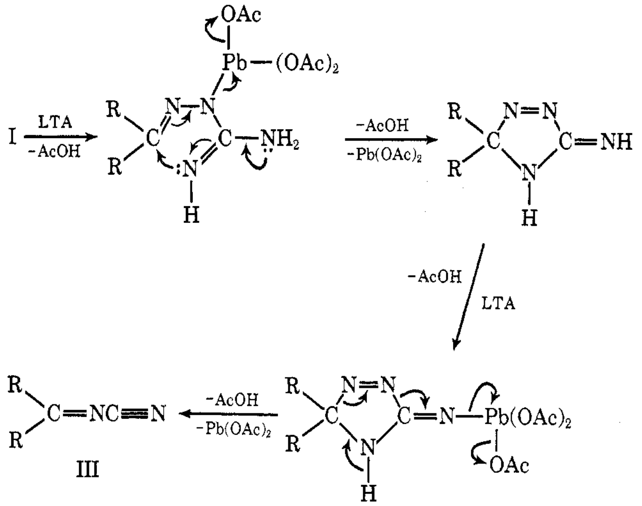
SCHEME I



According to this mechanism under the reaction conditions used the intermediate triazole sought is unstable and is further oxidized to give a cyanimino derivative.

The results (Table I) show that starting with a guanylhydrazone and using lead tetraacetate as an oxidant one can obtain a new class of ketone derivatives.

TABLE I
SYNTHESIS OF CYANIMINO KETONES
RR′C=NC≡N

Registry no.	R	R′	Yield, %	Mp, °C
34441-01-5	Phenyl	Methyl	76	68–69[b]
34441-02-6	α-Naphthyl	Methyl	79	71–72[c]
34427-53-7	β-Naphthyl	Methyl	84	118–119[d]
34414-10-3	Phenyl	Phenyl	74	81–83[b]

[a] Satisfactory analyses (±0.2% for C and H) were reported for all compounds: Ed. [b] Recrystallized from ether-petroleum ether. [c] Recrystallized from ether. [d] Recrystallized from acetone.

Experimental Section

All melting points were taken with a Kofler hot stage apparatus and are uncorrected. Nmr spectra were determined using a Varian A-60A spectrometer. Infrared spectra were obtained from a Leitz Model III. Mass spectra were run on a Varian Model CH5 instrument.

General Procedure for the Oxidation of Guanylhydrazones.—To a solution of 0.02 mol of the guanylhydrazone in a mixture of 10 ml of glacial acetic acid and 90 ml of dichloromethane, at room temperature, was added a solution of 0.04 mol of lead tetraacetate (70% in acetic acid) in 50 ml of dichloromethane dropwise, during a period of 30 min. The mixture was allowed to stand for 1 hr. Water was added and the dichloromethane layer was separated, washed with sodium bicarbonate solution, and dried. After evaporation of the dichloromethane the residue was recrystallized from an appropriate solvent. Melting points are given in Table I.

Hydrolysis of Cyaniminoacetophenone.—Cyaniminoacetophenone (1.0 g) in 20 ml of 6 *N* HCl was refluxed for 0.5 hr. The solution was extracted with chloroform. The chloroform layer was dried and evaporated. The liquid residue was found to be identical with acetophenone. The aqueous layer was evaporated to dryness. The solid residue gave an infrared spectrum that was superimposable on that given by a sample of material obtained from the treatment of acetophenone and cyanamide hydrochloride as above.

Registry No.—Lead tetraacetate, 546-67-8.

7-Trimethylsilylcycloheptatriene

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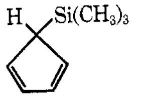
5-Trimethylsilylcyclopentadiene (**1**)[1–6] and 1-trimethylsilylindene (**2**)[7–9] show thermal [1,5] sigmatropic migrations of hydrogen and silicon. However, silicon migration occurs approximately 10^6 faster than that of hydrogen in both systems.[4,9,10] In order to test the generality of these rapid silicon migrations, we have examined 7-trimethylsilylcycloheptatriene (**3**) and have found that hydrogen migration occurs exclusive of silicon in this case.



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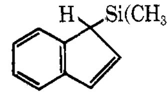

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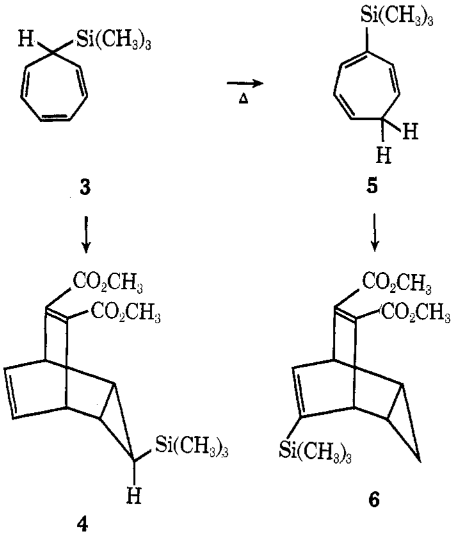

7-Trimethylsilylcycloheptatriene can be prepared by the CuCl-catalyzed addition of trimethylsilyldiazomethane[11] to benzene. The yellow **3** was identified by elemental analysis and its pmr spectrum: (CDCl$_3$) τ 9.9 (s) [9 H, Si(CH$_3$)$_3$], 8.5 (t) (1 H, allylic), 4.0 (t) (2 H, vinylic), 3.8–4.2 (m) (4 H, vinylic). Reaction with dimethyl acetylenedicarboxylate gave a 1:1 adduct, assigned structure **4** on the basis of its pmr spectrum: (CDCl$_3$) τ 10.1 (s) [9 H, Si(CH$_3$)$_3$], 9.7 (t) (1 H, CHSi), 8.7 (m) (2 H, *tert*-cyclopropyl), 6.2 (s) (6 H, OCH$_3$), 5.9

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[2] Y. A. Ustynyuk, A. V. Kisin, and O. E. Oksinoid, *J. Gen. Chem. USSR*, **38**, 389 (1968).

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[8] R. B. Larrabee and B. F. Dowden, *Tetrahedron Lett.*, 915 (1970).

[9] A. J. Ashe, III, *ibid.*, 2105 (1970).

[10] For the rate of hydrogen migration in indene see W. R. Roth, *ibid.*, 1009 (1964).

[11] D. Seyferth, A. W. Dow, H. Menzel, and T. C. Flood, *J. Amer. Chem. Soc.*, **90**, 1080 (1968).

(m) (2 H, bridgehead position), and 3.9 (m) (2 H, vinyl). The stereochemistry has been assumed to be analogous to other cycloheptatriene–dienophile adducts.[12]

Heating **3** to 170° for 1 hr leads to irreversible changes in its pmr spectrum[13] indicating its isomerization to **5**. A new trimethylsilyl singlet at τ 9.8 and a new allylic triplet at τ 7.9 appear as well as a more complicated pattern in the vinyl region. Addition of dimethyl acetylenedicarboxylate to this mixture of **3** and **5** gave a new adduct **6** as well as **4**. The structure of **6** follows from its pmr spectrum: ($CDCl_3$) τ 9.9 (s) [10 H, $Si(CH_3)_3$ and one *sec*-cyclopropyl], 9.5 (t) (1 H, *sec*-cyclopropyl), 8.6 (m) (2 H, *tert*-cyclopropyl), 6.2 (s) (6 H, OCH_3), 5.9 (m) (2 H, bridgehead position), 3.8 (dd) (1 H, vinyl). Qualitatively the rate of [1,5] hydrogen migration of **3** is not greatly different from that of other cycloheptatrienes.[14]

In order to detect possible silicon migration in **3**, 7-trimethylsilylcycloheptatriene-1,2,3,4,5,6-d_6 (**7**) was prepared from benzene-d_6 and trimethylsilyldiazomethane. The pmr spectrum of this material showed only a broad singlet at τ 8.5 for the unique ring proton in addition to the trimethylsilyl peak. Silicon migration would be observed by the conversion of this proton from an allylic to a vinylic position. However the only changes in the pmr spectrum[13] of **7** on heating, to 170° for 1 hr were the appearance of the new allylic proton at τ 7.9 of hexadeuterio-**5** as well as its trimethylsilyl peak. No new vinylic protons could be detected after more than half of **7** was gone, indicating that the rate of silicon migration must be at least an order of magnitude slower than that of hydrogen.

The facile migration of silicon compared to hydrogen in systems **1** and **2** coupled with its relative inertness in **3** demonstrate the different requirements for migration of the two atoms. Perhaps it is more difficult for the large trimethylsilyl to bridge the concave face of the nonplanar cycloheptatriene ring.[14,15] This steric difficulty should be minimized in the nearly planar **1** and **2**.[16]

Experimental Section

General.—Glpc analyses were performed with a Varian Aerograph 90P chromatograph using a 20 ft × 0.25 in. column containing 20% Carbowax 20 M on Chromosorb W and a 5 ft × 0.25 in. column containing 20% Apiezon L on Chromosorb W. The pmr spectra were recorded using a Varian T-60 instrument. Peak positions were recorded to the nearest 0.1 ppm relative to internal TMS. Elemental analyses were performed by the Spang Microanalytical Laboratory, Ann Arbor, Mich.

Trimethylsilyldiazomethane.—The procedure of Seyferth[11] was modified slightly in that product was extracted with mineral oil instead of benzene to facilitate separation by distillation. It always contained approximately 30% hexamethyldisiloxane.

7-Trimethylsilylcycloheptatriene (3).—Trimethylsilyldiazomethane (4.0 g) in 50 ml of benzene was added dropwise over 6 hr to a stirred mixture of 0.3 g of CuCl in benzene at reflux. After an additional 1 hr at reflux the mixture was filtered and solvent was removed by distillation through a 30-cm tantalum spiral column. This left 5 g of crude product, which was purified by glpc on an Apiezon L column. Besides residual solvent the major component (retention time 3 min at 40 lb He, 140°) was 7-trimethylsilylcycloheptatriene. *Anal.* Calcd for $C_{10}H_{16}Si$: C, 73.09; H, 9.89. Found: C, 73.01; H, 9.86.

Dimethyl 3-Trimethylsilyltricyclo[3.2.2.0^{2,4}]-6,8-nonadiene-6,7-dicarboxylate (4).—Trimethylsilylcycloheptatriene (0.5 g) and dimethyl acetylenedicarboxylate (0.75 g) in 0.5 ml of benzene were sealed under nitrogen in a glass tube. The mixture was heated to 160° for 0.5 hr, causing considerable darkening. Glpc on the Carbowax column showed a single component (retention time 10.5 min at 60 lb He, 240°). The material was collected. Its spectra were consistent with structure **4**. *Anal.* Calcd for $C_{16}H_{22}O_4Si$: C, 62.72; H, 7.24. Found: C, 62.51; H, 7.15.

Dimethyl 8-Trimethylsilyltricyclo[3.2.2.0^{2,4}]-6,8-nonadiene-6,7-dicarboxylate (6).—7-Trimethylsilylcycloheptatriene (0.5 g) and 0.5 ml of benzene-d_6 were sealed in an nmr tube. The tube was heated to 170° for 1 hr, at which time the nmr spectrum was recorded and showed peaks associated with **5** in addition to those of **3**. Attempted separation of this mixture on a variety of glpc columns was unsuccessful.

Excess dimethyl acetylenedicarboxylate (0.75 g) was added to the mixture and it was heated to 160° for 0.5 hr. Glpc (Carbowax, 60 lb He at 240°) showed two peaks (retention time 9.5 and 10.5 min). Both were collected and the high retention time peak was shown to be **4**. The lower retention time peak was an isomer. *Anal.* Calcd for $C_{16}H_{22}O_4Si$: C, 62.72; H, 7.24. Found: C, 62.68; H, 7.17. The pmr spectrum was consistent with structure **6**.

Pyrolysis of 7.—This material was prepared from benzene-d_6 and trimethylsilyldiazomethane in the same manner as **3**. Heating to 170° for 1 hr in benzene-d_6 gave partial conversion to hexadeuterio-**5**, although no vinyl hydrogen peaks were noted in the pmr spectrum.

Registry No.—**3**, 34542-20-6; **4**, 34542-21-7; **6**, 34578-23-9.

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[13] Pmr spectrum in benzene-d_6.

[14] A. P. Ter Borg, H. Kloosterziel, and N. Van Meurs, *Recl. Trav. Chim. Pays-Bas*, **82**, 717 (1963); A. P. Ter Borg and H. Kloosterziel, *ibid.*, **82**, 741 (1963).

[15] For conformational studies of 7-substituted cycloheptatrienes see H. Günther, M. Görlitz, and H.-H. Hinrichs, *Tetrahedron*, **24**, 5665 (1968).

[16] R. B. Larrabee, *J. Amer. Chem. Soc.*, **93**, 1510 (1971), has found that [1,5] metal shifts occur faster than hydrogen shifts in 7-triphenylstannylcycloheptatriene. This contrasts with **3** and is perhaps due to the known greater migratory aptitude of tin. See footnotes 1, 3, 7, and 8.