Acknowledgment. This work was supported by grants from the National Institutes of Health (HL-16029) and the National Science Foundation.

Registry No. CH_2=$CHCH_2CN$, 109-75-1; CH_2=$CHCH_2OAc$, 591-87-7; CH_2=$CHCH_2OEt$, 557-31-3; CH_2=$CHCH_2Ph$, 300-57-2; $(CH_3)_3CCH_2CH$=CH_2, 762-62-9; $(CH_3)_3CCH$=CH_2, 558-37-2; $CH_3CH_2CH(CH_3)CH$=CH_2, 760-20-3; CH_2=CHOAc, 108-05-4; *trans*-$(CH_3)_3CCH$=$CHC(CH_3)_3$, 692-48-8; *cis*-$(CH_3)_2CHCH$=$CHCH_3$, 691-38-3; *trans*-$(CH_3)_2CHCH$=$CHCH_3$, 674-76-0; CH_2=$CHCH_2Cl$, 107-05-1; CH_2=$CHCH_2Br$, 106-95-6; CH_2=$CH(CH_2)_3CH_3$, 592-41-6; $PhCH$=CH_2, 100-42-5.

Communications to the Editor

Stereoselection in the Michael Addition Reaction. 1. The Mokaiyama–Michael Reaction[1]

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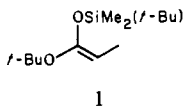
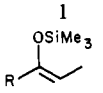
In the last decade, there has been a surge of interest in the stereoselective synthesis of acyclic and other conformationally flexible molecules.[2] As a part of this activity, considerable attention has been focused on stereoselective carbon–carbon bond-forming processes, particularly the aldol addition reaction[3] and the related reactions of crotylorganometallic reagents with aldehydes.[4] In contrast, much less is known about the stereochemistry of the Michael addition reaction, which may be considered to be a "vinylogous aldol addition reaction".[5] In this paper and others to follow, we will report initial results of a thorough investigation of this question.

In 1974–1976, Mukaiyama and co-workers introduced a version of the Michael addition reaction wherein an enolsilane reacts with an enone under conditions of Lewis acid catalysis.[5] Electronically, the Mukaiyama–Michael reaction is an acid-catalyzed 1,4-addition process and provides a mechanistic complement for the more well-studied base-catalyzed analogue. In the early work on the reaction[5] the focus was on the reaction itself, and stereochemistry was not investigated, although several examples that are capable of simple diastereoselection were included in the study. The current publication deals solely with the stereochemistry of the Mukaiyama–Michael reaction. Although the results at this time are preliminary, we have discovered several general structure–stereoselectivity relationships that should be of widespread utility in synthesis. Furthermore, we are also able to put forth a coherent transition-state hypothesis that explains the stereoselectivity observed.

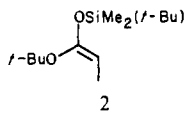
To investigate the stereoselectivity of the Mukaiyama–Michael addition, we have utilized the pair of stereoisomeric silyl ketene acetals **1** and **2** and enolsilanes In general, reactions were carried out by premixing the enone and an appropriate Lewis acid catalyst in methylene chloride at −78 °C, adding the enolsilane or ketene acetal at −78 °C, and working up by the addition of aqueous potassium carbonate after 30–120 min. In most cases, the isolated products were found to be stereoisomeric mixtures of anti and syn isomers (eq 1).[6] Isomeric ratios were determined by ^1H NMR, ^{13}C NMR, analytical HPLC, and capillary GLC. Stereostructures were assigned on the basis of X-ray crystallography, conversion to materials of known structure, and ^{13}C NMR chemical shift analogy; details are given in the supplemental material. Data are summarized in Table I.



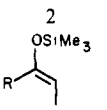
1



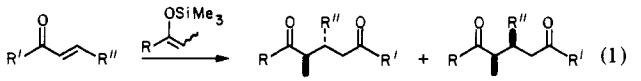
3, R = Et
4, R = *i*-Pr
5, R = *t*-Bu
6, R = Ph
7, R = *p*-$MeOC_6H_4$
8, R = 2,4,6-$Me_3C_6H_2$



2



9, R = Et
10, R = *i*-Pr
11, R = Ph
12, R = 2,4,6-$Me_3C_6H_2$



(1)

As shown in the table, enol silanes derived from ketones show a general tendency for anti addition, regardless of the stereostructure of the enolsilane (cf. inter alia entries 8–10 and 31, 14 and 34, 23 and 40, and 17 and 37). With the enolsilanes derived from aliphatic ketones, the observed anti selectivity ranges from modest (entry 15, 1.5:1) to good (entry 17, 10:1). The *Z* enol silanes derived from propiophenone and related aromatic ketones (**6–8**) show excellent anti selectivity (from a low of 10:1 to a maximum of >20:1). The *E* enolsilanes of aromatic ketones show lower anti selectivity (entries 40 and 41).

In striking contrast to the behavior of the foregoing enolsilanes, the silyl ketene acetals **1** and **2** show high syn selectivity with acyclic *tert*-butyl enones (entries 1–3 and 6). The latter compounds exhibit only low stereoselectivity with cyclohexenone (entries 5 and 7) and with 3-penten-2-one (entry 4). An interesting effect is seen in the reactions of the ketene acetals. If the ketene acetal is added slowly (syringe pump) to a -78 °C solution of the complex of the enone and $TiCl_4$, the sole product is the keto *tert*-butyldimethylsilyl ester. However, if the ketene acetal is added rapidly, the product is a mixture of *tert*-butyl and *tert*-butyldimethylsilyl esters.

The data may be explained in terms of the mechanism put forth in Scheme I. In this proprosal, the initial adduct A can undergo reversion to reactants (k_{-1}) or ionization to B. Desilylation of the latter intermediate to give C is effectively irreversible. We propose that, with ketene acetals, the initial equilibrium lies far to the right, because the oxonium ion is delocalized. In this case, desilylation of the (trialkylsilyl)oxonium ion is fast, relative to retro-Michael

(1) Part 29 in the series "Acyclic Stereoselection". For part 28, see: Heathcock, C. H.; Montgomery, S. H. *Tetrahedron Lett.* **1985**, *26*, 1001–1004.

(2) See, inter alia: Bartlett, P. A. *Tetrahedron*, **1980**, *36*, 2.

(3) For reviews of aldol stereoselectivity, see: (a) Evans, D. A.; Nelson, J. V.; Taber, T. R. *Top. Stereochem.* **1982**, *13*. (b) Heathcock, C. H. "Comprehensive *Carbanion Chemistry*"; Buncel, E., Durst, T. Eds.; Elsevier: Amsterdam, **1984**; Vol. 2. (c) Heathcock, C. H. "Asymmetric Syntheses"; Morrison, J. D., Ed.; Academic Press: New York, **1984**, Vol. 3. (d) Mukaiyama, T. *Org. React.* **1982**, *28*, 203.

(4) For review of crotylorganometallic stereoselectivity, see: Hoffmann, R. W. *Angew. Chem.* **1982**, *94* (8), 569–580.

(5) (a) Narasaka, K.; Soai, K.; Mukaiyama, T. *Chem. Lett.* **1974**, 1223. (b) Narasaka, K.; Soai, K.f Aikawa, Y.; Mukaiyama, T. *Bull. Soc. Chem. Jpn.* **1976**, *49*, 779. (c) Saigo, K.; Osaki, M.; Mukaiyama, T. *Chem. Lett.* **1976**, 163.

(6) For a definition of the syn/anti convention, see: Masamune, S.; Ali, Sk. A.; Snitman, D. L., Garvey, D. S. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 557.

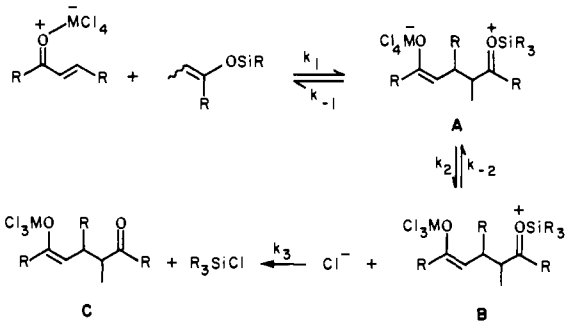
0002-7863/85/1507-2797$01.50/0

Table I. Stereochemistry of Reactions of Enolsilanes **1–12** with Enones

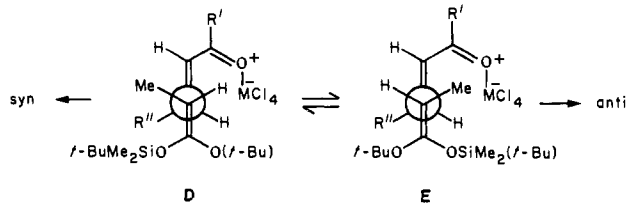
		prod (eq 1)					
entry	enol silane	R	R′	R″	Lewis acid	yield, %	anti/syn
1	**1**	RO[a]	*t*-Bu	Me	$TiCl_4$	88[b]	1:99
2	**1**	RO[a]	*t*-Bu	*i*-Pr	$TiCl_4$	87[b]	4:96
3	**1**	RO[a]	*t*-Bu	Ph	$TiCl_4$	77[b]	2:98
4	**1**	RO[a]	Me	Me	$TiCl_4$	74[c]	50:50
5	**1**	RO[a]	$-(CH_2)_3-$		$TiCl_4$	78[b]	25:75
6	**2**	RO[a]	*t*-Bu	*i*-Pr	$TiCl_4$	76[b]	2:98
7	**2**	RO[a]	$-(CH_2)_3-$		$TiCl_4$	78[b]	38:62
8	**3**	Et	*t*-Bu	Me	$SnCl_4$	74	88:12
9	**3**	Et	*t*-Bu	Me	$SnCl_4$	57[d]	89:11
10	**3**	Et	*t*-Bu	Me	$TiCl_4$	52[d]	88:12
11	**3**	Et	*i*-Pr	Me	$SnCl_4$	52	76:24
12	**4**	*i*-Pr	Et	Me	$SnCl_4$	42	59:41
13	**4**	*i*-Pr	*i*-Pr	Me	$SnCl_4$	87	65:35
14	**4**	*i*-Pr	*t*-Bu	Me	$SnCl_4$	63	85:15
15	**4**	*i*-Pr	Ph	Me	$SnCl_4$	78	60:40
16	**4**	*i*-Pr	*t*-Bu	Et	$SnCl_4$	68	83:17
17	**4**	*i*-Pr	*t*-Bu	*i*-Pr	$SnCl_4$	24	91:9
18	**4**	*i*-Pr	*t*-Bu	*t*-Bu	$SnCl_4$	0	
19	**4**	*i*-Pr	*t*-Bu	Ph	$SnCl_4$	91	85:15
20	**5**	*t*-Bu	*i*-Pr	Me	$SnCl_4$	37	59:41
21	**5**	*t*-Bu	*t*-Bu	Me	$SnCl_4$	10	69:31
22	**5**	Ph	*i*-Pr	Me	$SnCl_4$	50	91:9
23	**6**	Ph	*t*-Bu	Me	$SnCl_4$	69	>95:5
24	**6**	Ph	Ph	Me	$SnCl_4$	75	95:5
25	**6**	Ph	*t*-Bu	Et	$SnCl_4$	95	>95:5
26	**6**	Ph	*t*-Bu	*i*-Pr	$SnCl_4$	89	>95:5
27	**6**	Ph	*t*-Bu	*t*-Bu	$SnCl_4$	0	
28	**6**	Ph	*t*-Bu	Ph	$SnCl_4$	81	68:32
29	**7**	*p*-$MeOC_6H_4$	*t*-Bu	Me	$SnCl_4$	94	93:7
30	**8**	2,4,6-$Me_3C_6H_2$	*t*-Bu	Me	$TiCl_4$	68[e]	93:7
31	**9**	Et	*t*-Bu	Me	$SnCl_4$	59	87:13
32	**10**	*i*-Pr	Et	Me	$SnCl_4$	42	69:31
33	**10**	*i*-Pr	*i*-Pr	Me	$SnCl_4$	69	77:23
34	**10**	*i*-Pr	*t*-Bu	Me	$SnCl_4$	81	67:33
35	**10**	*i*-Pr	Ph	Me	$SnCl_4$	82	81:19
36	**10**	*i*-Pr	*t*-Bu	Et	$SnCl_4$	73	76:24
37	**10**	*i*-Pr	*t*-Bu	*i*-Pr	$SnCl_4$	26	89:11
38	**10**	*i*-Pr	*t*-Bu	*t*-Bu	$SnCl_4$	0	
39	**10**	*i*-Pr	*t*-Bu	Ph	$SnCl_4$	46	63:37
40	**11**	Ph	*t*-Bu	Me	$SnCl_4$	77	73:27
41	**12**	2,4,6-$Me_3C_6H_2$	*t*-Bu	Me	$TiCl_4$	87[e]	82:18

[a] The product is a mixture of *tert*-butyl and *tert*-butyldimethylsilyl esters; see text. [b] Yield given is for the keto acid, obtained by hydrolysis of the keto ester with aqueous NaOH. [c] This reaction gave 35% of 1,2-addition product and 65% of 1,4-addition product. [d] The Lewis acid was added at −78 °C to a premixed solution of enone and enolsilane. [e] This reaction was carried out at 0 °C and quenched immediately following the addition of enolsilane.

Scheme I

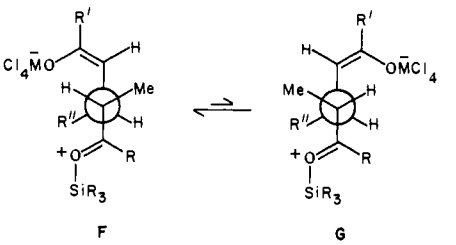


Scheme II



reaction. Therefore, the stereochemistry observed with ketene acetals is a result of interactions in the isomeric transition states

Scheme III



leading to syn and anti diastereomers. We believe that the syn selectivity observed with acyclic *tert*-butyl enones is the result of a preference for transition-state conformation D relative to E (Scheme II). This kinetic hypothesis is in agreement with the fact that the stereoselectivity is independent of ketene acetal geometry and that stereoselectivity disappears with the methyl enone (Table I, entry 4).[7]

(7) In Scheme II we illustrate a reacting conformation of the Lewis acid coordinated enone in which the Lewis acid is trans to R′ about the carbon–oxygen double bond and the enone chromophore is cisoid. This is probably the case when R′ is *tert*-butyl but probably is not when R′ is a smaller group. We are currently engaged in investigating other enones, to see if the two-point trend suggested by entries 1 and 4 is borne out (e.g., R′ = *i*-Pr, Et). A more extensive discussion of this mechanistic point will be deferred until the full paper on the subject.

In the case of enolsilanes, the initial equilibrium is not as favorable. Thus, retro-Michael reaction competes with desilylation of B, and the observed stereoselectivity is a result of either partial or complete thermodynamic control. With these compounds, we suggest that anti stereochemistry predominates because gauche interactions are minimized in conformation F, relative to G (Scheme III). This hypothesis nicely explains the observed anti stereoselectivity and the fact that stereoselectivity is largely independent of enol silane stereostructure.

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Registry No. 1, 89043-59-4; **2**, 89043-58-3; **3**, 51425-54-8; **4**, 19980-41-7; **5**, 61878-68-0; **6**, 66323-99-7; **7**, 95740-73-1; **8**, 72658-08-3; **9**, 51425-53-7; **10**, 19980-42-8; **11**, 71268-59-2; **12**, 72658-15-2; $TiCl_4$, 7550-45-0; $SnCl_4$, 7646-78-8; *t*-BuC(O)CH=CHMe, 20971-19-1; *t*-BuC(O)CH=CHPr-*i*, 38343-04-3; *t*-BuC(O)CH=CHPh, 29569-91-3; MeC(O)CH=CHMe, 3102-33-8; R′C(O)CH=CHR″ (R′, R″=$(CH_2)_3$), 930-68-7; *i*-PrC(O)CH=CHMe, 50396-90-2; EtC(O)CH=CHMe, 50396-87-7; PhC(O)CH=CHMe, 35845-66-0; *t*-BuC(O)CH=CHEt, 38343-01-0; *t*-BuC(O)CH=CHBu-*t*, 20859-13-6; *t*-BuOC(O)CH(Me)CH(Me)CH_2C(O)Bu-*t* (isomer 1), 95740-74-2; *t*-BuOC(O)CH(Me)CH(Me)CH_2C(O)Bu-*t* (isomer 2), 95740-75-3; *t*-BuOC(O)CH(Me)CH(*i*-Pr)CH_2C(O)Bu-*t* (isomer 1), 95740-76-4; *t*-BuOC(O)CH(Me)CH(*i*-Pr)CH_2C(O)Bu-*t* (isomer 2), 95740-77-5; *t*-BuOC(O)CH(Me)CH(Ph)CH_2C(O)Bu-*t* (isomer 1), 95740-78-6; *t*-BuOC(O)CH(Me)CH(Ph)CH_2C(O)Bu-*t* (isomer 2), 95740-79-7; *t*-BuOC(O)CH(Me)CH(Me)CH_2C(O)Me (isomer 1), 95740-80-0; *t*-BuOC(O)CH(Me)CH(Me)CH_2C(O)Me (isomer 2), 95740-81-1; *t*-BuOC(O)CH(Me)CH(R″)CH_2C(O)R′ (R′,R″ = $(CH_2)_3$) (isomer 1), 95740-83-3; *t*-BuOC(O)CH(Me)CH(R″)CH_2C(O)R′ (R′,R″ = $(CH_2)_3$) (isomer 2), 95740-84-4; EtC(O)CH(Me)CH(Me)CH_2C(O)Bu-*t* (isomer 1), 95740-85-5; EtC(O)CH(Me)CH(Me)CH_2C(O)Bu-*t* (isomer 2), 95740-86-6; EtC(O)CH(Me)CH(Me)CH_2C(O)Pr-*i* (isomer 1), 95740-87-7; EtC(O)CH(Me)CH(Me)CH_2C(O)Pr-*i* (isomer 2), 95740-88-8; *i*-PrC(O)CH(Me)CH(Me)CH_2C(O)Et (isomer 1), 95740-89-9; *i*-PrC(O)CH(Me)CH(Me)CH_2C(O)Et (isomer 2), 95740-90-2; *i*-PrC(O)CH(Me)CH(Me)CH_2C(O)Pr-*i* (isomer 1), 95740-91-3; *i*-PrC(O)CH(Me)CH(Me)CH_2C(O)Pr-*i* (isomer 2), 95740-92-4; *i*-PrC(O)CH(Me)CH(Me)CH_2C(O)Bu-*t* (isomer 1), 95740-93-5; *i*-PrC(O)CH(Me)CH(Me)CH_2C(O)Bu-*t* (isomer 2), 95740-94-6; *i*-PrC(O)CH(Me)CH(Me)CH_2C(O)Ph (isomer 1), 95740-95-7; *i*-PrC(O)CH(Me)CH(Me)CH_2C(O)Ph (isomer 2), 95740-96-8; *i*-PrC(O)CH(Me)CH(Et)CH_2C(O)Bu-*t* (isomer 1), 95740-97-9; *i*-PrC(O)CH(Me)CH(Et)CH_2C(O)Bu-*t* (isomer 2), 95740-98-0; *i*-PrC(O)CH(Me)CH(*i*-Pr)CH_2C(O)Bu-*t* (isomer 1), 95740-99-1; *i*-PrC(O)CH(Me)CH(*i*-Pr)CH_2C(O)Bu-*t* (isomer 2), 95741-00-7; *i*-PrC(O)CH(Me)CH(Ph)CH_2C(O)Bu-*t* (isomer 1), 95741-01-8; *i*-PrC(O)CH(Me)CH(Ph)CH_2C(O)Bu-*t* (isomer 2), 95741-02-9; *t*-BuC(O)CH(Me)CH(Me)CH_2C(O)Pr-*i* (isomer 1), 95741-03-0; *t*-BuC(O)CH(Me)CH(Me)CH_2C(O)Pr-*i* (isomer 2), 95741-04-1; *t*-BuC(O)CH(Me)CH(Me)CH_2C(O)Bu-*t* (isomer 1), 95741-05-2; *t*-BuC(O)CH(Me)CH(Me)CH_2C(O)Bu-*t* (isomer 2), 95741-06-3; PhC(O)CH(Me)CH(Me)CH_2C(O)Pr-*i* (isomer 1), 95741-07-4; PhC(O)CH(Me)CH(Me)CH_2C(O)Pr-*i* (isomer 2), 95741-08-5; PhC(O)CH(Me)CH_2C(O)Bu-*t* (isomer 1), 95741-09-6; PhC(O)CH(Me)CH(Me)CH_2C(O)Bu-*t* (isomer 2), 95741-10-9; PhC(O)CH(Me)CH(Me)CH_2C(O)Ph (isomer 1), 95741-11-0; PhC(O)CH(Me)CH(Me)CH_2C(O)Ph (isomer 2), 95741-12-1; PhC(O)CH(Me)CH(Et)CH_2C(O)Bu-*t* (isomer 1), 95741-13-2; PhC(O)CH(Me)CH(Et)CH_2C(O)Bu-*t* (isomer 2), 95741-14-3; PhC(O)CH(Me)CH(*i*-Pr)CH_2C(O)Bu-*t* (isomer 1), 95741-15-4; PhC(O)CH(Me)CH(*i*-Pr)CH_2C(O)Bu-*t* (isomer 2), 95741-16-5; PhC(O)CH(Me)CH(Ph)CH_2C(O)Bu-*t* (isomer 1), 95741-17-6; PhC(O)CH(Me)CH(Ph)CH_2C(O)Bu-*t* (isomer 2), 95741-18-7; *p*-$MeOC_6H_4$C(O)CH(Me)CH(Me)C(O)Bu-*t* (isomer 1), 95741-19-8; *p*-$MeOC_6H_4$C(O)CH(Me)CH(Me)C(O)Bu-*t* (isomer 2), 95741-20-1; 2,4,6-$Me_3C_6H_4$C(O)CH(Me)CH(Me)C(O)Bu-*t* (isomer 1), 95741-21-2; 2,4,6-$Me_3C_6H_4$C(O)CH(Me)CH(Me)C(O)Bu-*t* (isomer 2), 95741-22-3; *t*-$BuMe_2SiOC(O)CH(Me)CH(Me)CH_2C(O)Bu$-*t* (isomer 1), 95741-23-4; *t*-$BuMe_2SiOC(O)CH(Me)CH(Me)CH_2C(O)Bu$-*t* (isomer 2), 95741-24-5; *t*-$BuMe_2SiOC(O)CH(Me)CH(i\text{-}Pr)CH_2C(O)Bu$-*t* (isomer 1), 95741-25-6; *t*-$BuMe_2SiOC(O)CH(Me)CH(i\text{-}Pr)CH_2C(O)Bu$-*t* (isomer 2), 95741-26-7; *t*-$BuMe_2SiOC(O)CH(Me)CH(Ph)CH_2C(O)Bu$-*t* (isomer 1), 95741-27-8; *t*-$BuMe_2SiOC(O)CH(Me)CH(Ph)CH_2C(O)Bu$-*t* (isomer 2), 95741-28-9; *t*-$BuMe_2SiOC(O)CH(Me)CH(Me)CH_2C(O)Me$ (isomer 1), 95741-29-0; *t*-$BuMe_2SiOC(O)CH(Me)CH(Me)CH_2C(O)Me$ (isomer 2), 95740-82-2; *t*-$BuMe_2SiOC(O)CH(Me)CH(R'')CH_2C(O)R'$(R′,R″ = $(CH_2)_3$) (isomer 1), 95741-30-3; *t*-$BuMe_2SiOC(O)CH(Me)CH(R'')CH_2C(O)R'$(R′,R″ = $(CH_2)_3$) (isomer 2), 95741-31-4.

Supplementary Material Available: Methods used to assign stereostructures and ^{13}C NMR chemical shifts of the products of the reactions summarized in Table I (4 pages). Ordering information is given on any current masthead page.

Geometrical Isomers of a Bridgehead Imine: (*E*)- and (*Z*)-2-Azabicyclo[3.2.1]oct-1-ene and 2-Azabicyclo[2.2.2]oct-1-ene

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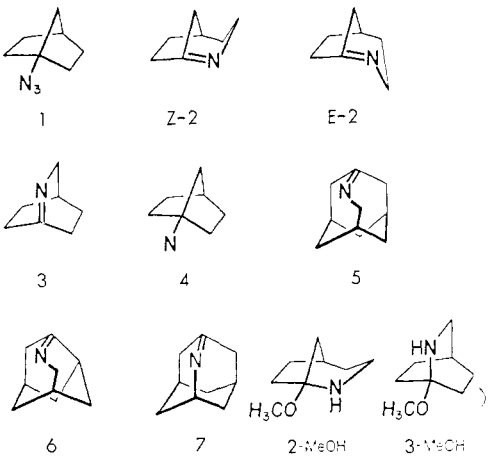
Irradiation of matrix-isolated bridgehead azides yields highly strained bridgehead imines.[2-6] 1-Azidonorbornane (**1**) would be expected to provide access to both 2-azabicyclo[3.2.1]oct-1-ene (**2**) and 2-azabicyclo[2.2.2]oct-1-ene (**3**), but only the IR of the



former was detected in recently reported matrix-isolation work and assigned to the less strained *Z* form.[4] Our results for matrix-isolated **1**, obtained by using monochromatic irradiation, IR, UV, and ESR spectroscopy and trapping with methanol, show that the situation is considerably more complicated: (*E*)-**2**, (*Z*)-**2**, **3**, and **4** are all formed, and (*E*)-**2** can be photoisomerized to (*Z*)-**2**.

UV irradiation[7a,b] of **1** isolated in Ar or polyethylene matrices at 12 K causes a gradual disappearance of its characteristic UV and IR absorption spectra[8] and a gradual growth of new peaks,

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(7) Irradiations were performed (a) at 308 nm by using a Lambda Physik XeCl excimer laser, (b) at 310 ± 15 nm by using a 2500-W high-pressure Xe–Hg lamp and an interference filter protected by a broad-band $NiSO_4/H_2O$ filter, (c) at 415 nm by using a Coherent krypton ion laser, (d) at $\lambda > 365$ nm by using a cutoff filter and a 200-W high-pressure Hg lamp, (e) at 254 nm by using a low-pressure Hg lamp;

(8) UV of **1** (polyethylene, 12 K) 222, 287 nm; (Ar, 12 K) 287 nm. IR of **1** (Ar, 12 K) 2103 (asym str), 1271 (sym str), 727 and 467 (bend) cm^{-1}. [3-^{15}N]-1-Azidonorbornane (49 atom % ^{15}N) was prepared according to the method given in ref 5 and had IR (neat, room temperature) 2099, 1237, 714, and 457 cm^{-1}.

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