of pyridine 17 (2.50 (2×), 2.75, and 2.93 ppm). The results are given in the text.

Preparation of 2-(Ethoxycarbonyl)-3,4,5,6-tetramethylpyridine (17). A solution of 6.25 g of ethyl cyanoformate (62.5 mmol) in 2 mL of CH_2Cl_2 was added at −50 °C to a solution of complex 1(Al_2Cl_6), prepared from 6.67 g of $AlCl_3$ (50 mmol) and 2.70 g of 2-butyne (50 mmol), in 50 mL of CH_2Cl_2.[1c] After slowly warming to room temperature, the reaction mixture was poured out into 200 mL of an aqueous 1 N NaOH solution under mechanical stirring. The water layer was extracted with pentane (2 × 100 mL). The combined organic layers were extracted with an aqueous 1 N HCl solution (3 × 100 mL), and the combined acidic layers were washed with 50 mL of pentane. The acidic layers were made alkaline with K_2CO_3 and subsequently extracted with CH_2Cl_2 (3 × 100 mL). The combined CH_2Cl_2 layers were dried over K_2CO_3, and the solvent was evaporated, affording 4.32 g (83% yield) of 17 (pure, according to the ^1H NMR spectrum[1e,7]).

Preparation of 2-Cyano-3,4,5,6-tetramethylpyridine (18). At 0 °C cyanogen was bubbled through a solution of complex 1(Al_2Cl_6), prepared from 2.7 g of $AlCl_3$ (20 mmol) and 1.08 g of 2-butyne (20 mmol),[1c] in 40 mL of CH_2Cl_2 under a hood. The reaction was followed by ^1H NMR spectroscopic measurements, and the addition of cyanogen was stopped when complex 1(Al_2Cl_6) had disappeared. Compound 18 was isolated as described above for pyridine 17 followed by sublimation at 100 °C (0.1 mmHg), giving 1.05 g (66% yield) of 18, which was resublimed twice at 100 °C (0.1 mmHg) to give analytically pure material: mp 83.5–85.0 °C; ^1H NMR 2.26 (s, 6 H), 2.43 (s, 3 H), 2.48 (s, 3 H); ^{13}C NMR 14.9 (2×), 15.6, 22.3 (3 q, J = 130 Hz), 116.5 (s), 128.8 (s), 133.5 (s), 133.7 (s), 144.5 (s), 155.1 (s); IR (Nujol) 2230 cm^{-1} (nitrile); mass spectrum, molecular ion peak at m/e 160. Anal. Calcd for $C_{10}H_{12}N_2$: C, 74.97; H, 7.55; N, 17.48. Found: C, 75.0; H, 7.6; N, 17.4.

Preparation of 2-(Cyanomethyl)-3,4,5,6-tetramethylpyridine (19). A solution of 5.0 g of malonitrile (75 mmol) in 10 mL of CH_2Cl_2 was added at −50 °C to a solution of complex 1(Al_2Cl_6), prepared from 8.0 g of $AlCl_3$ (60 mmol) and 3.24 g of 2-butyne (60 mmol), in 75 mL of CH_2Cl_2.[1c] Pyridine 19 was isolated as described for pyridine 17 and was purified by Kugelrohr distillation at 115 °C (0.01 mmHg) followed by recrystallization from methylcyclohexane (−50 °C), giving analytically pure 19: 1.15 g (22% yield); mp 109–110 °C; ^1H NMR 2.16 (s, 6 H), 2.21 (s, 3 H), 2.41 (s, 3 H), 3.73 (s, 2 H); ^{13}C NMR 14.9, 15.1, 15.6, 22.8 (4 q, J = 125 Hz), 25.4 (t, J = 135 Hz), 117.1 (s), 127.2 (s), 129.7 (s), 144.2 (s), 144.9 (s), 153.5 (s); IR ($CHCl_3$) 2240 cm^{-1} (nitrile); mass spectrum, molecular ion peak at m/e 174. Anal. Calcd for $C_{11}H_{14}N_2$: C, 75.83; H, 8.10; N, 16.38. Found: C, 75.6; H, 8.2; N, 16.2.

Preparation of 2-Phenyl-3,4,5,6-tetramethylpyridine (20). A solution of 7.7 g of benzonitrile (75 mmol) in 10 mL of CH_2Cl_2 was added at −50 °C to a solution of complex 1(Al_2Cl_6), prepared from 8.0 g of $AlCl_3$ (60 mmol) and 3.24 g of 2-butyne (60 mmol), in 75 mL of CH_2Cl_2.[1c] Pyridine 20 was isolated as described for pyridine 17 and purified by Kugelrohr distillation at 130 °C (0.01 mmHg), giving 1.12 g (18% yield) of 20 as an oil: ^1H NMR 2.13 (s, 3 H), 2.20 (s, 6 H), 2.48 (s, 3 H), 7.28 (br s, 5 H); ^{13}C NMR 14.7, 15.3, 16.2, 22.7 (4 q, J = 125 Hz), 126.0 (s), 126.6 (d, J = 160 Hz), 127.4 (d, J = 160 Hz), 127.6 (s), 128.6 (d, J = 160 Hz), 141.2 (s), 144.0 (s), 152.4 (s), 154.6 (s); mass spectrum, molecular ion peak at m/e 211; exact mass m/e 211.139, calcd for $C_{15}H_{17}N$ m/e 211.136.

Reaction of 1(Al_2Cl_6) with Acetonitrile. A solution of 0.82 g of acetonitrile (10 mmol) in 2 mL of CH_2Cl_2 was added at −50 °C to a solution of complex 1(Al_2Cl_6), prepared from 0.67 g of $AlCl_3$ (5 mmol) and 0.27 g of 2-butyne (5 mmol), in 10 mL of CH_2Cl_2.[1c] After warming to room temperature, the reaction mixture was poured out into 100 mL of an aqueous 1 N NaOH solution. The alkaline layer was extracted with pentane (2 × 100 mL), followed by drying of the combined organic layers over K_2CO_3. After evaporation of the solvent, 0.24 g of a slightly yellow semisolid was obtained. According to the ^1H NMR spectrum the crude product contained no 2,3,4,5,6-pentamethylpyridine (21); it consisted mostly of octamethyl-*syn*-tricyclo[4.2.0.$0^{2,5}$]octadiene (22).

Registry No. 1 ($AlCl_3$), 31886-99-4; 1 (Al_2Cl_6), 66085-77-6; 2 ($AlBr_3$), 80206-72-0; 2 (Al_2Br_6), 80206-70-8; 3 ($AlBr_3$), 80206-73-1; 3 (Al_2Br_6), 80206-74-2; 4 ($AlBr_3$), 80206-75-3; 4 (Al_2Br_6), 80206-71-9; 5 ($AlBr_3$), 80206-76-4; 5 (Al_2Br_6), 80206-77-5; 6 ($AlBr_3$), 80206-78-6; 6 (Al_2Br_6), 80206-79-7; 7 ($AlBr_3$), 80206-80-0; 7 (Al_2Br_6), 80206-81-1; **10a**, 80206-38-8; **10b**, 80206-39-9; **10c**, 80206-40-2; **12a**, 80206-41-3; **12b**, 80206-42-4; **13**, 80206-43-5; **14**, 80206-44-6; **15a**, 80206-45-7; **15b**, 80206-46-8; **16a**, 80206-47-9; **16b**, 80206-48-0; **17**, 61110-37-0; **18**, 80206-49-1; **19**, 80206-50-4; **20**, 80206-51-5; **22**, 1448-74-4; $AlBr_3$, 7727-15-3; propyne, 74-99-7; *tert*-butylacetylene, 917-92-0; 2-butyne, 503-17-3; 1,5-hexadiyne, 628-16-0; phenylacetylene, 536-74-3; 1,9-decadiyne, 1720-38-3; ethyl cyanoformate, 623-49-4; cyanogen, 460-19-5; malonitrile, 109-77-3; benzonitrile, 100-47-0; acetonitrile, 75-05-8.

One-Pot Nonphotochemical Synthesis of Dewar Pyridones from Alkynes and Isocyanates

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A one-pot synthesis of substituted 3-oxo-2-azabicyclo[2.2.0]hex-5-enes (Dewar pyridones) from alkynes, aluminum halides, and isocyanates is described. The mechanism of the reaction of isocyanates with the intermediate aluminum halide σ complexes of cyclobutadienes is discussed on the basis of the substitution pattern of the obtained bicyclic products. The thermal and acid-promoted reactions of some of the compounds are reported.

It has been shown previously that aluminum halide σ complexes of cyclobutadienes react with a variety of reagents to yield four-, five-, and six-membered-ring compounds.[1] These complexes are especially useful in the synthesis of Dewar benzene derivatives[1a] and substituted bicyclo[2.2.0]hexenes.[1b] In this paper, a new reaction of these complexes with isocyanates is described, leading to the formation of substituted 3-oxo-2-azabicyclo[2.2.0]-hex-5-enes ("Dewar pyridones"). This class of compounds is known to be accessible by irradiation of 2-pyridones.[2]

There exists an important difference between the presently reported reaction and comparable reactions involving organotransition-metal complexes. Thus, reactions

(1) (a) Driessen, P. B. J.; Hogeveen, H. *J. Organomet. Chem.* **1978**, *156*, 265. (b) Van Rantwijk, F.; Van der Stoel, R. E.; Van Bekkum, H. *Tetrahedron* **1978**, *34*, 569. (c) Hogeveen, H.; Kok, D. M. "The Chemistry of Acetylenes"; Patai, S., Ed.; Wiley: New York, in press (Supplement C).

(2) (a) Corey, E. J.; Streith, J. *J. Am. Chem. Soc.* **1964**, *86*, 950. (b) De Selms, R. C.; Schleigh, W. R. *Tetrahedron Lett.* **1972**, 3563. (c) Fürrer, H. *Chem. Ber.* **1972**, *105*, 2780.

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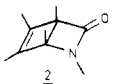
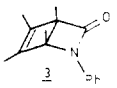
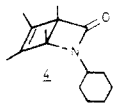
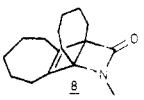
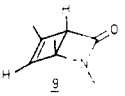
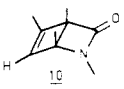
Table I. Reactions of Aluminum Halide σ Complexes of Cyclobutadienes with Isocyanates

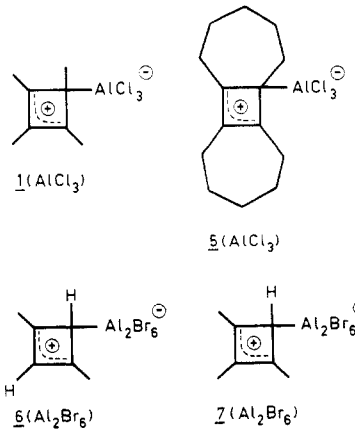
complex	isocyanate, R of RN=C=O	product	% yield[a]
1($AlCl_3$)	Me	 2	85
1($AlCl_3$)	Ph	 3	46
1($AlCl_3$)	c-Hex	 4	57
5($AlCl_3$)	Me	 8	62
6(Al_2Br_6)	Me	 9	69
7(Al_2Br_6)	Me	 10	85

[a] Yields are based on the amount of alkyne used.

of preformed cobaltocyclopentadiene complexes[2] with isocyanates[3] and catalytic cotrimerization of alkynes and isocyanates[4] lead to monocyclic six-membered-ring compounds (2-pyridones), rather than to the strained isomeric bicyclic Dewar pyridones. The Dewar pyridones are known to be easily converted to 2-pyridones by thermal isomerization.[2c] In this paper both thermal and acid-promoted isomerizations of some Dewar pyridones are described.

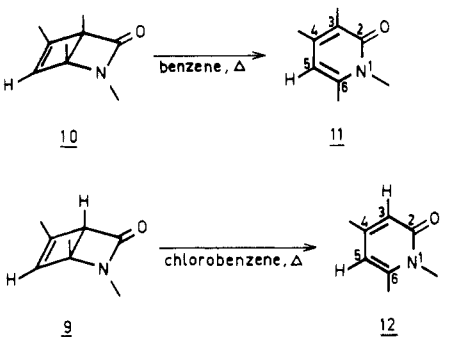
Results and Discussion

Reactions of Aluminum Halide σ Complexes of Cyclobutadienes with Isocyanates. Complex 1($AlCl_3$)[5] reacts at room temperature with methyl-, phenyl-, and cyclohexyl isocyanate to yield the substituted 3-oxo-2-azabicyclo[2.2.0]hex-5-enes ("Dewar pyridones") **2–4**, respectively (Table I). In addition, complexes **5**($AlCl_3$), **6**(Al_2Br_6), and **7**(Al_2Br_6) have been found to react with



methylisocyanate, and the only Dewar pyridones formed

Scheme I



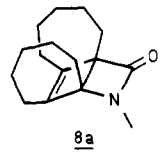
are **8–10**, respectively. The formation of these products was determined by ^1H NMR spectroscopic measurements, which show, in addition to absorptions due to unidentified material, only the absorptions of the Dewar pyridones mentioned. A ^{13}C NMR spectrum of crude Dewar pyridone **8** also shows that it is the sole Dewar pyridone formed in the reaction.

The preparation of Dewar pyridones via the procedure described above provides a new route for the synthesis of β-lactams.[6a] The continued search for novel routes to these lactams underlines the importance of this structural unit.[6b]

Structure Assignment of Dewar Pyridones 2–4 and 8–10. The cyclic Dewar pyridone structures of **2** and **9** are confirmed by comparison with published ^1H NMR and IR data for these compounds. Further evidence for the bicyclic structure of Dewar pyridones **2–4** and **8–10** is obtained from the ^{13}C NMR chemical shift values of the skeleton carbon atoms of the cyclobutene moiety. The bridgehead carbon atoms absorb in the range 58–70 ppm and the alkene carbon atoms in the region 130–152 ppm. In comparison, the alkene carbon atoms of 2-pyridones are observed as far upfield as 108 ppm (see Experimental Section). In the case of Dewar pyridones **9** and **10** a $^1J_{^{13}C,^1H}$ coupling of 170 Hz in the proton-coupled ^{13}C NMR spectrum indicates the presence of an olefinic hydrogen atom. Determination of the position of the olefinic proton of Dewar pyridone **10** is based on the ^1H NMR chemical shift value of the hydrogen atom in the corresponding 2-pyridone **11**, which was obtained from **10** by thermal ring opening (Scheme I) in 92% yield. By comparison of mono- and dimethyl-substituted *N*-methyl-2-pyridones, it has been shown that ^1H NMR chemical shift values of hydrogens in the 4- and 5-positions are 7.2 ± 0.1 and 6.05 ± 0.15 ppm, respectively.[7] The value of 5.90 ppm found for compound **11** is in reasonable agreement with a hydrogen in the 5-position. Similarly, evidence for the structure of Dewar pyridone **9** has been obtained from the ^1H NMR chemical shift value of 6.01 ppm for the hydrogen atom in the 5-position in 2-pyridone **12**, which was formed by thermal isomerization of **9** in almost quantitative yield. On the basis of common spectroscopic methods it is difficult to differentiate between Dewar pyridones **8** and **8a**. This question has therefore been resolved by an X-ray structural analysis performed by Van Bolhuis[8] (Figure 1), which shows that structure **8** is the correct one.

Mechanism of the Reaction of Aluminum Halide σ Complexes of Cyclobutadienes with Isocyanates. In the previous section the formation of Dewar pyridones **2–4**

(3) Hong, P.; Yamazaki, H. *Synthesis* **1977**, 50.
(4) Hong, P.; Yamazaki, H. *Tetrahedron Lett.* **1977**, 1333.
(5) The aluminum halide in parentheses indicates the Lewis acid which is attached to the cyclobutadiene moiety.
(6) For a review, see: Isaacs, N. S. *Chem. Soc. Rev.* **1976**, *5*, 181. (b) Elks, J., Ed. "Recent Advances in the Chemistry of β-Lactam Antibiotics"; The chemical Society: London, 1977.
(7) Elvidge, J. A.; Jackman, L. M. *J. Chem. Soc.* **1961**, 860.
(8) Van Bolhuis, F. Department of Chemical Physics, University of Groningen, The Netherlands.



8a

and 8–10 was described, the most notable fact being the exclusive formation of 8–10.

When Me_2SO is added to a solution of complex 1($AlCl_3$) and methyl isocyanate at −50 °C, at which temperature the latter two compounds do not react, formation of the dimer of tetramethylcyclobutadiene, **13**, is observed (Scheme II). This result indicates that at −50 °C tetramethylcyclobutadiene does not react with methyl isocyanate. It is therefore more likely that the reaction leading to a Dewar pyridone involves a direct attack of complex 1($AlCl_3$) on the isocyanate. From the structure of Dewar pyridone **10** it is concluded that the reaction proceeds via a nucleophilic attack of the isocyanate nitrogen atom at the 2(4)-carbon atom of the allylic cation, followed by a cyclization at the 3-position (Scheme III).

This mechanism does not yet explain the exclusive formation of Dewar pyridone 8 from complex 5($AlCl_3$) and methyl isocyanate. Inspection of a Dreiding model (Figure 2) of complex 5($AlCl_3$) [the cyclobutenyl ring structure being based on the X-ray structure of complex 1($AlCl_3$)[9]] indicates no steric preference for attack at C-2 (which leads to 8) or at C-4 (which would lead to **8a**). An alternative explanation for the exclusive formation of 8 might be a difference in positive charge values between C-2 and C-4. However, in the ^{13}C NMR spectrum of complex 5($AlCl_3$)[10] the cyclobutenyl ring carbon atoms of the allylic cation absorb at 167.3, 169.7, and 171.0 ppm, suggesting no great differences in positive charge values. A third alternative may be that there is no selectivity in the isocyanate addition to the C-2 or C-4 carbon atom and that both 8 and **8a** are formed; the exclusive formation of 8 might then be due to a rapid rearrangement, induced by aluminum trichloride, of **8a** to 8 via 14 (Scheme IV). This would mean that 8 is thermodynamically more stable than **8a**, which is in agreement with the fact that endocyclic bonds are found to be slightly more stable than exocyclic double bonds.[11] Compound **8a** contains two cycloheptane rings, having an exocyclic double bond, and 8 contains a cycloheptene ring and a cycloheptane ring, the latter therefore being thermodynamically favored.

The intermediacy of the dipolar structure **14** in a conversion of **8a** to 8 is not unlikely; comparable dipolar structures are thought to be intermediates in cycloaddition reactions of isocyanates,[12] and recently a similar intermediate was proposed for the thermal isomerization of 5-alkoxy-3-oxo-2-azabicyclo[2.2.0]hex-5-enes to 6-alkoxy-2-pyridones[13] (Scheme V).

Thermal and Acid-Promoted Isomerizations of Dewar Pyridones 2 and 8. The thermal behavior of Dewar pyridones, already investigated by Fürrer,[2c] leads to ring opening, affording 2-pyridone derivatives. As shown above, this thermal ring opening has been employed to assign the structures of Dewar pyridones **9** and **10**. The isomerization has also been studied under acidic condi-

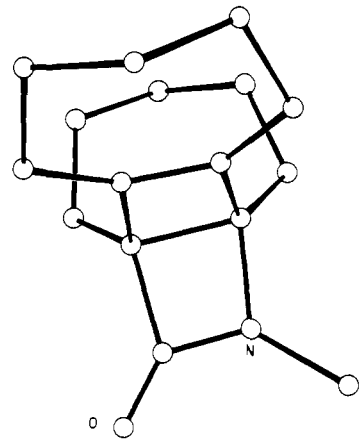


Figure 1. Representation of the spatial structure of Dewar pyridone 8.

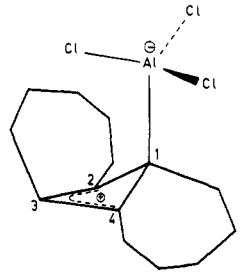
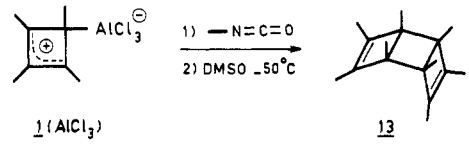
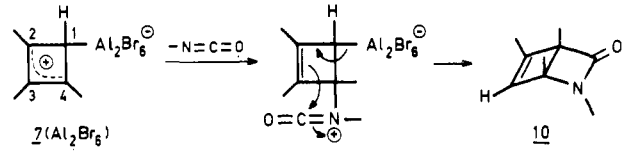


Figure 2. Representation of the spatial structure of complex 5($AlCl_3$).

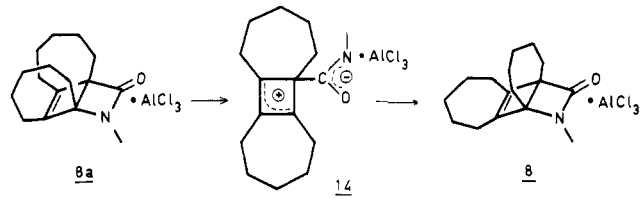
Scheme II



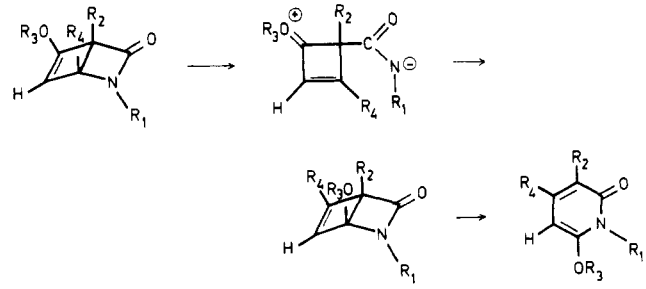
Scheme III



Scheme IV

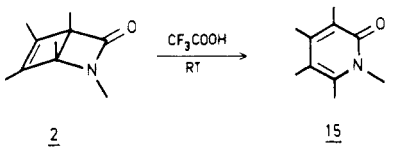


Scheme V

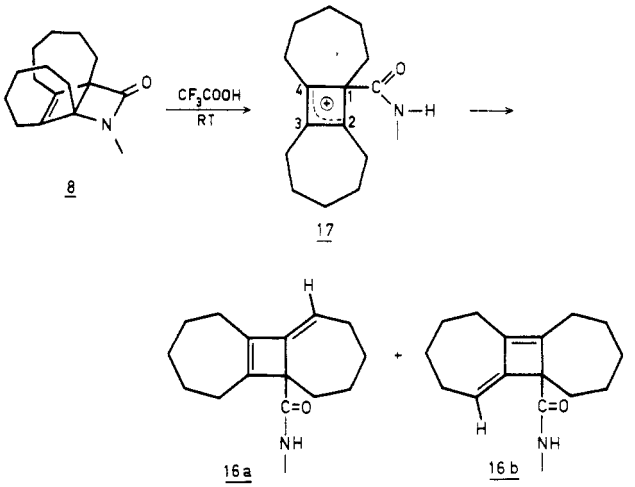


(9) Krüger, C.; Roberts, P. J.; Tsay, Y. H.; Koster, J. B. *J. Organomet. Chem.* **1974**, *78*, 69.
(10) Driessen, P. B. J.; Hogeveen, H. *J. Am. Chem. Soc.* **1978**, *100*, 1193.
(11) Labbauf, A.; Rossini, F. D. *J. Phys. Chem.* **1961**, *65*, 476.
(12) Richter, R.; Ulrich, H. In "The Chemistry of Cyanates and Their Thio Derivatives"; Patai, S., Ed.; Wiley: New York, 1977; Chapter 17.
(13) Kaneko, C.; Shiba, K.; Fujii, H.; Momose, Y. *J. Chem. Soc., Chem. Commun.* **1980**, 1177.

Scheme VI



Scheme VII



tions. When Dewar pyridone **2** is allowed to react with 2 equiv of trifluoroacetic acid, 2-pyridone **15** is isolated in 88% yield (Scheme VI). When Dewar pyridone **8** is subjected to treatment with 2 equiv of trifluoroacetic acid, however, the cyclobutene ring remains intact, and, as shown by the ^{13}C NMR spectrum of the isolated material, a mixture of cyclobutene derivatives **16a** and **16b** is obtained in quantitative yield (Scheme VII). A ring opening of the cyclobutene analogous to that of **2** would have led to a 2-pyridone which was 3,6-bridged by a pentamethylene chain, and this, for reasons of strain, is unlikely to be formed. The reaction probably involves a ring opening of a protonated β-lactam ring to a cyclobutenyl cation **17**, from which elimination of a proton from the methylene adjacent to C-2 or C-4 leads to **16b** or **16a**, respectively.

Experimental Section

General Remarks. Melting points (uncorrected) were determined on a Reichert apparatus by the Kofler method. Elemental analysis were performed in the Analytical Section of our department. Mass spectra were obtained on a AEI MS-902 mass spectrometer. IR spectra were obtained on a Perkin-Elmer 177 spectrometer. ^1H NMR spectra were recorded on a JEOL C 60-HL spectrometer equipped with a variable-temperature probe or on a Varian A-60 spectrometer. Unless stated otherwise, the ^1H NMR spectra were recorded on solutions in $CDCl_3$, and chemical shifts are given in parts per million downfield from tetramethylsilane (δ 0.00). ^{13}C NMR spectra were recorded by using a Varian XL-100 spectrometer with a variable-temperature probe and operating at 25.16 MHz, with the aid of Fourier transform, and were proton-noise decoupled. Proton-coupled ^{13}C NMR spectra were recorded in the gyrogate mode. Chemical shifts were measured relative to $CDCl_3$ and converted to δ_{Me_4Si} values by using δ_{CDCl_3} = 76.9 ppm. Splitting patterns are designated as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad. The solvents were distilled before use and stored over 3-4-Å molecular sieves. All reagents were commercially available and were used as such with the exception of $AlCl_3$ (Merck) which was sublimed before use.

The aluminum halide σ complexes of cyclobutadienes were prepared by previously published methods.[10,14] Reactions were carried out under a dry nitrogen atmosphere.

Preparation of 1,2,4,5,6-Pentamethyl-3-oxo-2-azabicyclo[2.2.0]hex-5-ene (2). A solution of 694 mg of methyl isocyanate (12 mmol) in 3 mL of CH_2Cl_2 was added dropwise to a magnetically stirred solution of complex **1**($AlCl_3$), prepared from 1.08 g of 2-butyne (10 mmol) and 1.47 g of $AlCl_3$ (11 mmol).[10] After 15 min complex **1**($AlCl_3$) had disappeared (according to the ^1H NMR spectrum), and the solution was poured into 200 mL of an aqueous 1 N NaOH solution under vigorous mechanical stirring. The water layer was extracted two times with CH_2Cl_2, and the combined organic layers were dried over K_2CO_3. After evaporation of the solvent, the residue was sublimed at 80–90 °C (15 mmHg), affording 1.41 g (85% yield) of ^1H NMR pure **2**, mp 45–46 °C. The ^1H NMR and IR spectral data were the same as those reported in the literature:[2c] ^1H NMR 1.21 (s, 3 H), 1.31 (s, 3 H), 1.66 (s, 6 H), 2.70 (s, 3 H); ^{13}C NMR 6.4, 9.0, 9.3, 9.4 (4 q, J = 130 Hz), 25.3 (q, J = 140 Hz), 63.0 (s), 63.7 (s), 140.1 (s), 141.4 (s), 172.9 (s); IR (Nujol) 1750 cm^{-1} (amide C=O); mass spectrum, molecular ion peak at m/e 165.

Preparation of 1,4,5,6-Tetramethyl-2-phenyl-3-oxo-2-azabicyclo[2.2.0]hex-5-ene (3). A solution of complex **1**($AlCl_3$), prepared from 1.08 g of 2-butyne (10 mmol) and 1.47 g of $AlCl_3$ (11 mmol),[10] and 1.42 g of phenyl isocyanate (12 mmol) in 12 mL of CH_2Cl_2 was stirred overnight. After a workup analogous to the procedure used for compound **2**, the crude residue was distilled in a Kugelrohr apparatus at 170 °C (0.03 mmHg), giving 1.03 g (46% yield of a slightly yellow solid. Analytically pure material was obtained by recrystallization from n-hexane: mp 147–148 °C (sublimes at 120 °C); ^1H NMR (CCl_4) 1.29 (s, 3 H), 1.56 (s, 3 H), 1.63–1.88 (m, 6 H), 6.63–7.43 (m, 5 H); ^{13}C NMR 7.3, 10.1, 10.8, 11.4 (4 q, J = 125 Hz), 63.8 (s), 64.0 (s), 116.1, 122.7, 128.6 (3 d, J = 160 Hz), 138.5 (s), 142.2 (s), 142.4 (s), 180.0 (s); IR (Nujol) 1725 cm^{-1} (amide C=O); mass spectrum, molecular ion peak at m/e 227. Anal. Calcd for $C_{15}H_{17}NO$: C 79.26; H, 7.54; N, 6.16. Found: C, 79.1; H, 7.6; N, 6.1.

Preparation of 1,4,5,6-Tetramethyl-2-cyclohexyl-3-oxo-2-azabicyclo[2.2.0]hex-5-ene (4). Compound **4** was prepared analogously to compound **2** by using 1.08 g of 2-butyne (10 mmol), 1.47 g of $AlCl_3$ (11 mmol), and 50 mL of CH_2Cl_2 for the synthesis of complex **1**($AlCl_3$),[10] and 1.50 g of cyclohexyl isocyanate (12 mmol). After the workup, analogous to the procedure used for compound **2**, the residue was sublimed at 100 °C (0.05 mmHg) by using a solid carbon dioxide cooled cold finger. In this way 1.57 g (57% yield) of **4** was isolated (^1H and ^{13}C NMR pure). Recrystallization from n-pentane (2×) at −50 °C gave an analytically pure sample: mp 42–44.5 °C; ^1H NMR 1.21 (s, 3 H), 1.35 (s, 3 H), 1.66 (s, 6 H), 0.78–2.15 (br, 10 H), 3.00–3.63 (br, 1 H); ^{13}C NMR 7.3, 10.0, 10.3, 12.8 (4 q, J = 125 Hz), 25.1, 31.7, 32.2 (3 t, J = 130 Hz), 51.6 (d, J = 135 Hz), 63.2 (s), 63.7 (s), 141.3 (s), 141.9 (s), 172.8 (s); IR (Nujol) 1730 cm^{-1} (amide C=O); mass spectrum, molecular ion peak at m/e 233. Anal. Calcd for $C_{15}H_{23}NO$: C, 77.21; H, 9.93; N, 6.00. Found: C, 76.9; H, 9.9; N, 6.0.

Preparation of 1,4-Pentamethylene-5,6-pentamethylene-2-methyl-3-oxo-2-azabicyclo[2.2.0]hex-5-ene (8). Compound **8** was prepared by stirring a solution of complex **5**($AlCl_3$), prepared from 1.88 g of 1,8-cyclotetradecadiyne (10 mmol) and 1.47 g of $AlCl_3$ (11 mmol),[10] and 684 mg of methyl isocyanate (12 mmol) in 28 mL of CH_2Cl_2 for 4 h. After the workup, as described for the synthesis of compound **2**, the residual oil (which slowly solidifies) contained only one compound according to the ^1H and ^{13}C NMR spectra. The oil was sublimed at 120 °C (0.08 mmHg), affording 1.51 g (62% yield) of **8** (^1H and ^{13}C NMR pure). Recrystallization from n-pentane at −50 °C gave an analytically pure sample: mp 87–90 °C; ^1H NMR 1.00–2.38 (br m, 20 H), 2.75 (s, 3H); ^{13}C NMR 24.9, 25.7, 26.4 (3 t[15]), 26.6 (q, J = 135 Hz), 27.1, 27.7, 27.8, 28.4, 28.8, 29.0, 32.5 (7 t[15]), 69.6 (s), 69.4 (s), 146.0 (s), 147.2 (s), 174.2 (s); IR (Nujol) 1725 cm^{-1} (amide C=O); mass spectrum, molecular ion peak at m/e 245. Anal. Calcd for $C_{16}H_{23}NO$: C, 78.32; H, 9.45; N, 5.71. Found: C, 78.4; H, 9.7; N, 5.6.

Preparation of 1,2,5-Trimethyl-3-oxo-2-azabicyclo[2.2.0]-hex-5-ene (9). To a solution of complex **6**(Al_2Br_6), prepared from

(14) Hogeveen, H.; Kingma, R. F.; Kok, D. M. *J. Org. Chem.*, preceding paper in this issue.

(15) In these cases $^1J_{^{13}C,^1H}$ values could not be determined, because, due to long-range couplings, several absorptions coincide.

0.80 g of propyne (20 mmol) and 5.4 g of $AlBr_3$ (20 mmol), in 50 mL of CH_2Cl_2[14] was added dropwise a solution of 1.43 g of methyl isocyanate (25 mmol) in 5 mL of CH_2Cl_2 at −80 °C. After the reaction mixture was warmed to 0 °C, the workup was carried out in a manner analogous to the procedure used for compound **2**. The residual oil of compound **9** was distilled at 20 °C (0.07 mmHg; −80 °C trap), affording 0.94 g (69% yield) of **9** (^1H NMR pure). The ^1H NMR spectrum of the oil before distillation gave no evidence for the presence of isomers of **9**: ^1H NMR (recorded on a Varian XL-100 spectrometer) 1.49 (s, 3 H), 1.87 (m, 3 H), 2.68 (s, 3 H), 3.71 (br s, 1 H), 6.20 (m, 1 H); ^{13}C NMR 13.4, 14.3 (2 q, J = 130 Hz), 26.3 (q, J = 140 Hz), 58.1 (s), 62.0 (d, J = 160 Hz), 133.5 (d, J = 175 Hz), 146.4 (s), 168.1 (s); IR (neat) 1730 cm^{-1} (amide C=O); mass spectrum, molecular ion peak at m/e 137. The ^1H NMR and IR spectral data were consistent with literature data for this compound.[2c]

Preparation of 1,2,4,5-Tetramethyl-3-oxo-2-azabicyclo[2.2.0]hex-5-ene (10). The synthesis of compound **10** was carried out analogously to that of compound **9**. Complex **7**(Al_2Br_6) was prepared from 0.54 g of 2-butyne (10 mmol), 0.40 g of propyne (10 mmol), and 5.4 g of $AlBr_3$ (20 mmol) in 50 mL of CH_2Cl_2;[14] 1.43 g of methyl isocyanate (25 mmol) was added. The residual oil, obtained after a workup analogous to the procedure used for compound **2**, was distilled at 22–24 °C (0.05 mmHg; −80 °C trap), affording 1.29 g (85% yield) of **10** (^1H NMR pure). The ^1H NMR spectrum of the oil before distillation showed no isomer of **10**: ^1H NMR 1.33 (s, 3 H), 1.40 (s, 3 H), 1.83 (d, J = 2.8 Hz, 3 H), 2.72 (s, 3 H), 6.25 (q, J = 2.8 Hz, 1 H); ^{13}C NMR 7.4 (q, J = 125 Hz), 11.9 (q, J = 130 Hz), 13.0 (q, J = 125 Hz), 27.1 (q, J = 140 Hz), 62.6 (s), 66.5 (s), 132.7 (d, J = 170 Hz), 151.4 (s), 173.1 (s); IR (neat) 1740 cm^{-1} (amide C=O); mass spectrum, molecular ion peak at m/e 151.

Thermal Isomerization of Compound 10 to 1,3,4,6-Tetramethyl-2-oxo-1-azacyclohexa-3,5-diene (11). A solution of 755 mg of compound **10** in 50 mL of benzene was refluxed for 1.5 h, after which compound **10** had isomerized to compound **11** (according to ^1H NMR). Benzene was removed by evaporation, and recrystallization of the solid residue from methylcyclohexane at −50 °C afforded 693 mg (92% yield) of analytically pure **11**: mp 124–125 °C (sublimes); ^1H NMR 2.08 (s, 6 H), 2.28 (s, 3 H), 2.97 (s, 3 H), 5.90 (s, 1 H); ^{13}C NMR 11.4, 18.2, 19.1 (3 q, J = 130 Hz), 29.8 (q, J = 140 Hz), 108.0 (d, J = 160 Hz), 120.7 (s), 140.2 (s), 143.6 (s), 162.2 (s); IR (Nujol) 1645 cm^{-1} (amide C=O); mass spectrum, molecular ion peak at m/e 151. Anal. Calcd for $C_9H_{13}NO$: C, 71.49; H, 8.67; N, 9.26. Found: C, 71.5; H, 8.7; N, 9.3.

Thermal Isomerization of Compound 9 to 1,4,6-Trimethyl-2-oxo-1-azacyclohexa-3,5-diene (12). A solution of 137 mg of compound **9** (1 mmol) in 10 mL of chlorobenzene was refluxed for 2.5 h. The ^1H NMR spectrum of the solution showed that compound **9** was converted into compound **12**. Evaporation of chlorobenzene left 136 mg of **12**: ^1H NMR 2.12 (s, 3 H), 2.35 (s, 3 H), 3.53 (s, 3 H), 5.89 (br s, 1 H), 6.24 (br s, 1 H). These ^1H NMR chemical shifts were in accord with the literature data for this compound.[7]

Attempted Methyl Isocyanate Addition to Complex 1($AlCl_3$) in the Presence of Me_2SO. A solution of 0.34 g of methyl isocyanate (6 mmol) in 1 mL of CH_2Cl_2 was added to a solution of complex **1**($AlCl_3$), prepared from 0.54 g of 2-butyne (10 mmol) and 0.67 g of $AlCl_3$ (10 mmol), in 10 mL of CH_2Cl_2 at −60 °C. After the mixture was warmed to −50 °C, 3.0 g of Me_2SO in 1 mL of CH_2Cl_2 was added dropwise. Thereafter the reaction mixture was poured into 100 mL of an aqueous 1 N NaOH solution under vigorous stirring. Further workup was carried out analogously to the procedure used for Dewar pyridone **2**, which afforded 0.5 g of a residue containing no Dewar pyridone **2** according to the ^1H NMR spectrum. The residue consisted largely of the dimer of tetramethylcyclobutadiene, **13**.

Preparation of 1,3,4,5,6-Pentamethyl-2-oxo-1-azacyclohexa-3,5-diene (15) from Compound 2. A solution of 684 mg of CF_3COOH (6 mmol) in 2 mL of CH_2Cl_2 was added to a magnetically stirred solution of 495 mg of **2** (3 mmol) in 8 mL of CH_2Cl_2. After 1.5 h Dewar pyridone **2** had disappeared according to a ^1H NMR spectrum of the solution. The reaction mixture was poured into an aqueous 1 N NaOH solution under vigorous stirring, and the alkaline layer was extracted with CH_2Cl_2 (3 × 50 mL). After drying the solution over K_2CO_3 the solvent was evaporated, and the solid white residue was sublimed at 100 °C (0.01 mmHg), giving 436 mg (88% yield) of 2-pyridone **15**: ^1H NMR 1.95 (s, 3 H), 2.03 (s, 6 H), 2.20 (s, 3 H), 3.44 (s, 3 H); mass spectrum, molecular ion peak at m/e 165. The ^1H NMR spectrum is in agreement with the literature data.[16]

Preparation of 1-[(Methylamino)carbonyl]tricyclo[7.5.0.0^{2,8}]tetradeca-$\Delta^{2,8}$,9-diene (16a) and 1-[(Methylamino)carbonyl]tricyclo[7.5.0.0^{2,8}]tetradeca-2,8-diene (16b) from Compound 8. A solution of 456 mg of CF_3COOH (4 mmol) in 2 mL of CH_2Cl_2 was added at room temperature to a magnetically stirred solution of 490 mg of Dewar pyridone **8** (2 mmol) in 5 mL of CH_2Cl_2. After 10 min **8** had disappeared (^1H NMR spectrum). A workup as for 2-pyridone **15** afforded 0.49 g (quantitative yield) of a mixture of **16a** and **16b** as a colorless oil: ^1H NMR 0.75–2.63 (br, 18 H), 2.75 (d, J = 5.3 Hz,[17] 3 H), 4.83–5.41 (m, 1 H), 5.63–6.30 (br, 1 H); ^{13}C NMR 25.1, 25.4, 25.7, 25.8, 26.4, 26.6, 27.3, 27.9, 28.1, 29.2, 30.6, 32.3, 33.3 (13 t[15]), 60.9 (s), 61.1 (s), 108.6 (d, J = 160 Hz), 143.2 (s), 143.6 (s), 145.0 (s), 145.9 (s), 148.2 (s), 153.5 (s), 173.0 (s), 174.0 (s); IR (neat) 3350 cm^{-1} (NH), 1640 cm^{-1} (C=O); mass spectrum, molecular ion peak at m/e 245; exact mass calcd for $C_{16}H_{23}NO$ m/e 245.178, found m/e 245.178. The presence of two isomers was concluded from the observation of two amide carbon atoms, seven alkene carbon atoms, and two cyclobutene sp^3 carbon atoms in the ^{13}C NMR spectrum.

Registry No. **1** ($AlCl_3$), 31886-99-4; **2**, 38052-13-0; **3**, 80206-52-6; **4**, 80206-53-7; **5** ($AlCl_3$), 66035-33-4; (Al_2Br_6), 80206-70-8; **7** (Al_2Br_6), 80206-71-9; **8**, 80206-54-8; **9**, 38052-12-9; **10**, 80206-55-9; **11**, 80206-56-0; **12**, 15031-89-7; **13**, 1448-74-4; **15**, 57147-44-1; **16a**, 80227-61-8; **16b**, 80206-57-1; methyl isocyanate, 624-83-9; phenyl isocyanate, 103-71-9; cyclohexyl isocyanate, 3173-53-3.

(16) Hart, H.; Dickinson, D. A.; Li, W. Y. *Tetrahedron Lett.* **1975**, 2253.

(17) By irradiation of the signal of the hydrogen atom attached to the nitrogen atom at 6.0 ppm (performed on a Varian XL-100 spectrometer), it was established that the presence of two absorptions was due to a coupling.