and stirring for 14 hr. These conditions gave the maximum yield of *tert*-butyl-2-naphthyl ether (38%) while keeping the yield of 2-naphthol to a minimum (27%). The naphthol is a degradation product of the *tert*-butylnaphthyl ether.[4] An excellent yield of purified *n*-butyl-2-naphthyl ether (84%) was obtained at 150° using this process.

The alkylnaphthyl sulfides are not as readily available. One preparative method is the acid-catalyzed reaction of naphthol and a mercaptan.[9] In our reaction, 2-bromonaphthalene was added to a mixture of DMSO, *n*-butyl mercaptan, and sodium methoxide and the resulting solution was refluxed for 1 hr. *n*-Butyl-2-naphthyl sulfide was obtained in a 58% yield. This reaction has been carried out on 1- and 2-fluoronaphthalene as well as 1- and 2-bromonaphthalene using both *n*-butyl and *tert*-butyl mercaptans.[5]

Experimental Section

Materials.—2-Fluoronaphthalene was obtained from P. C. R. Inc. 2-Bromonaphthalene and dimethyl sulfoxide (DMSO) were obtained from J. T. Baker Chemical Co. The DMSO was passed through silica gel and stored over Linde 4A, $^1/_{16}$-in. molecular sieves before using. Sodium methoxide (Olin Matheson Co.) and potassium *tert*-butoxide (M. S. A. Research Corp.) were kept in sealed containers. 1-Butanethiol was purchased from Aldrich Chemical Co. and stored over molecular sieves.

Preparation of *tert*-Butyl-2-naphthyl Ether.—A mixture of DMSO (140 g, 1.8 mol) and 30.5 g (0.41 mol) of *tert*-butyl alcohol was heated to 70° in a 500-ml, three-necked, round-bottom flask equipped with a magnetic stirrer, thermometer, reflux condenser, and addition funnel. Potassium *tert*-butoxide (31.0 g, 0.28 mol) was added and the mixture was stirred until all the base dissolved. 2-Fluoronaphthalene (20.0 g, 0.14 mol) dissolved in 20 g of DMSO (total DMSO in the reaction mixture = 160 g, 2.05 mol) was rapidly added and the resulting mixture was stirred at 70° for 14 hr. The reaction mixture was then added to 50 ml of ice water and extracted four times with 200-ml portions of ether. The combined ether extracts were washed with aqueous sodium hydroxide and dried over anhydrous magnesium sulfate. The filtered ether extract was distilled to give 4.67 g (23%) of starting 2-fluoronaphthalene, bp 75–90° (1 mm), and 8.2 g (38%, based on amount of starting material actually used) of *tert*-butyl-2-naphthyl ether, bp 95–105° (1 mm), $n^{22}\text{D}$ 1.5740 (lit.[10] $n^{22}\text{D}$ 1.5724). The infrared spectrum of this compound was the same as that previously reported.[10]

The aqueous reaction mixture was acidified to pH 1 with concentrated hydrochloric acid and extracted with ether. The ether extracted yielded 4.25 g (27%) of 2-naphthol.

Prepartion of *n*-Butyl-2-naphthyl Ether.—This reaction was carried out in the same manner as the above reaction except that potassium metal (10.1 g, 0.28 mol) was dissolved in 51 g (0.69 mol) of *n*-butyl alcohol to make the base-alcohol portion of the reaction mixture. A dark yellow solid (26.03 g) was obtained after the ether extract was evaporated. Five grams of this material was recrystallized twice from a 90% aqueous alcohol solution to yield 4.5 g of *n*-butyl-2-naphthyl ether, mp 33.5–34.5° (lit.[11] mp 33–35°). The total yield of purified ether would be 22.4 g (84%).

Preparation of *n*-Butyl-2-naphthyl Sulfide.—Twenty grams (0.096 mol) of 2-bromonaphthalene in 44 g of DMSO was added to a mixture of 70 g of DMSO, 43.6 g (0.48 mol) of 1-butanethiol, and 15.7 g (0.29 mol) of sodium methoxide at reflux temperature (110°) in the same apparatus as reported above. The reaction mixture was worked up as in the *tert*-butyl-2-naphthyl ether reaction to yield 12.12 g (58%) of *n*-butyl-2-naphthyl sulfide, bp 147–152° (1 mm), $n^{25}\text{D}$ 1.6205 (lit.[5] $n^{25}\text{D}$ 1.6195). The infrared spectrum for this compound was the same as that previously reported.[5]

Registry No.—*tert*-Butyl-2-naphthyl ether, 15052-11-6; *tert*-butyl alcohol, 75-65-0; 2-fluoronaphthalene, 323-09-1; *n*-butyl-2-naphthyl ether, 10484-56-7; *n*-butyl alcohol, 71-36-3; *n*-butyl-2-naphthyl sulfide, 5286-43-1; 2-bromonaphthalene, 580-13-2; 1-butanethiol, 109-79-5.

Acknowledgment.—The authors wish to thank Professor R. T. Hawkins for his many helpful discussions.

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Lead Tetraacetate Oxidation of Guanylhydrazones. A Novel Rearrangement

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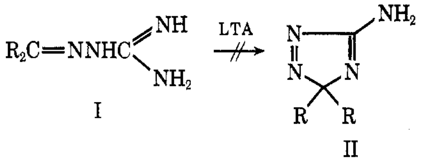
Nitrogen-containing heterocyclic compounds have been synthesized by the oxidative cyclization of ketone or aldehyde semicarbazones, acylhydrazones, *N*-alkylsemicarbazones, thiosemicarbazones, and carbohydrazones.[1]

By analogy, lead tetraacetate oxidation of a guanylhydrazone I should have led to the formation of a triazole derivative II.



Addition of molar quantities of lead tetraacetate to a dichloromethane solution of acetophenone guanylhydrazone[2] resulted in 35% yield of a compound which showed a molecular ion at *m/e* 144. Increasing the quantity of lead tetraacetate to 2 equiv gave a nearly quantitative yield. The infrared spectrum of this compound showed an intense band at 2200 cm^{-1}, in accordance with the structure III shown in Scheme I. Similarly, the nmr spectrum showed only the two signals for the methyl and the phenyl groups at 2.77 and 7.72 ppm, respectively.

Treatment of this compound with dilute boiling HCl followed by extraction with chloroform gave a liquid which was shown to be acetophenone. Evaporation to dryness of the aqueous layer gave a solid which had an identical infrared spectrum with that of a sample of cyanamide which had been treated with acetophenone and hydrochloric acid as above.

The oxidative conversion of guanylhydrazones into cyanimino derivatives is visualized as proceeding through the sequence shown in Scheme I.

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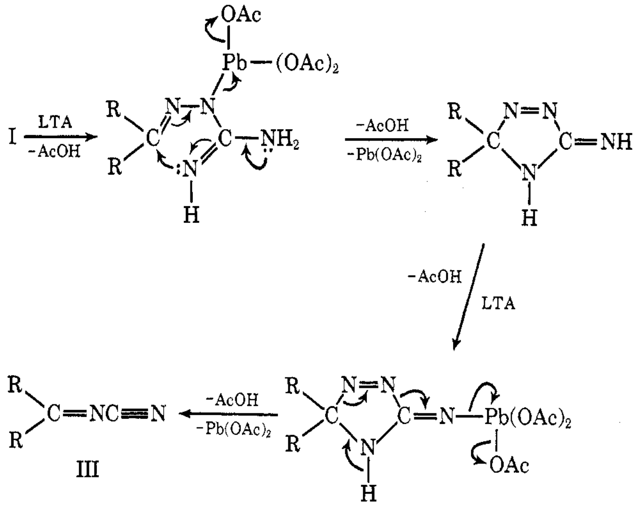
SCHEME I



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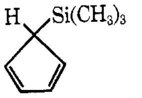
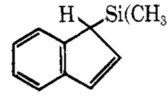
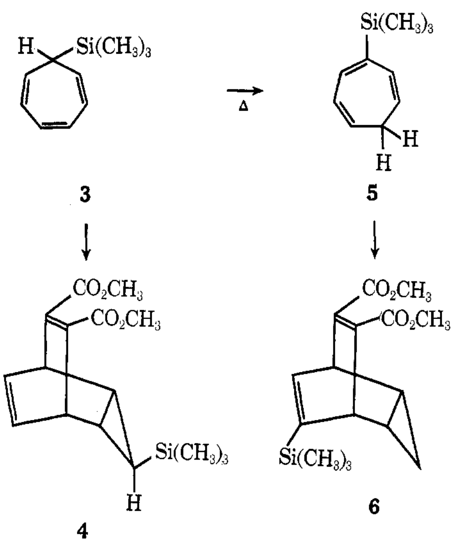
5-Trimethylsilylcyclopentadiene (**1**)[1–6] and 1-trimethylsilylindene (**2**)[7–9] show thermal [1,5] sigmatropic migrations of hydrogen and silicon. However, silicon migration occurs approximately 10^6 faster than that of hydrogen in both systems.[4,9,10] In order to test the generality of these rapid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



1



2



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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