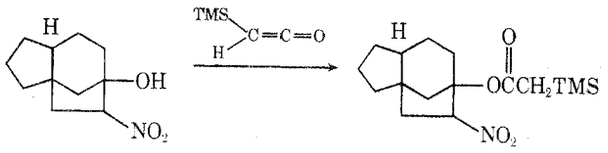
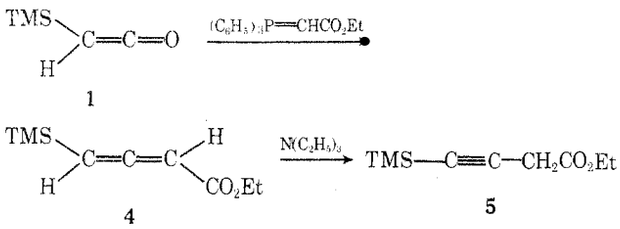
1 μl of $BF_3{\cdot}O(C_2H_5)_2$ to a solution of 1 mmol of *tert*-butyl alcohol and 1.1 mmol of trimethylsilylketene in 1 ml of CCl_4 affords the ester within 2 min of mixing. Alcohol **2** could not be successfully acetylated using the standard reagents (benzoyl chloride, acetyl chloride, and acetic 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**

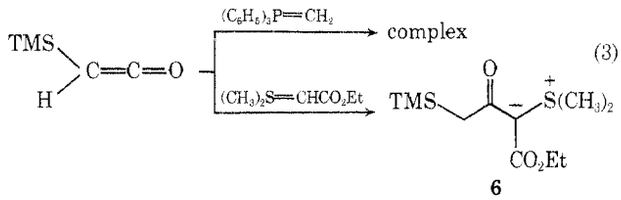
TMS-ketene also undergoes olefination with stabilized phosphorus ylides. Treatment of TMS-ketene with carbethoxymethylenetriphenylphosphorane in methylene chloride at −5° affords the allenic ester **4** in 85% yield.[5] This material could be quantitatively deconjugated to the acetylene **5** with triethylamine 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.

References and Notes

(1) L. Shchukouskaya and R. I. Pal'chik, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2228 (1964).
(2) Also prepared by dehydrohalogenation of trimethysilylacetyl chloride [I. F. Lutsenko, Y. I. Baukov, A. S. Kostyuk, N. I. Savelyava, and V. K. Krysina; *J. Organometall. Chem.*, **17**, 241 (1969)] and by pyrolysis of trimethysilylacetic acid anhydride [A. S. Kostyur, *et al.*, *J. Gen. Chem. USSR*, **39**, 441 (1969)].
(3) For other methods for protection of tertiary alcohols see the following: W. Stevens and A. Van Es, *Recl. Trav. Chim. Pays-Bas*, **83**, 1287, 1294 (1964); J. H. Brewster and C. J. Ciotti Jr., *J. Amer. Chem. Soc.*, **77**, 6214 (1955); W. Steglich and G. Höfle, *Angew Chem., Int. Ed. Engl.*, **8**, 981 (1969); H. Staab, **1**, 351 (1962).
(4) Unpublished work of E. J. Corey and R. L. Danheiser, Harvard University.
(5) Z. Hamlet and W. D. Barker, *Synthesis*, **2**, 543 (1970).
(6) Cyclopentene, cyclohexene, cyclohexadiene 2,3-dimethylbutadiene, and ethoxyacetylene were tried.
(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

F. Wudl* and M. L. Kaplan

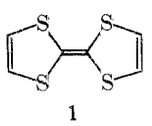
Bell Laboratories, Murray Hill, New Jersey 07974

E. J. Hufnagel and E. W. Southwick, Jr.

State University of New York at Buffalo, Buffalo, New York 14214

Received August 1, 1974

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

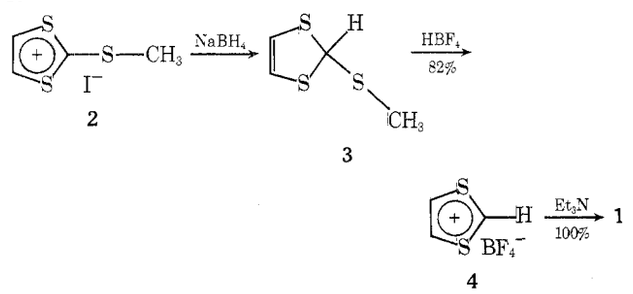


1

experimental procedures for the preparation of TTF which incorporate improvements leading to both high yields and a high purity product.

The syntheses of substituted tetrathiafulvalenes have been accomplished by deprotonation of 1,3-dithiolium salts.[7,8] The preparation of **1** was undertaken in a like manner although in one case analytically pure samples were not reported for the product.[9,10] The first published outline for the synthesis of carefully characterized **1**[3] involved preparation of 1,3-dithiole-2-thione[11] from acetylene, sulfur, and carbon disulfide followed by oxidation of the thione to 1,3-dithiolium hydrogen sulfate[12] and finally coupling of the salt with an appropriate base. A similar final step using 1,3-dithiolium perchlorate has also been reported;[4] however, another laboratory has informed us that a serious explosion was encountered in handling this perchlorate.

Various changes in this route to **1** have been effective in substantially increasing both the yields and the quality of **1**. The commercially available 2-thiomethyl-1,3-dithiolium iodide (**2**)[13] was reduced with sodium borohydride giving 2-*S*-methyl-1,3-dithiole (**3**) as an oil which was not isolated in its pure state. Upon treatment of **3** with fluoboric acid 1,3-dithiolium fluoborate (**4**) was formed which on deprotonation with excess amine resulted in a quantitative yield of **1**.



2 3

4

For large scale preparations of TTF, the method recently described by Melby, *et al.*,[6] is the most suitable. However, the preparation described here from the commercially available methiodide **2** is the preferred method for small amounts of **1**.

Experimental Section

Preparation of 1,4,5,8-Tetrahydro-1,4,5,8-tetrathiafulvalene (1). Into a 2-l. erlenmeyer flask containing a magnetic stirrer was placed 2-thiomethyl-1,3-dithiolium iodide (50.0 g, 0.18 mol, Strem Chemicals, Inc., Danvers, Mass.) and 500 ml of methanol (absolute). The mixture was stirred and cooled in an ice bath. While making certain that the temperature did not rise above 15°, $NaBH_4$ (34.5 g, 0.93 mol, Metal Hydrides, Inc.) was cautiously added in small portions. After the addition was complete, stirring was continued for 2 hr. One liter of anhydrous ether was added to precipitate the NaI which had formed. The solution was stored at −15° overnight and then decanted into a 2-l. separatory funnel, washed three times with water (200 ml each time), dried over $MgSO_4$, filtered, and concentrated on a rotary evaporator.

The resulting orange-yellow oil (**3**) had an nmr spectrum in $CDCl_3$ (TMS) (JEOL C6OHL spectrometer) which consisted of three singlets at τ 7.85, 4.03, and 3.93. Integration was difficult because of the proximity of the low-field lines to each other. However, the ratio of the areas of the low-field lines to the high-field line was 1:1. These resonances are assigned to the SCH_3, olefinic, and methine hydrogens, respectively.

To the stirred, cooled (0°) solution of **3** in 100 ml of acetic anhydride in a 500-ml erlenmeyer flask was added dropwise a fluoboric acid solution.[14]

When the addition was complete, anhydrous ether was added (~200 ml). The near-white 1.3-dithiolium fluoborate salt (**4**) was collected on a Büchner funnel and washed with anhydrous ether. The salt (~28 g, 0.15 mol, 82%) was used immediately for the next step. The nmr spectrum of **4** in CD_3CN consisted of a doublet at τ 0.33 (J = 2 Hz) and a triplet at τ − 1.65 (J = 2 Hz). The areas were 2:1, respectively. The lines are assigned to H-4 and -5 for the doublet and H-2 for the triplet.

The 1,3-dithiolium fluoborate was dissolved in 100 ml of acetonitrile in a 500-ml erlenmeyer flask. The solution was magnetically stirred at 0° and triethylamine was added until the formation of yellow crystals was obvious (~50 ml). Another quantity of amine (~10 ml) was then added. After stirring for 10 min water was added to precipitate the product. The yellow-orange crystals were collected, washed with water, and air-dried. The yield of crude product was 15.0 g (100%). Recrystallization from cyclohexane–hexane (500 ml:300 ml) (clarified with Norit and dried with $MgSO_4$) resulted in yellow-orange needles of **1** with mp 119.1–119.3° (corrected) (lit. mp 118.5–119°,[3] 120°[4]).

Registry No.—**1**, 31366-25-3; **2**, 53059-74-8; **3**, 45439-65-4; **4**, 53059-75-9.

References and Notes

(1) A. F. Garito and A. J. Heeger, *Accounts Chem. Res.*, **7**, 218 (1974), and references therein.
(2) Z. G. Soos, *Annu. Rev. Phys. Chem.*, in press.
(3) F. Wudl, G. M. Smith, and E. J. Hufnagel, *Chem. Commun.*, 1453 (1970).
(4) S. Hünig, G. Kiesslich, H. Quast, and D. Scheutzow, *Justus Liebigs Ann. Chem.*, 310 (1973).
(5) F. Wudl, D. Wobschall, and E. J. Hufnagel, *J. Amer. Chem. Soc.*, **94**, 670 (1972).
(6) L. R. Melby, H. D. Hartzler, and W. A. Sheppard, *J. Org. Chem.*, **39**, 2456 (1974).
(7) H. Prinzbach, H. Berger, and A. Lüttringhaus, *Angew. Chem., Int. Ed. Engl.*, **4**, 435 (1965).
(8) A. Takaminzawa and K. Hirai, *Chem. Pharm. Bull.*, **17**, 1931 (1969).
(9) D. L. Coffen, *Tetrahedron Lett.*, 2633 (1970).
(10) D. L. Coffen, J. Q. Chambers, D. R. Williams, P. E. Garrett, and N. D. Chambers, *J. Amer. Chem. Soc.*, **93**, 2258 (1971).
(11) R. Mayer and B. Gebhardt, *Chem. Ber.*, **97**, 1298 (1964).
(12) E. Klingsberg, *J. Amer. Chem. Soc.*, **86**, 5290 (1964).
(13) F. Challenger, E. A. Mason, E. C. Holdsworth, and R. Emmott, *J. Chem. Soc.*, 292 (1953).
(14) Fluoboric acid reagent consisted of fluoboric acid (33.3 g of 48% HBF_4, 0.18 mol) added dropwise to stirred, cooled (0°) acetic anhydride (100 ml). This reaction is very exothermic!