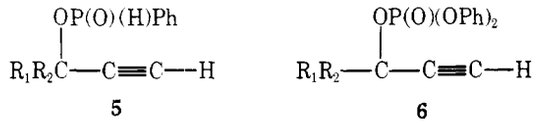

5 6

Preliminary results indicate that 3,3-dimethylallenyl acetate undergoes hydrolysis to 3-methyl-2-butenal at 45 °C at pH 7.8 with a half-life of 100 min. The corresponding diethyl phosphate appears to be even more reactive under the same conditions.

Experimental Section

Infrared spectra were recorded using a Perkin-Elmer Model 337 infrared spectrophotometer. Preparative gas–liquid chromatography was performed on a Hewlett-Packard chromatograph, Model 5750, using 8 ft × 0.5 in. SE-30 columns. The ^1H NMR spectra were run on an Hitachi Perkin-Elmer R-20B nuclear magnetic resonance spectrometer, 60 Hz. Melting points and boiling points are uncorrected. Elemental analyses were performed by Atlantic Microlabs, Inc., Atlanta, Ga.

Propargyl Esters. Acetates of secondary and tertiary propargyl alcohols were prepared according to the method of Hennion et al.[7] Diethyl phosphates were prepared by treatment of the alkoxide salt with diethyl chlorophosphate according to reported procedures.[8,9] Nitrobenzoates were prepared according to Hennion et al.[10] Propargyl tosylates and trifluoroacetates were prepared according to reported procedures.[11,12]

General Procedure for Ag^+-Catalyzed Rearrangement of Propargyl Esters. Propargyl ester (50 mmol) dissolved in 50 mL of CH_2Cl_2 is allowed to react at 35 °C under N_2 in the presence of 1.5 mmol of $AgClO_4$ or $AgBF_4$ until the appearance of a red-brown color (usually 1.75–2.75 h). Continued reaction leads to lower yields. The mixture is then diluted with 50 mL of ether and washed with 2 × 75 mL of 10% aqueous ammonia and 2 × 100 mL of H_2O before drying over K_2CO_3 and rotary evaporation. Distillation or recrystallization followed by preparative GC (8 ft × 0.5 in., SE-30) or column chromatography on neutral alumina (10 ft × 0.5 in.) with pentane afforded the desired allenyl ester in the yields reported. Variations for specific compounds and requisite analytical data are to be found in Table II.

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Registry No.—**7**, 61570-65-8; **8**, 17458-90-1; **9**, 17458-93-4; **10**, 61570-66-9; **11**, 50989-92-9; **12**, 61570-67-0; **13**, 61570-68-1; **14**, 61570-69-2; **15**, 61570-70-5; **16**, 42969-38-0; **17**, 42969-35-7; **18**, 61570-71-6; **19**, 61570-72-7; **20**, 61570-73-8.

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Pyrolysis of the Lithium Salts of the *p*-Toluenesulfonylhydrazones of 8,9-Dehydro-2-adamantanone and 2,4-Dehydro-5-homoadamantanone

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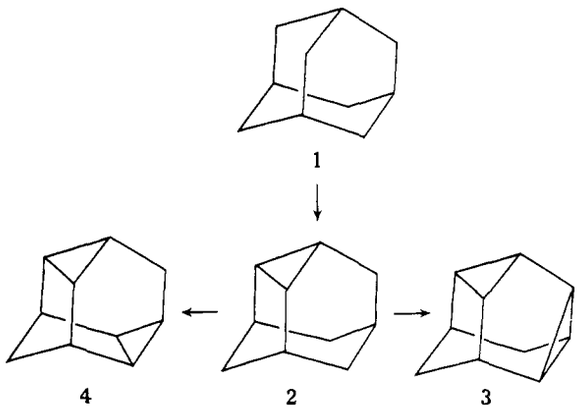
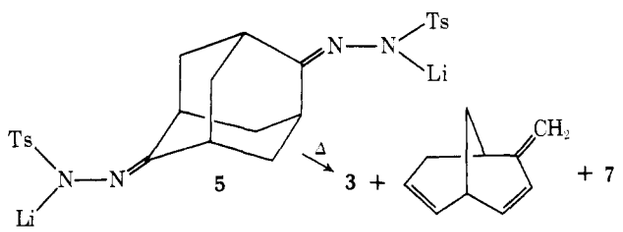
Adamantane (**1**) (T_d symmetry) allows for only one "nonbridgehead" dehydroadamantane (**2**). By contrast, two nonbridgehead didehydroadamantanes, **3** and **4**, are possible.



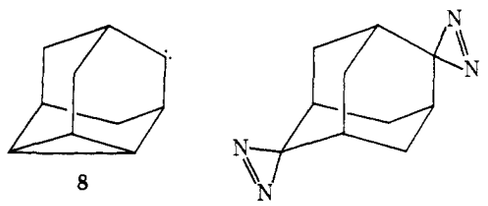
1 4 2 3

Geluk and de Boer have reported that thermolysis of the dilithium salt of 2,6-adamantanedione bistosylhydrazone (**5**) gives a mixture of three volatile $C_{10}H_{12}$ hydrocarbons: **3**, 2-methylenebicyclo[3.3.1]nona-3,6-diene (**6**), and an unknown compound **7** in yields of 12, 9, and 3%, respectively.[1] These



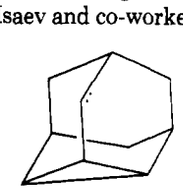
5 6

authors have suggested that the reaction proceeds via carbene **8**.[1] 2,4,6,9-Bisdehydroadamantane (**3**) has also been obtained in ca. 30% yield by pyrolysis of diazirine **9**.[2]



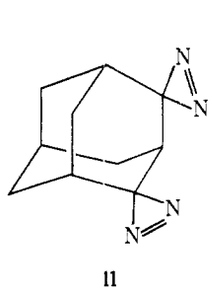
8 9

In principle, hydrocarbon **3** might also be generated from carbene **10**. Although Isaev and co-workers have reported that

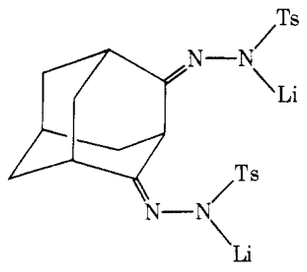


10

pyrolysis of diazirine **11** leads to a mixture of products containing **3** in ca. 30% yield,[2] Geluk and de Boer observed that pyrolysis of **12** only affords a condensate that consists of a



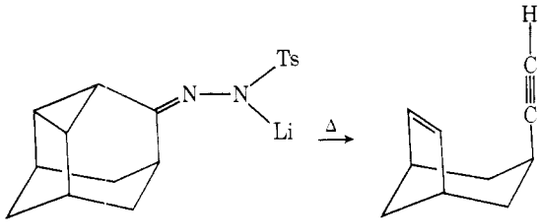
11



12

large number of products with low volatility.[1] Since it is well known that geometrically constrained cyclopropylcarbinyl carbenes frequently undergo fragmentation reactions,[3] it was of interest to explore the behavior of **10** generated from an alternative source.

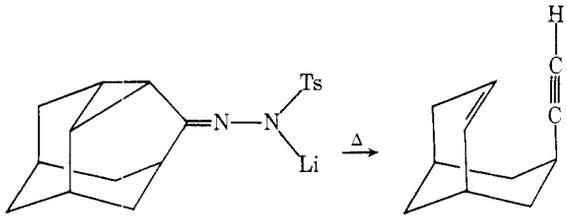
Pyrolysis of the dry lithium salt of the *p*-toluenesulfonylhydrazone of 8,9-dehydro-2-adamantanone[4] (**13**) at 190–200 °C for 1 h, according to the general procedure of Friedman and Shechter,[5] gives 3-*endo*-ethynylbicyclo[3.2.1]oct-6-ene (**14**)



13 14

as the sole volatile product in ca. 25% yield. Consistent with this structure assignment, **14** shows characteristic terminal acetylene absorptions in the infrared at 3320 and 2115 cm^{-1}, an apparent singlet for the olefinic hydrogens at δ 6.15 in its ^1H NMR spectrum, and a ^{13}C NMR spectrum which contains only seven signals with three of the signals being twice as intense as the others. As it has previously been shown that an ethynyl substituent is configurationally stable under the reaction conditions employed,[6] the stereochemistry at C-3 in **14** is determined by the mode of formation of **14**. Since **13** undoubtedly proceeds to **14** via carbene **10**,[7] it follows that **10** cannot be a discrete intermediate in the thermal decomposition of **11**.

Carbenoid decomposition of the *p*-toluenesulfonylhydrazone of 2,4-dehydro-5-homoadamantanone[8] leads to an analogous result. Pyrolysis of **15** at 190 °C for 1.5 h affords



15 16

7-*endo*-ethynylbicyclo[3.3.1]non-2-ene (**16**) as the only volatile product in ca. 50% yield. Hydrocarbon **16** also has terminal acetylene absorptions at 3320 and 2110 cm^{-1} in the infrared. Consistent with this structure assignment, the ^{13}C NMR spectrum of **16** consists of 11 signals. The stereochemistry at C-7 in **16** also follows from the mode of formation of **16**.

Experimental Section

Infrared spectra were obtained on a Perkin-Elmer 337 spectrophotometer and proton magnetic resonance spectra were recorded with Varian A-60A or Perkin-Elmer R-12B 60-MHz spectrometers. Carbon magnetic resonance spectra were taken at an operating frequency of 22.63 MHz on a Bruker HFX-90 spectrometer equipped for Fourier transform pulsed NMR with a Nicolet 1085 data system. Yields of the pyrolysis products were obtained by integration of the olefinic proton signals in the ^1H NMR spectrum of the condensate vs. the signal of a predetermined amount of an added standard and are regarded as being accurate to ca. ±10%. Elemental analyses were performed by Micro-Analysis, Inc., Wilmington, Del.

8,9-Dehydro-2-adamantanone Tosylhydrazone (17). Equimolar quantities of 8,9-dehydro-2-adamantanone[4] (1.00 g, 6.75 mmol) and *p*-toluenesulfonylhydrazine (1.26 g, 6.77 mmol) were dissolved in methanol (5 mL). The stirred solution was brought to a gentle boil and refluxed for 2 h. After slowly cooling to room temperature, the reaction mixture was stored overnight at −10 °C. The resulting white solid was filtered, washed with cold methanol, and dried in vacuo to give 1.72 g (80% yield) of **17**: mp 137.5–139.5 °C; δ_{Me_4Si} ($CDCl_3$) 0.9–2.9 (complex m, 13 H, containing CH_3 signal at δ 2.46) and 7.13–8.25 (4 H, d of d, aromatic protons).

3-*endo*-Ethynylbicyclo[3.2.1]oct-6-ene (14). *n*-Butyllithium (3 mL of a solution 2.4 M in hexane) was slowly added to a stirred solution of **17** (1.72 g, 5.4 mmol) in 15 mL of tetrahydrofuran (freshly distilled from lithium aluminum hydride) at 0 °C under nitrogen. The resulting pale yellow solution was stirred at 0 °C for 15 min and then at 25 °C for 1 h. At this point the solvent was evaporated at reduced pressure and the residue was dried at 60 °C and 0.1 mm for 0.5 h. The reaction flask was then connected to an all-glass pyrolysis apparatus leading to a trap maintained at −78 °C. The lithium salt of **17** was heated to 200 °C at 0.1 mm with an oil bath and kept at this temperature for 1 h (vigorous decomposition of the residue occurred at 190 °C). Analysis of the distillate by GLC (10 ft × 0.25 in. DC-550 column, 125 °C) indicated a single product. This material was purified by GLC to give **14** as an oil: ^1H NMR δ_{Me_4Si} ($CDCl_3$) 6.15 (s, 2 H, CH=CH) and 3.15–1.3 (complex m, 10 H); ^{13}C NMR, off-resonance decoupled, δ_{Me_4Si} ($CDCl_3$) 135.1 (d, C-6 and C-7), 92.8 (s, **C**≡CH), 69.4 (d, C≡**CH**), 43.9 (t, C-8), 38.7 (d, C-1 and C-5), 31.5 (t, C-2 and C-4), and 21.7 (d, C-3); ν (CCl_4) 3320, 3065, 2940, 2860, 2115, 1460, 1445, 1355, 1335, 1080, 990 cm^{-1}.

Anal. Calcd for $C_{10}H_{12}$: C, 90.85; H, 9.15. Found: C, 90.88; H, 9.05.

2,4-Dehydro-5-homoadamantanone Tosylhydrazone (18). Treatment of 2,4-dehydro-5-homoadamantanone[8] (631 mg, 3.89 mmol) with *p*-toluenesulfonylhydrazine (723 mg, 3.89 mmol) in methanol (10 mL) as described above for **17** provided 1.08 g (84% yield) of white, crystalline **18**. An analytical sample was obtained by recrystallizing a small amount of the material from methanol at 0 °C: mp 148.5–152 °C; δ_{Me_4Si} ($CDCl_3$) 0.95–2.8 (complex m, 15 H, containing CH_3 singlet at δ 2.38) and 7.13–8.02 (4 H, d of d, aromatic protons).

Anal. Calcd for $C_{18}H_{22}N_2O_2S$: C, 65.43; H, 6.71; N, 8.48; S, 9.70. Found: C, 65.51; H, 6.77; N, 8.62; S, 9.64.

7-*endo*-Ethynylbicyclo[3.3.1]non-2-ene (16). To a stirred solution of **18** (1.08 g, 3.27 mmol)in dry tetrahydrofuran (20 mL) maintained at 0 °C under nitrogen was slowly added *n*-butyllithium (2 mL of a solution 2.4 M in hexane). The resulting solution was stirred at 0 °C for 2 h and then the solvent was evaporated at reduced pressure and the residue was dried at 55 °C and 0.1 mm for 1 h. The reaction flask was then connected to an all-glass pyrolysis apparatus leading to a trap maintained at −78 °C. The lithium salt of **18** was heated to 190 °C at 0.1 mm with an oil bath and kept at this temperature for 1.5 h. Analysis of the distillate by GLC (10 ft × 0.25 in. SE-30 column, 130 °C) showed a single product to be present. Purification of this material by GLC provided **16** as an oil: ^1H NMR δ_{Me_4Si} ($CDCl_3$) 6.03–5.43 (m, 2 H, CH=CH) and 3.0–1.1 (complex m, 12 H); ^{13}C NMR δ_{Me_4Si} ($CDCl_3$) 131.1, 129.5, 90.2 (**C**≡CH), 67.0 (C≡**CH**), 36.4, 32.9, 32.5, 30.2, 27.9, 26.0, and 21.7 (C-7); ν ($CHCl_3$) 3320, 3030, 2930, 2905, 2110, and 1440 cm^{-1}.

Anal. Calcd for $C_{11}H_{14}$: C, 90.35; H, 9.65. Found: C, 90.15; H, 9.61.

Acknowledgment. This work was supported by grants from the Research Corporation and the University of Delaware Research Foundation.

Registry No.—**14**, 61665-63-2; **16**, 61665-64-3; **17**, 61665-65-4; **17** Li salt, 61665-66-5; **18**, 61665-67-6; **18** Li salt, 61665-68-7; 8,9-dehydro-2-adamantanone, 10497-56-0; *p*-toluenesulfonylhydrazine, 1576-35-8; 2,4-dehydro-5-homoadamantanone, 55638-01-2.

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N- vs. C-Acylation of Metalated *O*-Methyllactims. Synthesis of 5,6,7,8-Tetrahydropyrido[2,3-*d*]-pyrimidines through C-Acylation by Nitriles[1]

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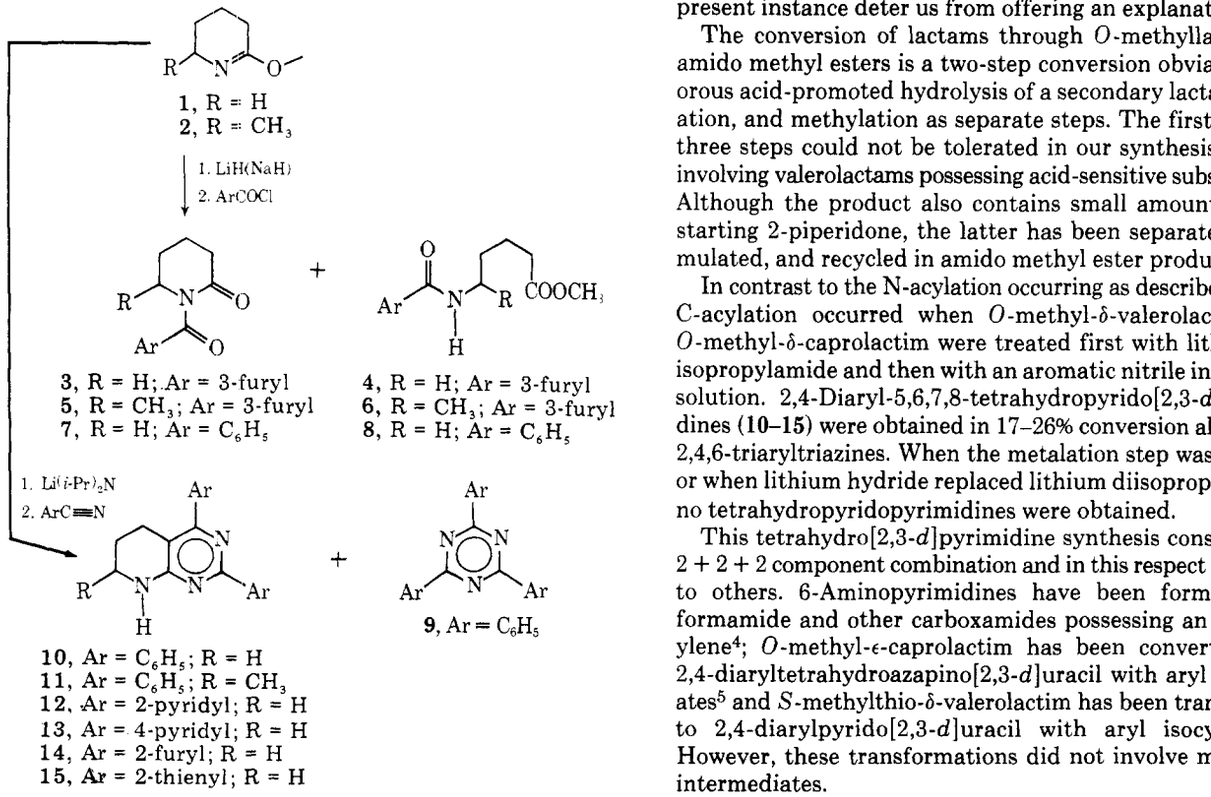
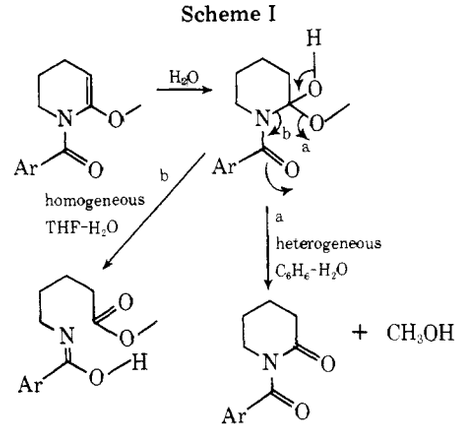
Our search for methods utilizing 2-piperidones as intermediates in the synthesis of piperidine alkaloids led us to examine the acylation of metalated *O*-methyl-δ-valerolactim (**1**) and *O*-methyl-δ-caprolactim (**2**), which were readily generated from the corresponding lactams.[2] The alkylations of metalated *O*-alkyllactims has been observed recently.[3] We report here the two different routes taken in the acylation of *O*-alkyllactims **1** and **2** by aroyl chlorides and aromatic nitriles and wish to emphasize the potential of one of these routes in the synthesis of 2,4-diaryl-5,6,7,8-tetrahydropyrido[2,3-*d*]-pyrimidines.

Treatment of **1** and **2** in benzene or tetrahydrofuran (THF) solution with alkali metal hydrides followed by the addition of the aroyl chloride gave mixtures containing N-acylated lactams, such as **3**, and amido methyl esters, such as **4**, in the yields and in relative amounts indicated in the Experimental Section. Omission of the metalation step resulted in the formation of both N-acylated lactams and amido methyl esters as before but in very low conversions. Metal hydrides were used as the base rather than lithium diisopropylamide, which was used in the C-acylations described below, in order to avoid the consumption of aroyl chloride through carboxamide formation. Lithium hydride suspended in THF and an acidic or basic aqueous treatment prior to workup favored the production of amido methyl esters (**4**, **6**, **8**) while sodium or lithium hydride suspended in benzene and a water, aqueous lithium hydroxide, or aqueous acidic treatment prior to workup favored *N*-acyllactam (**3**, **5**, **7**) formation. Scheme I



Scheme I



illustrates the two hydrolysis pathways which follow N-acylation and result from changing the acylation solvent from THF to benzene. The essential difference is that the homogeneous aqueous treatment carried out in THF strongly favored amido ester formation (path b) while the heterogeneous aqueous treatment carried out in benzene favored *N*-acyllactam formation (path a). The complexities of comparing homogeneous with heterogeneous systems in general and the need for considerably more experimental evidence in the present instance deter us from offering an explanation.

The conversion of lactams through *O*-methyllactims to amido methyl esters is a two-step conversion obviating vigorous acid-promoted hydrolysis of a secondary lactam, acylation, and methylation as separate steps. The first of these three steps could not be tolerated in our synthesis scheme involving valerolactams possessing acid-sensitive substituents. Although the product also contains small amounts of the starting 2-piperidone, the latter has been separated, accumulated, and recycled in amido methyl ester production.

In contrast to the N-acylation occurring as described above, C-acylation occurred when *O*-methyl-δ-valerolactim and *O*-methyl-δ-caprolactim were treated first with lithium diisopropylamide and then with an aromatic nitrile in benzene solution. 2,4-Diaryl-5,6,7,8-tetrahydropyrido[2,3-*d*]pyrimidines (**10–15**) were obtained in 17–26% conversion along with 2,4,6-triaryltriazines. When the metalation step was omitted or when lithium hydride replaced lithium diisopropylamide, no tetrahydropyridopyrimidines were obtained.

This tetrahydro[2,3-*d*]pyrimidine synthesis constitutes a 2 + 2 + 2 component combination and in this respect is similar to others. 6-Aminopyrimidines have been formed from formamide and other carboxamides possessing an α-methylene[4]; *O*-methyl-ε-caprolactim has been converted to a 2,4-diaryltetrahydroazapino[2,3-*d*]uracil with aryl isocyanates[5] and *S*-methylthio-δ-valerolactim has been transformed to 2,4-diarylpyrido[2,3-*d*]uracil with aryl isocyanates.[6] However, these transformations did not involve metalated intermediates.