

- (10) J. F. Endicott, *Inorg. Chem.*, in press.
 (11) C. Y. Mok and J. F. Endicott, submitted.
 (12) The macrocyclic ligands employed were [14]aneN = 1,3,8,11-tetraazacyclotetradecane and [14]tetraeneN₄ = 2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene.
 (13) (a) J. F. Endicott, G. J. Ferraudi, and J. R. Barber, *J. Phys. Chem.*, **79**, 630 (1975); (b) J. F. Endicott and G. J. Ferraudi, *Inorg. Chem.*, **14**, 3133 (1975); (c) J. F. Endicott in "Concepts in Inorganic Photochemistry", A. W. Adamson and P. D. Fleischauer, Ed., Wiley, New York, N.Y., 1975, Chapter 3, p. 83.
 (14) (a) T. S. Roche and J. F. Endicott, *Inorg. Chem.*, **13**, 1575 (1974); (b) *J. Am. Chem. Soc.*, **13**, 1575 (1974).
 (15) A. M. Tait, M. Z. Hoffman, and E. Hayon, *J. Am. Chem. Soc.*, **98**, 86 (1976).
 (16) In order for dissolved O₂ in aerated solutions ([O₂] ~ 2 × 10⁻⁴ M) to react at a diffusion limited rate ($k \leq 10^{10} \text{M}^{-1} \text{s}^{-1}$) with an excited species, the lifetime of that species must exceed 5 × 10⁻⁷ s. Such an excited species would have to luminesce. However, no such luminescence has been detected for cobalt(III) complexes with excited states lower in energy than 1.5 μm⁻¹,¹⁷⁻²⁰ and there are reasons to believe that such cobalt excited states should be very short lived.¹⁷⁻²¹ It is further to be observed that the slow decay in Figure 1b may be used to set an upper limit of [O₂] ≤ 10⁻⁷ M in our experiments; under such conditions we would observe any and all reactions between dioxygen and photochemical intermediates or excited states. The homolysis reactions were observed to occur during the flash pulse and could not have been the result of reaction with O₂.
 (17) V. Balzani and V. Carassiti, "Photochemistry of Coordination Compounds", Academic Press, New York, N.Y., 1970.
 (18) (a) P. D. Fleischauer and P. Fleischauer, *Chem. Rev.*, **70**, 199 (1970); (b) P. D. Fleischauer, private communication.
 (19) P. D. Fleischauer, A. W. Adamson, and G. Sartori, *Prog. Inorg. Chem.*, **17**, 1 (1972).
 (20) V. Balzani, L. Moggi, M. F. Manfrin, F. Bolletta, and G. S. Laurence, *Coord. Chem. Rev.*, **15**, 321 (1975).
 (21) J. F. Endicott and G. J. Ferraudi, *J. Phys. Chem.*, **80**, 949 (1976).
 (22) The macrocyclic ligand abbreviated as [14]dieneN₄ = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11⁴-diene. We have found Ni([14]dieneN₄) to be "photoinert" ($\phi < 10^{-4}$).
 (23) For descriptions of the techniques used see (a) T. L. Kelly and J. F. Endicott, *J. Am. Chem. Soc.*, **94**, 1797 (1972); (b) W. L. Wells and J. F. Endicott, *J. Phys. Chem.*, **75**, 3075 (1971); (c) G. J. Ferraudi and J. F. Endicott, *Inorg. Chem.*, **12**, 2389 (1973).
 (24) λ_{max} 470 nm, ε_{max} 9.4 × 10³ for B_{12r} and λ_{max} 520 nm, ε_{max} 9.8 × 10³ for Me-B₁₂; C. P. Dunne, Ph. D. dissertation, Brandeis University, 1971.
 (25) W. A. Pryor, "Free Radicals", McGraw-Hill, New York, N.Y., 1966, p. 161.
 (26) J. K. Thomas, *J. Phys. Chem.*, **71**, 1919 (1967).
 (27) E. R. Kantrowitz, M. Z. Hoffman, and J. F. Endicott, *J. Phys. Chem.*, **75**, 1914 (1971).
 (28) For examples of reactions analogous to eq 7 and 8 see J. Butler, G. G. Jayson, and A. J. Swallow, *J. Chem. Soc., Faraday Trans. 1*, **70**, 1394 (1974).
 (29) (a) J. F. Endicott, J. Lillie, J. M. Kuszaj, B. S. Ramaswamy, W. G. Schmonsees, M. G. Simic, M. D. Glick, and D. P. Rillema, *J. Am. Chem. Soc.*, in press; (b) B. Durham, D. P. Rillema, and J. F. Endicott, manuscript in preparation.
 (30) λ_{max} 460 nm, ε_{max} 3.84 × 10³; A. Adin and J. H. Espenson, *Inorg. Chem.*, **11**, 686 (1972).

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Received August 31, 1976

Photolysis of *tert*-Butyl Peroxylaurate

Sir:

It has been reported¹ that the photolysis of neat *tert*-butyl peroxycaprate and *tert*-butyl peroxylaurate produces high yields of the corresponding carboxylic acids, capric, and lauric acids. By reinvestigation² of the photolysis, using *tert*-butyl peroxylaurate as substrate, we have found that little or no carboxylic acid is formed.

The titration procedure used to determine the acid in the original work¹ was tested and found erroneous principally because the perester itself is saponified in the procedure. We then tried other methods of analysis and found them suitable for the detection of lauric acid in the presence of peroxylaurate. The methods employed thin-layer chromatography, and infrared and NMR spectroscopy. Using those methods, no lauric acid was detected in the photolyzed *tert*-butyl peroxylaurate.

We have also discovered some striking effects caused by a

small pyridine impurity such as was present in the peresters studied originally. Those peresters were prepared by the pyridine-acylation method of Silbert and Swern³ and the recrystallization procedure of that method does not remove the pyridine completely. When we came to suspect the effects of that slight impurity, we were able to remove it completely by chromatography on a silica gel column, using a 10% solution of diethyl ether in petroleum ether as eluting agent.⁴

The UV spectrum of *tert*-butyl peroxylaurate reported in the original work¹ showed a band at 2700 Å. That band is spurious and disappears when the perester is completely freed of pyridine. The highly purified perester has a structureless spectrum in the range 3000–2100 Å, the absorbance rising smoothly with decreasing wavelength. Pyridine has a strong band close to 2700 Å ($\epsilon \sim 3000$).⁵ The very strong absorption by the pyridine in that spectral region plays an important role when peresters are photolyzed with 2537-Å radiation.

The radiation photolyzes the pyridine as well as the perester and produces a coloration that progresses from yellow to reddish brown during the process. The strong absorption by the pyridine also diminishes the quantum yield of decomposition of the perester. The value of ϕ_D for the *tert*-butyl peroxylaurate was 1.76 in the original work¹ but rose to 7.0 at the same radiation intensity with the pyridine-free perester. In the absence of pyridine the photolyzed perester was colorless and the ϕ_D value was not lowered by saturation of the perester with oxygen gas.

The rate of photodecomposition of the chromatographed *tert*-butyl peroxylaurate followed a three-halves-order dependence on the perester concentration over times up to 3 h. Since that kinetic behavior and the high ϕ_D value indicated a chain reaction, EPR spectroscopy was used to detect any radicals produced during photolysis. The neat perester was photolyzed directly in the spectrometer cavity at 10 °C. A single-line spectrum was observed and the radical was apparently an alkyl peroxy radical ($g = 2.0150$, peak-to-peak width ~6 G). It was observed that if pyridine was present the signal was enhanced, showing a stabilization of the radical. Such stabilization might be expected to lower the induced decomposition of the perester.

References and Notes

- (1) W. H. Simpson and J. G. Miller, *J. Am. Chem. Soc.*, **90**, 4093 (1968).
 (2) Details of the reinvestigation are given in the Ph.D. Dissertation of John J. Davis, University of Pennsylvania, 1975.
 (3) L. S. Silbert and D. Swern, *J. Am. Chem. Soc.*, **81**, 2364 (1959).
 (4) We are grateful to L. S. Silbert for suggesting this method of pyridine removal.
 (5) A. Albert, "Heterocyclic Chemistry", 2nd ed, Athlone Press, London, 1968, pp 401, 415.

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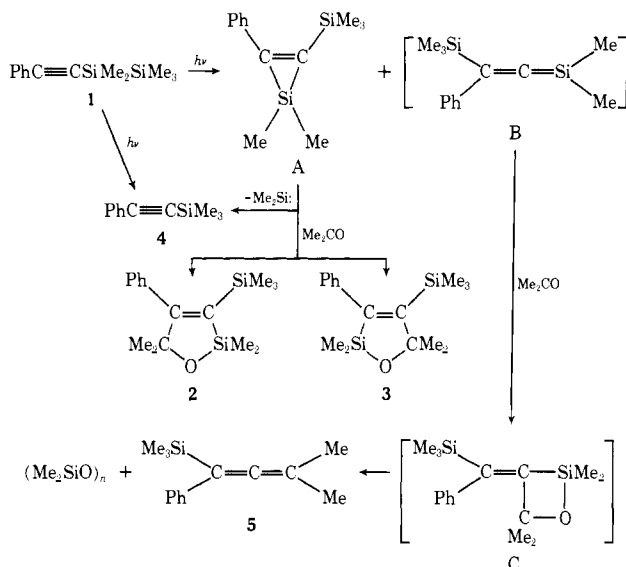
Received September 28, 1976

Photolysis of Organopolysilanes. Formation and Reactions of Substituted 1-Silacyclopentene and 1-Sila-1,2-propadiene

Sir:

Despite widespread interest in the photochemical studies of the organopolysilanes,¹⁻⁵ there have been no reports of the photolysis of 1-alkynylpolysilanes. Recently we demonstrated that irradiation of vinylsilanes produces reactive silicon-carbon double-bonded intermediates in high yields *via* photorearrangement of a silyl group to the terminal carbon of a vinyl group.⁶ In this communication we report a novel photo-

Scheme I

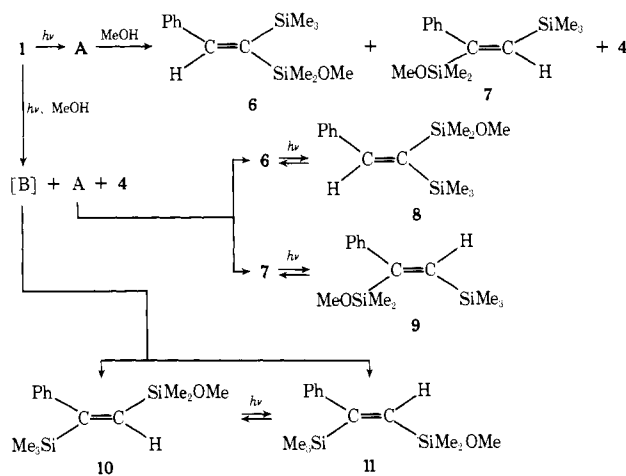


chemical behavior of (pentamethyldisilanyl)phenylacetylene (1). In marked contrast with vinylsilanes, the photolysis of 1 has been found to proceed simultaneously by two different routes, one of which, a main route, involves the production of 1-silacyclopropene (A), and the other, a minor one, comprises the transient formation of a new type of silicon-carbon double-bonded intermediate (B) (see Scheme I).

When a solution of 1 (4.31 mmol) in 110 ml of dry benzene in the presence of 0.5 ml of acetone was irradiated at room temperature for 6 h with a low-pressure mercury lamp bearing a Vycor filter (2537Å) under a purified nitrogen atmosphere, four products, 2,2,5,5-tetramethyl-3-trimethylsilyl-4-phenyl-1-oxa-2-silacyclo-3-pentene^{7,8} (2) (NMR (CCl₄) δ -0.25 (CH₃-SiMe₂, s, 9 H), 0.26 (CH₃-SiMe, s, 6 H), 1.23 (CH₃-CMe, s, 6 H), 6.9-7.4 (ring protons, m, 5 H); m/e 290 (M⁺)), 2,2,5,5-tetramethyl-3-phenyl-4-trimethylsilyl-1-oxa-2-silacyclo-3-pentene (3) (NMR (CCl₄) δ -0.10 (CH₃-SiMe₂, s, 9 H), 0.16 (CH₃-SiMe, s, 6 H), 1.40 (CH₃-CMe, s, 6 H), 6.9-7.4 (ring protons, m, 5 H); m/e 290 (M⁺)), phenyltrimethylsilylacetylene⁹ (4), and 1-phenyl-1-trimethylsilyl-3-methyl-1,2-butadiene (5) (NMR (CCl₄) δ 0.19 (CH₃-SiMe₂, s, 9 H), 1.77 (CH₃-CMe, s, 6 H), 7.14 (ring protons, broad s, 5 H), m/e 216 (M⁺), IR (neat) 1940 cm⁻¹) were obtained in 51, 2, 10, and 5% yield, respectively, with 81% conversion of the starting disilane. The formation of products 2-5 can be best understood by assuming intermediacy of both 1-silacyclopropene (A) and a silicon-carbon double-bonded species, 1-sila-1,2-propadiene (B). Insertion of acetone into the silicon-carbon bond in silacyclopropene A generates five-membered compounds 2 and 3. Liberation of dimethylsilylene species from either direct photolysis of 1 or decomposition of A results in the formation of 4. The dimethylsilylene could easily be trapped by diethylmethylsilyl-ane.¹⁰ Compound 5 can be rationalized in terms of cycloaddition of acetone¹¹ to intermediate B to afford silaoxetane¹² (C) followed by loss of the Me₂SiO moiety.

To establish whether or not acetone was involved in the photoisomerization, we irradiated 1 (3.43 mmol) with a low-pressure mercury lamp in the absence of acetone at -78 °C for 4 h in 110 ml of dry toluene. After the irradiation was stopped, 2 ml of acetone was added to the reaction mixture. Here, three products derived from A, 2, 3, and 4, were obtained in 44, 2, and 7% yield,¹³ respectively. However, as expected, no compound 5 arising from the reaction of short-lived intermediate B with acetone was detected by GLC analysis.

Scheme II



Further evidence for the photochemical generation of A and B was obtained from photolysis of 1 in the presence or absence of methyl alcohol (see Scheme II). Irradiation of 1 (4.50 mmol) at -78 °C for 5 h in 110 ml of toluene, followed by addition of 2 ml of dry methyl alcohol at the same temperature, afforded two compounds which can be expected from reaction of the silacyclopropene with methyl alcohol,¹⁴ (*E*)-1-methoxydimethylsilyl-1-trimethylsilyl-2-phenylethylene (6) (NMR (CCl₄) δ -0.06 (CH₃-SiMe₂, s, 9 H), 0.24 (CH₃-SiMe, s, 6 H), 3.41 (CH₃-O, s, 3 H), 7.0-7.3 (ring protons, m, 5 H), 7.77 (vinyl proton, s, 1 H), m/e 264 (M⁺)) and (*E*)-1-phenyl-1-methoxydimethylsilyl-2-trimethylsilylethylene (7) (NMR (CCl₄) δ -0.20 (CH₃-SiMe₂, s, 9 H), 0.09 (CH₃-SiMe, s, 6 H), 3.34 (CH₃-O, s, 3 H), 6.35 (vinyl proton, s, 1 H), 6.8-7.3 (ring protons, m, 5 H), m/e 264 (M⁺)) in 62 and 7% yield, respectively, in addition to 5% yield of 4. On the other hand, photolysis of 1 in the presence of dry methyl alcohol under similar conditions gave, *via* the expected addition of methyl alcohol across the silicon-carbon double bond on intermediate B, (*E*)-1-phenyl-1-trimethylsilyl-2-methoxydimethylsilylethylene (10) (NMR (CCl₄) δ -0.24 (CH₃-SiMe, s, 6 H), 0.06 (CH₃-SiMe₂, s, 9 H), 3.25 (CH₃-O, s, 3 H), 6.25 (vinyl proton, s, 1 H), 6.8-7.3 (ring protons, m, 5 H), m/e 264 (M⁺)) and (*Z*)-1-phenyl-1-trimethylsilyl-2-methoxydimethylsilylethylene (11) (NMR (CCl₄) δ 0.12 (CH₃-SiMe₂, s, 9 H), 0.23 (CH₃-SiMe, s, 6 H), 3.44 (CH₃-O, s, 3 H), 6.17 (vinyl proton, s, 1 H), 6.8-7.3 (ring protons, m, 5 H), m/e 264 (M⁺)) in 12 and 9% yield, in addition to 6 (33%) and 7 (7%). Moreover, in this case, photochemical isomerization of the initial products, 6 and 7, took place to give (*Z*)-1-methoxydimethylsilyl-1-trimethylsilyl-2-phenylethylene (8)¹⁵ and (*Z*)-1-phenyl-1-methoxydimethylsilyl-2-trimethylsilylethylene (9)¹⁶ in 18 and 4% yield, respectively. Such photochemical isomerization was confirmed by the fact that the photolysis of the isolated pure compounds, 6, 7, and 10, gave the corresponding equilibrium mixture (6/8 = 1.2, 7/9 = 1.4, and 10/11 = 1.6) under the same conditions.¹⁷

The structure of photoisomers, 8, 9, and 11, could be distinguished from that of 6, 7, and 10, respectively, on the basis of comparison of the NMR spectra of the isomer pairs. For example, the proton NMR of 8 showed an upfield shift for the dimethylmethoxysilyl group due to the ring current of the phenyl ring *cis* to this dimethylmethoxysilyl group, while its isomer 6 showed the upfield shift for the trimethylsilyl group but not for dimethylmethoxysilyl group, and we therefore assign the *E* structure to 6 and *Z* structure to 8.

We could also confirm the formation of 1-silacyclopropene A by means of NMR techniques.¹⁸ The proton NMR spectrum

of a mixture containing 25%¹⁹ of A produced by photolysis of **1** in benzene at room temperature showed two sharp resonances at δ 0.23 and 0.30 with relative intensities of 3:2, in addition to two peaks at δ 0.19 and 0.31 assignable, respectively, to Me₃Si and Me₂Si protons of **1**.

The silacyclopentene A in solution seems to be relatively stable at room temperature. When a reaction mixture containing 44%¹⁹ of A and 22% of unchanged **1** was allowed to stand for 8 h at room temperature, only 6.6% of A was decomposed to give mainly a nonvolatile product. We are continuing this investigation to stabilize intermediate A.

Acknowledgment. The cost of this research was defrayed in part by a Grant-in-Aid for Scientific Research by the Ministry of Education and Toray Science and Technology Grants to which the author's thanks are due. They also express their appreciation to Toshiba Silicon Co., Ltd., and Shin-etsu Chemical Co., Ltd., for a gift of organochlorosilanes.

References and Notes

- M. Ishikawa, T. Fuchikami, T. Sugaya, and M. Kumada, *J. Am. Chem. Soc.*, **97**, 5923 (1975), and references cited therein.
- P. Boudjouk and R. D. Koob, *J. Am. Chem. Soc.*, **97**, 6595 (1975).
- M. Ishikawa, T. Fuchikami, and M. Kumada, *Tetrahedron Lett.*, 1299 (1976).
- A. G. Brook and J. W. Harris, *J. Am. Chem. Soc.*, **98**, 3381 (1976).
- M. Ishikawa, T. Fuchikami, and M. Kumada, *J. Organomet. Chem.*, **118**, 139, 155 (1976).
- M. Ishikawa, T. Fuchikami, and M. Kumada, *J. Organomet. Chem.*, **117**, C58 (1976).
- All compounds reported here gave satisfactory elemental analyses and spectral data.
- Protodesilylation of **2** by dry hydrogen chloride in dry ethyl ether gave 2,2,5,5-tetramethyl-4-phenyl-1-oxa-2-silacyclo-3-pentene and 2-methyl-3-phenyl-1,3-butadiene in 31 and 33% yield, respectively, indicating that the two silyl groups are attached to the same carbon atom.
- L. Q. Minh, J. C. Billiotte, and P. Cadiot, *C. R. Acad. Sci.* 730 (1960).
- Photolysis of **1** in the presence of diethylmethylsilane gave 1,1-diethyl-1,2,2-trimethyldisilane and **4** in 4 and 12% yield, respectively.
- One of the referees has raised a question as to the absence of a silyl enol ether which might be expected to form from H-O addition of the enol form of acetone across the silicon-carbon double bond, as observed by Sommer and his co-workers.¹² We have established that, unlike the thermally generated Si=C intermediates,¹² photochemical ones from either vinyl-disilanes⁶ and arylsilanes²⁰ in the presence of an enolizable ketone such as acetone, cyclohexanone, and acetophenone never afford silyl enol ethers.
- C. M. Golino, R. D. Bush, D. N. Roark, and L. H. Sommer, *J. Organomet. Chem.*, **66**, 29 (1974).
- Yields reported here are based on unrecovered **1**, with its conversion being always approximately 70–80%.
- (a) W. H. Atwell and D. R. Weyenberg, *Intra-Sci. Chem. Rep.*, **7**, 139 (1973); (b) R. T. Conlin and P. P. Gaspar, *J. Am. Chem. Soc.*, **98**, 3715 (1976).
- Compound **8**: NMR (CCl₄) δ -0.05 (CH₃-SiMe, s, 6 H), 0.17 (CH₃-SiMe₂, s, 9 H), 3.30 (CH₃-O, s, 3 H), 7.18 (ring protons, broad s, 5 H), 7.65 (vinylic proton, s, 1 H).
- Compound **9**: NMR (CCl₄) δ 0.16 (CH₃-Si, s, 15 H), 3.14 (CH₃-O, s, 3 H), 6.44 (vinylic proton, s, 1 H), 6.8–7.3 (ring protons, m, 5 H).
- D. Seyferth and L. G. Vaughan, *J. Organomet. Chem.*, **1**, 138 (1963).
- The proton NMR spectrum of tetramethyl-1-silacyclopent-2-ene prepared from thermally generated Me₂Si: and 2-butyne has recently been reported.^{14b}
- The amount of the 1-silacyclopentene is taken to be equal to the sum of yields of methoxysilanes **6** and **7** formed by methanolysis of the photo-product.
- M. Ishikawa, T. Fuchikami, and M. Kumada, manuscript in preparation.

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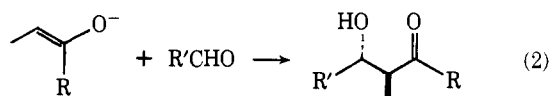
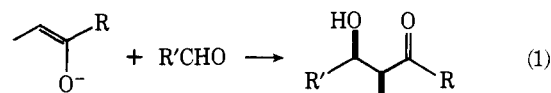
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Stereoselection in the Aldol Condensation

Sir:

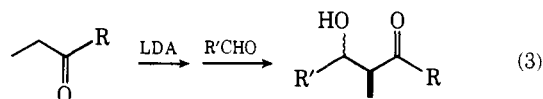
Dubois and co-workers have shown that the aldol condensation is subject to kinetic stereoselection, with (*Z*)-enolates giving predominantly the *erythro* aldol (eq 1), and (*E*)-enolates leading preferentially to the *threo* isomer (eq 2).¹ House and co-workers found that the use of preformed lithium eno-

lates in the presence of chelating divalent cations such as Zn²⁺ and Mg²⁺ leads to product mixtures rich in the more stable *threo* aldol, regardless of enolate geometry.² We have examined the use of preformed lithium enolates and find that, under the proper conditions, *complete kinetic stereoselection* may be achieved.

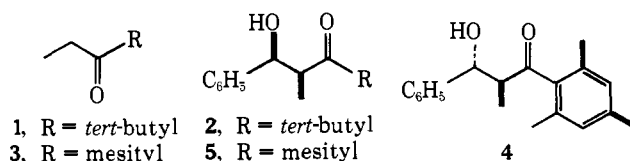


Reactions are carried out by preforming the enolate at -72 °C in THF or ether by addition of the ketone to a 1 M solution of lithium diisopropylamide (LDA).³ After 15 min, the aldehyde is added in one portion to the rapidly stirring enolate solution. The reaction mixture is quenched by the addition of saturated aqueous NH₄Cl 5 s after addition of the aldehyde. After separation of the layers, the aqueous layer is extracted with ether and the combined organic layers are dried (anhydrous MgSO₄) and evaporated to afford the aldol in good yield. Further purification is achieved by distillation and/or recrystallization of the crude product. Diastereomer ratios were determined from the carbinol resonances in the ¹H NMR spectra of the crude aldol product, using the well-established fact that *J*_{threo} > *J*_{erythro}.² In cases where both diastereomeric aldols are not produced in the condensation, the kinetic aldol was equilibrated so that both stereoisomers were in hand.

Our results may be summarized as follows: In aldol condensations of the type typified by eq 1 and 2, complete kinetic stereoselection is observed, with the (*Z*)-enolate giving the *erythro* aldol and the (*E*)-enolate giving the *threo* aldol when R is bulky (*tert*-butyl, 1-adamantyl, mesityl, trimethylsilyl). When R is smaller (ethyl, isopropyl, phenyl, methoxy, *tert*-butoxy, diisopropylamino), stereoselectivity diminishes or disappears.



An example is provided by the condensation of ethyl *tert*-butyl ketone (**1**, 100% (*Z*)-enolate) with benzaldehyde to yield *erythro* aldol **2**. The crude aldol product in this reaction, obtained in quantitative yield, shows no measurable amount of *threo* aldol. Pure aldol **2** (mp 55–56 °C) is obtained in 78% yield after distillation (bp 105°/0.3 Torr) and trituration with a small amount of hexane. On the other hand, ethyl mesityl ketone (**3**, 92% (*E*)-enolate, 8% (*Z*)-enolate) reacts with benzaldehyde to afford 92% of *threo* aldol **4** and 8% of *erythro* aldol **5**. Pure **4** (mp 97–99 °C) is obtained in 52% yield after two recrystallizations from hexane. To gain further support for the supposition that (*Z*)-enolates give *erythro* aldols and (*E*)-enolates give *threo* aldols, we have prepared mixtures of (*E*)- and (*Z*)-enolates of varying composition from ketone **3**⁵ and allowed these mixtures to react with benzaldehyde. In each case, the *erythro*/*threo* ratio is identical within experimental error to the (*Z*)/(*E*) ratio.



Our results are explicable in terms of a six-center transition state, depicted in structure I for a (*Z*)-enolate, in which the