selective for like molecules that **4** and **5** can be fractionally crystallized from one another.

Syn dimers **4** and **5** have strongly bent cyclobutane rings (torsion angles around cyclobutane ring 13.6–14.3° in **4** and 19.4–20.5° in **5**) in contrast to anti dimer **3**, whose center of symmetry requires a planar cyclobutane ring with 0° torsion angles.[3] The cyclobutane bonds connecting the two halves of syn dimers **4** and **5** are slightly lengthened (average of four such bonds, 1.59 Å; average of other four cyclobutane bonds, 1.55 Å), presumably to relieve steric repulsions between halves; in anti dimer **3**, where steric repulsions between halves are minimal, the bonds joining the two halves are normal (1.56 Å) but the *other* cyclo-
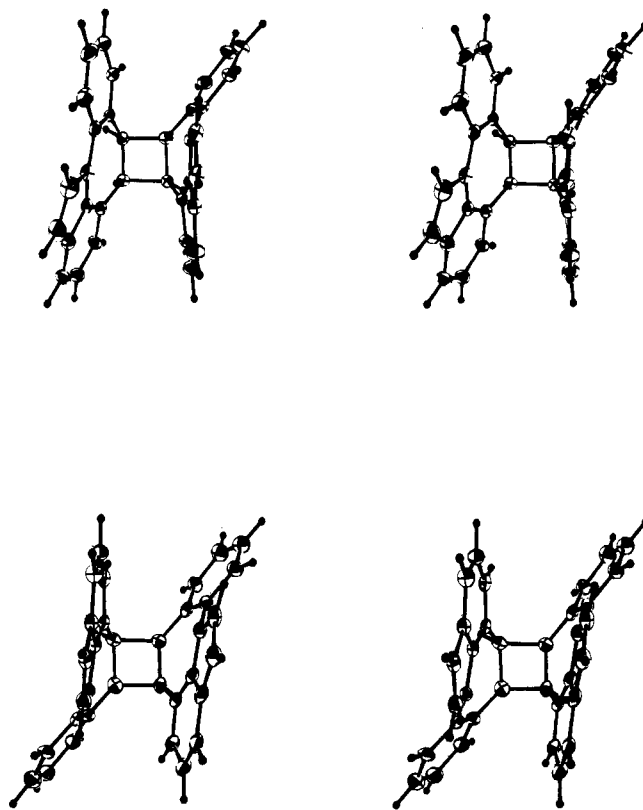

Figure 1. Stereoscopic views of a molecule of **4** (top) and **5** (bottom), with 20% thermal ellipsoids for non-hydrogens and spheres for hydrogens.

butane bonds are lengthened (1.61 Å) to relieve repulsion between eclipsed aryl groups.[3]

In anti dimer **3**, the seven-membered ring adopts a highly puckered boat conformation, with torsion angles starting from the 5a–6–7–7a type bond and proceeding clockwise around the ring of 0°, 42°, -7°, -70°, 72°, 2°, and -40°.[3] The indole groupings in **4** and **5** serve to flatten the seven-membered rings considerably: average values for the corresponding bonds in the four such rings of **4** and **5** are -30°, 41°, -4°, -33°, 24°, 8°, and -4°.

This flattening provides a clue to the very different photochemical behavior of indole-containing monomer **1** and non-indole monomers like **2**.[5] The monomer **2** is almost as puckered as its dimer **3** (torsion angles in **2**, in the same order as above, are -1°, 34°, 3°, -68°, 68°, -4°, and -32°[3]), and thus does not easily form eximers; its dimerization, shown to proceed via a triplet,[6] gives for steric reasons exclusively anti dimer **3**. **1**, in contrast, is much flatter[7] and readily forms eximers which lead exclusively to syn dimers **4** and **5**. Acenaphthalene is believed to give syn dimer via an eximer, but it also gives some anti dimer by a noneximer route.[8] We have not been able to detect any anti dimer from **1**.

It remains to explain the regiochemistry observed. The solid-state photodimerization favoring of **4** is an example of crystal lattice control of a photorearrangement, observed in some other alkene photodimerizations.[9] **5** is probably favored in solution because it comes from an intermediate

(4) Main, P.; Hull, S. E.; Lessinger, L.; Germain, G.; Declercq, J. P.; Woolfson, M. M. "Multan 80"; Universities of York and Louvain: England and Belgium, 1978.

(5) The number of substances known to spontaneously resolve is now in the hundreds: Collett, A.; Brienne, M.-J.; Jacques, J. *Bull. Soc. Chim. Fr.* **1972**, 127; **1977**, 494.

(6) Anti dimers have been obtained not only from **2**,[3] but also from five related amides (Kricka, L. J.; Lambert, M. C.; Ledwith, A. *J. Chem. Soc., Perkin Trans. 1* **1974**, 52) and from several related dibenzocycloheptatrienes.[1] It was not known at that time that the amide dimers were anti, and they were mistakenly believed to arise via exiplexes.

(7) We were unable to obtain a crystal of **1** suitable for an X-ray study, partly because of its facile conversion to **4** and **5**.

(8) Cowan, D. O.; Drisko, L. E. *J. Am. Chem. Soc.* **1970**, *92*, 6286.

(9) Scheffer, J. R. *Acc. Chem. Res.* **1980**, *13*, 283.

Figure 2. Bond distances (±0.006–0.015 Å) and angles (±0.6–0.8°) in **4** (left) and **5**.

Table I. Positional Parameters (×10⁴) with Estimated Standard Deviations in Parentheses

atom		x		y		z	
4	5	4	5	4	5	4	5
	N	5413 (4)	5713 (6)	6334 (3)	6497 (3)	9577 (2)	9390 (3)
	C1	6445 (6)	6803 (8)	7216 (4)	7211 (5)	9666 (3)	9513 (4)
	C2	6535 (6)	6986 (8)	7447 (4)	7330 (5)	10312 (3)	10251 (5)
	C2a	5512 (6)	5977 (7)	6767 (4)	6700 (4)	10657 (3)	10627 (4)
	C2b	4863 (5)	5253 (7)	6057 (4)	6167 (4)	10195 (2)	10085 (4)
	C3	5122 (7)	5725 (9)	6671 (5)	6557 (5)	11320 (3)	11381 (4)
	C4	4095 (8)	4696 (10)	5892 (5)	5880 (6)	11506 (3)	11578 (4)
	C5	3509 (6)	3967 (9)	5176 (5)	5315 (5)	11051 (3)	11032 (4)
	C5a	3941 (5)	4278 (7)	5168 (4)	5419 (4)	10381 (2)	10272 (4)
	C6	3553 (5)	3605 (7)	4192 (4)	4685 (5)	9990 (2)	9772 (4)
	C7	3870 (6)	3975 (9)	4163 (4)	4733 (5)	9226 (2)	8925 (4)
	C7a	3916 (6)	4102 (8)	5183 (5)	5624 (5)	8808 (2)	8489 (4)
	C8	3175 (7)	3300 (10)	5092 (5)	5643 (7)	8195 (3)	7803 (4)
	C9	3193 (8)	3330 (12)	5953 (7)	6416 (9)	7745 (3)	7346 (5)
	C10	3957 (9)	4145 (13)	6906 (6)	7203 (7)	7912 (3)	7579 (5)
	C11	4699 (7)	4895 (9)	7016 (4)	7207 (5)	8505 (3)	8254 (4)
	C11a	4680 (6)	4925 (8)	6159 (4)	6417 (5)	8957 (2)	8708 (4)
	N'	7953 (5)	7643 (7)	4517 (3)	4440 (3)	10271 (2)	10437 (3)
	C1'	9104 (7)	8818 (8)	5005 (5)	4898 (5)	10631 (3)	10854 (4)
	C2'	9062 (7)	9676 (8)	4698 (6)	5413 (5)	11260 (3)	10409 (5)
C2a'	C11'	7829 (6)	7352 (9)	3934 (5)	3250 (9)	11336 (3)	11373 (4)
C2b'	C11a'	7127 (5)	6754 (9)	3868 (4)	3681 (8)	10715 (2)	10737 (7)
C3'	C10'	7273 (8)	6587 (10)	3360 (5)	2535 (10)	11873 (3)	11711 (4)
C4'	C9'	6004 (8)	5210 (11)	2739 (5)	2198 (11)	11795 (3)	11413 (5)
C5'	C8'	5276 (6)	4649 (9)	2693 (4)	2600 (9)	11195 (2)	10772 (4)
C5a'	C7a'	5799 (5)	5387 (8)	3256 (4)	3353 (8)	10640 (2)	10427 (4)
C6'	C7'	4803 (5)	4607 (8)	3253 (3)	3735 (8)	10044 (2)	9763 (4)
C7'	C6'	5362 (6)	5377 (9)	3467 (4)	4044 (4)	9347 (2)	9037 (4)
C7a'	C5a'	6814 (6)	6947 (9)	4059 (4)	4495 (4)	9169 (2)	9061 (4)
C8'	C5'	7005 (7)	7569 (11)	4149 (5)	4858 (5)	8487 (3)	8392 (4)
C9'	C4'	8159 (10)	8902 (10)	4683 (7)	5404 (6)	8195 (3)	8342 (5)
C10'	C3'	9213 (10)	9655 (9)	5190 (6)	5627 (5)	8587 (5)	8975 (6)
C11'	C2a'	9129 (7)	9179 (8)	5149 (4)	5276 (5)	9270 (3)	9655 (5)
C11a'	C2b'	7932 (5)	7874 (7)	4566 (4)	4690 (4)	9566 (3)	9686 (4)

which has two benzene–pyrrole stacking interactions; the cyclobutane ring in dimer **5** is twisted strongly in the direction which permits such interactions. Whichever way **4** twists, it achieves only one such interaction.

Computer simulation of the cyclobutane proton NMR absorptions gave the parameters given in the Experimental Section. The vicinal couplings are all within experimental error of 8.6 Hz, consistent with either a cis or trans arrangement.[10] The four-bond couplings in **4**, which has an AA'BB' spectrum, are 1.6 Hz, which is large enough to be suggestive of but not definitive for the cis arrangement

(10) Wiberg, K. B.; Barth, D. E.; Pratt, W. E. *J. Am. Chem. Soc.* 1977, **99**, 4286.
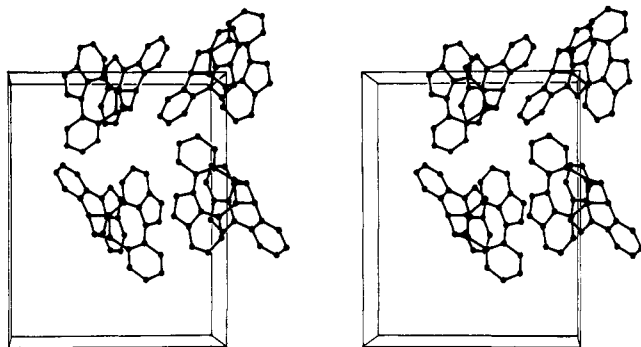
Figure 3. Stereoscopic views of a unit cell of **5**, with b axis horizontal and c axis vertical.

actually present. The spectrum of **5** is unfortunately insensitive to the four-bond couplings, since $J_{6,7}$ is sufficiently close in value to $J_{6,7'}$ that no lines other than those expected from an A_2B_2 spectrum were observed.[11]

(11) Günther, H. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 861.

The aromatic proton peaks of **4** and **5** (see Experimental Section) are almost all upfield of those in the spectrum of dihydro **1**,[12] which might have suggested that **4** and **5** are syn. Assignments on this basis were not considered safe in the absence of a good model for the anti dimers of **1**; **3** is not a good model as the electronic situation and geometry around the nitrogen are so different. Compared to those of **5**, the indole protons (on C1–C5) of **4** all absorb downfield and most of the other aromatic protons absorb upfield; this suggests that in solution, as in the crystals, the aromatic systems in each half of **4** are more nearly coplanar with one another than are the corresponding systems in **5**.

(12) Hallberg, A.; Dahlgren, T.; Martin, A.; Christensen, K. *J. Heterocycl. Chem.* **1983**, *20*, 37.

Reactions of 2,3-Dimethylenebutadiene Dianion with Electrophiles. Synthesis and Conformations of 2,3-Disubstituted-1,3-butadienes

Robert B. Bates,* Bernard Gordon, III,[1] Thomas K. Highsmith, and James J. White

Department of Chemistry, University of Arizona, Tucson, Arizona 85721

Received January 27, 1984

Reactions of 2,3-dimethylenebutadiene dianion **1** with monofunctional electrophiles were found to provide the best routes to symmetrically substituted 1,3-butadienes such as **2c–n**. Evidence that at least some of these reactions go by single electron-transfer mechanisms is presented. Possible mechanisms for the formation of some unusual byproducts are discussed. Reactions of **1** with dichlorides and dibromides were found to provide the best routes to most 1,2-dimethylenecycloalkanes **3**, the corresponding dimers **4** and trimers **5**, and 1,1-dimethyl-3,4-dimethylene-1-metallacyclopentanes **26**. From their UV spectra, the dienes **2** contain about 60% transoid conformations, except 2,3-dimethyl-1,3-butadiene (**2a**) which shows about 100% and 2,3-dineopentyl-1,3-butadiene (**2h**) which shows about 30%. 1,2-Dimethylenecycloalkanes **3** display cisoid conformations in rings smaller than 9-membered and transoid conformations in rings larger than 11. When the ring size exceeds 15, the homoallylic methylene groups on both sides are also anti coplanar. With rings larger than about 30, the next methylene group on each side is also anti coplanar, and when the ring size exceeds about 45, an additional methylene on each side is anti coplanar.

Dianion **1** (Chart I) has been prepared in 70–80% yield by metalating 2,3-dimethyl-1,3-butadiene (**2a**) as judged by the conversion of **1** to **2b** with D_2O and to **2d** with diethyl sulfate.[2] We report that symmetrical 2,3-disubstituted 1,3-butadienes like **2–5** can be synthesized in two-step, one-pot reactions. The mechanisms by which these reactions occur, the byproducts which were found, and the preferred conformations of dienes **2–5** are discussed below.

Reactions of Dianion 1 with Monofunctional Electrophiles

As can be seen from the first four entries in Table I, sulfates give higher yields than the corresponding halides; this is presumably because the sulfates go by an S_N2

Table I. Yields of Products from Dianion 1 and Monofunctional Electrophiles

electrophile	products (yield from 2a)
MeI	2c (43)
Me₂SO₄	2c (61)
EtBr	2d (43)
Et₂SO₄	2d (71)[2]
n-PrBr	2e (34)
n-BuBr	2f (30)
i-PrBr	2g (41); 6a (3); 7g (2)
t-BuBr	2h (15); 6a (12); 7h (15); 4, n = 4 (15)
t-BuI	2h (20); 6a (14); 7h (5); 4, n = 4 (16)
allyl chloride	2i (70); 6i (10)
PhCH₂Cl	2j (53); PhCH₂CH₂Ph (22)
PhCH₂Br	2j (21); PhCH₂CH₂Ph (30)
Me₃SiCl	2k (47)
Me₃GeBr	2l (54); 6l (5); 8 (4)
Me₃SnCl	2m (32); 6m (6)
Me₃PbCl	2n (30)

(1) Current address: Department of Materials Science, Pennsylvania State University, University Park, PA 16802.
(2) Bahl, J. J.; Bates, R. B.; Gordon, B., III *J. Org. Chem.* **1979**, *44*, 2290.

mechanism, whereas the halides go at least partly by single electron transfer (SET) which can lead to other than