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Chromous Chloride Promoted Cyclization of Olefinic *N*-Chloro Amides. Synthesis of Nitrogen Heterocycles[1]

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The chromous chloride promoted cyclization of a variety of olefinic *N*-chloro-*N*-methyl carboxamides was compared to the cyclization of the analogous *N*-chloro-*N*-alkenylacetamides. In all cases but one, the yields were higher with the former than with the latter. The high yield of cyclization (95%) of *N*-chloro-*N*-methylcycloheptenecarboxamide (**13b**) is noteworthy since a six-membered ring is formed and contrasts with the failure of the analogous *N*-chloro-*N*-cycloheptenylacetamide (**16b**) to cyclize. A number of nitrogen heterocycles were synthesized in good to excellent yields, including the azahomoadamantanone derivative **28** and the azaadamantane derivatives **30** and **31**. An attempt to prepare an azatwistanone derivative from *N*-chloro carboxamide **26b** failed. Comparison with photochemical and peroxide cyclizations of a few *N*-chloro amides showed that better yields were usually obtained with the chromous chloride method. The reaction mechanism is discussed from the following points of view: comparison of reactivity of the *N*-chloro carboxamides and *N*-chloro acetamides; comparison of the relative reactivity of amido radicals (complexed or not) in intramolecular addition to double bonds and intramolecular allylic hydrogen abstraction; stereochemistry; nature of the transfer step of the radical chain reaction.

Introduction

The chromous chloride promoted intermolecular addition of *N*-halo amides (ZCONHX) to a variety of olefins has been shown to proceed in good to excellent yields,[2] whereas *N*-alkyl-*N*-halo amides (ZCONRX) failed to add under the same conditions.[2a] This failure could be due to the fact that chromium(II) reduction of an *N*-alkylamido radical would be faster than its addition to the olefin as already suggested.[2b] However, intramolecular addition of *N*-alkylamido radicals would be expected to compete favorably with their chromium(II) reduction (an intermolecular process). Indeed, as we will see, the chromous chloride promoted cyclization of olefinic *N*-chloro amides does occur in good to excellent yields.

In the preceding paper,[3] we have compared the intramolecular behavior of *N*-chloro amides toward double bonds under photochemically and peroxide-initiated decomposition. Due to the special design of the models used, it was possible to gain information on the electronic structure of *N*-alkylamido radicals. Because of the possible complexation of these radicals with chromium ions,[2b] their electronic structure will not be considered in this paper.

In the present paper, we are going to (i) evaluate the scope and limitations of the chromous chloride method for the synthesis of nitrogen heterocycles, comparing the cyclization of olefinic *N*-chloro carboxamides A and *N*-chloro acetamides B; (ii) see whether the cyclization would occur when a six-membered transition state is involved; (iii) examine the competition between intramolecular abstraction of allylic hydrogens by the amido radical, and its intramolecular addition to double bonds; and (iv) study the stereochemistry of the cyclization reaction.

A B

As will be seen, most of the questions raised could be answered in a satisfactory manner and an efficient process for the synthesis of functionalized nitrogen heterocycles was devised. This method constitutes a useful complement to the synthesis of azabicyclic and polycyclic molecules efficiently

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achieved by intramolecular reactions of olefinic N-chloramines.[4,5]

Results

Preparation of N-Chloro Amides. The N-chlorination of olefinic amides is more difficult than that of the corresponding amines because amides are less reactive than amines toward the various chlorinating agents generally used. Two methods gave satisfactory results: room temperature treatment of the amide by sodium hypochlorite, and treatment of the lithium amide salt by N-chlorosuccinimide in ether, a method developed by Kuehne and Horne.[6] The yields as well as the purity of the N-chloro amides are recorded in Table I. The N-chlorination of the olefinic N-methyl carboxamides by the first method was usually faster than that of the corresponding N-alkenyl acetamides. It was necessary to follow the reaction by ^{1}H NMR spectroscopy or by TLC, since partial hydrolysis of the amide to the carboxylic acid occurred, particularly in the case of the N-methyl carboxamides.[7] Buffering the chlorinating solution at pH 12.5 was expected to reduce the amide hydrolysis. This occurred efficiently in the case of the preparation of **1b**, but presented no real advantage over the standard method for the preparation of N-chloro carboxamides **7b** and **17b**. The crude N-chloro amides prepared by the sodium hypochlorite method were used without further purification, the unreacted amide being essentially the sole other product present according to the ^{1}H NMR spectra. The second method proved to be efficient to prepare **26b**, **27b**, and **29b** where the sodium hypochlorite method, with or without buffer, and other methods[8] have failed. In the case of **27b**, these methods gave the chloro lactone **32** (54% yield with sodium hypochlorite). This product is most likely to be formed by the hydrolysis of the N-chloro amide and electrophilic chlorination of the double bond, followed by trapping of the intermediate cation by the carboxylate anion. The source of positive halogen is not clear, but it might be the N,N-dichloromethylamine formed by hydrolysis of the amide[7] or eventually the acylhypochlorite.

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Cyclization of Olefinic N-Chloro Amides. The results of the chromous chloride promoted cyclization of various olefinic N-chloro amides are summarized in Table I.[10] The reactions were carried out as described for the intermolecular additions[2a] at −78 °C (cooling bath temperature) in a chloroform/methanol mixture, adding the chromous chloride slowly and monitoring the reaction by an iodometric test. The various examples studied illustrate the synthetic potential of the method, as the yields of cyclization vary from good to excellent (except for the N-chloro amides **16b** and **26b**, which did not cyclize).

Inspection of Table I leads to the following general comments. It is noteworthy that the cyclization of the olefinic N-chloro-N-methyl carboxamides is generally more efficient than the cyclization of the analogous N-chloro-N-alkenyl acetamides. The material balance (cyclized products plus recovered parent amide) is very good (>90% in most cases) as in the peroxide-initiated cyclizations[3] and thus generally much better than in the photochemical cyclizations.[3,12] The chromous chloride method appears to be the most efficient except in the case of N-chloro carboxamide **7b**, where the three methods gave similar yields, and of N-chloro acetamide **16b** where the chromous chloride and benzoyl peroxide methods failed (the photochemical cyclization of **16b** was not studied).

The cyclization of N-chloro amides **1b** and **4b** led to a relatively large proportion of the nonchlorinated products **3** and **6** (1,H cyclic adducts), respectively, whereas no such product was isolated in the case of the other N-chloro amides.

The N-chloro amides **13b** and **16b** were chosen to test the hydrogen abstraction ability of the amido radical vs. its addition to double bonds in intramolecular reactions. As already pointed out in the preceding paper,[3] the cyclization was expected to be more difficult than that of N-chloro amides **7b** and **10b** (formation of a six-membered ring, boat-like conformation of the cycloheptene ring in the transition state), whereas the intramolecular allylic hydrogen abstraction process should involve the normally preferred 1,5 transfer.[13] Surprisingly, cyclization of **13b** was very efficient (95%). In contrast, **16b** gave only the parent amide **16a** as in the case of the peroxide-initiated reaction.[3]

The N-chloro amides **17b**, **19b**, **21b**, and **24b** were studied to see if their behavior would parallel that of the corresponding N-chloramines.[4d,e] As in the case of N-chloramines, the cyclization was almost quantitative and the chlorine-atom transfer onto the intermediate adduct radical occured almost exclusively from the less-hindered exo face, leading to the tricyclic products **18**, **20**, **22**, and **25**, respectively. Interestingly, N-chloro amides **7b** and **10b** yielded a mixture of endo and exo epimers in contrast to the corresponding N-chloramine, which has been reported to give exclusively the exo derivative.[5a]

We had hoped to obtain an azatwistanone derivative from N-chloro amide **26b**, but its cyclization failed. The N-chloro amides **27b** and **29b** led, in good yields, respectively, to the azahomoadamantanone derivative **28** and to the azaadamantanes **30** and **31**.

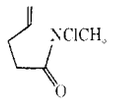
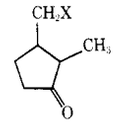
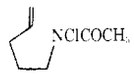
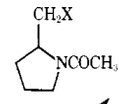
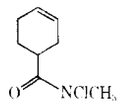
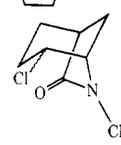
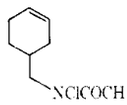
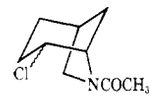
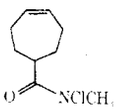
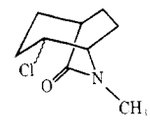
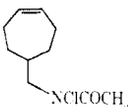
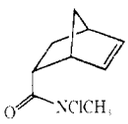
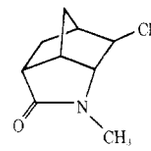
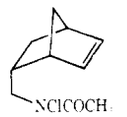
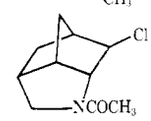
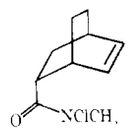
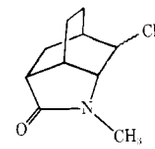
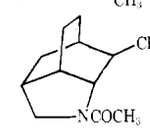
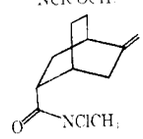
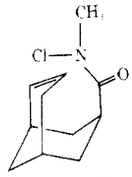
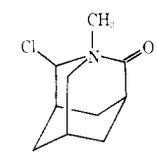
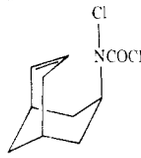
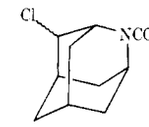
Discussion

The emphasis of this work had initially been placed on the synthetic aspects and the results clearly show the synthetic potential of the chromous chloride promoted cyclization of olefinic N-chloro amides for the synthesis of nitrogen heterocycles. This method turns out to be generally more efficient than the corresponding photocyclization[3,6] or benzoyl peroxide initiated cyclization.[3] It compares well with the cyclization of olefinic and enol ether N-chloramines,[4] although it was not possible to use an enol ether N-chloro amide because of the difficulty in chlorinating the corresponding amides [e.g., N-methyl(4-methoxy-3-cyclohexenyl)carboxamide].

The reactivity of amido radicals and the reaction mechanism of the chromous chloride promoted additions of N-halo amides to olefins have been already discussed.[2] However, the results obtained during the present work allow some further comments.

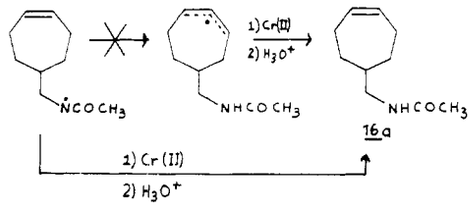
Comparative Reactivity of N-Chloro Acetamides and N-Chloro Carboxamides. The difference in favor of a greater reactivity of N-chloro carboxamides is particularly clear if the behavior of **13b** and **16b** is compared (Table I). This difference cannot be attributed to the greater reactivity of an amido radical toward an allylic hydrogen on the alkyl moiety than toward an allylic hydrogen on the acyl moiety (compare also the cyclization of **7b** and **10b**) as has been shown to be the case for intramolecular abstraction of nonactivated hydrogens by N-alkylamido radicals,[15] since a 1,5-hydrogen transfer is not operating in the case of **16b** (see below). Furthermore, the amido radicals derived from **17b** and **19b** (or **21b** and **24b**) have no hydrogen suitably oriented for the usual 1,5-transfer into the nitrogen,[13] and those derived from **1b** and **4b** have only an unreactive vinylic hydrogen in a 1,5 relationship with respect to the nitrogen, but the same difference in reactivity is still observed. Although electronic factors could be involved, this difference can be explained in terms of steric (torsional and nonbonded) interactions which would be expected to be larger for the cyclization of an N-alkenylace-

Table I. Preparation and Chromous Chloride Promoted Cyclization of Olefinic *N*-Chloro Amides

N-chloro amide	*N*-chloro amide no.	prepa-ration method[a]	reac-tion time, h	yield, %	iodo-metric purity, %	cyclization products: product	no.	yield,[b] %	parent amide: no.	yield,[b] %
	**1b**	NaOCl buff. NaOCl	8 3	23 74	70 84		**2** (X = Cl) **3** (X = H)	44 61	**1a**	0
	**4b**	NaOCl	9.5	90	100		**5** (X = Cl) **6** (X = H)	0 6	**4a**	90
	**7b**	NaOCl buff. NaOCl	18 11	71 76	92 79		**8** (exo) **9** (endo)	28 70	**7a**	0
	**10b**	NaOCl	100	83	96		**11** (exo) **12** (endo)	44 36	**10a**	20
	**13b**	NaOCl	40	82	91		**14** (exo) **15** (endo)	70 25	**13a**	tr
	**16b**	NaOCl	100	90	92			0	**16a**	95
	**17b**	NaOCl buff. NaOCl	34 78	70 64	80 100		**18**	92[c]	**17a**	7
	**19b**	NaOCl	100	85	91		**20**	85[d]	**19a**	20
	**21b**	NaOCl	48	76	89		**22** (exo) **23** (endo)	80 5	**21a**	<2
	**24b**	NaOCl	100	81	91		**25**	80	**24a**	10
	**26b**	*n*-BuLi/NCS		73	100			0	**26a**	70[e]
	**27b**	*n*-BuLi/NCS		54	100		**28** (exo)	74	**27a**	15
	**29b**	*n*-BuLi/NCS		52	100		**30** (exo) **31** (endo)	19 43	**29a**	21

[a] See text. [b] Yields based on the *N*-chloro amide present in the starting product and determined by VPC. [c] This corresponds to a quantitative yield of cyclization considering that the parent amide contained 8–10% of unseparable exo isomer. [d] Another unidentified product containing chlorine (*m/e* 185, 187) was isolated in about 12% yield. [e] The sample of amide **26a** used to prepare **26b** contained about 10% of the isomer with the amido group exo and this 10% was still present in the recovered parent amide (^{1}H NMR spectra); in addition to **26a**, we isolated (preparative VPC and TLC) 32% of the isomer with the double bond endo.

Scheme I



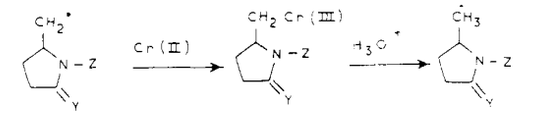
tamido radical than for the cyclization of the analogous olefinic N-methylcarboxamido radical according to the inspection of models. This led us to hypothesize that N-alkylamido radicals would be less reactive toward a double bond on the alkyl moiety than toward a double bond on the acyl moiety. Work is in progress to verify this hypothesis on substrates where an amido radical will have the choice between the two possibilities in an intramolecular process.

Five- or Six-Membered Transition State Leading to Cyclization. It is well known that radical cyclizations usually lead to five-membered rings.[17] Our results essentially confirm this trend. However, we noticed three exceptions with the cyclization of **13b**, **27b**, and **29b**. Cyclization of **29b** through a five-membered transition state would have led to a protoadamantane skeleton known to be more strained than the adamantane skeleton.[18] Cyclization of **27b** could have led either to a six-membered ring or to a seven-membered ring. The seven-membered ring was preferred (e.g., **28**) probably as a result of the greater stability of an homoadamantane derivative relative to a homoprotoadamantane derivative. N-Chloro amide **13b** can only give a six-membered ring. The entropy factor and the absence of strain in the transition state seem in fact to be the most important factors allowing or forbidding the cyclization.

Addition to Double Bond vs. Allylic Hydrogen Abstraction. The efficient cyclization of N-chloro amides **7b**, **10b**, and **13b** shows that the amido radical prefers to add to a double bond rather than to abstract an allylic hydrogen in intramolecular processes, even if the abstraction would involve the prefered 1,5 transfer to the nitrogen,[13] and even when the cyclization occurs through a six-membered transition state and a less favorable conformation of the ring as in the case of **13b**. This behavior cannot be attributed to the complexation of the amido radicals by chromium ions, since it has been observed in the peroxide-induced cyclization of **7b** and **13b**,[3] and in the photochemical cyclization of **7b**;[3,11] it is marked contrast with the assumed preference of N-alkylamido radicals for allylic hydrogen abstraction in intermolecular reactions with olefins.[14c] In the case of N-chloro amide **16b**, the parent amide **16a**, the sole product isolated, could have been formed by allylic hydrogen abstraction followed by chromium(II) reduction of the resulting allylic radical then protonolysis[19] (Scheme I). However, when compound **16b** was submitted to chromous chloride cyclization conditions in totally deuterated medium,[2b] then the workup carried out with D_2O, and the crude product passed over a silica gel column (in order to exchange the amide deuterium and also for purification purposes), the resulting product did not contain any deuterium as shown by mass spectroscopy. Consequently, the parent amide **16a** is most likely to be formed by chromium(II) reduction of the amido radical followed by protonolysis[2b] (Scheme I).

It therefore appears that, in the radical decomposition of olefinic N-chloro amides, the amido radical shows little reactivity in intramolecular abstraction of allylic hydrogens so that its intramolecular addition to the double bond competes mainly with intermolecular processes. In the chromous chloride promoted reactions, the main intermolecular competing process is most probably chromium(II) reduction of the amido

Scheme II



33 (Y = O; Z = CH_3) 3 (Y = O; Z = CH_3)

34 (Y = H, H; Z = $COCH_3$) 6 (Y = H, H; Z = $COCH_3$)

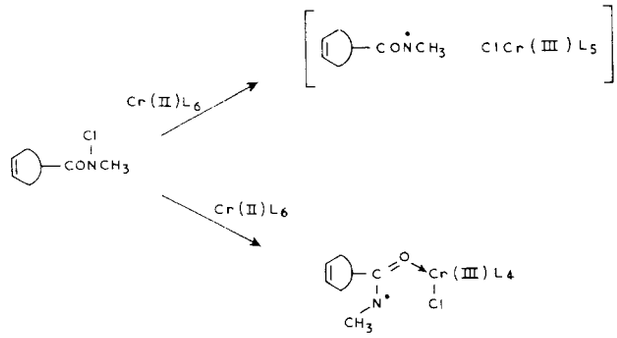
radical leading to the formation of the parent amide. In the peroxide-initiated reactions,[3] it is most likely the abstraction of hydrogen from dioxane by the amido radical, which leads also to the parent amide. In the photochemical cyclizations,[3,12] the most probable intermolecular process is the abstraction of allylic hydrogen by chlorine atoms formed in the initiation step, which leads to chlorinated derivatives and the parent amide according to the Goldfinger mechanism.[20] This then would explain the poorer material balance, cyclized products plus parent amide, obtained with the photochemical method as compared to the other two methods.

1,H-Cyclic Adducts. In intermolecular additions initiated by chromous chloride, nonhalogenated adducts, termed 1,H-adducts, were currently observed.[2a] Deuterium incorporation experiments have shown that their formation results mainly from chromium(II) reduction of an intermediate adduct–radical followed by protonolysis.[2b] By analogy, we propose a similar mechanism (Scheme II) for the formation of the 1,H-cyclic adducts **3** and **6** in the cyclization of **1b** and **4b**, respectively. A primary carbon radical should be reduced more readily than a secondary one. Indeed, no 1,H-cyclic adducts were isolated in the cyclization of the other olefinic N-chloro amides where the intermediate adduct–radical is secondary. A primary carbon radical should also be a more efficient hydrogen abstractor than a secondary one. This accounts for the fact that, whereas no 1,H-cyclic adduct was isolated from the photochemical cyclization of **7b**, **13b**, and **17b**,[3] some 15% of **3** and 9% of **6** was obtained from **1b** and **4b**, respectively.[12]

Stereochemistry. The stereochemistry is strongly dependent on the substrate (Table I). Interestingly, only two N-chloro amides gave predominantly the endo isomer, N-chloro carboxamide **7b** (endo/exo = 2.5) and N-chloro carboxamide **29b** (endo/exo = 2.3). The stereochemistry was found to be also dependent on the method of initiation in the case of N-chloro amides **7b** and **13b**. For **7b**, the endo/exo ratio varies from 2.5 with chromous chloride to 1.3 by irradiation in methylene chloride[3] (0.94 in benzene[11]), and 0.86 with benzoyl peroxide.[3] For **13b**, the following endo/exo ratios were observed: 0.35 with chromous chloride, 0.57 by irradiation in methylene chloride,[3] and 0.39 with benzoyl peroxide.[3] In order to see whether these differences in stereoselectivity could be due, at least in part, to variations of solvent and temperature, we carried out the photochemical cyclization of **7b** under conditions similar to those used for chromous chloride cyclization, and obtained an endo/exo ratio (2.0) close to that observed with chromous chloride (2.5).[21]

Reaction Mechanism. The fact that the chromous chloride method generally gives better yields of cyclization than the benzoyl peroxide method[3] and the photochemical method[3,12] could be due, to some extent, to an association complex between the metal ion and the amido radical. The "complexed radical" could then be more reactive toward a double bond than a "noncomplexed radical". The generation of an amido radical in the presence of chromous chloride is in itself quite different from the same generation in the presence of peroxides or under photochemical conditions. As already suggested for intermolecular additions,[2b] the formation of a monodentate complex, in the initiation step, will liberate an amido radical which could remain associated with the metal ion[23]

Scheme III



(Scheme III); and/or the *N*-chloro amide could also act as a bidentate ligand leading to an amido radical bonded to the chromium ion (Scheme III), a process which would be more favorable than the former because of the entropy factor. Whether or not the geometry of the substrate can accommodate the octahedral structure of chromium(II), a tridentate complex could also be involved as depicted in Scheme IV. This would be the case for *N*-chloro amides **7b** and **29b** according to the inspection of models. The formation of such a complex could result in a larger proportion of endo epimer by allowing an intramolecular ligand (chlorine) transfer as shown in Scheme IV. The *N*-chloro amides **7b** and **29b** are the two *N*-chloro amides that did give predominantly the endo isomer as already pointed out. However, as mentioned above, the photochemical cyclization of **7b** under conditions of solvent and temperature similar to those used for the chromous chloride reactions led to an endo/exo ratio of 2.0 as compared to 2.5 with chromous chloride. We therefore have no conclusive evidence for or against a ligand-transfer mechanism. The same situation was encountered for the intermolecular additions;[2b] a classical chain mechanism was considered more probable than a ligand-transfer mechanism mainly on the basis of the low redox potential of the chromic ion. However, it is likely that both mechanisms are involved.

Conclusion

The present work allowed us to show the synthetic potential of the chromous chloride promoted cyclization of olefinic *N*-chloro amides for the preparation of functionalized nitrogen heterocycles. It also allows us to compare the effectiveness and convenience of three methods of cyclization.

The benzoyl peroxide method appears to be quite effective for the cyclization of olefinic *N*-chloro carboxamides (e.g., **7b**, **13b**, and **17b**).[3] Whenever it works, it could be the method of choice, since it is very simple (technical operation and workup are easy) and amenable to large-scale reactions.

The chromous chloride method is more general, giving good to high yields of cyclization with olefinic *N*-chloro acetamides as well as with olefinic *N*-chloro carboxamides. It is amenable to large-scale work and furthermore, the larger the scale, the higher the yield of cyclization. Indeed, the reduction of the amido radical competes with its intramolecular addition to the double bond. Thus the smaller the relative amount of chromous chloride added at a time (which can be achieved by working on larger scales and adding the chromous chloride solution slowly), the better should be the yield of cyclization (as in the case of intermolecular additions[2a]). For instance, the cyclization of *N*-chloro acetamide **4b** carried out on a 3.5-mmol scale, adding the chromous chloride solution over 45 min led to 6% of **6** (Table I). When the reaction was carried out on a 8-mmol scale, adding the chromous chloride solution over 90 min, a 20% yield of **6** was obtained.

The photochemical method is very simple from the point of view of technical operation and workup. However, it is limited to small-scale reactions and proved generally less effective than the two other methods.[3,12] In addition, it may give a more complex mixture of products due to the competing reactions of the chlorine atoms produced in the initiation step.

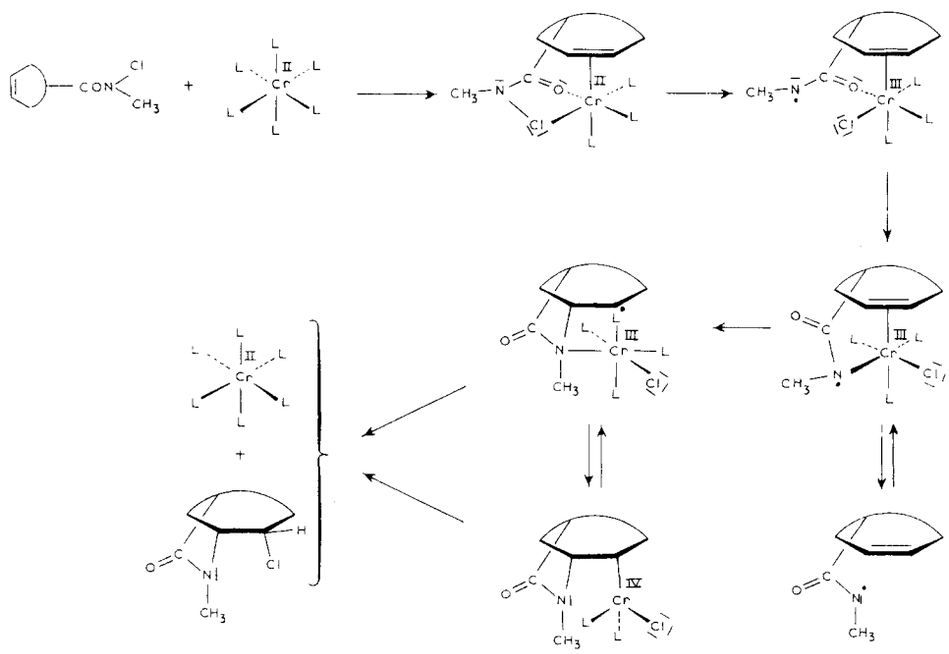
Experimental Section

The pertinent general information has been given in the preceding paper.[3]

Preparation of Olefinic Amides. The preparation of amides **7a**, **10a**, **13a**, **16a**, **17a**, and **19a** has been described in the preceding paper,[3] and that of amide **21a** in ref 4d. Amides **1a** and **4a** have been prepared from 4-pentenoic acid by standard procedures: **1a**,[24] 75% yield; **4a**,[6] 52% yield [after purification by microdistillation at 55–60 °C (1 mm)]. Amide **29a** was prepared according to the method described by Staas and Spurlock:[25] 55% yield; mp 89–92 °C (lit.[25] mp 94–96 °C).

***N*-[(2-Bicyclo[2.2.2]octen-5-yl)methyl]acetamide (24a).** A Diels–Alder reaction between acrolein and cyclohexadiene afforded

Scheme IV



5-formylbicyclo[2.2.2]oct-2-ene.[26] Treatment of this aldehyde by means of hydroxylamine hydrochloride in methanol gave a quantitative yield of oxime. Reduction of this oxime by aluminum hydride afforded the primary amine in 24% yield. Acetamide **24a** was obtained by the usual acetylation procedure in 77% yield: mp 75–77 °C; IR ($CHCl_3$) 3460, 3380, 1670, and 1520 cm^{-1}; NMR ($CDCl_3$) δ 0.8 (m, 1 H), 1.1–2.6 (m, 8 H), 1.98 (s, 3 H), 2.92 (t, 2 H), and 6.2 (m, 3 H).

***N*-Methyl-2-methylene-5-bicyclo[2.2.2]octanecarboxamide (26a).** 5-Carbomethoxybicyclo[2.2.2]octan-2-one was prepared as described by Lee.[27] A Wittig reaction on this ketone (8 g, 44 mmol) in dry benzene (200 mL) using methyltriphenylphosphonium iodide (41.6 g, 103 mmol) and potassium *tert*-butoxide (11.2 g, 0.1 mol) afforded 5-carbomethoxy-2-methylenebicyclo[2.2.2]octane (5.5 g, 70%). Treatment with methylamine (50 mL of a 30% solution in methanol) for 10 days gave, after sublimation of the crude product, the amide **26a** (30% yield): mp 79–85 °C (sealed tube); IR ($CHCl_3$) 3460, 1650, and 1530 cm^{-1}; NMR ($CDCl_3$) δ 1.45–2.8 (m, 11 H), 2.74 (d, 3 H), 4.50 and 4.68 (two m, 2 H), and 7.45 (m, 1 H); mass spectrum *m/e* (rel intensity) 179 (M^+, 14), 24 (18), 86 (100), 79 (26).

Anal. Calcd for $C_{11}H_{17}NO$: C, 73.71; H, 9.56; N, 7.81. Found: C, 73.92; H, 9.51; N, 7.82.

***N*-Methyl-3-bicyclo[3.3.1]non-6-enecarboxamide (27a).** This amide was prepared from 6-bicyclo[3.3.1]non-3-enecarboxylic acid.[28] The preparation of the acid chloride gave a mixture containing 60% of the acid chloride and 37% of 4-chloroadamantan-2-one.[29] Addition of the acid chloride to a dry solution of methylamine in benzene afforded amide **27a** in 60% yield. The crude amide was recrystallized from cyclohexane: mp 74 °C; IR ($CHCl_3$) 3520, 3440, 1675, and 1540 cm^{-1}; NMR ($CDCl_3$) δ 1.5–2.5 (m, 11 H), 2.75 (d, 3 H), and 5.6 (m, 3 H).

Preparation of Olefinic *N*-Chloro Amides. The *N*-chloro amides **26b**, **27b**, and **29b** were prepared from the parent amide by the method described by Kuehne and Horne.[6] The yields are recorded in Table I.

Typical Procedure for the Sodium Hypochlorite Method. *N*-Chloro-*N*-methyl-5-cycloheptenecarboxamide (13b). Amide **13a** (0.775 g, 5 mmol) dissolved in methylene chloride (10 mL) was treated with sodium hypochlorite (12.1 mL of a 0.83 N solution, 10 mmol). Sulfuric acid (1.2 mL of a 1 N solution) was then added. The mixture was stirred vigorously at room temperature in the dark. The reaction was followed by NMR until the complete disappearance of the *N*-methyl doublet at 2.8 ppm. The organic layer was separated and the aqueous solution extracted with methylene chloride (5 × 10 mL). The combined organic phases were dried (Na_2SO_4). Evaporation of the solvent gave **13b** (0.865 g, 91% active chlorine by iodometry, 82% yield): NMR ($CDCl_3$) δ 2.2 (m, 6 H), 3.1 (m, 1 H), 3.4 (s, 3 H), and 5.8 (m, 2 H).

The *N*-chloro amides **4b** to **24b** (Table I) were prepared in the same way on a 5–10-mmol scale with 0.8–1.3 M sodium hypochlorite solutions. Better yields could be obtained by stopping the reaction before the complete disappearance of the starting amide.

2-Chloro-4-oxahomoadamantane-5-one (32). An attempt to N-chlorinate amide **27b** by the above method led to a mixture which after separation on silica gel plates (ether–hexane 1:1) gave the chloro lactone **32** (54%). The analytical sample was obtained after recrystallization from cyclohexane (it sublimed readily and no melting point was recorded): IR ($CHCl_3$) 1740 cm^{-1}; NMR ($CDCl_3$) δ 1.4–2.6 (10 H), 3.09 (m, 1 H), 4.26 (m, 1 H), and 4.46 (m, 1 H); mass spectrum *m/e* (rel intensity) 200 (M^+, 2), 156 (8), 121 (30), 79 (100), and 39 (42); *m/e* calcd for $C_{10}H_{13}ClO_2$ 200.060404, found 200.059763.

Anal. Calcd for $C_{10}H_{13}ClO_2$: C, 59.86; H, 6.53. Found: C, 59.46; H, 6.81.

Typical Procedure for the Buffered Sodium Hypochlorite Method. *N*-Chloro-*N*-methyl-4-pentenecarboxamide (1b). The phosphate buffer (3 M solution) was prepared by adding a saturated potassium hydroxide solution to phosphoric acid until pH 12.5. The amide **1a** (1.50 g, 13 mmol) was dissolved in chloroform (10 mL). The buffer (37 mL) was added, then sodium hypochlorite (37 mL of a 0.71 N solution). The reaction was followed by NMR and was stopped when the integration ratio of the singlet at 3.33 ppm and the doublet at 2.75 ppm reached a maximum. Workup as above gave *N*-chloro amide **1b** (2.04 g, 84% active chlorine, 74% yield). The crude product still contained chloroform and 14% of parent amide **1a** by NMR. It was used without further purification.

Chromous Chloride Promoted Cyclizations. Typical Procedure. Cyclization of *N*-Chloro-*N*-methyl-4-pentenecarboxamide (1b). The reaction was carried out as described for the intermolecular additions,[2a] adding slowly a 1 M methanolic chromous chloride solution (10 mL added over 90 min) to a solution of **1b** (2.17 g, 78% active chlorine, 11.5 mmol) in chloroform (10 mL)–methanol (2 mL) cooled at −78 °C (dry ice–methanol bath) until a negative starch–iodide test. The crude product obtained after the usual workup and methylene chloride extraction was diluted in a 10-mL volumetric flask. An aliquot (2 mL) was separated by preparative TLC (hexane–ether–methanol 10:10:1) to yield three fractions. The less polar fraction consisted of *N*-methyl-5-chloromethyl-2-pyrrolidone (**2**; 0.121 g, 36%), which was purified by microdistillation at 70 °C (0.5 mm): NMR ($CDCl_3$) δ 1.9–2.7 (m, 4 H), 2.79 (s, 3 H), 3.64 (m, 2 H), and 3.80 (m, 1 H); mass spectrum *m/e* 147, 149 (3:1, M^+). The second fraction consisted of *N*-methyl-5-methyl-2-pyrrolidone (**3**; 0.131 g, 50%), which proved identical (IR, ^1H NMR) with an authentic sample (Aldrich). The third fraction consisted of the parent amide **1a** (0.063 g). Continuous extraction of the aqueous phases (from the extraction above) with methylene chloride yielded additional quantities of **1a**, **2**, and **3**. VPC analysis (OS-138) of this fraction and of the crude product obtained above, using authentic samples as standards, gave the following results: **1a**, 22% (amount present in the starting material); **2**, 44%; **3**, 61%.

The same procedure was followed for the cyclization of *N*-chloro amide **4b** (addition of the chromous chloride solution over 45 min). For the other *N*-chloro amides of Table I, it was not necessary to carry out a continuous extraction of the aqueous phases. The yields were determined by VPC using authentic samples as standards. These samples were obtained either by preparative VPC or preparative TLC.

Cyclization of *N*-Chloro-*N*-(4-penten-1-yl)acetamide (4b). The cyclic products **5** and **6** proved identical (IR, ^1H NMR) with samples prepared as follows. (2-Pyrrolidino)methanol was converted to its diacetate (95%) by acetylation under the usual conditions (1 h). Mild hydrolysis (potassium hydroxide, 1 equiv, in aqueous methanol) at room temperature for 3 h afforded *N*-acetyl(2-pyrrolidino)methanol (quantitative). It was treated with triphenylphosphine and chlorine in dry methylene chloride at 25 °C for 3 h. The solution was washed with a saturated solution of sodium bisulfite and dried, and the solvent was evaporated. Most of the triphenylphosphine oxide was removed by crystallization. Short-path distillation at 68°C (0.5 mm) afforded pure **5** in 58% yield: IR ($CHCl_3$) 1645 and 1405 cm^{-1}; NMR ($CDCl_3$) δ 2.00 (m, 4 H), 2.08 (s, 3 H), 3.50 (t, 2 H), 3.76 (m, 2 H), and 4.30 (m, 1 H); *m/e* 161, 163 (3:1, M^+). 5-Methyl-2-pyrrolidone was reduced with $LiAlH_4$ in ether to 2-methylpyrrolidine, which was then acetylated (Ac_2O, aqueous Na_2CO_3) to afford pure *N*-acetyl-2-methylpyrrolidine (**6**) as a liquid (26% yield): IR (CCl_4) 1645 and 1405 cm^{-1}; NMR ($CDCl_3$) δ 1.17 (d, 3 H), 1.5–2.3 (m, 4 H), 2.0 and 2.06 (two s, 3 H), 3.43 (m, 2 H), and 4.06 (br m, 1 H).

Cyclization of *N*-Chloro Amides 7b, 13b, 17b, and 19b. The physical constants and characterization of the corresponding cyclization products have been already described in the preceding paper.[3]

Cyclization of *N*-Chloro-*N*-[(3-cyclohexen-1-yl)methyl]-acetamide (10b). Cyclization of the olefinic *N*-chloro acetamide **10b** afforded a mixture of the two isomers **11** and **12**. The less polar isomer **11** was identified as *exo*-4-chloro-6-acetyl-6-azabicyclo[3.2.1]octane: mp 35 °C; IR ($CHCl_3$) 1630 cm^{-1}; NMR ($CDCl_3$, 250 MHz) δ 1.5–2.1 (m, 5 H), 2.11 and 2.06 (2 s, 3 H), 2.42 (m, 2 H), 3.31 and 3.37 (2 d, 1 H), 3.51 and 3.56 (2 q, 1 H), 4.18 and 4.38 (2 t, 1 H), 4.08 and 4.5 (2 t, 1 H).

Anal. Calcd for $C_9H_{14}ClNO$: C, 57.60; H, 7.52; N, 7.46. Found: C, 57.83; H, 7.13; N, 7.26.

The more polar isomer **12** was *endo*-4-chloro-6-acetyl-6 azabicyclo[3.2.1]octane: IR ($CHCl_3$) 1625 cm^{-1}; NMR ($CDCl_3$, 250 MHz) δ 1.5–2.18 (m, 5 H), 2.23 (br, 1 H), 2.27 (s, 3 H), 2.5 (br, 1 H), 3.34 (m, 1 H), 3.6 (q, 1 H), 4.05 (q, 1 H), and 4.26 (d, 1 H). The mass spectra of the two isomers were identical: *m/e* (rel intensity) 187 (M^+, 18), 110 (53), 68 (100), 43 (20); for these and all the other cyclization products P/(P + 2) = 2.8–3.

Reaction of *N*-Chloro-*N*-[(4-cyclohepten-1-yl)methyl]-acetamide (16b) in a Deuterated Medium. Chromous Chloride Solution (1 M). Anhydrous chromous chloride (2.46 g, 20 mmol) (Merck) was dissolved in 20 mL of methanol-d_1 containing 2 mL of heavy water and 0.3 mL of deuterated hydrochloric acid (37%) under nitrogen atmosphere.

Reaction. Olefinic *N*-chloro amide **16b** (1.03 g, 5 mmol) was dissolved in a chloroform–methanol-d_1 (5:1) mixture and the solution was cooled to −78 °C (methanol–dry ice). Then 10 mL (10 mmol) of the chromous chloride solution was added very slowly. The reaction was followed by iodometric test and stopped after completion; 20 mL of heavy water was added before the reaction mixture was allowed to warm up to room temperature. Extraction followed by silica gel column chromatography afforded quantitatively the parent amide **16a**. The mass spectrum of the reaction product showed no incorporation

of deuterium in the molecule and was identical with the mass spectrum of an authentic sample of **16a**.

Cyclization of *N*-Chloro-*N*-methyl-5-bicyclo[2.2.2]oct-2-enecarboxamide (21b). Cyclization of *N*-chloro amide **21b** gave 85% of cyclized products. One could isolate 80% of the tricyclic exo isomer **22** and detect a product (5%) which could be the endo isomer **23** on the basis of its mass spectrum. The exo isomer **22** was recrystallized from cyclohexane to give pure *exo*-10-chloro-3-methyl-3-azatricyclo[4.3.1.0^{1,5}]decan-2-one (**22**): mp 65–66 °C; IR ($CHCl_3$) 1690 cm^{-1}; NMR ($CDCl_3$) δ 1.3–2.43 (m, 9 H), 2.9 (s, 3 H), 3.46 (d, 1 H), and 4.0 (d, 1 H). The mass spectra of **22** and **23** were identical: *m/e* (rel intensity) 199 (M^+, 69), 164 (53), 136 (68), 96 (100), 78 (21), 42 (34).

Cyclization of *N*-Chloro-*N*-[(2-bicyclo[2.2.2]octen-5-yl)-methyl]acetamide (24b). *exo*-10-Chloro-3-acetyl-3-azatricyclo[4.3.1.0^{1,5}]decane (**25**) was obtained from the cyclization of olefinic *N*-chloro amide **24b** in 85% yield: IR ($CHCl_3$) 1635 cm^{-1}; NMR ($CDCl_3$, 250 MHz) δ 1.28 (m, 2 H), 1.6–2.5 (m, 7 H), 2.03 and 2.19 (2 s, 3 H), 2.84 and 3.20 (2 d, 1 H), 3.29 and 3.4 (2 q, 1 H), 3.84 and 4.19 (2 d, 1 H); mass spectrum *m/e* (rel intensity) 213 (M^+, 26), 178 (19), 136 (61), 80 (100), 68 (48), 43 (34).

Reaction of *N*-Chloro-*N*-methyl-2-methylene-5-bicyclo[2.2.2]octanecarboxamide (26b). Attempts to cyclize the *N*-chloro amide **26b** yielded a mixture containing 70% of parent amide **26a** and 32% of a product which was identified as *N*-methyl-2-methyl-5-bicyclo[2.2.2]oct-2-enecarboxamide: IR ($CHCl_3$) 1660, 1520 cm^{-1}; NMR ($CDCl_3$) δ 1.1–2.88 (m, 9 H), 1.83 (d, 3 H), 2.77 (d, 3 H), 5.5 (m, 1 H), and 5.83 (br, 1 H); mass spectrum *m/e* (rel intensity) 139 (M^+, 18), 94 (48), 86 (100), 79 (58).

Cyclization of *N*-Chloro-*N*-methyl-3-bicyclo[3.3.1]non-6-enecarboxamide (27b). Cyclization of *N*-chloro amide **27b** afforded 74% of *anti*-5-chloro-3-methyl-3-azahomoadamantan-2-one (**28**) and 15% of parent amide **27a**. The tricyclic lactam **28** was recrystallized from cyclohexane: mp 98 °C; IR ($CHCl_3$) 1650 cm^{-1}; NMR ($CDCl_3$, 250 MHz) δ 1.47–2.45 (m, 10 H), 2.88 (m, 1 H), 3.02 (s, 3 H), 3.45 (m, 1 H), and 4.22 (br, 1 H); mass spectrum *m/e* (rel intensity) 213 (39), 178 (100), 122 (21), 80 (23), 57 (26).

Anal. Calcd for $C_{11}H_{16}ClNO$: C, 61.83; H, 7.55; N, 6.55. Found: C, 61.69, H, 7.24; N, 6.28.

Cyclization of *N*-Chloro-*N*-(6-bicyclo[3.3.1]nonen-3-yl)-acetamide (29b). Cyclization of the olefinic *N*-chloro amide **29b** afforded a mixture of 62% of isomers **30** and **31**, 21% of parent amide **29a**, and 15% of an unidentified product. The less polar isomer was identified as *anti*-4-chloro-2-acetyl-2-azaadamantane (**30**): IR ($CHCl_3$) 1625 cm^{-1}; NMR ($CDCl_3$, 250 MHz) δ 1.56–2.46 (m, 10 H), 2.09 (s, 3 H), 3.98 (br, 1 H), 4.18 and 4.22 (2 br, 1 H), 4.81 and 4.86 (2 br, 1 H).

Anal. Calcd for $C_{11}H_{16}ClNO$: C, 61.83; H, 7.55; N, 6.55. Found: C, 61.66; H, 7.55; N, 6.52.

The more polar isomer was *syn*-4-chloro-2-acetyl-2-azaadamantane (**31**): mp 35 °C; IR ($CHCl_3$) 1630 cm^{-1}; NMR ($CDCl_3$, 250 MHz) δ 1.52–2.52 (m, 10 H), 2.12 (s, 3 H), 4.01 and 4.1 (2 br, 1 H), 4.31 (br, 1 H), 4.86 and 5.0 (2 br, 1 H).

Anal. Calcd for $C_{11}H_{16}ClNO$: C, 61.83; H, 7.55; N, 6.55. Found: C, 61.85; H, 7.50; N, 6.51.

The mass spectra of the two isomers were identical: *m/e* (rel intensity) 213 (M^+, 41), 178 (80), 171 (52), 136 (96), 94 (30), 80 (100), 43 (35).

Registry No.—**1a**, 52565-61-4; **16**, 66769-76-4; **2**, 66769-85-5; **3**, 5075-92-3; **4a**, 54385-21-6; **4b**, 54385-04-5; **5**, 54385-06-7; **6**, 18912-61-3; **7a**, 54385-24-9; **7b**, 36393-98-3; **8**, 36394-04-4; **9**, 36394-03-3; **10a**, 54385-23-8; **10b**, 54385-09-0; **11**, 66769-86-6; **12**, 66769-87-7; **13a**, 53102-89-9; **13b**, 66769-77-5; **14**, 66769-88-8; **15**, 66791-98-8; **16a**, 66769-67-3; **16b**, 66769-78-6; **17a**, 13295-40-4; **17b**, 66769-79-7; **18**, 66769-89-9; **19a**, 66769-68-4; **19b**, 66769-80-0; **20**, 66769-90-2; **21a**, 62460-73-5; **21b**, 66769-81-1; **22**, 66769-91-3; **23**, 66791-99-9; **24a**, 66769-69-5; **24b**, 66769-82-2; **25**, 66792-17-4; **26a**, 66769-70-8; *exo*-**26a**, 66791-96-6; **26b**, 66769-83-3; **27a**, 66769-71-9; **27b**, 66787-43-7; **28**, 66769-65-1; **29a**, 53092-79-8; **29b**, 66769-84-4; **30**, 66769-66-2; **31**, 66791-95-5; **32**, 66769-72-0; 5-formylbicyclo[2.2.2]oct-2-ene, 40570-95-4; 5-formylbicyclo[2.2.2]oct-2-ene oxime, 66769-73-1; bicyclo[2.2.2]oct-2-ene-5-methanamine, 66791-97-7; 5-carbomethoxybicyclo[2.2.2]octan-2-one, 49826-55-3; 5-carbomethoxy-2-methylenebicyclo[2.2.2]octane, 66769-74-2; 6-bicyclo[3.3.1]non-3-enecarboxylic acid, 21932-98-9; 6-bicyclo[3.3.1]non-3-enecarbonyl chloride, 57438-49-0; (2-pyrrolidino)methanol, 498-63-5; (2-pyrrolidino)-methanol diacetate, 42366-60-9; *N*-acetyl-(2-pyrrolidino)methanol, 27822-68-0; *N*-methyl-2-methyl-5-bicyclo[2.2.2]oct-2-enecarboxamide, 66769-75-3; chromous chloride, 10049-05-5.

References and Notes

(1) (a) See ref 1a to 1c of the preceding paper in this issue. (b) Most of the work reported here is part of Ph. Mackiewicz, "Thèse d'Ingénieur—Docteur", University d'Aix-Marseille III, 1977. (c) Part of this work has been presented at the Congress of Heterocyclic Chemistry, Teheran, Iran, July, 1977, and at the 2nd International Symposium on Organic Free Radicals, Aix-en-Provence, France, July, 1977.

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(8) We have tried different additional chlorinating agents next to the previously described ones, i.e., calcium hypochlorite, *tert*-butyl hypochlorite,[9] *N*-chlorosuccinimide, and tetra-*n*-butylammonium hypochlorite.

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(10) All the cyclization products reported in Table I had IR and ^1H NMR spectra, and elemental analysis, and/or a mass spectrum consistent with their structure and stereochemistry. The interpretation and analysis of the ^1H NMR and IR spectra are generally quite straightforward and are presented in the Experimental Section. Compounds **8** and **9** had spectral data similar to those reported.[6,11] The *N*-acetyl derivatives are of particular interest from the ^1H NMR point of view as the two rotamers could be observed. These data will be reported in full details elsewhere.

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(12) We have also performed the photochemical cyclization of *N*-chloro amides **1b** and **4b**, as described in the preceding paper,[3] and obtained the following results: from **1b**, 56% of **2**, 15% of **3**, no parent amide; from **4b**, 6% of **5**, 21% of **6**, 10% of parent amide. Kuehne and Horne[6] reported a 35% yield of **5** after distillation. However we obtained, under the same conditions, a mixture of products.

(13) The preference for 1,5 transfer of hydrogen in amido radicals[14,15] and other heteroradicals[16] is documented by many examples.

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