to this explanation.

First, the calculations reproduce observed changes in the secondary effect when the primary hydrogen is changed from H to D, and vice versa. Experimentally, deuteration at one of the sites *reduces* the isotope effect at the other by factors of 1.03 ± 0.02 (Kurz and Frieden[5,13]) or around 1.14 (cited as ref 11 by Cook, Oppenheimer and Cleland[6]). The calculation for point A predicts a factor of 1.09. Those for points B, C, and D predict respectively 0.99, 0.99, and 1.00.

Second, if the mass of the transferring atom is increased to 16 amu, thus (crudely) simulating solvolysis[8] and acyl-transfer reactions,[9-12] anomalous phenomena disappear. If this mass change but no other alteration is made in the model for point A, $k_{\alpha H}/k_{\alpha D}$ becomes 1.060 and $K_{\alpha H}/K_{\alpha D}$ 1.100. As with deuteration, an increase in reduced mass for the reaction coordinate has greatly reduced the importance of tunneling and the associated anomalies.

The results are consistent with, but do not demand, a ubiquitous importance of tunneling in hydrogen transfer. The similar observations of Saunders and his co-workers[15-17] for proton transfer in elimination reactions add reinforcement to such a suggestion. It is possible that enzymes that catalyze hydrogen transfer have developed part of their catalytic power by not only altering the *height* of the reaction barrier but also its *shape*, thus altering the contribution of tunneling.

(14) The calculations shown in Figure 2 correspond to a total bond order about H_1 of approximately unity, which is usually assumed in hydrogen-transfer reactions (a practice that derives from: Johnston, H. S. "Gas Phase Reaction Rate Theory", Ronald Press: New York, 1966). Any of the models that reproduces approximately the observed secondary and primary isotope effects yet maintains a low imaginary frequency and thus has no tunneling contribution requires extremely low bond orders about the transferring hydrogen. Such models are probably unreasonable for hydrogen-transfer reactions but perhaps not for heavy-atom transfers.

(15) Miller, D. J.; Subramanian, R.; Saunders, W. H., Jr. *J. Am. Chem. Soc.* **1981**, *103*, 3519-3522.

(16) Kaldor, S. B.; Fredenberg, M. E.; Saunders, W. H., Jr. *J. Am. Chem. Soc.* **1980**, *102*, 6297-6299.

(17) Miller, D. J. Saunders, W. H., Jr. *J. Org. Chem.* **1981**, *46*, 4246-4247.

(18) Wolfsberg, M.; Stern, M. J. *Pure. Appl. Chem.* **1964**, *8*, 225-242.

(19) Stern, M. J.; Wolfsberg, M. *J. Chem. Phys.* **1966**, *45*, 4105-4124.

(20) Rodgers, J.; Femec, D. A.; Schowen, R. L. *J. Am. Chem. Soc.* **1982**, *104*, 3263.

(21) Bell, R. P. *Trans. Faraday Soc.* **1959**, *55*, 1-4.

Group-Transfer Polymerization. 1. A New Concept for Addition Polymerization with Organosilicon Initiators[1]

O. W. Webster,* W. R. Hertler, D. Y. Sogah,
W. B. Farnham, and T. V. RajanBabu

Central Research & Development Department†
E. I. du Pont de Nemours & Company
Experimental Station, Wilmington, Delaware 19898

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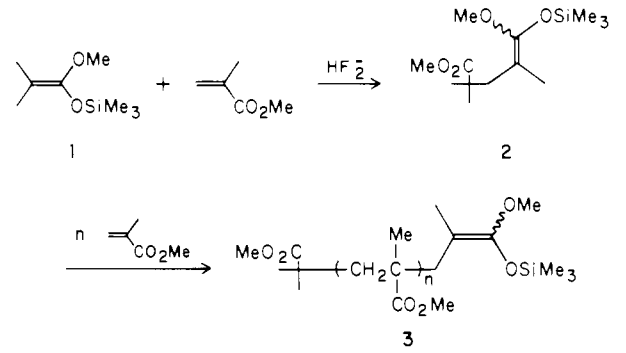
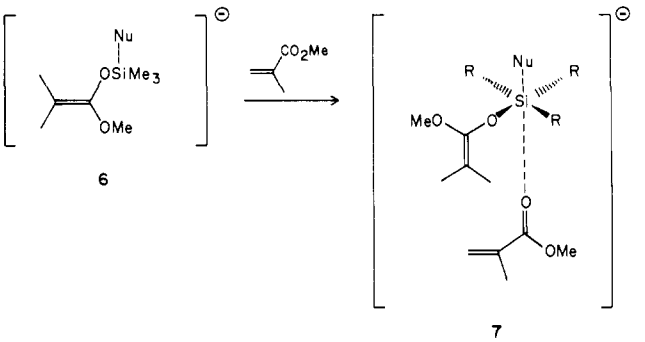
Although the conjugate addition of silyl ketene acetals to α,β-unsaturated carbonyl compounds has been used in organic synthesis,[2] application of this chemistry to polymer formation by sequential additions is unprecedented. This communication describes such a process for the controlled polymerization of α,β-unsaturated esters, ketones, nitriles, and carboxamides. *This new method offers new dimensions in the construction and design of polymer chains from these monomers.*

Scheme I



Scheme II



Scheme I illustrates the polymerization of methyl methacrylate (MMA) with dimethylketene methyl trimethylsilyl acetal[3] (**1**) as initiator. This new method of addition polymerization is termed "group-transfer polymerization" (GTP)[4] since the trimethylsilyl group is transferred from **1** (or **2** or **3**) to the incoming monomer.

A catalyst is required for the polymerization to proceed, and surprisingly, one of the most generally useful catalysts is bifluoride ion. Although fluorides have been widely used for the catalysis of nucleophilic reactions of organosilanes,[2g] this is the first report of the general utility of bifluoride ion in the catalysis of such reactions. Other anions that catalyze GTP are Me_3SiF_2,[5] CN, and N_3.[6,7] Table I summarizes the results.

In general, GTP proceeds rapidly at room temperature and gives living polymer of narrow molecular weight distribution in quantitative yield.[8] The degree of polymerization is controlled by the ratio of monomer to **1**. The living polymers are isolable and characterizable.[9] Hence, further addition of monomer leads to

† Contribution No. 3191.

(1) Webster, O. W.; Farnham, W. B.; Sogah, D. Y. E.P.O. Patent Application 0068887, Jan 5, 1983.

(2) (a) Gerlach, H.; Künzler, P. *Helv. Chim. Acta* **1978**, *61*, 2503. (b) Boyer, J.; Corriu; R. J. P.; Perz, R.; Reye, C. *J. Organomet. Chem.* **1980**, *184*, 157. (c) Saigo, K.; Osaki, M.; Mukaiyama, T. *Chem. Lett.* **1976**, 163. (d) Kita, Y.; Segawa, J.; Haruta, J.; Yasuda, H.; Tamura, Y. *J. Chem. Soc., Perkin Trans 1* **1982**, 1099. (e) Yamamoto, K.; Suzuki, S.; Tsuji, J. *Chem. Lett.* **1978**, *6*, 649. (f) Chan, T. H.; Brownbridge, P. *J. Chem. Soc., Chem. Commun.* **1979**, 578. (g) For a review, see: Colvin, E. "Silicon in Organic Synthesis" Butterworths: London, 1981.

(3) Ainsworth, C.; Chen, F.; Kuo, Y.-N. *J. Organomet. Chem.* **1972**, *46*, 59.

(4) This name was suggested by Professor B. M. Trost, University of Wisconsin.

(5) Middleton, W. J. U.S. Patent 3 940 402, Feb 1976; Middleton, W. J. *Org. Synth.*, in press.

(6) Lewis acids such as zinc halides and alkylaluminum chlorides also catalyze group-transfer polymerization (most likely by activation of the monomer). This work will be published in the near future by O. W. Webster, B. M. Trost, W. R. Hertler, and D. Y. Sogah.

(7) Although tetraalkylammonium bifluorides or even potassium bifluoride can be used, we found tris(dimethylamino)sulfonium bifluoride (TAS HF_2) to give the best overall results. Tris(dimethylamino)sulfonium bifluoride was prepared in quantitative yield by treatment of tris(dimethylamino)sulfonium difluorotrimethylsilicate (27.5 g, 0.10 mol) with water (1.0 mL, 0.055 mol) in acetonitrile (20 mL). Purification was achieved by crystallization from MeCN/THF (1/10, v/v). The product has the expected ^1H and ^{19}F NMR spectral properties, and the elemental analysis was within 0.3% of theory.

(8) In a typical procedure, MMA (360 mmol) is slowly added to a solution of 1-methoxy-1-(trimethylsiloxy)-2-methyl-1-propene (**1**, 8.5 mmol) and tris(dimethylamino)sulfonium bifluoride (0.01 mmol) in tetrahydrofuran (20 mL) at room temperature with exclusion of moisture. When the exothermic reaction is complete, methanol (3 mL) is added, and the solution is evaporated to give a quantitative yield of poly(methyl methacrylate), M_n 4300, M_w 5300 (theory, 4343), dispersity (D) = M_w/M_n = 1.24, as determined by GPC.

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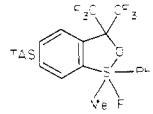
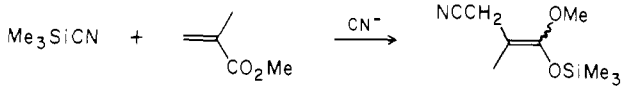
Table I. Polymers by Group-Transfer Polymerization

entry	monomer(s)	initiator	catalyst[a]	solvent	polymer M_n	polymer M_w	polymer D	polymer theor
1	methyl methacrylate	1	$TASF_2SiMe_3$	THF, −78 °C	1120	1750	1.56	2040
2[b]	methyl methacrylate	1	$TASN_3$	CH_3CN	3000	3100	1.03	3700
3	methyl methacrylate	1		CH_3CN	1700	1900	1.10	2000
4[b]	methyl methacrylate	Me_3SiCN	TASCN	CH_3CN	800	800	1.03	1000
5[c]	methyl methacrylate (35%) *n*-butyl methacrylate (65%)	9a	$TASHF_2$	THF	22100	24500	1.11	20307
6[d]	methyl methacrylate (35%) ethyl acrylate (65%)	9a	$TASHF_2$	THF	3400	6500	1.92	3466
7[e]	methyl methacrylate (57%) *n*-butyl methacrylate (32%) allyl methacrylate (11%)	1	$TASHF_2$	THF	3800	4060	1.07	4060
8[c]	methyl methacrylate (58%) *n*-butyl methacrylate (17%) glycidyl methacrylate (25%)	1	$TASHF_2$	THF	3910	4290	1.10	4092
9	*N,N*-dimethylmethacrylamide	$Me_3SiCH_2CO_2Et$	$TASF_2SiMe_3$	THF	1400	2000	1.43	2260
10	methyl vinyl ketone	1	$TASF_2SiMe_3$	CH_3CN/THF	490	944	1.93	800
11	methyl methacrylate		$TASF_2SiMe_3$	CH_3CN/THF	2100	2400	1.14	2000

[a] TAS = $(Me_2N)_3S$. [b] Induction period observed. [c] Random copolymer, composition in mole per cent. [d] Diblock copolymer. [e] Triblock terpolymer. Glass transition temperatures are −19, +38, and +108 °C.

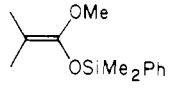
Scheme III



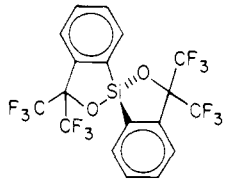
8

the anticipated molecular weight increase while sequential addition of other monomers gives block copolymers. GTP can be terminated by either desilylation or removal of catalyst.

Our mechanistic studies of GTP of MMA with tris(dimethylamino)sulfonium (TAS) bifluoride and TAS Me_3SiF_2 as catalysts show that a fluorosilane is not produced in a reversible, dissociative step. As evidence, polymerization of MMA with phenyldimethylsilyl initiator **4** in the presence of an equimolar



4

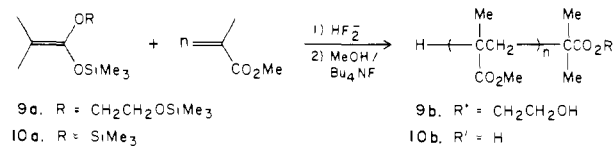


5

quantity of tolyldimethylsilyl fluoride with $TASHF_2$ catalyst (25–50 °C, 0.75 h) provided phenyldimethylsilyl oligomer **3** with less than 5% of the corresponding tolyldimethylsilyl derivative. A similar experiment using $TASMe_3SiF_2$ catalyst (−95 to −90 °C, 5 min), followed by an irreverisible catalyst quench with spirosilane **5**,[10] resulted in only ca. 10% incorporation of the tolyldimethylsilyl fragment.

We propose an intramolecular transfer mechanism in which the silyl group is transferred directly from **1** or **3** to the carbonyl oxygen of the monomer via hypervalent silicon intermediates **6** and **7** (Scheme II). Results with appropriately labeled **3** ($n \geq 10$) show that silyl group exchange is not involved.

Scheme IV



Other organosilicon compounds such as ethyl trimethylsilylacetate (entry 9, Table I) and trimethylsilyl cyanide (entry 4, Table I; Scheme III) operate as initiators.[11] With Me_3SiCN as initiator, a reactive intermediate **8** (Scheme III) is formed.

Polymers with terminal functional groups can be prepared by GTP using an initiator containing a protected functional group (entries 5 and 6, Table I). Thus, initiation of MMA polymerization with **9a** gives, after deprotection, PMMA with a terminal hydroxy group,[12] **9b** (Scheme IV). Similarly, initiator **10a**[13] leads to **10b**.

GTP provides a route to polymers containing a pendent functionality sensitive to free radicals; e.g., a copolymer containing 11% allyl ester group is readily synthesized (entry 7, Table I). A copolymer with this level of allyl functionality prepared by free radical polymerization would be heavily cross-linked.

In conclusion, group-transfer polymerization of α,β-unsaturated esters appears to be a more versatile method of polymerization than previously known methods, allowing for superior control of molecular structure and functionality.

Acknowledgment. We thank Professor Barry M. Trost, University of Wisconsin, for helpful discussions. B. C. Anderson, T. Fukunaga, and B. E. Smart also contributed substantially.

Registry No. 1, 31469-15-5; **9a**, 85248-36-8; Me_3SiCN, 7677-24-9; $Me_3SiCH_2CO_2Et$, 4071-88-9; $TaASF_2SiMe_3$, 59218-87-0; $TASN_3$, 59094-58-5; TASCN, 59094-55-2; $TASHF_2$, 85248-37-9; MMA, 80-62-6; PMMA, 9011-14-7; *n*-butyl methacrylate, 97-88-1; ethyl acrylate, 140-88-5; allyl methacrylate, 96-05-9; glycidyl methacrylate, 106-91-2;

(9) The intermediates **2** and **3** (n = 5, 9) have been isolated and characterized by ^1H NMR and GPC. Comparison of 100.6-MHz ^{13}C NMR spectra of **3** (n = 9), PMMA (of the same tacticity), and **1** provided accurate peak assignment. For a detailed 25-MHZ ^{13}C NMR analysis of PMMA, see: Randall, J. C. "Polymer Sequence Determination, Carbon-13 Method"; Academic Press: New York, 1977; pp 11–114, and references therein.

(10) Farnham, W. B.; Harlow, R. L. *J. Am. Chem. Soc.* **1981**, *103*, 4608. Perozzi, E. F.; Martin, J. C. *Ibid.* **1979**, *101*, 1591. Perozzi, E. F.; Michalak, R. S.; Figuly, G. D.; Stevenson, W. H., III; Dess, D. B.; Ross, M. R.; Martin, J. C. *J. Org. Chem.* **1981**, *46*, 1049.

(11) Germanium and tin analogues of **1** also initiate group-transfer polymerization of MMA.

(12) Hydroxyl-terminated PMMA is readily distinguished from PMMA by HPLC. See: Andrews, G. D.; Vatvars, A. *Macromolecules* **1981**, *14*, 1603.

(13) Ainsworth, C.; Kuo, Y.-N. *J. Organomet. Chem.* **1972**, *46*, 73.

N,N-dimethylmethacrylamide, 6976-91-6; methyl vinyl ketone, 78-94-4; n-butyl methacrylate•methyl methacrylate copolymer, 25608-33-7; ethyl acrylate•methyl methacrylate copolymer, 9010-88-2; allyl methacrylate•n-butyl methacrylate•methyl methacrylate copolymer, 51053-21-5; n-butyl methacrylate-glycidyl methacrylate•methyl methacrylate copolymer, 25766-58-9; poly(N,N-dimethylmethacrylamide), 81665-88-5; poly(methyl vinyl ketone), 25038-87-3; [(4,5-dihydrofuran-2-yl)oxy]trimethylsilane, 51425-66-2; tris(dimethylamino)sulfur [α,α-bis(trifluoromethyl)benzenemethanolato]fluoromethylphenyl silicate, 79218-03-4.

Picosecond Observation of Kinetic vs. Thermodynamic Hydrogen Atom Transfer

Lewis E. Manring and Kevin S. Peters*†

Department of Chemistry, Harvard University
Cambridge, Massachusetts 02138

Received May 13, 1983

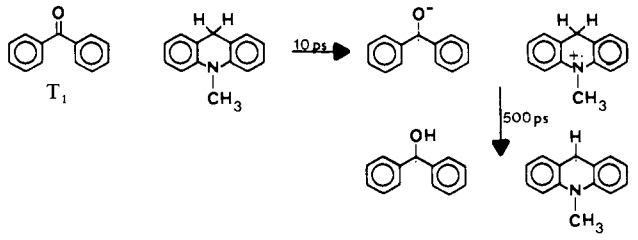
In an earlier paper,[1] it was demonstrated that the photoinduced reduction of benzophenone (Bph) by N-methylacridan (NMA) occurs via an electron–proton–electron mechanism (Scheme I). The initial step (within 10 ps after 355-nm laser excitation in benzene) is electron transfer from NMA to ^{3}Bph yielding the corresponding radical ions $Bph^{-}\cdot$ and $NMA^{+}\cdot$, which have visible absorbances with λ_{max} of 720 and 640 nm, respectively. Subsequent to electron transfer, proton transfer occurs from $NMA^{+}\cdot$ to $Bph^{-}\cdot$ ($t_{1/2}$ = 500 ps) yielding the benzophenone ketyl radical (λ_{max} = 550 nm) and the N-methylacridanyl radical (λ_{max} = 520 nm). Previously,[1] it was assumed that proton transfer occurred from the 9-position of $NMA^{+}\cdot$ (rather than from the N-methyl position) since the more stable, and observed, acridanyl radical would be the immediate product.[2] We now report that initial proton transfer occurs from the N-methyl position of $NMA^{+}\cdot$, followed by a fast ($t_{1/2}$ < 500 ps) intramolecular [1,5] proton shift yielding the acridanyl radical.

The experimental procedure for obtaining absorption spectra of photolysis intermediates with a time resolution of 25 ps has been described in detail.[1,4] Three systems observed simultaneously contained 0.05 M Bph and 1.0 M either NMA or the two deuterated analogues NMA-9,9-d_2 and N-(methyl-d_3)acridan.[5]

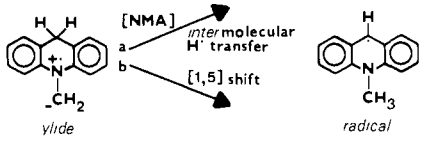
The rate of proton transfer from $NMA^{+}\cdot$ and $NMA^{+}\cdot$-9,9-d_2 were identical (within 3% as determined by the disappearance of $Bph^{-}\cdot$ and $NMA^{+}\cdot$); however, the N-(methyl-d_3)acridan gave a slower rate of proton transfer yielding $k_H/k_D = 1.4 \pm 0.05$. These results indicate that initial proton transfer occurs from the N-methyl position rather than the 9 position of $NMA^{+}\cdot$. The ratios of ketyl radical to N-methylacridanyl radical (determined by the ratio of the 550- and 520-nm peaks) were constant for all three systems studied indicating that although initial proton transfer occurs from the N-methyl position, the N-methylacridanyl radical appears at a rate similar to ketyl radical formation.

Further evidence that initial proton transfer occurs from the N-methyl position with subsequent formation of the acridanyl radical was obtained by NMR analysis. A solution of 1 M Bph with 0.015 M N-(methyl-d_3)acridan in C_6D_6 was photolyzed to ~50% conversion of the acridan. The remaining starting material contained >20% N-(methyl-d_2)acridan. Furthermore, the 9,9′-acridanyl dimer (one of the major products) contained ~100% N-methyl-d_2 groups.[7]

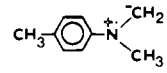
Scheme I



Scheme II



Initial proton transfer from the N-methyl position will create an ylide. Since the acridanyl radical appears as fast as the ketyl radical, the ylide must be converted to the acridanyl radical within 500 ps. Two mechanisms can account for conversion of the ylide to the radical, paths a and b, Scheme II. Path a is an *intermolecular* hydrogen atom transfer from the 9-position of acridan to the ylide yielding acridanyl radical and acridan. If path a is occurring, we anticipate that other ylides similar to the NMA ylide will also abstract a hydrogen atom from NMA. N,N-Dimethyl-p-toluidine (DMT) undergoes electron–proton transfer to ^{3}Bph in C_6H_6 at rates similar to those for NMA. Proton transfer from $DMT^{+}\cdot$ to $Bph^{-}\cdot$ will create a DMT ylide similar to the NMA ylide. Laser excitation of 0.05 M Bph with 1 M



DMT–*ylide*

NMA and 1 M DMT in C_6H_6 showed the same amount of ketyl radical (5 ns after excitation) as a solution with only 1 M NMA but showed only half as much acridanyl radical. This result shows that the DMT ylide does not abstract a hydrogen atom from acridan and rules out path a as the mechanism for acridanyl radical formation. By exclusion pathway b, an *intra*molecular [1,5] sigmatropic shift, must be occurring.

The reason for kinetically favored proton abstraction from the N-methyl group rather than the thermodynamically favored 9-position must be due to the geometry of the ion pairs in solution. It is anticipated that the favored geometry would allow maximum π system overlap between the two aromatic systems and strong

†Camille and Henry Dreyfus Teacher-Scholar and Alfred P. Sloan Fellow.

(1) Peters, K. S.; Pang, E.; Rudzki, J. *J. Am. Chem. Soc.* **1982**, *104*, 5535.

(2) Mass spectral analysis of NMA and NMA-9,9-d_2 has shown that hydrogen atom loss occurs predominantly from the 9 position.[3] Our mass spectral analysis of NMA, NMA-9,9-d_2, and N-(methyl-d_3)acridan confirm this previous conclusion, indicating that <1% of the hydrogen loss occurs from the N-methyl position in the gas phase.

(3) Clark, J.; Bakavoli, M. *J. Chem. Soc., Perkin Trans. 1* **1977**, 1966.

(4) Simon, J. D.; Peters, K. S. *J. Am. Chem. Soc.*, in press.

(5) NMA was prepared as described previously.[6] The NMA-9,9-d_2 was prepared by $NaBD_4$ reduction of N-methylacridone in 2-propanol at 80 °C, 14 h, 75% yield, NMR and mass spectrum indicated it was >93% d_2, ~6% dH, and <1% H_2. N-(methyl-d_3)acridan was prepared similar to NMA using CD_3I rather than CH_3I. NMR and mass spectrum indicated it was >99.8% methyl-d_3.

(6) Colter, A. K.; Saito, G.; Sharom, F. J. *Can. J. Chem.* **1977**, *55*, 2741.

(7) Photolysis was done with a 300-W medium-pressure Hg arc lamp filtered through a 330-nm cutoff filter. NMR analysis of the mixture (1.0 M Bph and 0.015 M N-(methyl-d_3)acridan in C_6D_6) before photolysis showed a peak at 3.66 ppm due to the methylene bridge protons (9 position) and a very small peak at 2.80 ppm due to the <0.2% N-(methyl-d_2)acridan in the starting material (along with many peaks between 6.5 and 8 ppm due to the Bph and NMA aromatic protons). After photolysis to 50% conversion, N-(methyl-d_2)acridan (2.80 ppm, pentet) accounts for >20% of the remaining starting material and pentets appear at 2.69 and 2.60 ppm. We assign the pentet at 2.60 ppm to the 9,9′-(N-(methyl-d_2)acridanyl) dimer (a sample of 9,9′-(N-methylacridanyl) dimer shows a singlet at 2.63 ppm). The pentet at 2.69 is possibly due to the mixed dimer from the acridanyl and ketyl radicals. The position of the N-methyl-d_2 NMR peaks in the starting material (2.80 ppm) and in the 9,9′-acridanyl dimer (2.60 ppm) are shifted upfield from the N-methyl groups in the corresponding compounds, 2.84 and 2.63 ppm, respectively. Isotope shifts of these magnitudes for CHD_2 vs. CH_3 groups are common in proton NMR.[8] NMR spectra were recorded on a Bruker 300 MHz.

(8) Gutowsky, H. S. *J. Chem. Phys.* **1959**, *31*, 1683.

0002-7863/83/1505-5708$01.50/0