and actual spectral absorption is very good (0.20 ppm vs. 0.23 ppm). By this analysis, the initially formed isomer A corresponds to structure IV and B to structure V.

When IIIa was treated as described above except for the presence of 15 equiv of $DNMe_2$, 0.6 D was incorporated at C_6 in the product aminofulvene. On the other hand, when the 4,6-dibromobicyclo[3.1.0]hexene was treated under similar conditions, only 0.2 D was incorporated.[2] This may indicate that the lifetime of 2-*tert*-butylbicyclo[3.1.0]hexatriene, IIa, is somewhat longer than that of unsubstituted bicyclo[3.1.0]-hexatriene, thereby allowing IIa more time to exchange.

In view of the chemistry of bicyclo[3.1.0]hexatriene, the nucleophilic addition of $HNMe_2$ should entail protonation either at C_2 or C_4 of IIa. Proton delivery to C_2 of IIa should be disfavored for the same reason that protonation at the tertiary carbon of methylcyclopentadienyl anion does not occur.[7] A mechanism consistent with that elucidated for bicyclo[3.1.0]-hexatriene entails an initial trans nucleophilic addition of dimethylamine to IIa with protonation occurring at the unsubstituted C_4. A subsequent [1,5] sigmatropic shift of the hydrogen syn to the nitrogen generates the less strained diene VIa.[9] At this point, the diene VIa, instead of undergoing a disrotatory electrocyclic opening to yield the sterically conjested 4-*tert*-butyl-6-dimethylaminofulvene (VIIIa),[10] is converted to the isomeric diene VII via a base catalyzed [1,5] sigmatropic shift. VII then undergoes a ring opening to form the comparatively stable IV.

By this analysis a less bulky alkyl at C_2 of I should lead to the formation of the 4-substituted aminofulvene since the counterpart of diene VI should open directly. To test this prediction, 2-methyl-4,6-dibromobicyclo[3.1.0]hex-2-ene (IIIb) was subjected to the standard conditions. The predominant product was 6-bromo-4-methylenebicyclo[3.1.0] hex-2-ene. However, a single methyl-6-dimethylaminofulvene (C) was obtained as a minor product. Unlike the *tert*-butylfulvene IV, fulvene C did not epimerize upon purification via column chromatography.

To confirm the structure of C, methylcyclopentadienyl anion was converted to a mixture of three methyl-6-dimethylaminofulvenes using a procedure devised by Hafner.[12] By ^1H NMR and ^{13}C NMR the product, after purification by column chromatography, consisted of a 2:1:1 mixture. The major component was assigned as 4-methyl-6-dimethylaminofulvene (VIII) since under these equilibrating conditions, equal amounts of 2- and 3-methyl-6-dimethylaminofulvenes IVb and Vb should be present.[13] By ^1H NMR and ^{13}C NMR, product C corresponds to structure VIII. Just as was observed for the unsubstituted case, the disrotary opening of VI is fast compared to further [1,5] hydrogen shifts provided that the alkyl group at C_2 does not sterically interfere with ring opening.

In view of the increased rate of exchange at C_6, sterically demanding substituents may provide a means of sufficiently stabilizing I to permit observation of chemistry other than nucleophilic attack. We are presently pursuing this line of investigation.

Acknowledgment. We thank Research Corporation for financial support.

References and Notes

(1) W. N. Washburn and R. Zahler, *J. Am. Chem. Soc.*, **98,** 7827 (1976).
(2) W. N. Washburn and R. Zahler, *J. Am. Chem. Soc.*, **98,** 7828 (1976).
(3) ^1H NMR ($CDCl_3$) δ 1.21 (s, 9 H), 1.41 (s, 9 H), 6.01–6.58 (m, 3 H), 7.11 (s, 1 H, H_6); ^{13}C NMR ($CDCl_3$, proton decoupled) ppm from Me_4Si 28.08 (CMe_3), 30.06 ($OCMe_3$ methyl), 107.85, 123.86, 126.54 (tertiary ring carbon), 114.15, 116.97 (quaternary ring carbon), 147.51(C_6).
(4) ^1H NMR ($CDCl_3$) δ, isomer A 1.28 (s, 9 H), 3.24 (s, 6 H), 6.39 (m, 3 H), 7.00 (s, 1 H, H_6); isomer B 1.28 (s, 9 H), 3.24 (s, 6 H), 6.15 (m, 1 H), 6.62 (m, 2 H), 7.05 (s, 1 H, H_6); ^{13}C NMR ($CDCl_3$, proton decoupled) ppm from Me_4Si, 1:1 A and B 31.20 (CMe_3), 43.11 (NMe_2), 107.00, 114.73, 117.14, 119.28, 125.04, 125.32 (tertiary ring carbons), 147.00, 147.17 (C_6); mass spectrum mixture A and B (*m*/e) parent 177 (%RA = 29), 162 (%RA = 100).
(5) ^1H NMR ($CDCl_3$) δ, mixture of two isomers, 1.10 (s, 9 H), 3.84 (s, 6 H), 4.27 (m, 1 H), 4.77 (m, 1 H), 5.38 (m, 1 H), 6.50 (m, 1 H), 7.27 (m, 5 H); mass spectrum (*m/e*) parent 352 (%RA = 86), 292 (%RA = 100).
(6) A. Mannschreck and U. Kolle, *Chem. Ber.*, **102,** 243 (1969).
(7) Lithium methylcyclopentadienyl anion was protonated in acetic acid–THF at −75 °C and trapped with *N*-phenylmaleamide at −15 °C overnight. By ^1H NMR only the adduct of 1-methylcyclopentadiene was formed. Our controls established that 5-methylcyclopentadiene[8] did not rearrange under the trapping conditions.
(8) S. McLean and P. Haynes, *Tetrahedron*, **21,** 2313 (1965).
(9) The implicit assumption is that the rearrangement of II to VI proceeds with the same selectivity with respect to hydrogen migration as did the analogous transformation of the unsubstituted bicyclo[3.1.0]hexatriene.[1,2] Consequently, only the hydrogen syn to the heteroatom at C_6 of IXa should undergo a [1,5] sigmatropic migration. Additional support for this mechanism is provided by the exclusive formation of IV as the initial product. If both the syn and anti methylene hydrogens of IXa were equally prone to migration, both IV and V would have been produced. Compound VI and VII cannot be in equilibrium with each other in order for the results to be consistent with those obtained from the analogous deuterium labeled compounds.
(10) One measure of the steric crowding induced by a *tert*-butyl group at C_1 of C_4 of 6-dimethylaminofulvene (X) is provided by the fact that alkylation of X with *t*-BuCl/$AlCl_3$ leads exclusively to the formation of 2- and 3-*tert*-butyl-6-dimethylaminofulvene. On the other hand, less hindered electrophiles exclusively attacked positions 1 and 4, the sites of highest electron density.[6,11]
(11) K. Hafner, K. H. Hafner, C. Konig. M. Kreuder, G. Ploss, G. Schulz, E. Sturm, and K. H. Vopel, *Angew. Chem., Int. Ed. Engl.*, **2,** 123 (1963).
(12) K. Hafner, K. H. Vopel, G. Ploss, and C. Konig, *Justus Liebigs Ann. Chem.*, **661,** 52 (1963).
(13) 4-Methyl-6-dimethylaminofulvene: ^1H NMR (CCl_4) δ, 2.08 (s, 3 H), 3.02 (s, 6 H), 5.70–6.37 (m, 3 H), 6.65 (s, 1 H, H_6); ^{13}C NMR ($CDCl_3$, proton decoupled) ppm from Me_4Si 15.16 (CH_3), 42.52 (NMe_2), 111.04, 121.57, 124.93 (tertiary ring carbon), 146.18 (C_6).

William N. Washburn,* Robert Zahler
Department of Chemistry, University of California, Berkeley
Berkeley, California 94720

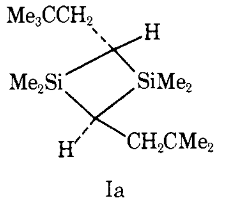
Received November 3, 1976

The Addition of *tert*-Butyllithium to Vinylhalosilanes. A Novel, High Yield Route to 1,3-Disilacyclobutanes

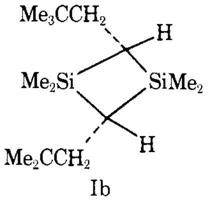
Sir:

Since the initial discovery of the addition of organolithium reagents to vinylsilanes by Cason and Brooks,[1] there have been relatively few reports of such reactions.[2] To our knowledge, the only example of the addition of an organolithium reagent to a vinylsilane bearing substituents susceptible to nucleophilic displacement on silicon is contained in the original report. Cason and Brooks observed a 4% yield of β-phenethyltriphenylsilane after hydrolytic workup of the mixture resulting from the reaction of excess phenyllithium with vinyltrichlorosilane in ether.[1] However, alkoxy and chloro groups on silicon have been found to activate vinylsilanes toward the addition of Grignard reagents.[3] We report here a novel, high yield synthesis of substituted 1,3-disilacyclobutanes, from the reaction of *tert*-butyllithium with vinyldimethylchlorosilane.

In an attempt to prepare vinyldimethyl-*tert*-butylsilane, 100 mmol of *tert*-butyllithium in 141 mL of pentane was added slowly to 100 mmol of vinyldimethylchlorosilane in 50 mL of dry hexane, under an argon atmosphere at room temperature. An exothermic reaction with the immediate formation of a white precipitate occurred. Hydrolytic workup gave, instead of the desired product, 6.55 g (46%) of I; bp 72–98 °C (1 mm); identified on the basis of data given below as a mixture of the *E* (Ia) and *Z* (Ib) isomers of 1,1,3,3-tetramethyl-2,4-di-



Ia



Ib

neopentyl-1,3-disilacyclobutane. In addition, 4.25 g (30%) of a higher boiling material, tentatively identified as a mixture of substituted 1,3,5-trisilacyclohexanes was obtained.

Yields of greater than 80% may be obtained for the 1,3-disilacyclobutanes, I, by combination of the vinyldimethylchlorosilane and *tert*-butyllithium in pentane/hexane, at −78 °C, to give a clear solution. On warming, precipitation of lithium chloride begins at about −30 to −20 °C. The order of addition of the reactants has no appreciable effect on the yield of I.

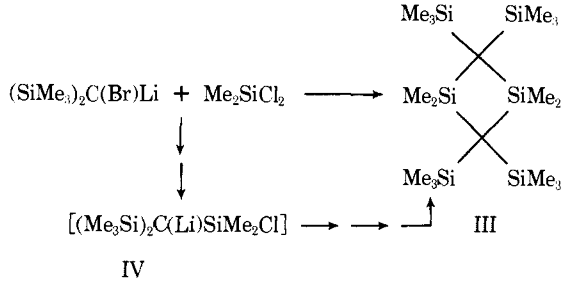
Gas chromatographic analysis of I permits separation of two colorless solids, Ia (47%) and Ib (53%). Ia has a mass, *m/e* (M^+) 284, and elemental analysis (Calcd for $C_{16}H_{36}Si_2$: C, 67.52; H, 12.75. Found: C, 67.67; H, 12.90) consistent with the 1,3-disilacyclobutane structure. Its NMR spectrum ((CCl_4) δ 0.15 (s, 12 H), 0.75 (s, 18 H), 1.28 (d, 4 H, J = 7.5 Hz), 0.2–0.4 (2 H)[4]), with a single absorbance for the dimethylsilyl protons, indicates that it is the *E* isomer in which the silicon methyl groups are equivalent. For Ib, the mass, *m/e* (M^+) 284, and analysis (Found: C, 67.81; H, 12.61) are again consistent with the 1,3-disilacyclobutane formulation. The NMR spectrum of Ib ((CCl_4) δ 0.08 (s, 6 H), 0.21 (s, 6 H), 0.76 (s, 18 H), 1.32 (d, 4 H, J = 7.0 Hz), 0.2–0.4 (2 H)[4]) with two sets of equivalent dimethylsilyl protons indicates that it is the *Z* isomer. In all of our experiments to date, the reaction of *tert*-butyllithium with vinyldimethylchlorosilane has given approximately equal amounts of Ia and Ib.

It seems reasonable that the first step in this reaction is the addition of *tert*-butyllithium to the vinylsilane producing an α-lithiochlorosilane, II.[2d] In this light, the reaction

$$RLi + CH_2{=}CHSi(Cl)Me_2 \longrightarrow RCH_2\underset{Li}{CH}—\underset{Cl}{SiMe_2}$$

II, R = *t*-Bu

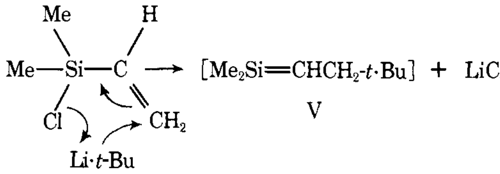
bears a marked similarity to a reaction recently reported by Seyferth and Lefferts. They observed that the reaction of bis(trimethylsilyl)bromomethyllithium with dimethyldichlorosilane at low temperature in ether solvents gave moderate yields (36%) of 1,1,3,3-tetramethyl-2,2,4,4-tetrakis(trimethylsilyl)-1,3-disilacyclobutane, III as the major product.[5] Subsequently, they demonstrated that the α-lithio compound, IV, could be an intermediate in the formation of III, using trapping experiments with trimethyltin chloride or bromine.[6]



It is also significant to note that the bromine derivative of IV, $(Me_3Si)_2C(Br)SiMe_2Cl$, when treated with *tert*-butyllithium, gave a 14% yield of III,[6] presumably by lithium–halogen exchange to re-form IV. In our system, when the reaction of *tert*-butyllithium with vinyldimethylchlorosilane is carried out in tetrahydrofuran, products which may be ascribed to coupling of intermediate lithium compounds with chlorosilanes are obtained in addition to I.[8]

In attempts to trap the analogous α-lithiochlorosilane intermediate, II, in our reaction, a mixture of excess trimethylchlorosilane and vinyldimethylchlorosilane was added to *tert*-butyllithium in hexane at −78 °C. A 48% yield of the 1,3-disilacyclobutane mixture, I, was obtained. Not a trace of $ClMe_2SiCH(SiMe_3)CH_2C(CH_3)_3$, the anticipated derivative of II, was obtained. In another experiment, the solution resulting from the addition of 1 equiv of vinyldimethylchlorosilane to *tert*-butyllithium in hexane at −78 °C was warmed to −40 °C for 15 min. No precipitation of lithium chloride, a process which always accompanies the formation of I in hydrocarbon solvents, had occurred. The reaction mixture was cooled to −78 °C and excess trimethylchlorosilane in tetrahydrofuran was added. The immediate formation of a white precipitate was observed. Workup, after warming to room temperature gave a 74% yield of I. None of the expected products from coupling of organolithium reagents with trimethylchlorosilane was observed. When the reaction of *tert*-butyllithium with vinyldimethylchlorosilane in hydrocarbons is monitored over the temperature range −78 to 25 °C by NMR, peaks corresponding to I grow as peaks corresponding to vinyldimethylchlorosilane diminish. At no time are peaks which could be attributed to the possible intermediate, II, observed. These results indicate that, at least in hydrocarbon solvents, the α-lithiochlorosilane, II, has an extremely short lifetime, and that the coupling of II with trimethylchlorosilane is slow in comparison to the production of the disilacyclobutanes, I.[7] Competition experiments in which equimolar amounts of vinyltrimethylsilane and trimethylchlorosilane are treated with 0.5 equiv of *tert*-butyllithium give only products arising from an initial addition of the *tert*-butyllithium to vinyltrimethylsilane. In both hexane and ether solvents, but not in tetrahydrofuran, the *elimination* of lithium hydride to give *trans*-1-*tert*-butyl-2-trimethylsilylethylene competes favorably with coupling of the alkyllithium adducts when the reactions are carried out under conditions analogous to those used for the preparation of I.[8]

It is possible that the reaction between *tert*-butyllithium and vinyldimethylchlorosilane in hydrocarbon involves a six-center transition state, analogous to that proposed by Magid and co-workers for the alkylation of allyl chlorides by phenyllithium,[9] leading to the silaethylene intermediate, V. It is well known that, in the absence of trapping reagents, silaethylene analogues of V dimerize to give 1,3-disilacyclobutanes both in the gas phase,[10] and in solution.[11]



At the present time it is not possible to differentiate between a series of coupling reactions leading to I,[6] or the formation of V as the precursor to I. In light of the known sluggishness of coupling reactions between organolithium reagents and chlorosilanes in hydrocarbon solvents,[12] the high yields obtained for I in our system, and our lack of success in trapping II in hydrocarbon solvents, we are inclined to favor a pathway to the 1,3-disilacyclobutanes involving the silaethylene intermediate, V. Experiments are presently underway in our laboratories to differentiate between the two possible routes, and to determine the generality of the reaction.

Acknowledgment. The authors gratefully acknowledge the support of the Robert A. Welch Foundation and the North Texas State University Faculty Research Fund.

References and Notes

(1) L. F. Cason and H. G. Brooks, *J. Am. Chem. Soc.*, **74**, 4582 (1952); *J. Org. Chem.*, **19**, 1278 (1954).

(2) (a) J. E. Mulvaney and Z. G. Gardlund, *J. Org. Chem.*, **30**, 917 (1965); (b) M. R. Stober, K. W. Michael, and J. L. Speier, *ibid.*, **32**, 2740 (1967); (c) A. G. Brook, J. M. Duff, and D. G. Anderson, *Can. J. Chem.*, **48**, 561 (1970); (d) R. F. Cunico, *J. Organomet. Chem.*, **60**, 219 (1973).

(3) G. R. Buell, R. Corriu, C. Guerin, and L. Spialter, *J. Am. Chem. Soc.*, **92**, 7424 (1970).

(4) The ring protons, signals which presumably would be triplets from coupling with methylene protons of the neopentyl group, lie in the methylsilyl region and were too weak to be resolved.

(5) D. Seyferth and J. L. Lefferts, *J. Am. Chem. Soc.*, **96**, 6237 (1974).

(6) D. Seyferth and J. L. Lefferts, *J. Organomet. Chem.*, **116**, 257 (1976).

(7) It should be noted that, when the reaction of *tert*-butyllithium with vinyldimethylchlorosilane in the presence of various trapping reagents is carried out in tetrahydrofuran, products which could possibly arise from II are obtained,[8] analogous to the derivatization of α-lithiobenzyldiphenylchlorosilane with trimethylchlorosilane reported by K. G. Rutherford and R. J. Seidewand, *Can. J. Chem.*, **53**, 3103 (1975).

(8) T. F. O. Lim, D. Mapel, and P. R. Jones, unpublished results.

(9) R. M. Magid, E. C. Nieh, and R. D. Gandor, *J. Org. Chem.*, **36**, 2099 (1971); R. M. Magid and E. C. Nieh, *ibid.*, **36**, 2105 (1971).

(10) L. E. Gusel'nikov, N. S. Nametkin, and V. M. Vdovin, *Acc. Chem. Res.*, **8**, 18 (1975), and references therein.

(11) P. Boudjouk and L. H. Sommer, *J. Chem. Soc., Chem. Commun.*, 54 (1973).

(12) A. E. Bey and D. R. Weyenberg, *J. Org. Chem.*, **31**, 2036 (1966).

Paul R. Jones,* Thomas F. O. Lim

Department of Chemistry
North Texas State University
Denton, Texas 76203

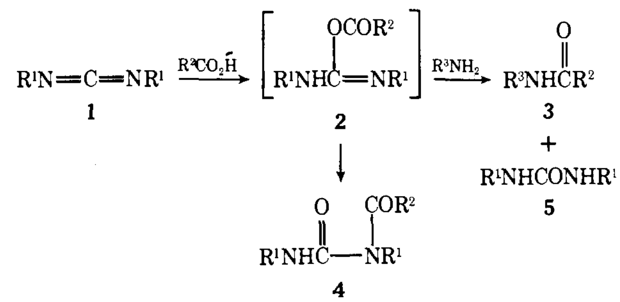
Received October 19, 1976

Isolation and Reactivity of a Model for the Carbodiimide–Carboxylic Acid Adduct. *O*-Benzoyl-*N*,*N*-dimethyl-*N*'-(*N*-methyl-2,4-dinitroanilino)isourea

Sir:

We wish to report the crystal structure and reactivity of an analogue of the adduct **2** which is the proposed intermediate in carbodiimide mediated condensations. The isourea undergoes acid-catalyzed inter- and intramolecular acyl transfer in the pH range 3-6 but the complex pH dependency favors the intermolecular reaction (which is necessary for condensation) in more acidic solution.

Carbodiimides, such as dicyclohexylcarbodiimide (DCC, **1**, R^1 = cyclohexyl), have received wide use as reagents to promote condensations, particularly in peptide (**3**) synthesis. However, the exact nature of the intermediates responsible for these reactions remains obscure, although it has been suggested that *O*-acylisoureas (**2**), formed on reaction of the carbodiimide with the carboxylic acid component, might be involved in this reaction[1] and in the related condensations with Woodward's reagent.[2] The failure to isolate or detect **2** was attributed to the occurrence of a rapid[3] O → N acyl transfer to give **4**, which is the product isolated in the absence of added nucleophile; indeed the undesirable formation of **4** can be the major problem in the use of **1** in peptide synthesis.[4]



Reaction of dichloromethylene dimethylammonium chloride[5] with *N*-methyl-*N*-(2,4-dinitrophenyl)hydrazine in chlorobenzene gave the formamidine chloride **6** (88%, mp 102 °C) which on treatment with silver benzoate in chloroform gave the *O*-benzoylisourea **8** (90%, mp 125.5 °C), uncontaminated by isomeric **9** and urea **11**.

Crystals of **8** are monoclinic, space group $P2_1/c$ with four molecules in a cell of dimensions a = 15.732 (3) Å, b = 16.246 (5) Å, c = 7.628 (1) Å, β = 108.94 (1)°. The structure was solved by direct methods and refined by full-matrix least-squares calculations to an R value of 0.0438 for 1281 independent observed reflections measured with a Hilger and Watts four-circle computer-controlled diffractometer.[10] In the structure (Figure 1) the benzoyl group is clearly trans to the position of the lone pair on the imine nitrogen atom. The C═N bond length is 1.286 (6) Å; other distances are in accord with expected values. (See paragraph at end of paper regarding supplementary material.)

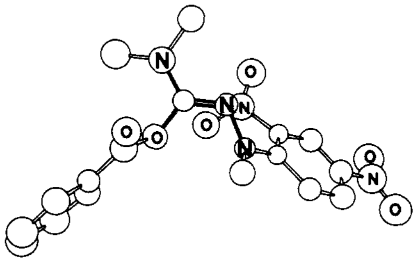


Figure 1. (*Z*)-*O*-Benzoyl-*N*,*N*-dimethyl-*N*'-(*N*-methyl,2,4-dinitroanilino)-isourea (**8**), viewed normal to the plane of the imine moiety.

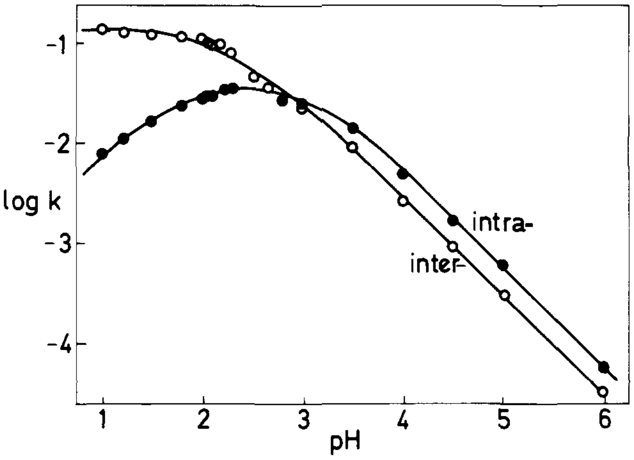
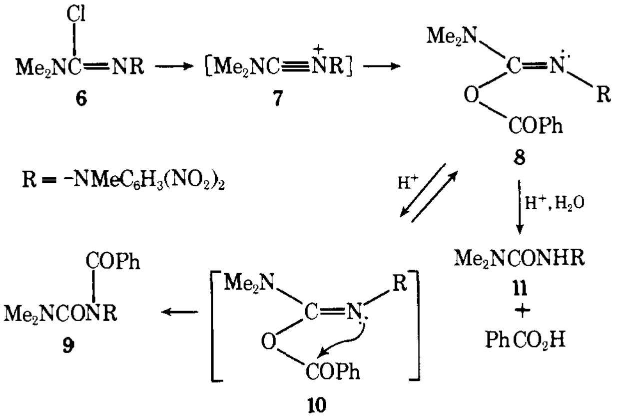


Figure 2. Observed rate constants for the intermolecular conversion of **8** to **11** (open circles) and intramolecular conversion to **9** (closed circles) at 25 °C in 4:1 water–dioxane. The points are experimental and the curves theoretical; for **8** → **11**, $k_{\mathrm{obsd}} = k_1 a_{\mathrm{H}}/(a_{\mathrm{H}} + K_{\mathrm{a}})$, $k_1 = 1.50 \times 10^{-1}\ \mathrm{s}^{-1}$, $K_{\mathrm{a}} = 4.4 \times 10^{-3}$; for **8** → **9**, $k_{\mathrm{obsd}} = k_2 a_{\mathrm{H}} K_{\mathrm{a1}}/(a_{\mathrm{H}}^2 + a_{\mathrm{H}} K_{\mathrm{a1}} + K_{\mathrm{a1}} K_2)$ (see ref 9) with $k_2 = 3 \times 10^{-2}\ \mathrm{s}^{-1}$, $K_2 = 5.2 \times 10^{-4}$.



The stereospecific formation of the *Z* isomer **8** by this route is consistent with the intermediacy of the ion **7** in the reaction sequence; we have recently shown[6] that nucleophiles react with simple nitrilium ions (-C≡N⁺-) to yield only the Z isomer (i.e., that in which the adjacent lone pair and nucleophile are mutually trans). Consistent with this, solvolysis of **6** at pH 6