constant-temperature bath held to ±0.05 °C of reaction temperature, and then, at appropriate times, titrated as previously described.[4a]

Treatment of Kinetic Data. The thermodynamic activation parameters were calculated by regression analysis on an IBM 370 computer. The linear correlations, slope values, and correlation coefficients were also calculated by IBM 370 computer regression analysis.

Registry No. Neophyl-OPms, 74592-21-5; neopentyl-OTs, 2346-07-8; neophyl-OTs, 21816-03-5; pentamethylbenzenesulfonyl chloride, 52499-94-2; neophyl alcohol, 2173-69-5; *p*-toluenesulfonyl chloride, 98-59-9; neopentyl alcohol, 75-84-3.

Tetramethyl-1,2,3,4,5-hexapentaene[1]

Lawrence T. Scott* and Gary J. DeCicco

Department of Chemistry, University of Nevada, Reno, Nevada 89557

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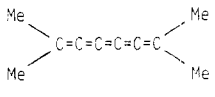
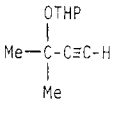
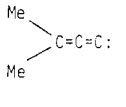
Peculiar conjugation effects and unusual reactivity have long been associated with the cumulenes, an interesting family of highly unsaturated hydrocarbons.[2] In the parent series, C_nH_4, a proclivity for polymerization has prevented isolation of all but the smallest members (n = 2, 3, 4).[3] Study of the more extended cumulenes, therefore, has necessarily focused on derivatives in which stabilizing groups have replaced the hydrogen atoms.[2] We report here a short, convenient procedure for preparing and purifying the title compound (1), an extended cumulene substituted only by methyl groups.



1



2



3

The tetrahydropyranyl ether of 3-methyl-1-butyn-3-ol (2) can be cleanly deprotonated with ethylmagnesium chloride to give a solution of the corresponding acetylide which is stable under ordinary conditions. Subsequent treatment with a catalytic amount of cuprous chloride, however, induces a γ-elimination which leads to the formation of cumulene **1**, presumably via a copper carbenoid related to **3**.[4] Chromatography on silica gel provides a yellow pentane solution of pure **1** which was characterized by hydrogenation to 2,7-dimethyloctane (Rh/alumina/−78 °C) and by spectroscopic means: ^{1}H NMR ($CDCl_3$) δ 1.95 (s); UV max (EtOH) 214, 226, 306, 320 nm (relative ε 29, 100, 17, 19).

It is interesting to note the large downfield shift of the methyl hydrogen NMR signal of **1** relative to that of tetramethylethylene (δ 1.67). The magnitude of this downfield shift appears to correlate with the number of double bonds in the tetramethyl cumulene family.[5] The longer wavelength UV absorptions of **1** relative to those of lower homologues[5] likewise reflect the more extended π system in **1**.

This cumulene does polymerize rapidly in the absence of solvent but can be kept for many hours in dilute solutions protected from oxygen. By working quickly, one can remove the solvent under reduced pressure and redissolve the cumulene in a different solvent without undue losses to polymerization. In $CDCl_3$ (ca. 5% solution) at 37 °C, the ^{1}H NMR signal of **1** disappears with a half-life of about 2 h; a precipitate appears, but no new ^{1}H NMR signals are observed. Bubbling oxygen through a freshly prepared NMR sample of **1** for 10 min completely destroys the cumulene.

The title compound has previously been prepared by Skattebøl by reductive dechlorination of 2,7-dichloro-2,7-dimethyl-3,5-octadiyne, although no purification method was reported.[5] The close correspondence of UV data [lit.[5] UV max (EtOH) 215, 228, 308, 321 nm (relative ε 35, 100, 20, 22)] confirms the identity of the hydrocarbons obtained by these different routes. Skattebøl reports an IR (2002 and 1625 cm^{-1}) but no ^{1}H NMR spectrum and notes that heating the polymer obtained from **1** produced an explosion on one occasion.[5] We intend by this note to supplement the sparse published information available on the title compound and to provide a procedure for its preparation and purification which other interested chemists should find easy and convenient.

Experimental Section

Tetramethyl-1,2,3,4,5-hexapentaene (1).[1] A solution of 1.680 g (10.0 mmol) of **2**[6] in 10 mL of dry THF[7] was added dropwise to 3.6 mL (10.0 mmol) of 2.79 M ethylmagnesium chloride[8] in THF. The solution was heated under reflux for 1 h and then cooled to room temperature. To the acetylide solution was added 50 mg (0.50 mmol) of anhydrous cuprous chloride.[9] The mixture was then heated under reflux for 1 h more, cooled to room temperature, and poured into dilute HCl and ice. The resulting mixture was extracted with 50 mL of ether, which was then shaken with 50 mL of saturated $NaHCO_3$, dried ($MgSO_4$), and concentrated under reduced pressure; the vacuum was released by readmitting nitrogen rather than air. The residue was rapidly taken up in minimal pentane and chromatographed on a column of silica gel (25 g), using pentane as the eluant. The yellow fraction contained pure cumulene **1** (5–10% yield); no other compounds were eluted from the column with pentane. Evaporation of the pentane under reduced pressure gave a yellow-orange solid which could be redissolved in $CDCl_3$, EtOH, THF, or other solvents with only minor losses to polymerization, provided the operation was performed quickly under nitrogen. (See text for spectra.)

Hydrogenation of 1. The pentaene (**1**) was prepared and chromatographed as above, only the yellow fraction from the column chromatography was collected in a flask flushed with nitrogen and cooled to −78 °C. When all the cumulene had been collected, 100 mg of 5% Rh/alumina was added to the pentane solution, and hydrogen gas was slowly bubbled through the mixture, still at −78 °C. The yellow color slowly faded over a period of 45 min. The mixture was allowed to warm to room temperature, and the addition of hydrogen was continued for 15 min more. The mixture was then filtered and concentrated under reduced pressure to give 41 mg (6%) of 2,7-dimethyloctane as a colorless liquid: mass spectrum, m/e (relative intensity) 142 (1, M^+), 127 (5, M − CH_3), 113 (no peak for M − Et), 99 (53, M − Pr),

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85 (47), 71 (57), 57 (100), 43 (79); ^{1}H NMR ($CDCl_3$) δ 1.5 (br m, 2, $CHMe_2$), 1.22 (br s, 6, CH_2), 0.85 (d, 12, J = 6 Hz, CH_3); IR (neat) 2950, 2880, 1460, 1380, 1360, 1170 cm^{-1}.

Acknowledgment. We thank the National Science Foundation, the Research Corporation and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for financial support of this work.

Registry No. 1, 2590-12-7; 2, 27943-46-0; 2,7-dimethyloctane, 1072-16-8.

Reductive Debromination of Some Purine and Purine-Like Nucleosides

Fung-Lung Chung, Robert A. Earl, and Leroy B. Townsend*[‡]

Department of Medicinal Chemistry, College of Pharmacy, and Department of Chemistry, The University of Michigan, Ann Arbor, Michigan 48109, and Department of Medicinal Chemistry and Department of Chemistry, The University of Utah, Salt Lake City, Utah 84112

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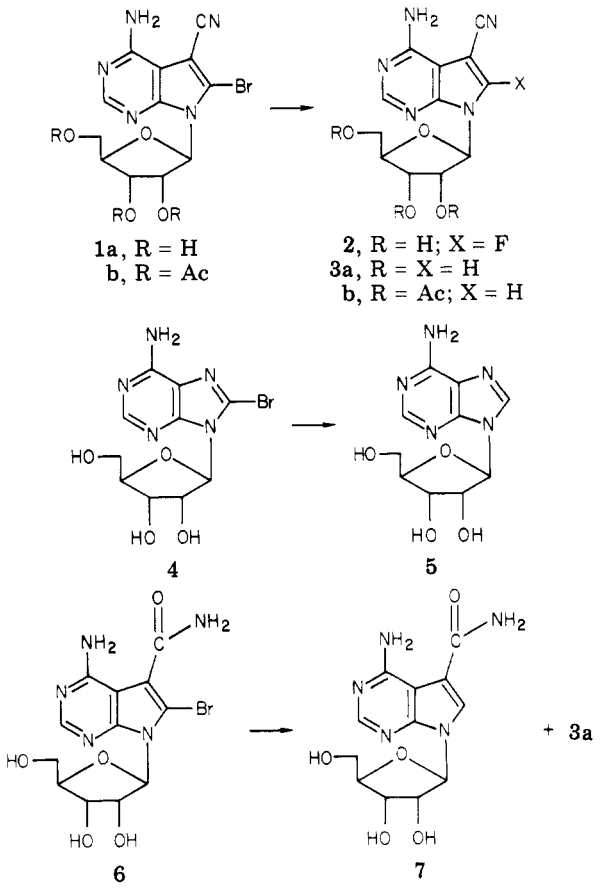
The synthetic applications of trialkylsilylating agents in the field of nucleoside and nucleotide chemistry are well-documented.[1] The three most commonly used silylating agents are hexamethyldisilazane (HMDS), trimethylsilyl chloride, and *N,O*-bis(trimethylsilyl)acetamide (BSA). It has been shown that BSA is a versatile and reactive agent for the synthesis of silylated heterocycles. These silylated heterocycles can then be condensed with a suitably blocked derivative to provide a great variety of nucleoside analogues. Due to the ubiquitous use of BSA in this area, we report a novel reaction where BSA functions as a debrominating agent in the presence of potassium fluoride and a crown ether.

In an attempt to synthesize 6-fluorotoyocamycin (**2**) from 6-bromotoyocamycin (**1**), a solution of 6-bromotoyocamycin and an excess of BSA in acetonitrile was mixed with a suspension of potassium fluoride and dicyclohexyl-18-crown-6 in acetonitrile. The reaction mixture was heated at reflux temperature in an oil bath for 48 h. After removal of the solvent, a nucleoside product was isolated by chromatography. This product (40% yield) was found to be toyocamycin (**3a**) by a comparison of the UV, ^{1}H NMR, and IR spectra and mixture melting point with an authentic sample of toyocamycin. This interesting observation prompted us to study a series of similar reactions (see Scheme I); e.g., adenosine (**5**) was isolated in 44% yield when 8-bromoadenosine (**4**) was treated with BSA, potassium fluoride, and crown ether under the same conditions. Similarly, 6-bromosangivamycin (**6**) afforded sangivamycin (**7**) in 30% yield. The isolation of toyocamycin (**3a**) in 20% yield from this same reaction would indicate that perhaps this may be a new method for the transformation of a carboxamide group into a nitrile group.

2′,3′,5′-Tri-*O*-acetyl-6-bromotoyocamycin (**1b**) was prepared and then treated under the standard conditions (9-h reflux) to provide a 60% yield of 2′,3′,5′-tri-*O*-acetyltoyocamycin (**3b**) and established that BSA is indispensible in these reactions. However, when the reaction was repeated without the addition of BSA, there was no apparent reaction even after heating for more than 48 h. We also found that the attempted reaction of 6-bromotoyocamycin (**1a**) with BSA and crown ether in the absence of potassium fluoride afforded, after heating at reflux for 72 h, only starting material. On the basis of these experiments, we have concluded that BSA and potassium fluoride are both required for the debromination reaction.

Scheme I



1a, R = H
b, R = Ac

2, R = H; X = F
3a, R = X = H
b, R = Ac; X = H

4 5

6 7

It is not clear at this time what species is responsible for the observed reductions. It is interesting to note, however, that the trimethylsilyl anion has been reported[2-4] to function not only as a nucleophile in reactions with organic halides but also as a reducing agent due to its one-electron-transfer properties. Trimethylsilyl anion[5] has been prepared[2-4] through the action of alkali alkoxides on hexamethyldisilane in polar aprotic solvents. It has also been shown[6,7] that crown ethers are capable of complexing with alkali metal ions, resulting in an increased separation of charge between the alkali metal ion and its counterion. The use[6-7] of crown ethers also serves to increase the solubility of alkali metal ions in nonpolar solvents (e.g., benzene, ether, or tetrahydrofuran). It seems likely that the "naked" fluoride ion,[8] formed under our reaction conditions, may be interacting with BSA or (monotrimethylsilyl)acetamide in such a manner as to produce[9]

[‡] University of Michigan.

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