zation bands with spacings of 1650 ($\tilde{X}$), 580 ($\tilde{A}$), and 2250 and 560 cm^{-1} ($\tilde{C}$). For the radical cation ground state ($\tilde{X}$), no additional vibrational progression can be detected, which would correspond to the large-amplitude motion v_7 observed in the first PE band of the iso(valence)electronic radical cation O=C=C=C=O$^{\bullet+}$.[11] A fifth PE band appears at about 16.5 eV (Figure 1), if the PE spectrum of OC_3S is recorded while increasing the count rate. As concerns its assignment, the MNDO calculations predict a C_3 skeleton ionization within the He(I) measurement region, although with a rather large Koopmans deviation. Altogether, however, the MNDO calculations, which are geometry-optimized assuming a linear arrangement, seem to be reliable; e.g., the known microwave structure of OC_3S[5b]

	O=C	=C	=C	=S		
exptl	113.43	126.96	125.40	158.25	(pm)	(2)
MNDO	118	128	126	150	(pm)	

is approximately reproduced.

Tricarbon oxide sulfide (O=C=C=C=S) is a thermally rather stable molecule: On further heating in a short-pathway molybdenum furnace[10] up to 1000 °C no CO elimination to C_2S or any other thermal decomposition can be detected PE spectroscopically.

Acknowledgment. The research project has been supported by Land Hessen, the Deutsche Forschungsgemeinschaft, and the Fonds der Chemischen Industrie. We all enjoyed the stimulating discussions with M. Winnewisser, University Giessen.

Registry No. $C_8O_4S_2$, 70597-76-1; OC_3S, 2219-62-7.

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[11] Cf., e.g.: Rabalais, J. W. *"Principles of Ultraviolet Photoelectron Spectroscopy*; Wiley: New York, 1977; pp 65–68, as well as Ginsberg, A. P.; Brundle, C. R. *J. Chem. Phys.* **1978**, *68*, 5231 and literature cited therein.

Ruthenium-Catalyzed Amidation of Nitriles with Amines. A Novel, Facile Route to Amides and Polyamides

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In the field of amide synthesis, a problem of continuing interest is the development of a general method for the conversion of amines to amides under neutral conditions.[1] Toward this end we have devised a new type of highly efficient method, which is applicable for synthesis of various amides and polyamides.

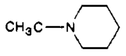
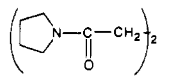
Ruthenium-catalyzed condensation of nitriles with amines in the presence of 2 equiv of water provides the corresponding amides along with ammonia as depicted in eq 1. The reaction appears

$$R^1CN + HNR^2R^3 + H_2O \xrightarrow{\text{Ru catalyst}} R^1CONR^2R^3 + NH_3 \quad (1)$$

to proceed generally, cleanly, and highly efficiently under neutral conditions in a single step, although the reaction temperature is high.

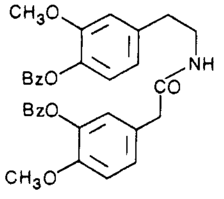
As the catalyst, $RuH_2(PPh_3)_4$ (**1**) has proved to be the most effective. The reaction does not proceed in the absence of the catalyst. The efficiency of the catalyst has been demonstrated by the following experiments. Acetonitrile (2.0 mmol) was treated with butylamine (2.2 mmol) and H_2O (4.0 mmol) in the presence of a catalyst (0.06 mmol) in 1,2-dimethoxyethane (DME, 0.5 mL) at 160 °C for 24 h in a sealed tube under argon: $RuH_2(PPh_3)_4$ (conversion 100%, yield of BuNHCOMe 93%); $RuCl_2(PPh_3)_3$ (87%, 70%); $RuH(OH)(PPh_3)_2(H_2O)$ (86%, 88%); $[Ru(NH_3)_5Cl]Cl_2$ (54%, 90%); $Mo(CO)_6$ (66%, 77%).

Table I. Amide Synthesis

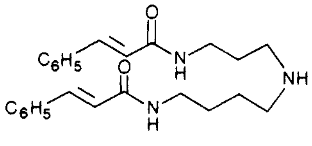
amides[a]	yield,[b,c] %
$CH_3CNHC_4H_9$	93
	97
$CH_3C(CH_3)N(CH_3)CH_2C_6H_5$	95
$CH_3OCH_2CONHC_4H_9$	93
	91
2	80
3	74
4	99
6a	93
6b	86
6c	70

[a] The product amides in eq 1. A mixture of nitrile (1 equiv), amine (1.1 equiv), H_2O (2 equiv), and $RuH_2(PPh_3)_4$ (3 mol %) in DME was heated at 160 °C for 24 h in a sealed tube under argon. [b] Isolated yield. [c] The products showed satisfactory IR, NMR, and mass spectra.

Table I summarizes the representative examples. Acetylation of amines with CH_3CN is practical, because of simple isolation of the acetamides without a washing process. The single-step preparation of amides from nitriles is highly useful. Typically, amide **2**, which is an important precursor of isoquinoline alkaloids such as reticuline or *N*-norreticuline,[2] has been prepared readily upon treatment of 3-(benzyloxy)-4-methoxytoluene-α-carbonitrile[3] with [3-methoxy-4-(benzyloxy)-β-phenethyl]amine (80% yield).[4]



2 (Bz = $CH_2C_6H_5$)



6c

The intramolecular version of the present reaction provides an efficient method for synthesis of lactams. 6-Hexanelactam (**3**) has been obtained from 6-aminohexanenitrile. Boiling 5-(methylamino)pentanenitrile and boiling 5-(hexylamino)pentanenitrile were also converted into the corresponding *N*-methyl- (**4**) and *N*-hexylpiperidones in quantitative yields, respectively.

To explore the scope of the reaction with respect to the chemoselectivity of primary amines toward secondary amines, nitriles were allowed to react with triamines **5** under the present reaction conditions (eq 2). Acetonitrile underwent the condensation with

$$RCN + \underset{\mathbf{5}}{H_2N(CH_2)_mNH(CH_2)_nNH_2} \xrightarrow[H_2O]{\text{catalytic } \mathbf{1}} \underset{\mathbf{6}}{RCONH(CH_2)_mNH(CH_2)_nNHCOR} \quad (2)$$

spermidine (**5a**, $m = 3$, $n = 4$) to give N^1,N^8-bisacetylspermidine (**6a**) in 93% yield after chromatographic separation (SiO_2, $CHCl_3$/MeOH). Similarly, the reaction of $C_6H_5CH_2CN$ with dipropylenetriamine (**5b**, $m = 3$, $n = 3$) gave N^1,N^7-bis(phenylacetyl)dipropylenetriamine (**6b**) in 86% yield along with only 3% of the triacyl compound. Further, maytenine[5] (**6c**) has been

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[1] For review, see: (a) Beckwith, A. L. J. In *The Chemistry of Amides*; Zabicky, J., Ed.; Interscience: New York, 1970; p 73. (b) Sandler, S. R.; Karo, W. *Organic Functional Group Preparations*; Academic Press: New York, 1968, p 269.

[2] Shamma, M.; Moniot, J. L. *Isoquinoline Alkaloids Research 1972–1977*; *Plenum Press*: New York, 1978.

[3] Schwartz, M. A.; Zoda, M.; Vishnuvajjala, B.; Mami, I. *J. Org. Chem.* **1976**, *41*, 2502.

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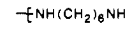
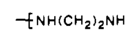
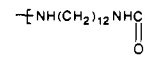
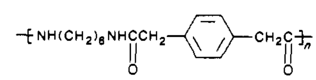
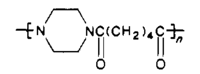
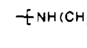
Table II. Polyamide Synthesis

polyamides[a]	mp, °C	M_n[b]	yield,[c] %
 $\text{-}[NH(CH_2)_6NH\underset{\underset{O}{\|}}{C}(CH_2)_4\underset{\underset{O}{\|}}{C}]_n\text{-}$	255	8900	98
 $\text{-}[NH(CH_2)_2NH\underset{\underset{O}{\|}}{C}(CH_2)_4\underset{\underset{O}{\|}}{C}]_n\text{-}$	>300	3700	97
 $\text{-}[NH(CH_2)_{12}NH\underset{\underset{O}{\|}}{C}(CH_2)_{10}\underset{\underset{O}{\|}}{C}]_n\text{-}$	>300	3800	99
	>300	14000	93
	230	7200	73
 $\text{-}[NH(CH_2)_2\underset{\underset{O}{\|}}{C}]_n\text{-}$	175	1600	98

[a] The product polyamide **9** in eq 3. Polymerization was carried out with 2 mmol of each monomer in the presence of 4 mmol of water and 3 mol % of $RuH_2(PPh_3)_4$ in DME at 160 °C for 24 h in a sealed tube under argon. The precipitated polymer was washed with $CHCl_3$ and dried in vacuo. [b] Molecular weight was determined by the titration of the terminal amino group with *p*-toluenesulfonic acid using Thimol-Blue. [c] The IR spectra and elemental analyses are consistent with the general polyamide structure.

prepared by the reaction of *trans*-cinnamonitrile with **5a** in 70% yield. Evidently, the acylation of primary amines proceeds chemoselectively in the presence of secondary amines. Direct selective acylation of polyamines, particularly spermidines and spermines, is of considerable importance, because their derivatives have potent antibiotic and antineoplustic properties.[6] However, the methods available are limited to a few, because of the higher nucleophilicity of secondary amines with most electrophilic reagents.[6]

The efficiency of our new process is highlighted by the synthesis of various, industrially important polyamides.[7] The ruthenium-catalyzed reaction of dinitriles **7** with diamines **8** in the presence of water gives polyamides **9** generally (eq 3).[8] As a model reaction

$$\underset{\mathbf{7}}{NCCH_2\text{-}X\text{-}CH_2CN} + \underset{\mathbf{8}}{RNH\text{-}Y\text{-}NHR} \xrightarrow[H_2O]{\text{Ru catalyst}} \underset{\mathbf{9}}{\text{-}(COCH_2\text{-}X\text{-}CH_2CONR\text{-}Y\text{-}NR)_n\text{-}} \tag{3}$$

the polycondensation of hexanedinitrile with 1,6-hexanediamine was investigated in the presence of water (2 equiv) and catalyst **1** (3 mol %) in DME at 160 °C for 24 h. The polyamide was obtained in 98% yield. The molecular weight ($\overline{M}_n$) was determined to be 8900 by titration of the terminal amino group.[9] The viscosity η in *m*-cresol was 0.7 dL g^{-1}, which corresponds to $\overline{M}_n$ 7900 and is consistent with the $\overline{M}_n$ value obtained above. Other representative examples of the polyamide synthesis are shown in Table II. Since various dinitriles have been prepared as the precursor of diamines,[10] the present reaction provides a wide-scope method for synthesis of polyamides without using diacids and diesters. Finally, aminonitriles undergo similar polycondensation efficiently. The ruthenium-catalyzed reaction of 3-aminopropionitrile gave nylon 3, $-(NH(CH_2)_2CO)_n-$ (mp 175 °C, $\overline{M}_n$ 1600), in 98% yield.

Work is in progress to investigate the interesting mechanism of the present reaction and to apply our method to other systems.

Registry No. 1, 19529-00-1; **2**, 1699-40-7; **3**, 105-60-2; 4, 931-20-4; **6a**, 82414-35-5; **6b**, 95245-15-1; **6c**, 41590-65-2; $H_2N(CH_2)_5CN$, 2432-74-8; $H_3CNH(CH_2)_4CN$, 6066-89-3; $H_3C(CH_2)_5NH(CH_2)_4CN$, 104807-50-3; CH_3CN, 75-05-8; **5a**, 124-20-9; **5b**, 56-18-8; $C_6H_5CH_2CN$, 140-29-4; *trans*-$C_6H_5CH{=}CHCN$, 1885-38-7; $H_3CCONHC_4H_9$, 1119-49-9; $H_3CCON(CH_3)CH_2C_6H_5$, 29823-47-0; $H_3COCH_2CONHC_4H_9$, 53848-63-8; 3-(benzyloxy)-4-methoxybenzenecarbonitrile, 1699-39-4; [3-methoxy-4-(benzyloxy)-β-phenethyl]amine, 22231-61-4; *N*-hexylpiperidone, 89013-13-8; 1-(*N*-piperidino)ethanone, 618-42-8; 1,4-dipyrrolidinyl-1,4-dioxobutane, 63958-62-3; $(H_2N(CH_2)_6NH_2)(NC(CH_2)_4CN)$(copolymer), 51937-09-8; $(H_2N(CH_2)_6NH_2)(NC(CH_2)_4CN)$(copolymer, SRU), 3213-17-2; $(H_2N(CH_2)_2NH_2)(NC(CH_2)_4CN)$(copolymer), 70087-99-9; $(H_2N(CH_2)_2NH_2)(NC(CH_2)_4CN)$(copolymer, SRU), 26951-61-1; $(H_2N(CH_2)_{12}NH_2)(NC(CH_2)_{10}CN)$(copolymer), 104807-51-4; $(H_2N(CH_2)_{12}NH_2)(NC(CH_2)_{10}CN)$(copolymer, SRU), 36348-71-7; $(H_2N(CH_2)_6NH_2)(NCCH_2C_6H_4\text{-}p\text{-}CH_2CN)$(copolymer), 104807-52-5; $(H_2N(CH_2)_6NH_2)(NCCH_2C_6H_4\text{-}p\text{-}CH_2CN)$(copolymer, SRU), 52236-37-0; (1,6-hexanedinitrile)(1,4-piperazine)(copolymer), 104807-53-6; (1,6-hexanedinitrile)(1,4-piperazine)(copolymer, SRU), 26967-89-5; poly(3-aminopropionitrile)(homopolymer), 28157-83-7; poly(3-aminopropionitrile)(SRU), 104807-54-7.

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Electrocatalytic Four-Electron Reduction of Dioxygen by Iridium Porphyrins Adsorbed on Graphite

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The electrocatalytic reduction of dioxygen by macrocyclic transition-metal complexes adsorbed on electrodes has been studied extensively in conjunction with the search for an inexpensive cathode material for oxygen fuel cells.[1] We and other laboratories have shown that dicobalt cofacial porphyrin dimers can catalyze dioxygen reduction to water without producing significant amounts of hydrogen peroxide.[2] To our knowledge, however, no monomeric macrocyclic metal complex has been reported to catalyze the direct four-electron reduction of dioxygen in acidic solution.[3,4] In a survey of electrocatalytic oxygen reduction by various metalloporphyrins adsorbed on activated carbon, iridium complexes were reported to be the most active catalysts.[5] Since the reduction

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