

Figure 3. Time-resolved emission spectra obtained at 3 and 15 μ s after the laser pulse for $[\text{Ru}(\text{bpy})(\text{HDP A})_2]^{2+}$ in 2-PrOH at 77 K. Assignments of the emission are given (see text).

The $[\text{Ru}(\text{bpy})_2(\text{HDP A})]^{2+}$ complex exhibits absorption bands characteristic of the HDP A and bpy unit; however, the emission band position and structure as well as the emission lifetime (Table I) and emission photoselection (Figure 1) indicate that this emission is an MLCT emission involving only the bpy ligand. In contrast $[\text{Ru}(\text{bpy})(\text{HDP A})_2]^{2+}$ has a new low-energy absorption band and two emissions depending upon the excitation wavelength and solvent (Figure 2). Subsequently, lifetimes were measured as a function of emitting wavelength (Table I) and time-resolved spectra were obtained (Figure 3). Excitation spectra and emission photoselection spectra (Figure 1) were measured and found to be consistent with the results in Figures 2 and 3 and Table I, indicating a higher energy, longer lived (13 μ s) emission and a lower energy, shorter lived (5.0 μ s) emission.

The broad emission band measured at room temperature can be time resolved to show the presence of two bands, a higher energy emission with $\tau = 1.05 \pm 0.04 \mu$ s and a lower energy with $\tau = 0.33 \pm 0.02 \mu$ s.

Since a small amount of luminescent impurity¹⁴ can result in erroneous identification of a dual emission, the following precautions have been taken: (1) Repeated recrystallization and chromatographic separations have been used and the emission has been monitored as a function of the number of repurifications. (2) The samples have been prepared in the dark and light and irradiated for long periods, and no difference in the emission or absorption bands could be determined in any case. (3) The $[\text{Ru}(\text{phen})(\text{HDP A})_2]^{2+}$ analogue has been synthesized, and a dual emission is also obtained for it. $[\text{Ru}(\text{bpy})_2(\text{HDP A})]^{2+}$ would be the most likely impurity since its emission is coincident with the higher energy emission band of $[\text{Ru}(\text{bpy})(\text{HDP A})_2]^{2+}$, but the lifetime of the emissions from the two complexes are 4.6 and 13 μ s, respectively. Therefore, $[\text{Ru}(\text{bpy})_2(\text{HDP A})]^{2+}$ can be eliminated as an impurity in $[\text{Ru}(\text{bpy})(\text{HDP A})_2]^{2+}$. The 13- μ s emission has also been shown to disappear in H_2O leaving only a single emission band which was found to be excitation wavelength independent verifying the purity of the $[\text{Ru}(\text{bpy})(\text{HDP A})_2]^{2+}$ complex. Moreover, the absorption spectra and emission spectra of the dual emitter have been measured as a function of concentration (10^{-4} – 10^{-6} M) and no change is noted, consequently dimer emission can be excluded.

A criterion for dual emission that the zero point energies of the two emitting excited states are near degenerate is apparently met in the $n = 1$ complex, yet the two emission bands can be

resolved, thereby implying that the two excited-state manifolds are displaced by different amounts. In addition, the different contours for the two emissions and the difference in the lifetime enable ready resolution of the two emission bands. For the $n = 2$ compound, the single emission implies that the separation between the lowest energy levels must be sufficient to allow non-radiative relaxation to the lowest lying state consistent with Kasha's rule.

The short-lived, lower energy emission in $[\text{Ru}(\text{bpy})(\text{HDP A})_2]^{2+}$ and the single emission observed in $[\text{Ru}(\text{bpy})_2(\text{HDP A})]^{2+}$ are characteristic of the Ru-bpy chromophore and permit identification of these emissions as from a Ru-bpy MLCT state.

A key to the assignment of the second emission in the $n = 1$ species is the occurrence of the new absorption band at 19 600 cm^{-1} . Careful examination of the absorption spectrum of $[\text{Ru}(\text{bpy})_2(\text{HDP A})]^{2+}$ indicates that this band does occur but with lower intensity than in $[\text{Ru}(\text{bpy})(\text{HDP A})_2]^{2+}$, therefore it is nearly covered by the more intense MLCT (Ru-bpy) band. This band does not occur in either of the parent compounds; in fact, it is only visible in complexes in which an HDP A and a bpy ligand are present. Upon examination of spectroscopic properties of $[\text{Ru}(\text{bpy})(\text{py})_4](\text{ClO}_4)_2$ where no bridging amine is present, the unusual absorption and emission bands are not observed. Moreover, this absorption blue shifts as the hydrogen bonding ability of the solvent is increased (Figure 2), a characteristic of $n-\pi^*$ transitions in organic chromophores.¹⁵ Indeed, this absorption band disappears in H_2O , likely due to hydrogen bonding to the amine lone pair, and now only a single emission band is observed. Consequently, this emission is assigned as an *interligand* $n-\pi^*$ transition involving the nonbonding electrons of the amine nitrogen on HDP A and the π^* orbital of the adjacent bpy ligand.

Further data and details on these and related systems are to be published.

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(15) Kasha, M. *Radiat. Res., Suppl.* 1960, 2, 264-269.

Gas-Phase Reactions. 55.¹ $\text{O}=\text{C}=\text{C}=\text{C}=\text{S}$: Synthesis and PE Spectrum

Hans Bock,* Ralph Dammel, and Dieter Jaculi

Department of Chemistry, University of Frankfurt
Niederurseler Hang, D-6000 Frankfurt 50, West Germany
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3-Thioxo-1,2-propadien-1-one ($\text{O}=\text{C}=\text{C}=\text{C}=\text{S}$), a five-atomic linear molecule, is of considerable interest to both astronomers²⁻⁴ and spectroscopists.⁵ Recently, the novel interstellar molecule $\text{O}=\text{C}=\text{C}=\text{C}$ has been discovered in the cold dark cloud Taurus TMC 1,³ which is rich in carbon chain compounds such as HC_nN ($n = 1, 3, 5, 7, 9$).² It could well be a precursor of $\text{O}=\text{C}=\text{C}=\text{C}=\text{S}$,^{5a} which according to previous evidence occurs most likely in other interstellar molecular clouds.⁴ The need to provide precise spectroscopic data, measured on earth, for an unequivocal assignment in space coincides with the interest of spectroscopists to know more about OC_3S , which in contrast to

(1) Part 54: $\text{H}_3\text{C}-\text{P}=\text{CH}_2$: Bock, H.; Bankmann, M. *Angew. Chem.* 1986, 98, 287; *Angew. Chem., Int. Ed. Engl.* 1986, 25, 265.

(2) For a recent summary on "Interstellar Molecules and Microwave Spectroscopy" cf.: Winniewisser, M. *Chem. Z.* 1984, 18, 1-16, 54-61 and literature cited therein. Especially on carbon chain molecules like HC_nN with $n = 1, 3, 5, 7, 9$ in the interstellar dark cloud Taurus TMC 1.

(3) Matthews, H. E.; Irvine, W. M.; Freiberg, P.; Brown, R. D.; Godfrey, P. D. *Nature (London)* 1984, 310, 125.

(4) Turner, B. E. *Astrophys. Lett.* 1983, 23, 17.

(5) (a) Winniewisser, M.; Holland, F. *Astron. Astrophys.*, in press. (b) Winniewisser, M.; Peau, E. W. *Acta Phys. Hung.* 1984, 55, 33. (c) Winniewisser, M.; Peau, E. W.; Yamada, K.; Christiansen, J. J. *Z. Naturforsch.* 1981, 36A, 819. (d) Winniewisser, M.; Christiansen, J. J. *Chem. Phys. Lett.* 1976, 37, 270 and literature cited in each.

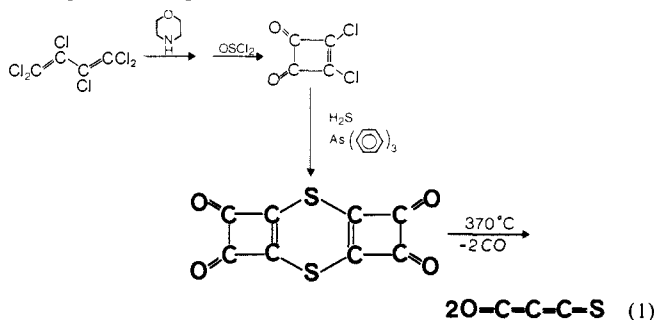
(12) Cocks, A. T.; Wright, R.; Seddon, K. R. *Chem. Phys. Lett.* 1982, 85, 369.

(13) Juris, A.; Barigelletti, F.; Balzani, V.; Belser, P.; Von Zelewsky, A. *Isr. J. Chem.* 1982, 22, 87.

(14) Belser, P.; Von Zelewsky, A.; Juris, A.; Barigelletti, F.; Balzani, V. *Chem. Phys. Lett.* 1984, 104, 100. This reference indicates in detail why the results of ref 12 and 13 cannot describe a bona fide dual emission for Ru(II) complexes.

its iso(valence)electronic analogue OC₃O does not exhibit quasi-linear behavior,⁵ i.e., a large-amplitude bending motion around its carbon center.⁶ The so far only known and tedious synthesis of OC₃S from moistured OC₃O and P₄S₁₀ in 0.2% yield,^{5d} however, constitutes a nasty obstacle to its further investigation.

Our interest in ion-pair formation between chelate radical anions and alkali-metal counterions [Me⁺M⁻]⁺ in aprotic solution⁷ has stimulated the three-step synthesis⁸ of 4,5,9,10-tetraoxo-2,7-dithia[6.2.0.0.3⁶]deca-1(8),3(6)-diene, a heterotricycle, containing no atoms with nuclear spin moments in high natural abundance, i.e., well suited for ESR measurements without multiplet blurring:



Looking again at the compound C₈O₄S₂ with an eye on CO as a thermodynamically most favorable pyrolytic leaving group,⁹ thermal decomposition to yield either C₂S, another unknown carbon sulfide, or the actually observed OC₃S seemed to be feasible.

The pyrolysis of C₈O₄S₂ in a standard flow reactor⁹ has been monitored by PE spectroscopic real-time gas analysis⁹ (Figure 1). CO elimination from C₈O₄S₂ already starts at 200 °C needed for evaporation under 10⁻² mbar of pressure and is completed at 370 °C (Figure 1). OC₃S, cool-trapped with liquid nitrogen, can be reevaporated at -90 °C to record its PE and MS spectra,¹⁰ which both show no detectable impurities. The sequence of OC₃S⁺ radical cation states is assigned by Koopmans' correlation, IE_n^v = -ε_j^{MNDO}, with MNDO eigenvalues: The predominant contribution to the doubly degenerate OC₃S⁺ ground state, $\tilde{X}(^2\Pi)$, stems from the thiocarbonyl group. The excited states start with $\tilde{A}(^2\Pi)$, exhibiting each one node through the formally perpen-

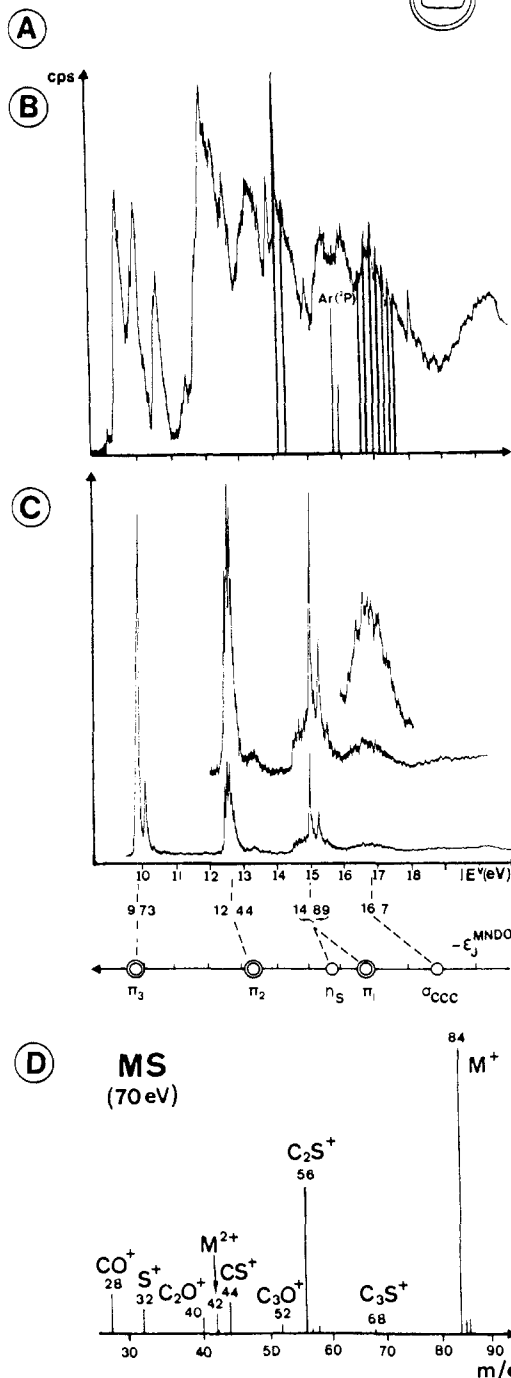
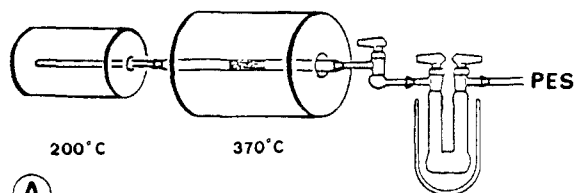


Figure 1. Flow reactor with vaporizer and cooling trap (A) for generation and isolation of OC₃S. (B) He(I) PE spectra of C₈O₄S₂ at 200 °C evaporation temperature, already contaminated by CO (blackened needles) and minor amounts of CO₂. OC₃S, generated by pyrolysis at 370 °C and cool-trapped at -196 °C, can be reevaporated at -90 °C to record its PE spectrum (C), assigned via Koopmans' theorem, IE_n^v = -ε_j^{MNDO}, based on MNDO eigenvalues (see text), and also its mass spectrum (D) exhibiting the expected dominant pattern with m/e = 84 (M⁺), 56 (CCS⁺) and 28 (CO⁺).

dicular π-components, followed by the adjacent single σ_{CS}(²Σ⁻) and degenerate totally bonding π_{OCCCS}(²Π) states, the bands of which partly overlap (Figure 1). This tentative assignment, based on a well-parametrized semiempirical calculation, is supported by the pronounced vibrational fine structures of all π-type ioni-

(6) OC₃S with a lowest lying bending mode ν₇ = 82.6 cm⁻¹ has a strictly linear structure in sharp contrast to OC₃O, the complex dynamics of which with ν₇ = 18.2 cm⁻¹ require a model almost halfway between linear and bent.⁵

(7) Bock, H.; Jaculi, D. *Angew. Chem.* **1984**, *96*, 298; *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 305, or Bock, H.; Hierholzer, B.; Vögtle, F.; Hollmann, G. *Angew. Chem.* **1984**, *96*, 74; *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 57.

(8) The synthesis of 4,5,9,10-tetraoxo-2,7-dithiatricyclo[6.2.0.0.3⁶]deca-1(8),3(6)-diene largely follows known literature procedures: According to a German patent application (Hegenburg, P.; Maahs, G. DOS 1568291, Chem. Werke Hüls, 1970) hexachlorobutadiene is advantageously converted to 3,4-dihydroxycyclobutene-1,2-dione by (i) stirring with a 10-fold molar excess of morpholine for 5 h at 100 °C. After the excess of morpholine is distilled off, the reaction mixture is neutralized by adding aqueous HCl, stirred for 1 h at 60 °C, acidified for 20 min to pH 5, neutralized again, and stirred for another 4 h. After concentrating the solution in a rotary evaporizer, the residue is refluxed for 6 h in concentrated HCl. After the mixture is cooled squaric acid recrystallized from water is obtained in 40% yield. (ii) Chlorination to squaric acid dichloride is best achieved with OSeCl₂ (Schmidt, A. H. *Synthesis* **1980**, 963). (iii) The last step to the heterotricycle C₈O₄S₂ (cf.: Schmidt, A. H.; Aime, A.; Hoch, M. *Synthesis* **1984**, 754) has been slightly modified as follows: 2.0 g (13 mmol) of squaric acid dichloride is stirred in 50 mL of absolute benzene at a temperature between 5 and 8 °C. H₂S, dried by passing it through a 4-Å molecular sieve, is bubbled into the solution for 10 min, and within 15 min a solution of 4.06 g (13 mmol) of triphenylarsane in absolute benzene is slowly added. After another 3-h H₂S treatment, the orange solid is filtered off and recrystallized from acetonitrile. Yield 0.6 g (41%) with mp 174–176 °C dec, mass spectrum, m/e = 224. Cyclic voltammetry in THF/0.1 M LiB(C₆H₅)₄ using GCE vs. SCE with v = 100 mV/s yields an irreversible first cathodic peak at -0.48 V.

(9) Cf. the summary on PE spectroscopic real-time gas analysis in flow systems: Bock, H.; Solouki, B. *Angew. Chem.* **1981**, *93*, 425–442; *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 427–444.

(10) The measurements were performed by using a photoelectron spectrometer Leybold Hereaus UPG 200⁹ and a mass spectrometer Varian MAT CH7. For a detailed description of the short-pathway molybdenum furnace, cf.: Solouki, B.; Bock, H.; Appel, R.; Westerhaus, A.; Becker, G.; Uhl, G. *Chem. Ber.* **1982**, *115*, 3748.

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 ν_7 observed in the first PE band of the iso(valence)electronic radical cation $\text{O}=\text{C}=\text{C}=\text{O}^{\bullet+}$.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 $\text{OC}_3\text{S}^{\text{5b}}$

	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 ($\text{O}=\text{C}=\text{C}=\text{C}=\text{S}$) is a thermally rather stable molecule: On further heating in a short-pathway molybdenum furnace¹⁰ up to 1000 °C no CO elimination to C_2S or any other thermal decomposition can be detected PE spectroscopically.

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Registry No. $\text{C}_8\text{O}_4\text{S}_2$, 70597-76-1; OC_3S , 2219-62-7.

(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

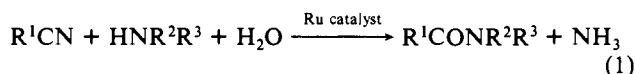
Shun-Ichi Murahashi,* Takeshi Naota, and Eiichiro Saito

Department of Chemistry, Faculty of Engineering
Science, Osaka University
Machikaneyama, Toyonaka, Osaka 560, Japan

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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

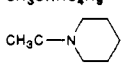
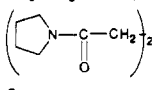


to proceed generally, cleanly, and highly efficiently under neutral conditions in a single step, although the reaction temperature is high.

As the catalyst, $\text{RuH}_2(\text{PPh}_3)_4$ (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)

(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.

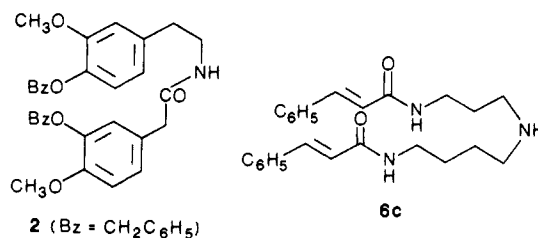
Table 1. Amide Synthesis

amides ^a	yield, ^{b,c} %
$\text{CH}_3\text{CNHC}_4\text{H}_9$	93
	97
$\text{CH}_3\text{C}(\text{CH}_3)\text{N}(\text{CH}_3)\text{CH}_2\text{C}_6\text{H}_5$	95
$\text{CH}_3\text{OCH}_2\text{CONHC}_4\text{H}_9$	93
	91
2	80
3	74
4	99
6a	93
6b	86
6c	70

^aThe product amides in eq 1. A mixture of nitrile (1 equiv), amine (1.1 equiv), H_2O (2 equiv), and $\text{RuH}_2(\text{PPh}_3)_4$ (3 mol %) in DME was heated at 160 °C for 24 h in a sealed tube under argon. ^bIsolated yield. ^cThe products showed satisfactory IR, NMR, and mass spectra.

at 160 °C for 24 h in a sealed tube under argon: $\text{RuH}_2(\text{PPh}_3)_4$ (conversion 100%, yield of BuNHCOMe 93%); $\text{RuCl}_2(\text{PPh}_3)_3$ (87%, 70%); $\text{RuH}(\text{OH})(\text{PPh}_3)_2(\text{H}_2\text{O})$ (86%, 88%); $[\text{Ru}(\text{N}(\text{H}_3)\text{Cl})\text{Cl}]_2$ (54%, 90%); $\text{Mo}(\text{CO})_6$ (66%, 77%).

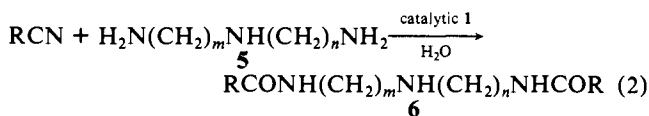
Table I summarizes the representative examples. Acetylation of amines with CH_3CN is practical, because of simple isolation of the acetamides without a washing process. The single-step preparation of amides from nitriles is highly useful. Typically, amide **2**, which is an important precursor of isoquinoline alkaloids



such as reticuline or *N*-norreticuline,² has been prepared readily upon treatment of 3-(benzyloxy)-4-methoxytoluene- α -carbonitrile³ with [3-methoxy-4-(benzyloxy)- β -phenethyl]amine (80% yield).⁴

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



spermidine (**5a**, $m = 3$, $n = 4$) to give *N*¹,*N*⁸-bisacetylspermidine (**6a**) in 93% yield after chromatographic separation (SiO_2 , $\text{CHCl}_3/\text{MeOH}$). Similarly, the reaction of $\text{C}_6\text{H}_5\text{CH}_2\text{CN}$ 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, maytenine⁵ (**6c**) has been

(2) Shamma, M.; Moniot, J. L. *Isoquinoline Alkaloids Research 1972-1977*; Plenum Press: New York, 1978.

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(4) Battersby, A. R.; Binks, R.; Francis, R. J.; McCaldin, D. J.; Ramuz, H. *J. Chem. Soc.* **1964**, 3600.

(5) (a) Englert, G.; Klinga, K.; Raymond-Hamet; Schlittler, E.; Vetter, W. *Helv. Chim. Acta* **1973**, *56*, 474. (b) McManis, J. S.; Ganem, B. *J. Org. Chem.* **1980**, *45*, 2041.