icals **3** and **4**, but allow a check to be made on the stability of the syn lithium reagent **6** under conditions similar to those of the reaction of **1a** with lithium–Et_2O (run 4). Run 6 was repeated and the reaction mixture allowed to warm up to 0°; neutralization with D_2O generated a ratio of **2a**:**2b** which was determined to be >30:1 establishing the stability of the syn lithium reagent. On the basis of these experiments, it seems reasonably certain, therefore, that the stereoselectivity in the reactions of alkali metals and lithium naphthalenide with **1a** is governed primarily by a radical preequilibrium such as that of Scheme I, the initially formed anti radical **3** being less stable than the syn radical **4** due to the greater severity of syn C_8-H–syn C_3-H nonbonding interactions relative to those of the syn C_8-H and the half-filled orbital at C-3. In the reactions of **1a** with lithium (run 4), the greater amount of anti-3-deuterio substrate relative to that observed in the reaction of **1a** with lithium naphthalenide is due to more efficient trapping of the initially formed radical on the surface of the metal, while in the reactions of **1a** with sodium and potassium the greater amount of anti-3-deuterio product is due, perhaps, to both an efficient trapping of initially formed radical and equilibration of **5** and **6**.[6]

Experimental Section

Analytical. Nuclear magnetic resonance spectra were obtained on a Varian Associates HA-100 spectrometer equipped with a digital time averaging accessory. Gas chromatography columns used include a 0.25 in. × 6 ft 5% CW20M on 60–40 Chromosorb PAW and a 0.25 in. × 10 ft 10% XF-1150 on 60–40 Chromosorb PAW. Halides **1a**[2] and **1b**[2] were purified by preparative glpc before use.

Work-up, in all cases, consisted of dilution of the reaction mixture with water followed by extraction with pentane. Pentane extracts were dried over Na_2SO_4 and most of the pentane was distilled off the product through a Vigreux column followed by preparative glpc of the residue.

Deuteration patterns of C-3 deuterated *exo*-tricyclooctane **2** were obtained by integration of the nmr signals of the syn C-3-H (δ 0.28, $J_{3,3}$ = 6, $J_{2,3}$ = 3 Hz) and anti C-3-H (δ −0.11, $J_{2,3}$ = 7.4 Hz), referenced to the C-1 and C-5 protons (δ 2.23). The syn and anti C-3 protons are cleanly separated from all other signals. The identity of the C-3 syn and anti proton signals was firmly established by a Eu(fod)$_3$ shift reagent study on the epoxide prepared from a partly C-3 deuterated sample of *exo*-tricyclo[3.2.1.0^{2,4}]oct-6-ene and comparison with the nmr spectrum of the *exo*-tricyclooctane **2** obtained by hydrogenation of the same starting sample of *exo*-tricyclo[3.2.1.0^{2,4}]oct-6-ene.

Alkali Metal-*t*-BuOD–THF Reduction of *anti*-3-Chloro-*exo*-tricyclo[3.2.1.0^{2,4}]octane (1a). To a refluxing solution of **1a** (50 mg, 0.35 mmol) in a mixture of 1 ml of *t*-BuOD (98% d_1) and 2 ml of anhydrous THF was added 5 mmol of the alkali metal. Heating at reflux was continued until aliquots indicated the absence of **1a**. Reaction time, yield, and syn to anti deuterio ratio were for Na, 1.5 hr, 70%, 2.11; for K, 30 min, 50%, 1.25; and for Li, 1 hr, 16%, and 1.70. Deuterium incorporations were above 95% as determined from nmr integrations.

Reaction of 1a with Lithium in Ether. A suspension of Li was prepared leaching 200 mg of a 20% Li (1% Na:99% Li) dispersion in paraffin with two 3-ml portions of pentane followed by the addition of 3 ml of anhydrous ether. To this mixture was added 50 mg of **1a** and after 1 min at room temperature the flask was cooled to 0°. After 5 min the reaction was 75% complete and after 15 min all chloride was absent. D_2O (0.5 ml) was then added and followed by the work-up described above; 40% yield, syn/anti = 2.1 ± 0.3, 87% deuterium incorporation.

Reaction of 1b with *n*-BuLi. To 1 ml of 1 *M* *n*-BuLi (Ventron) and 3 ml of anhydrous ether was added 55 mg of **1b**. After 10 min at 0°, reaction was complete. D_2O (1 ml) was added after 45 min and work-up as above gave 20 mg (85% yield) of hydrocarbon; >95% deuterium incorporation; syn/anti ≤0.061:1.

Reaction of 1a with Lithium Naphthalenide. A solution of lithium naphthalenide was prepared from 0.1 g of Li and 2 g of naphthalene in 20 ml of anhydrous THF. After 1 hr at room temperature the deep green solution was cooled to −78° and 50 mg of **1a** in 3 ml of THF was slowly added *via* a dropping funnel. After stirring for 10 min, 1 ml of D_2O in THF was added dropwise. Glpc collection gave 10 mg of hydrocarbon **2** with >96% deuterium incorporation. The ratio of the anti C_3-H pmr integration to syn C_3-H integration was 28:1 with the splitting pattern of the residual syn C_3-H indicating that at least 75% of this signal originated from the undeuterated species. The syn to anti deuteration ratio corrected for the presence of undeuterated hydrocarbon is, therefore, at least 100:1.

Stability Study of 6. Chloride **1a** (50 mg) was allowed to react with lithium naphthalenide as above except the reaction mixture was allowed to warm from −78 to 0° over a period of 6 hr before being quenched with D_2O. The deuterium incorporation was only 82% and the syn to anti deuterium incorporation ratio could thus not be determined directly from the integration of the pmr signals. A consideration of the relative intensities of the splitting of the syn C_3-H pmr signal indicates that at least 92% of the signal is due to the undeuterated compound. The correct syn:anti deuterium ratio is >30:1.

Acknowledgment. The authors are grateful to the National Science Foundation for partial support of this work.

Registry No.—**1a**, 6518-27-0; **1b**, 15598-75-1; **2a**, 52882-74-3; **2b**, 52882-75-4.

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Trimethylsilylketene. Acylation and Olefination Reactions

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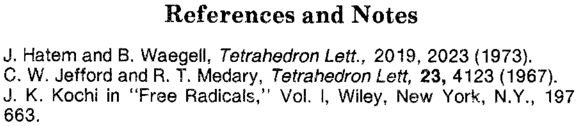
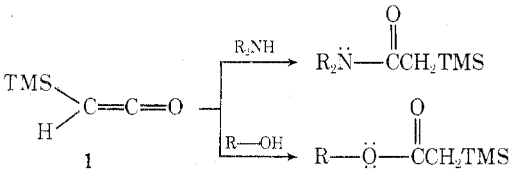
Trimethylsilylketene (TMS-ketene), **1**, a remarkably stable yet reactive ketene has been prepared by the pyrolysis of trimethylsilylethoxyacetylene[1,2] (eq 1). We wish to record its use as a potent acylating agent for hindered amines and tertiary alcohols[3] and for the preparation of trimethylsilyl-substituted allenes and acetylenes.



$$(CH_3)_3Si{-}C{\equiv}C{-}OC_2H_5 \xrightarrow{120^\circ} (CH_3)_3Si(H)C{=}C{=}O \quad (1)$$

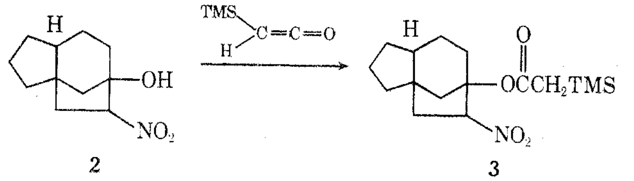
1

TMS-ketene reacts almost instantly in carbon tetrachloride with hindered amines such as diisopropyl- and isopropylcyclohexylamine to produce the amide in essentially quantitative yield (eq 2), the work-up consisting merely of short-path distillation. *tert*-Butyl alcohol also reacts with TMS-ketene in CCl_4, but the reaction is quite slow, requiring 48 hr for 80% completion. We have found however, that $BF_3 \cdot O(C_2H_5)_2$ strongly catalyzes the reaction. Addition of



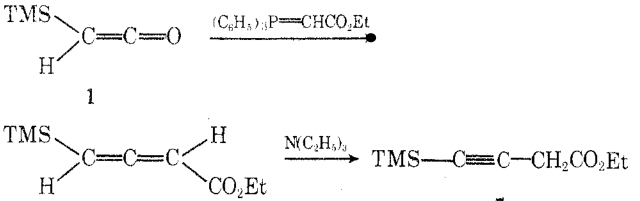
$$\text{TMS(H)C=C=O} \;\begin{cases} \xrightarrow{R_2NH} R_2N{-}C(=O)CH_2TMS \\ \xrightarrow{R{-}OH} R{-}O{-}C(=O)CH_2TMS \end{cases} \quad (2)$$

1 μl of $BF_3{\cdot}O(C_2H_5)_2$ to a solution of 1 mmol of *tert*-butyl alcohol and 1.1 mmol of trimethylsilylketene in 1 ml of CCl_4 affords the ester within 2 min of mixing. Alcohol **2** could not be successfully acetylated using the standard reagents (benzoyl chloride, acetyl chloride, and acetic anhydride with 4-dimethylaminopyridine). This material however, upon treatment with TMS-ketene in the presence of $BF_3 \cdot O(C_2H_5)_2$, afforded the trimethylsilylacetate **3** in 89% yield after preparative-layer chromatography.[4]



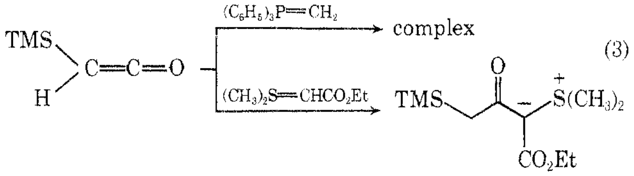
2 3

TMS-ketene also undergoes olefination with stabilized phosphorus ylides. Treatment of TMS-ketene with carbethoxymethylenetriphenylphosphorane in methylene chloride at −5° affords the allenic ester **4** in 85% yield.[5] This material could be quantitatively deconjugated to the acetylene **5** with triethylamine in CCl_4. Indeed, if the olefination is conducted at room temperature, a mixture of allene **4** and acetylene **5** is produced. Presumably the ylide is basic enough to effect this isomerization.



1 4 5

Unstabilized phosphorus ylides such as methylenetriphenylphosphorane give complex mixtures, while stabilized sulfur ylides produce the acylated product, **6** (eq 3).



(3)

6

TMS-ketene does not dimerize upon standing. Samples kept under nitrogen at room temperature show no noticeable decomposition after many weeks. Unfortunately, attempted 2 + 2 cycloaddition with a variety of dienes and olefins[6] was not successful. We are continuing to explore the chemistry and utility of trimethylsilylketene.[7]

Experimental Section[8]

Preparation of Trimethylsilylketene, 1. Methyllithium (105 mmol, 62 ml of 1.7 *M*) was added dropwise *via* syringe to a cooled (0°) solution of 7.0 g (100 mmol) of ethoxyacetylene in 250 ml of anhydrous ether. A white precipitate formed during the addition and the solution became difficult to stir. After stirring an additional 0.5 hr, trimethylsilyl chloride (11.0 g, 102 mmol) was added and the mixture stirred overnight at room temperature. The mixture was filtered and the precipitate washed well with dry ether. Careful removal of the solvent at reduced pressure afforded trimethylsilylethoxyacetylene (λ_{max}^{film} 4.55, 8.02, 11.88 μm) contaminated with lithium chloride. The acetylene was redissolved in dry pentane and filtered. After removal of the pentane, the residue was slowly distilled (bath temperature 120°) to produce trimethysilylketene as a colorless mobile oil. A second distillation gave pure trimethylsilylketene: 7.37 g, 65%, bp 81–82°; λ_{max}^{film} 4.70, 7.90, 8.00, 11.70 μm; $\delta_{TMS}^{CCl_4}$ 1.5 ppm (CH, s).

(I) Acylation. $BF_3 \cdot O(C_2H_5)_2$ (1 μl) was added to a cooled (0°) solution of trimethylsilylketene (120 mg 1.1 mmol) and *tert*-butyl alcohol (74 mg 1 mmol) in 1 ml of CCl_4. After 5 min, the product was isolated with hexane and evaporatively distilled, bp 50° (bath temperature, 0.1 mm), affording 179 mg (93%) of the ester: λ_{max}^{film} 5.79, 8.00, 9.15, 11.68 μm; $\delta_{TMS}^{CCl_4}$ 1.62 ($CH_2C(=O)$–, s), 1.15 ppm ($C(CH_3)_3$, s).

(II) Olefination. To a cooled (−5°) solution of carbethoxyethylidenetriphosphorane (348 mg, 1 mmol) in 5 ml of CH_2Cl_2 was added 115 mg (1.02 mmol) of trimethylsilylketene. The reaction appeared to be almost instantaneous (ir). Isolation of the product with pentane afforded 157 mg (85%) of the allenic material contaminated with a trace of the deconjugated acetylene: λ_{max}^{film} 5.18, 5.81, 8.02, 11.80 μm; $\delta_{TMS}^{CCl_4}$ 5.16 (allenic H's, AB quartet, J_{AB} = 6.1 Hz), 4.00 (CH_2, q, J = 7.0 Hz), 1.10 ppm (CH_3, t, J = 7.0 Hz); mass spectrum *m/e* calcd for $C_9H_{16}O_2Si$, 184.0915; found, 184.0885. Treatment of a CCl_4 solution of allene with a catalytic amount of triethylamine afforded the deconjugated acetylene: λ_{max}^{film} 4.62 μm; $\delta_{TMS}^{CCl_4}$ 4.02 (CH_2, q, J = 7.0 Hz), 3.04 ($CH_2C(=O)OEt$, s), 1.15 ppm (CH_3, t, J = 7.0 Hz).

Registry No.—**1,** 4071-85-6; **2,** 53059-32-8; **3,** 53059-33-9; **4,** 53059-23-7; **5,** 53059-24-8; $BF_3 \cdot O(C_2H_5)_2$, 109-63-7; ethoxyacetylene, 927-80-0; trimethylsilyl chloride, 75-77-4; trimethylsilylethoxyacetylene, 1000-62-0; *tert*-butyl alcohol, 75-65-0; *tert*-butyl trimethylsilylacetate, 41108-81-0; carbethoxymethylenetriphenylphosphorane, 53059-25-9.

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(7) The support of the Rutgers Research Council and the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

(8) Boiling points are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 137; nmr spectra were recorded on Varian T-60; chemical shifts were recorded as downfield from the internal trimethylsilyl group.

A Convenient Synthesis of 1,4,5,8-Tetrahydro-1,4,5,8-tetrathiafulvalene

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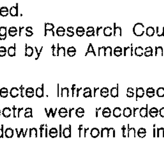
Recent interest by experimental physicists[1] and theoreticians[2] in the organic solid state has been prompted by the observation of electrical conductivity in such systems. One compound which has been the subject of numerous investigations is 1,4,5,8-tetrahydro-1,4,5,8-tetrathiafulvalene (TTF) (**1**). Although the physical[3,4] and electrical properties[5] of **1** have been reported, only one detailed synthesis exists in the recent literature.[6] Therefore, we present here



1