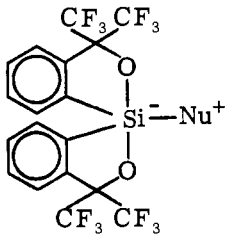
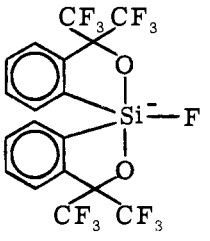


2



3

is not necessary to explain the inversion of **1** promoted by weak nucleophiles. The structure of the initially formed intermediate is not known. Although **2** might be expected to be the most stable structure, it may not be the kinetically favored product of nucleophilic attack. If attack of nucleophile were to occur opposite one of the oxygen ligands, inversion of configuration could be obtained by a sequence of three pseudorotations (B ⇄ C ⇄ C′ ⇄ B′) followed by loss of the nucleophile (Figure 1). This sequence has an advantage energetically over the five-step sequence starting from **2** in that the intermediate having a diequatorial five-membered ring has two apical oxygens, one of them being a highly apicophilic oxonium ligand.

An even shorter (and possibly lower energy) pathway for racemization is possible if one invokes attack on the C_1, O_2 edge (or the C_2, O_1 edge) of the tetrahedron of **1**. This three-step inversion (A ⇄ C ⇄ C′ ⇄ A′) involves only one pseudorotation step interconverting enantiomers C and C′, energetically equivalent species with one apical carbon and without a diequatorial five-membered ring.

Some of these mechanisms for inversion propose edge (equatorial) attack of the nucleophile rather than face (apical) attack to give the initial intermediate. A similar mode of attack has been proposed to explain retention of configuration in nucleophilic substitution at silicon,[8] i.e., equatorial attack of the nucleophile to give a pentacoordinate intermediate followed by apical departure of the leaving group. Alkoxy-substituted silanes are thought to be particularly susceptible to equatorial attack, as these compounds usually give retention of configuration upon nucleophilic substitution. Apical attack on **1** may be strongly disfavored since it always leads to a high-energy intermediate having a five-membered rink linking equatorial sites. It may nevertheless be kinetically favored, with subsequent pseudorotation leading to more stable intermediates.[13]

Silane **1** is remarkably electrophilic, forming 1:1 adducts with such nucleophiles as pyrrolidine[14] and 4-(*N*,*N*-dimethylamino)-pyridine.[2] In contrast, **1** does not easily form hexacoordinate compounds by the addition of two nucleophiles—none have yet been isolated or observed spectroscopically. For example, the ^{29}Si spectra of **1** in the presence of 1–5 equiv of sodium methoxide show only a peak at −76.4 ppm (±0.3 ppm), characteristic of a pentacoordinate compound.[15] Furthermore, in solution with a large excess of the nucleophile pyrrolidine, the isolated stable adduct of pyrrolidine and **1** shows no evidence in its ^{19}F NMR spectrum of the inversion which could accompany nucleophilic displacement at silicon via a hexacoordinate transition state.[14]

The bidentate ligands of **1** are exceptionally well suited to stabilize pentacoordinate silicon, but they are less capable of stabilizing hexacoordinate structures. The reversible formation of pentacoordinate intermediates in weakly nucleophilic media is thus expected. Pseudorotation of these intermediates provides the most probable mechanism to account for the observed rapid nucleophile-induced inversion of configuration.

Acknowledgment. We are grateful to Professor A. J. Arduengo for assistance in adapting the LAOCOON programs and Professor R. Corriu for helpful suggestions. This research was supported in part by a grant from the National Science Foundation (CHE 81-13142). NMR experiments were conducted at the University of Illinois Midwest NSF Regional NMR Facility (CHE 79-16100).

Registry No. **1**, 70091-69-9; **2** (Nu = pyrrolidine), 80145-68-2.

(13) Inversion of **1** by a series of fluoroalkoxy O–Si bond dissociation and recombination steps of the pentacoordinate intermediate cannot be rigorously excluded but seems unlikely. The rate of inversion shows no relation to solvent polarity, and the breaking of a relatively strong silicon–oxygen bond of a five-membered ring is expected to be energetically unfavorable.

(14) The pyrrolidine adduct was synthesized by addition of 1 equiv of pyrrolidine to **1** in dichloromethane, removal of the solvent under reduced pressure, and recrystallization from dichloromethane–pentane (72% isolated yield): mp 198–199 °C; ^1H NMR ($PhNO_2$-d_5) δ 8.4 (m, 2.0, H ortho to Si on spirobicyclic rings), 7.9–7.4 (m, 6.0, remaining *H* on spirobicyclic rings), 6.9–6.0 (br s, 1.3, HN), 3.5 (t, 4.1, CH_2N), 1.95 (m, 4.1, remaining H on pyrrolidine); ^{19}F NMR ($PhNO_2$-d_5) (A_3B_3) δ −74.5, −75.1, J_{FF} = 9.9 Hz; ^{29}Si NMR ($PhNO_2$-d_5) δ −82.4 (s); MS (70 eV) *m/e* (relative intensity) 512 (55.0, $M^{+\cdot} - C_4H_9N$), 443 (100.0, $M^{+\cdot} - C_4H_9N - CF_3$), 71 (23.2, $C_4H_9N^{+\cdot}$). Anal. ($C_{22}H_{17}F_{12}NO_2Si$) C, H, N.

(15) Silane **1** exhibits a ^{29}Si signal at δ 8.6 (downfield of tetramethylsilane); pentacoordinate compounds derived from **1** give signals between δ −64.1 and −82.4, an upfield shift characteristic of pentacoordinate silicon. See: Cella, J. A.; Cargioli, J. D.; Williams, E. A. *J. Organomet. Chem.* **1980**, *186*, 13.

Stereochemical Control of the Internal Michael Reaction. A New Construction of *trans*-Hydrindane Systems.

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Department of Chemistry, Columbia University New York, New York 10027

Received June 29, 1981

Vicinal stereochemistry can often be controlled very effectively via cycloadditions: The Diels–Alder reaction immediately comes to mind. This vicinal control has been very important in the construction of bicyclic systems but has been somewhat limited in that it leads most directly to cis fusions. The important system represented by the trans "angularly methylated" hydrindanes is a case in point: they can be reached via Diels–Alder addition only by subsequent more or less elaborate further manipulation of the initial cis adducts.[1] We now report that the intramolecular Michael addition provides a new approach to the construction of bicyclic systems and illustrate this here with the synthesis of *trans*-hydrindanes. We show that, using **1** below, (a) the intramolecular Michael addition takes precedence over the formally possible vinylogous aldol condensation and (b) the stereochemical result can be controlled to give the very desirable trans arrangement of the two carbonyl chains, thus leading to a simple route to *trans*-hydrindenones (Scheme I).

The synthesis of the model system **1** is outlined in Scheme II.

Reaction of silyl enol ether **4**[2] with *m*-chloroperbenzoic acid in tetrahydrofuran at 0 °C followed by treatment of the intermediate α-silyloxy ketone with tetrabutylammonium fluoride furnished the α-hydroxy ketone[3] which was cleaved with $Pb(OAc)_4$ in methanol to provide the aldehydo ester **6** (in 57% yield from **4**): IR (neat) 1715, 1730, 2700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.1 (3 H, d, *J* = 7 Hz, CH_3), 3.7 (3 H, s, CH_3), 9.75 (1 H, t, *J* = 2 Hz, CHO). Condensation of **6** with dimethyl (2-oxopropyl)-phosphonate in aqueous potassium hydroxide/methanol (0 °C) furnished enone ester **7** in 81% yield: IR (neat) 1630, 1680, 1740 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.15 (3 H, d, *J* = 7 Hz), 2.25 (3 H,

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(1) Woodward, R. B.; Sondheimer, F.; Taub, D.; Heusler, K.; McLamore, W. M. *J. Am. Chem. Soc.* **1952**, *74*, 4223. Stork, G.; Stotter, P. L. *Ibid.* **1969**, *91*, 7780. Trans, as well as cis, hydrindanes are produced in internal Diels–Alder reactions (Jung, M. E.; Halweg, K. *Tetrahedron Lett.* **1981**, 3929. Bal, S.; Helquist, P. *Ibid.* **1981**, 3933. Roush, W.; Peseckis, S. *J. Am. Chem. Soc.* **1981**, *103*, 6696. Kametani, T.; Matsumoto, H.; Honda, T.; Fukumoto, K. *Tetrahedron Lett.* **1980**, 4847.

(2) Stork, G.; Hudrlik, P. *Ibid.* **1968**, *90*, 4462.

(3) Rubottom, G. M.; Vasquez, M. A.; Pelagrince, D. R. *Tetrahedron Lett.* **1974**, 4319. Rubottom, G. M.; Gruber, J. M.; Boeckman, R. K., Jr.; Ramaiah, M.; Medwid, J. B. *Tetrahedron Lett.* **1978**, 4603.

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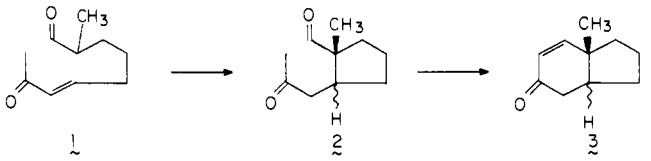
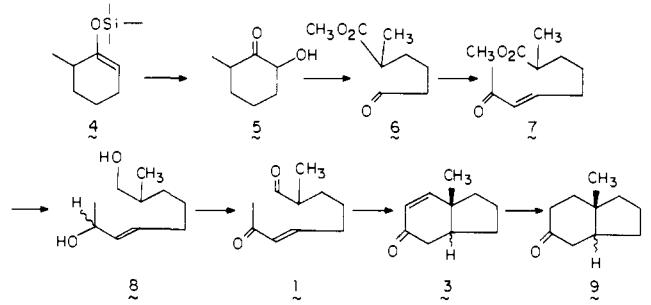
Scheme I



Scheme II

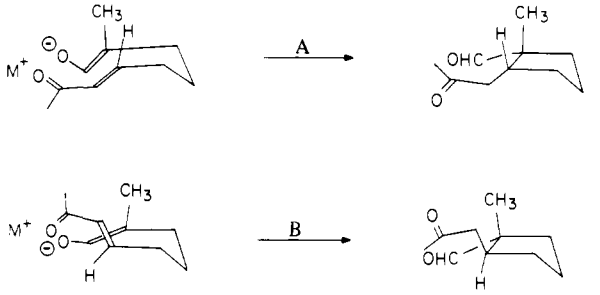


s, $COCH_3$), 6.05 (1 H, d, J = 16 Hz), 6.80 (1 H, dt, J = 6, 16 Hz). Reduction of **7** with diisobutylaluminum hydride in diethyl ether (−78 °C → room temperature) followed by oxidation of diol **8** with pyridinium chlorochromate–sodium acetate[4] in CH_2Cl_2 at room temperature furnished key intermediate **1** (in 65% yield from **6**): ^{1}H NMR ($CDCl_3$) δ 1.05 (3 H, d, J = 7 Hz, CH_3), 2.2 (3 H, s, $COCH_3$), 6.05 (1 H, d, J = 16 Hz), 6.80 (1 H, dt, J = 6, 16 Hz), 9.6 (1 H, d, J = 2 Hz).

Treatment of **1** with a catalytic amount of sodium methoxide in methanol furnished a mixture of ketols which was dehydrated with sodium methoxide in diethyl ether to provide a 3:1 mixture of hydrindenones (**3**) (in 80% yield from **1**): ^{1}H NMR δ 0.95 (major), 1.25 (minor) (3 H, s, CH_3), 5.90 (1 H, d, J = 10 Hz, H_α of enone for both isomers), 6.64 (minor), 7.27 (major) (1 H, d, J = 10 Hz, H_β). That the major product formed is the trans fused isomer was demonstrated by comparison of **9**, obtained by H_2/Pd–C reduction of **3**: ^{1}H NMR δ 0.95 (major), 1.12 (minor) with authentic samples of *cis*-[5] and *trans*-[6] hydrindanones (**9**). The premise that *trans*-hydrindane systems could be made by intramolecular Michael addition had thus been demonstrated. It now remained to test the assumption that the relatively unimpressive stereoselectivity could be improved by suitable variation of the reaction conditions, especially the nature of the base. Indeed, the latter markedly affected the stereochemical outcome of the reaction (trans/cis ratios: KOH/CH_3OH = 2/1; $NaOCH_3/CH_3OH$ = 3/1; $LiOH/CH_3OH$ = 4/1).

The stereochemical results are consistent with the transition states shown. If the two oxygens are held closely to the metal cation, the resulting repulsion of the negative charges spread over the π systems (Scheme III) should favor transition-state B, leading

Scheme III

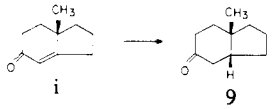


to the trans product.[7] These considerations led us to attempt the cyclization with the readily available zirconium *n*-propoxide in benzene.[8,9] This proved very successful: A solution of the enone aldehyde **1** (15 mg, 0.09 mmol) in 1 mL of dry benzene was treated with 1 equiv of $Zr(OPr)_4$. After 1 h at room temperature, the reaction mixture was diluted with 1 mL of dry methanol, and 0.1 mL of a 0.5 M aqueous solution of LiOH was added. After stirring overnight, workup with EtOAc/pH 7 phosphate buffer afforded 16 mg of crude bicyclic ketol. The ketol was dissolved in 1 mL of dry methylene chloride [with a crystal of 4-(*N*,*N*-dimethylamino)pyridine], cooled to −40 °C under Ar, and treated with 3 equiv of trifluoroacetic anhydride and 5 equiv of diazabicycloundecene. The reaction mixture was warmed slowly (over 1 h) to 0 °C and then treated with a second portion of DBU (5 equiv) and allowed to warm to room temperature. Chromatography (silica gel) furnished hydrindenone (**3**) (13 mg, 90% of theory). VPC analysis (3% FFAP, 120 °C) of the product obtained on H_2/Pd-C reduction of **3** showed a 40:1 trans/cis ratio of hydrindanones **9**.[10]

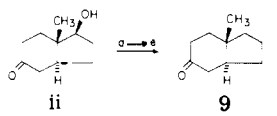
The suggestion that those cations which form the least dissociated bonds to oxygen should lead to more and more trans product has been further examined by studying the cyclization of the ketal **10**.[12] The results which were obtained in this more complex case

(4) Corey, E. J.; Suggs, J. W. *Tetrahedron Lett.* **1975**, 2647.

(5) An authentic sample of the *cis*-hydrindanone [NMR δ 1.12 (3 H, s)] was prepared from the known hydrindenone i (Caine, D.; Alejande, A. M.; Ming, K.; Powers, W. J., III *J. Org. Chem.* **1972**, *37*, 706) by catalytic hydrogenation (Chaykovsky, M. Ph.D. thesis, University of Michigan, Ann Arbor, MI, 1961).



(6) The authentic *trans*-hydrindanone (**9**) (^{1}H NMR δ 0.95) was prepared from the known ketoalcohol ii (Hajos, Z. G.; Parrish, D. R. *J. Org. Chem.* **1973**, *38*, 3239.



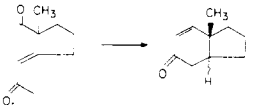
(a) $HOCH_2CH_2OH$, H^+; (b) MsCl, Et_3N; (c) DBU, 180 °C; d) H_2/Pd-$CaCO_3$; (e) aqueous H_2SO_4

(7) We are not explicitly giving a role to the geometry of the aldehyde enolates. Although the connection with our work is unclear, it is interesting that it has recently been shown that the stereochemistry of the aldol products obtained from *zirconium* enolates is unaffected by the enolate geometry: cf. Evans, D. A.; McGee, L. R. *Tetrahedron Lett.* **1980**, 3975. Evans, D. A.; McGee, L. R. *J. Am. Chem. Soc.* **1981**, *103*, 2876.

(8) Available from Alfa Products, Danvers, MA.

(9) As an indication of the strength of the metal–oxygen bonds we note the following solubilities in aqueous solution: (g/100 g of H_2O) (cf.: "CRC Handbook of Chemistry and Physics"; CRC Press: Cleveland, OH, 1970) KOH, 107; NaOH, 42; LiOH 28; ZrO_2, 0.02; $Mg(OH)_2$, 0.009; $Ca(OH)_2$, 0.18

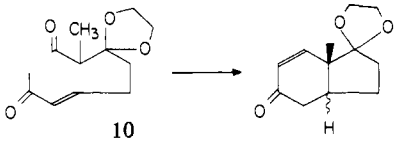
(10) To determine the effect of the double bond geometry of enone **1** on the stereochemical outcome of the Michael cyclization, the *cis*-enone iv[11] was cyclized with $LiOH/CH_3OH$, followed by dehydration with TFAA/DBU in CH_2Cl_2 to give **3** (70% overall yield), in a 2:1 trans/cis ratio. This was not very different from the 4:1 ratio obtained with the trans enone **1**. Attempted cyclization of iv with $Zr(OnPr)_4$ in benzene unfortunately caused destruction of the starting material iv with no formation of the desired ketols or of **3**.



(11) Prepared by alkylation (72% yield) of propionitrile anion (cf. Watt, D. S. *Tetrahedron Lett.* **1974**, 707) with (*Z*)-6-(*tert*-butyldimethylsilyloxy)-4-hexenyl bromide prepared in a straight forward manner from 3-butyn-2-ol, followed by hydrogenation (Pd–$BaSO_4$/H_2/CH_3OH-py), DIBAL-H reduction to the aldehyde, hydrolysis of the silyl ether with aqueous acetic acid, and oxidation with Collins reagent in CH_2Cl_2: IR (CH_2Cl_2) 1610, 1690, 1725; ^{1}H NMR δ 1.1 (3 H, d, J = 7 Hz, CH_3), 2.2 (3 H, s, CH_3CO), 5.8–6.4 (2 H, m, olefinic H's), 9.6 (1 H, d, J = 2 Hz).

(12) This was synthesized from ethyl 2-methyl-3-oxobutanoate by the following sequence: alkylation of the dianion with allyl bromide (cf. Huckin, S. N.; Weiler, L. *J. Am. Chem. Soc.* **1974**, *96*, 1082), dioxolane formation, ozonolysis, condensation with dimethyl (2-oxopropyl)phosphonate, reduction (LAH) and modified Collins oxidation (cf.; Ratcliffe, R., Rodehorst, R. *J. Org. Chem.* **1970**, *35*, 4000) of the resulting diol to the required aldehydo enone **10**: ^{1}H NMR ($CDCl_3$) δ 1.1 (3 H, d, J = 7 Hz), 2.2 (3 H, s), 2.7 (1 H, dq, J = 2,8 Hz), 4.0 (4 H, s), 6.05 (1 H, d, J = 16 Hz), 6.8 (1 H, d, J = 16 Hz), 9.75 (1 H, d, J = 2 Hz).

were in complete agreement with those obtained in the cyclization of **1**, using the same base systems already mentioned. It is further remarkable that examination of the results obtained with the additional systems $Mg(OCH_3)_2$, $Ca(OCH_3)_2$, and $Ba(OH)_2$, all in methanol, again showed that the ratio of *trans*- to *cis*-hydrindenones eventually formed follows the order expected on the assumption that the metals forming the tighter bond to oxygen would lead to more *trans* product. The observed trans/cis ratios (determined by NMR integration) were as follows: LiOH, 4/1; $Mg(OCH_3)_2$, 12/1; $Ca(OCH_3)_2$, 10/1; $Ba(OH)_2$, 3/1; $Zr(OnPr)_4$, 25/1 (determined by VPC analysis, 3% FFAP, 180 °C).[13]



10

It is clear that the internal Michael addition is a useful route to angularly methylated *trans*-hydrindanes and an important method in the control of vicinal stereochemistry.

Acknowledgment. We thank the National Institutes of Health and the National Science Foundation for their support of this work.

Registry No. (*E*)-**1**, 79971-12-3; (*Z*)-**1**, 79971-13-4; **2**, 79971-14-5; *cis*-**3**, 79971-15-6; *trans*-**3**, 17429-25-3; **4**, 19980-33-7; **5**, 52456-90-3; **6**, 76712-36-2; **7**, 79971-16-7; **8**, 79971-17-8; *cis*-**9**, 79971-18-9; *trans*-**9**, 62719-12-4; **10**, 79971-19-0; *cis*-2′,3′,3′a,7′a-tetrahydro-7′a-methylspiro[1,3-dioxolane-2,1′-[1*H*]inden]-5′(4′H)-one, 79971-20-3; *trans*-2′,3′,3′a,7′a-tetrahydro-7′a-methylspiro[1,3-dioxolane-2,1′-[1*H*]inden]-5′(4′H)-one, 79971-21-4; dimethyl (2-oxopropyl)phosphonate, 4202-14-6.

(13) The stereochemistry of the hydrindenones was easily established by hydrogenation followed by ketal hydrolysis to give the well-known *cis*- (Boyce, C. B. C.; Whitehurst, J. S. *J. Chem. Soc.* **1960**, 4547) and *trans*-hydrindanediones (Baggaley, K. H.; et al. *J. Chem. Soc. C* 1971, 2671; Hajos, Z. G., Parrish, D. R. *J. Org. Chem.* **1973**, *38*, 3239).

Thioacrolein[1]

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Received August 19, 1981

The preparation of reactive organic intermediates by means of thermal decomposition in the gas phase can be optimized advantageously by following the PE spectroscopic "molecular fingerprints" in the respective flow system:[2] those of the starting materials vanish and those of the products emerge. Applying this technique, many thiocarbonyl derivates like $H_2C{=}S$[3a], or $H_2C{=}C{=}S$,[3b] or alkyl derivatives thereof[3a] have been detected and characterized. Still missing is the PE spectroscopic proof for monomeric $H_2C{=}CH{-}HC{=}S$,[4] the thio analogue to well-known acrolein, although MNDO calculations[5] predict it to be the most

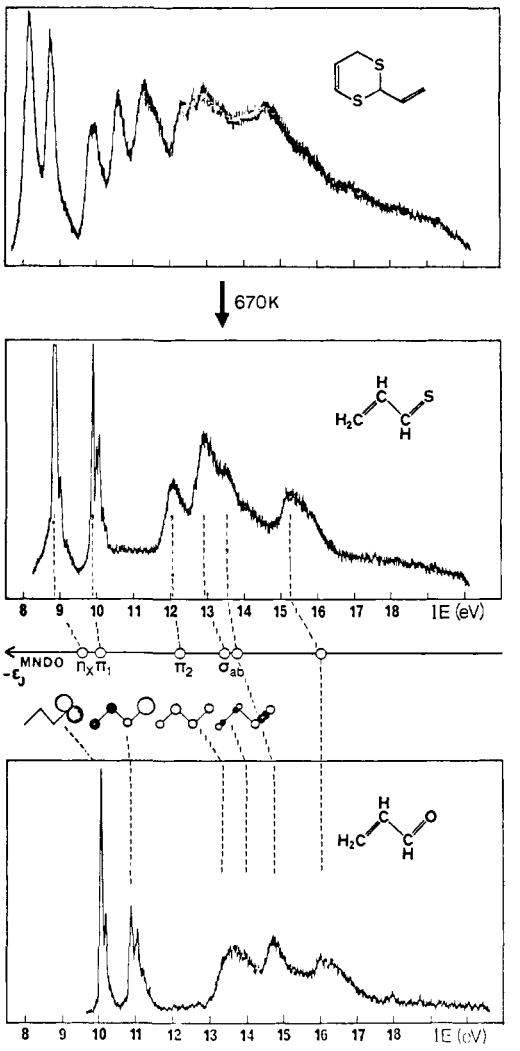
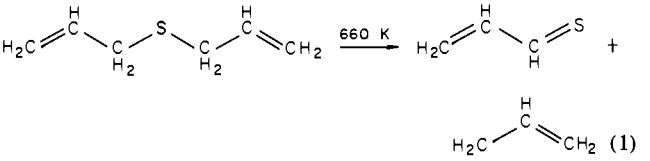


Figure 1. PE spectra of thioacrolein.

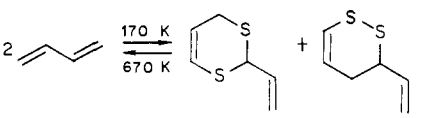
stable isomer out of the set of 12 which can be constructed for the ensemble C_3H_4S by using normal valency rules.

One of the most favorable leaving groups in thermal decompositions from allylic compounds is propene,[2,6] and expectedly, diallyl sulfide[4] chosen as precursor yields quantitatively thioacrolein at the PE spectroscopically optimized temperature of 660 K.



(1)

The PE spectra recorded on heating the flow system show the developing 8.87 eV ionization peak of thioacrolein (Figure 1), but all other bands at higher energies overlap with those of propene (reaction 1). The PE spectrum of pure thioacrolein (Figure 1), however, could be obtained after cool trapping the Diels–Alder dimer mixtures



(2)

and evaporating the slowly polymerizing liquid again while heating

(1) Gas-phase Reactions. 29. Part 28: H. Bock. *Chem. Rundsch.*, **34** (29), 3 (1981).

(2) For a recent review, see H. Bock and B. Solouki, *Angew. Chem.*, *93*, 425 (1981); *Angew. Chem., Int. Ed. Engl.*, **20**, 427 (1981).

(3) (a) Cf. E. Block, E. R. Corey, R. E. Penn, T. L. Renken, P. F. Sherwin, H. Bock. T. Hirabayashi, S. Mohmand, and B. Solouki, *J. Am. Chem.Soc.*, in press; H. Bock, T. Hirabayashi, and S. Mohmand, Chem. Ber., in press; see the literature reviewed, e.g., H. W. Kroto and R. J. Suffolk, *Chem. Phys. Lett.*, **15**, 545 (1972);B. Solouki, P. Rosmus, and H. Bock, *J. Am. Chem. Soc.*, **98**, 6054 (1976); H. Bock, B. Solouki, S. Mohmand, E. Block, and L. K. Revelle, *J. Chem. Soc., Chem. Commun.* **1977**, 287; (b) H. Bock, B. Solouki, G. Bert, and P. Rosmus, *J. Am. Chem. Soc.*, **99**, 1663 (1977). See also P. Rosmus, B. Solouki, and H. Bock, *Chem. Phys. Letts.*, *22*, 453 (1977).

(4) Cf. W. J. Bailey and M. Isogawa, *Am. Chem. Soc., Div. Polymer Chem.*, **14** (1), 300 (1973); G. Giles, R. A. Marty, and P. de Mayo, *J. Chem. Soc., Chem. Commun. 1974*, 409; *Can. J. Chem.*, **54**, 537 (1976).

(5) H. Bock, S. Mohmand, T. Hirabayashi, and A. Semkow, *Chem. Ber.*, in press.

(6) Cf., e.g., R. F. C. Brown "Pyrolytic Methods in Organic Chemistry", Academic Press, New York, 1980 and literature cited. See also F. A. Houle and J. J. Beauchamp, *J. Am. Chem. Soc.*, **100**, 329o (1978); H. Bock, A. Bowling, B. Solouki, T. J. Barton, and G. T. Burns, *ibid.*, **102**, 429 (1980).

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