Highly Reduced Organometallics. 10.[1] Synthesis and Chemistry of the Pentacarbonylmetallate(3-) Ions of Niobium and Tantalum, $M(CO)_5^{3-}$

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In this paper we report on the syntheses and characterizations of the pentacarbonylmetallate trianions of niobium and tantalum, which are the first compounds to contain these elements in a formal oxidation state of −3. Although metal carbonyl trianions of other second- and third-row transition elements have been claimed,[2] these are also the first examples to have been isolated as analytically pure substances.

Substantial differences in the carbonyl chemistry of first-row transition metals and that of second and third row homologues are often observed. For example, while $Cr(CO)_6$ readily reacts with $Na-NH_3$ to provide high yields of $Na_2Cr(CO)_5$, corresponding reductions of $M(CO)_6$ (M = Mo, W) give only very low yields of thermally unstable $Na_2M(CO)_5$.[3,4] For these reasons it was by no means obvious whether reductions of the isoelectronic $M(CO)_6^-$ (M = Nb, Ta) would provide species analogous to the previously reported $V(CO)_5^{3-}$.[5]

Unlike the $Na-NH_3$ reductions of $Mo(CO)_6$ and $W(CO)_6$, however, $[Na(diglyme)_2][M(CO)_6]$[6] are smoothly reduced by 3 equiv of sodium in liquid ammonia at −78° C to provide deep red solutions containing thermally unstable $Na_3[M(CO)_5]$, according to eq 1. After filtration and cation exchange, deep red (M = Nb) or deep brown-red (M = Ta), slightly soluble, and apparently amorphous solids are obtained in 40–50% yields, which provide satisfactory analyses for unsolvated $Cs_3[M(CO)_5]$.[7] These materials have infrared spectra that are nearly superimposable on those of $Cs_3[V(CO)_5]$.[5] Although they appear to be only slightly less thermally stable than the vanadium analogue, as dry solids they are much more *shock sensitive*. One sample of $Cs_3[Ta(CO)_5]$ *exploded* on standing at room temperature under an inert atmosphere. In this respect they resemble the unstable $K_3[V(CO)_5]$.[5] For these reasons, their chemical studies have been largely limited to the reactions of $M(CO)_5^{3-}$ formed in situ in liquid ammonia.

$$Na[M(CO)_6] + 3Na \rightarrow Na_3[M(CO)_5] + {}^1/_2[Na_2C_2O_2]\downarrow \quad (1)$$

Treatment of liquid ammonia solutions of $Na_3[M(CO)_5]$ dropwise with 1 equiv of Ph_3SnCl in THF provides, after metathesis, 70–80% yields of orange to orange-red, crystalline $[Et_4N]_2[Ph_3SnM(CO)_5]$.[8] These oxygen-sensitive materials have infrared spectra in the ν(CO) region that are consistent with the presence of a substituted dianion of C_{4v} symmetry.[8] Also, nearly quantitative yields of the previously unknown $Na[M(CO)_5NH_3]$ are obtained from the reaction of $Na_3[M(CO)_5]$ with ammonium chloride in liquid ammonia. Although the sodium salts are thermally unstable, 40–45% yields of red violet (M = Nb) to deep violet (M = Ta) crystalline $[Ph_4As][M(CO)_5NH_3]$ may be obtained by metathesis.[9] These ammine complexes, like their vanadium analogue,[10] are very labile in solution and readily react at −20 to 0 °C with a variety of π-acceptor ligands such as PR_3, $P(OR)_3$, and RNC to provide 50–80% isolated yields of the corresponding $M(CO)_5L^-$. For example, the first isocyanide derivatives of tantalum and niobium carbonyls were obtained by treating ammonia solutions of $Na[M(CO)_5NH_3]$ with *t*-BuNC followed by cation exchange and crystallization. Orange $[Et_4N][M(CO)_5CN$-*t*-Bu] were thereby obtained in 50–60% yields.[11] The chemistry of $M(CO)_5^{3-}$ reported herein is summarized in eq 2 and 3.

$$Ph_3SnM(CO)_5^{2-} \xleftarrow{Ph_3SnCl} M(CO)_5^{3-} \xrightarrow{2NH_4^+} M(CO)_5NH_3^- + H_2 \quad (2)$$

(M = Nb, Ta)

$$M(CO)_5NH_3^- + L \xrightarrow{-20 \text{ to } 0\ ^\circ C} M(CO)_5L^- + NH_3 \quad (3)$$

(L = PR_3, $P(OR)_3$, RNC)

It is anticipated that the carbonyl trianions of niobium and tantalum will be especially important as precursors to new metal clusters containing these elements. Studies in this latter area are in progress.

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation (CHE82-10496) for continuing support of this research.

(1) Part 9: Lin, J. T.; Hagen, G. P.; Ellis, J. E. *J. Am. Chem. Soc.*, in press.

(2) Ellis, J. E.; Barger, P. T.; Winzenburg, M. L. *J. Chem. Soc., Chem. Commun.* **1977**, 686 and references cited therein.

(3) Behrens, H. *Adv. Organomet. Chem.* **1980**, *18*, 2.

(4) Maher, J.; Beatty, R. P.; Cooper, N. J. *Organometallics* 1982, *1*, 215.

(5) Ellis, J. E.; Fjare, K. L.; Hayes, T. G. *J. Am. Chem. Soc.* **1981**, *103*, 6100.

(6) Dewey, C. G.; Ellis, J. E.; Fjare, K. L.; Pfahl, K. M.; Warnock, G. F. P. *Organometallics*, in press.

(7) Anal. Calcd for $C_5Cs_3NbO_5$: C, 9.61; Cs, 63.12; H, 0.00. Found, C, 9.47; Cs, 63.35; H, 0.07. IR Nujol, (ν(CO) region) 1810 w (sharp), 1566 vs. (br) cm^{-1}. Anal. Calcd for $C_5Cs_3O_5Ta$: C, 8.34; Cs, 55.40; Ta, 25.14; H, 0.00. Found: C, 8.23; Cs, 55.68; Ta, 25.03; H, 0.12. IR Nujol, (ν(CO) region) 1813 w (sharp), 1562 vs (br) cm^{-1}.

(8) Anal. Calcd for $C_{39}H_{55}N_2O_5SnTa$: C, 50.29; H, 5.95; N, 3.01. Found: C, 49.95; H, 5.83; N, 3.03. IR (ν(CO), in CH_3CN) 1942 m, 1785 vs, 1755 sh cm^{-1}. Anal. Calcd for $C_{39}H_{55}N_2O_5NbSn$: C, 55.54; H, 6.57; N, 3.32. Found: C, 55.42; H, 6.48; N, 3.45. IR (ν(CO), CH_3CN) 1948 m, 1790 vs, 1750 sh cm^{-1}. ^1H NMR spectra in CD_3CN show integrations of phenyl and ethyl protons that are consistent with these formulations.

(9) Anal. Calcd for $C_{29}H_{23}O_5AsNNb$: C, 55.26; H, 3.20; N, 2.22. Found: C, 55.13; H, 3.26; N, 2.34. IR (ν(CO), Nujol) 1963 m, 1781 vs (br), 1759 vs (br) cm^{-1}. Anal. Calcd for $C_{29}H_{23}O_5AsNTa$: C, 48.49, H, 2.81; N, 1.95. Found: C, 48.03; H, 2.91; N, 1.90. IR (ν(CO), Nujol) 1960 m, 1775 s (br), 1755 vs (br) cm^{-1}.

(10) (a) Ellis, J. E.; Fjare, K. L. *Organometallics* **1982**, *1*, 898. (b) Fjare, K. L.; Ellis, J. E. *Ibid.* **1982**, *1*, 1373.

(11) Anal. Calcd for $C_{18}H_{29}N_2NbO_5$: C, 48.44; H, 6.55; N, 6.28. Found: C, 48.21; H, 6.75; N, 6.23. IR (CH_3CN) (ν(CN)) 2090 w, ν(CO): 1966 m, 1830 s cm^{-1}; ^1H NMR (CD_3CN) δ 1.46 s (9 H) (Et_4N^+ signals omitted). Anal. Calcd for $C_{18}H_{29}N_2O_5Ta$: C, 40.46; H, 5.47. Found: C, 40.79; H, 5.53. IR (CH_3CN) (ν(CN)) 2090 w, (ν(CO)) 1960 m, 1828 s cm^{-1}; ^1H NMR (CD_3CN) δ 1.48 s (9 H) (Et_4N^+ signals omitted).

Olefinic Cyclizations Promoted by Beckmann Rearrangement of Oxime Sulfonate

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The title reaction, if successful, would result in the direct formation of a wide variety of ring systems.[1-3]

(1) For reviews of the Beckmann rearrangement, see: Blatt, A. H. *Chem. Rev.* **1933**, *12*, 215. Jones, B. *Chem. Rev.* **1944**, *35*, 335. Moller, F. In "Methoden der Organischen Chemie"; Müller, E., Ed.; Thieme Verlag: Stuttgart, 1957; Vol. XI, Part 1, p 892. Donaruma, I. G.; Heldt, W. Z. *Org. React. (N.Y.)* **1960**, *11*, 1. Beckwith, A. L. J. In "The Chemistry of Amides"; Zabicky, J., Ed.; Interscience: New York, 1970; p 131. McCarty, C. G. In "Chemistry of the Carbon-Nitrogen Double Bond"; Patai, S., Ed.; Wiley-Interscience: New York, 1970; p 408.

(2) The present rearrangement–cyclization process may proceed via nitrilium ions as intermediates, which can also be generated by the Ritter reaction. For an excellent review of the Ritter reaction, see: Meyers, A. I.; Sircar, J. C. In "The Chemistry of Cyano Group"; Rappoport, Z. Ed.; Interscience: New York, 1970; p 341. See also: Johnson, F.; Madronero, R. In "Advances in Heterocyclic Chemistry"; Katritzky, A. R., Boulton, A. J., Eds.; Academic Press: New York, 1966; Vol. 6, p 95. Krimen, L. I.; Cota, D. J. *Org. React. (N.Y.)* **1969**, *17*, 213. Meyers, A. I.; Singh, H. *J. Org. Chem.* **1968**, *33*, 2365. Shome, M.; Smith, P. W.; Southam, R. M.; Oxford, A. W. *Tetrahedron Lett.* **1980**, *21*, 2927.

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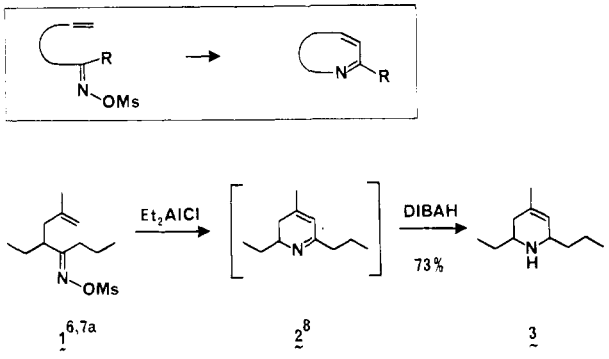
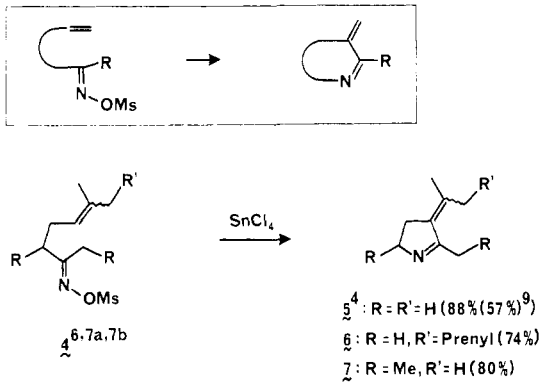
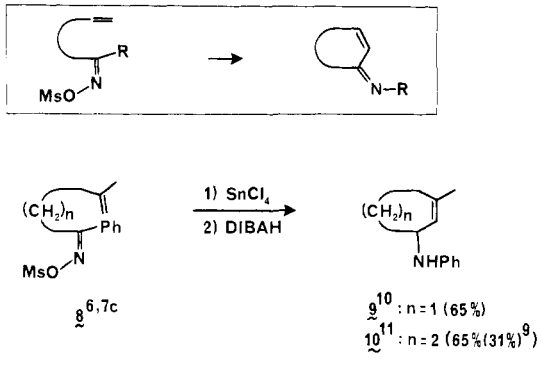
Scheme I. Endo(B)-Endo



Scheme II. Endo(B)-Exo



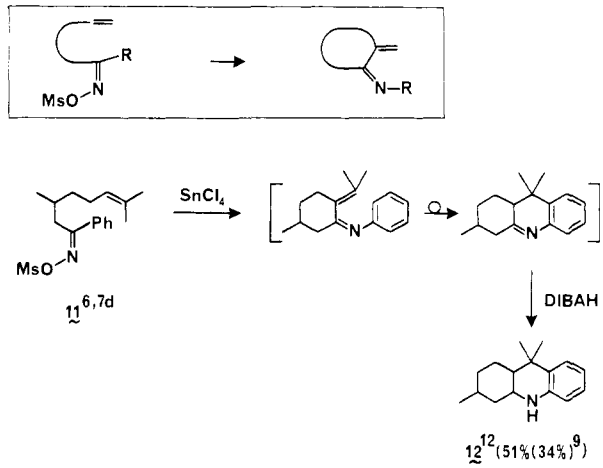
Scheme III. Exo(B)-Endo



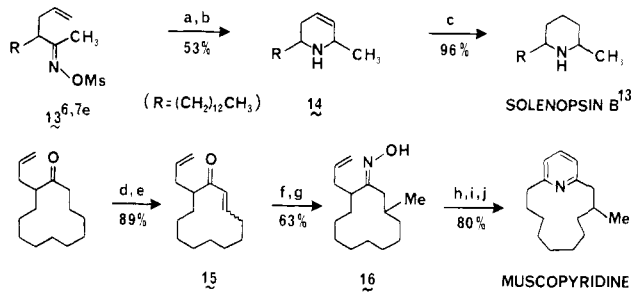
We began our studies by developing a method for efficient chemoselective activation of oxime derivatives in the presence of olefinic linkages. *In fact, the lack of a satisfactory functional group for such selective activation is presumably why this type of reaction has never been developed to a useful level.*[4] The use of oxime methanesulfonates was quickly found to be promising[5,6] because of their high reactivity and easy accessibility by simple treatment of oximes with methanesulfonyl chloride–triethylamine at −20 °C, which we introduced recently.[5]

A priori, four distinct cyclization modes are possible in these systems. Since the Beckmann rearrangement proceeds by mi-

Scheme IV. Exo(B)-Exo



Scheme V



[a] Et_2AlCl. [b] DIBAH. [c] H_2-Pd/C. [d] *i*-Pr_2NLi, PhSeBr. [e] 30% H_2O_2. [f] Me_2CuLi. [g] H_2NOH·HCl, NaOH. [h] MsCl, NEt_3. [i] Me_3SiOTf. [j] MnO_2, NEt_3.

(3) This work was presented by H. Y. at the 4th International Conference on Organic Synthesis (IUPAC), Tokyo, Aug 1982.

(4) The P_2O_5 promoted cationic cyclization of 6-methyl-5-hepten-2-one oxime under forcing conditions was previously reported. See: Wallach, O. *Justus Liebigs Ann. Chem.* **1901**, *319*, 77. Wagner-Jauregg, T.; Roth, M. *Helv. Chim. Acta* **1962**, *45*, 771. The structure of the cyclization product was recently reexamined and corrected to be **5** by Gawley. See: Gawley, R. E.; Termine, E. J.; Onan, K. D. *J. Chem. Soc., Chem. Commun.* **1981**, 568. For the choice of Lewis acids in the similar reactions, see: Gawley, R. E.; Termine, E. J. *Tetrahedron Lett.* **1982**, *23*, 307.

(5) Hattori, K.; Matsumura, Y.; Miyazaki, T.; Maruoka, K.; Yamamoto, H. *J. Am. Chem. Soc.* **1981**, *103*, 7368.

(6) Noncrystalline oxime mesylates may be conveniently stored at −20 °C or as a CH_2Cl_2 solution at 0 °C.

(7) The parent oximes can be prepared according to one of the following methods: (a) alkylation of lithium enolates followed by oximation of the resulting α-alkyl ketones; (b) oximation of commercially available ketones, and chromatographic separation of the anti and syn oximes; (c) alkylation of acetophenone oxime dianion (Jung, M. E.; Blair, P. A.; Lowe, J. A. *Tetrahedron Lett.* **1976**, 1439); (d) oximation of the ketone derived from citronellal and chromatographic separation of the anti and syn isomers; (e) oximation of 3-allyl-2-hexadecanone [derived from alkylation of ethyl acetoacetate dianion (Huckin, S. N.; Weiler, L. *J. Am. Chem. Soc.* **1974**, *96*, 1082) followed by decarboxylation] and chromatographic separation of the anti and syn oximes.

(8) The clean formation of **2** was observed in the NMR tube upon treatment of **1** in $CDCl_3$ with Et_2AlCl. Attempted isolation of **2** was unsuccessful with some decomposition.

(9) The values in parentheses refer to the yields by the use of Et_2AlCl.

(10) An independent synthesis of **9** via an alternate route aided our analysis.

(11) The experimental procedure for the Beckmann-rearrangement-promoted cyclization is given in detail here: To a solution of the oxime mesylate **8** (n = 2; 281 mg, 1 mmol) in CH_2Cl_2 (10 mL) was added $SnCl_4$ (0.13 mL, 1.1 mmol) at −20 °C under argon atmosphere. After 5 min, the mixture was stirred at 0 °C for 1 h, poured into a 10% NaOH solution (30 mL), and extracted with CH_2Cl_2 (3 × 15 mL). The combined extracts were dried over Na_2SO_4, concentrated to ~10 mL, and treated with DIBAH (4 mL of a 1 M hexane solution, 4 mmol) at 0 °C for 1 h. The reaction was terminated by dilution with CH_2Cl_2 (~20 mL) followed by sequential treatment with NaF (672 mg, 16 mmol) and H_2O (0.22 mL, 12 mmol) at 0 °C. The resulting suspension was vigorously stirred at 25 °C for 30 min. Filtration by the aid of CH_2Cl_2 and removal of solvent left an oil, which was purified by column chromatography on silica gel (1:20 ether–hexane) to give *N*-(3-methyl-2-cyclohexenyl)aniline (**10**; 121 mg, 65% yield) as a colorless oil.

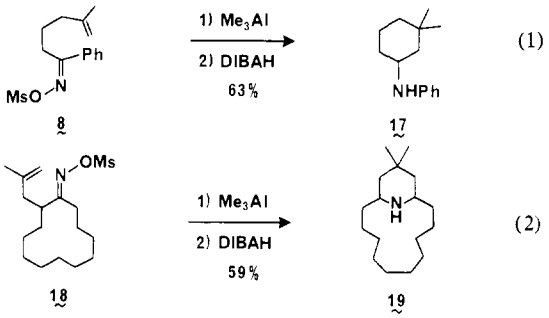
(12) An alternative mechanism that involves the capture of the intermediary carbocation by the neighboring phenyl group leading to the tricyclic compound may also be considered.

grating the group anti to the departing sulfonate group in either an endocyclic or an exocyclic mode to the so-formed ring, we refer to them as endo(B) and exo(B) rearrangements, respectively. Further, when the breaking double bond is endocyclic to the so-formed ring, we refer to them as suffix endo and exo correspondingly. Thus, four possible cyclization modes are endo(B)-endo, endo(B)-exo, exo(B)-endo, and exo(B)-exo as depicted in Scheme I–IV each of which also illustrates the representative examples. Another example of the endo(B)-exo cyclization by use of an oxime–P_2O_5 system was previously reported by Gawley.[4]

The following features of our new process are noteworthy: (1) The reaction proceeds at low temperature in aprotic solvent (CH_2Cl_2) with only 1 equiv of Lewis acid. (2) Aliphatic and aromatic ketones with acyclic and cyclic structures are equally employable. (3) The products are easily predictable, since our mild reaction conditions are free from the complicated syn/anti equilibrium of oximes. (4) Both carbocyclic and heterocyclic structures are prepared efficiently via exo(B) and endo(B) cyclizations, respectively.

Two unusually short syntheses illustrated in Scheme V heavily depend on our new process. Thus, solenopsin B was prepared in two steps from a simple acyclic precursor.[13] The similar endo(B) cyclizations provided a direct entry to a variety of heterophanes from macrocyclic ketones as illustrated in the facile synthesis of muscopyridine. The requisite oxime **16** was readily available from 2-allylcyclododecanone in four steps.[14] Reaction of **16** with MsCl (1.1 equiv)–NEt_3 (1.5 equiv) in CH_2Cl_2 at −20 °C for 30 min produced the corresponding oxime mesylate quantitatively, which was converted cleanly to muscopyridine (80% yield) as the sole product by treatment with Me_3SiOTf (1.1 equiv)[15] in $CHCl_3$ at 25 °C for 1.5 h followed by exposure with active MnO_2 (20 equiv)[16] in the presence of NEt_3 (5 equiv) at 50 °C for 1.5 h.[17]

Up to this point the cyclization was terminated by the deprotonation, yielding α,β-unsaturated imines. The intermediary cations, however, may also be captured by carbon nucleophiles to afford saturated imines. Initial efforts are given in eq 1 and 2. Treatment of a solution of the oxime mesylate **8** (n = 2) in



CH_2Cl_2 with Me_3Al (4 equiv) at 25 °C for 1 h followed by reduction with DIBAH (3 equiv) produced the methylated product **17** in 63% yield.[18] Similarly, the amine **19** was obtained in 59% yield from the oxime mesylate **18**.[19] It should be noted that neither **17** or **19** may be synthesized in a single operation by an alternative method.[2]

Acknowledgment. This work was supported by the Ministry of Education, Japanese Government (Grant-In-Aids 57102008 and 57118006).

Registry No. (*E*)-**1**, 84099-04-7; **2**, 84099-05-8; **3**, 84099-06-9; (*E*)-**4** (R = R′ = H), 84099-07-0; (*E*,*X*)-**4** (R = H; R′ = prenyl), 84099-08-1; (*E*)-**4** (R = Me; R′ = H), 84099-09-2; **5**, 5194-85-4; **6**, 84099-10-5; **7**, 84099-11-6; (*E*)-**8** (n = 1), 84099-12-7; (*E*)-**8** (n = 2), 84099-13-8; **9**, 84099-14-9; **10**, 84099-15-0; (*E*)-**11**, 84099-16-1; **12**, 84099-17-2; **12** (4a,10-didehydro), 84099-18-3; (*E*)-**13**, 84099-19-4; **14**, 84099-20-7; **14** (1,2-didehydro), 84099-21-8; (±)-**15**, 84099-22-9; **16**, 84099-23-0; **16** (mesylate), 84099-24-1; **17**, 84099-25-2; **18**, 84099-26-3; **19**, 84099-27-4; **19** (1,16-didehydro), 84099-28-5; (*Z*)-3-(phenylimino)-1-methylcyclopentene, 84099-29-6; (*Z*)-3-(phenylimino)-1-methylcyclohexene, 84099-30-9; (±)-2-allylcyclododecanone, 84099-31-0; 2-allyl-12-(phenylselenyl)cyclododecanone, 84099-32-1; 2-allyl-11-methylcyclododecanone, 84099-33-2; 1,16-dihydromuscopyridine, 84099-34-3; (±)-muscopyridine, 56912-83-5; solenopsin B, 32778-77-1; *cis*-2-methyl-6-tridecylpiperidine, 35285-26-8; (*Z*)-1-isopropylidene-4-methyl-2-(phenylimino)cyclohexane, 84099-35-4.

Supplementary Material Available: Spectroscopic data for new compounds described in this paper (1 page). Ordering information is given on any current masthead page.

(13) Solenopsin B possesses the trans structure. The ratio of cis/trans isomers was determined by GC assay (silicone OV-101, 185 °C) to be 46:54: t_r of the cis isomer = 14.55 min; t_r of the trans isomer = 16.55 min. See: Matsumura, Y.; Maruoka, K.; Yamamoto, H. *Tetrahedron Lett.* **1982**, *23*, 1929.

(14) The syn oxime was produced in 33% yield. The stereochemical assignments for **16** and its syn isomer are tentative and based in part on ^1H NMR analysis according to ref 7c.

(15) A number of Lewis acids were screened for a new pyridine synthesis by using 2-allylcyclododecanone oxime mesylate as a substrate and active MnO_2 as an oxidant. The yields of [10](2,6)pyridinophane thus obtained follow: Et_2AlCl (39%); $SnCl_4$ (65%); Me_3SiI (68%); Me_3SiOTf (80%).

(16) It should be worthy of note that active MnO_2 was the reagent of choice and other oxidizing agents (DDQ, O_2, H_2O_2–$FeCl_3$, Br_2, etc.) gave less satisfactory results.

(17) The spectra of the synthetic muscopyridine were identical in all respects with those of the authentic specimen, which are kindly provided from Dr. K. Utimoto.

(18) In addition to the methylated amine **17**, the deprotonated amine **10** was produced in 8% yield.

(19) The yield of the deprotonated product was 19%.

A New Approach to Construction of Artificial Monolayer Assemblies

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Preparation of artificial supermolecular organizates represents an important new goal of modern chemistry. Within this framework, the study of monolayer assemblies and their applications has expanded tremendously in recent years, encompassing now a wide variety of subjects ranging from biological membranes to solid-state electronic devices.[1] Modern film-building techniques have evolved; however, the basic approach common to all of them is still that devised by Langmuir and Blodgett (LB) some 50 years ago.[2] Although the LB procedure is powerful as a tool for handling molecular entitites, it suffers from some inherent drawbacks, mainly due to the extensive use of mechanical manipulation in the formation and transfer of the monolayer films.[3]

We are hereby describing a different approach to assembling of artificial layered structures based on self-association and self-organization of molecules occurring spontaneously at solid–fluid interfaces. Our approach takes advantage of the possibility of obtaining oriented compact monolayers by adsorption of amphiphiles from a fluid (solution, melt, or vapor) onto a polar solid surface contacting the fluid phase.[4] We have recently shown that under suitable conditions adsorption may be used to prepare organized mixed monolayers of several components (including dyes

(1) See for example: Kuhn, H.; Möbius, D.; Bücher, H. In "Techniques of Chemistry"; Weissberger, A., Rossiter, B. W., Eds.; Wiley: New York, 1972; Vol. 1, Part IIIB, pp 577–702. Vincett, P. S.; Roberts, G. G. *Thin Solid Films* **1980**, *68*, 135.

(2) Blodgett, K. B. *J. Am. Chem. Soc.* **1935**, *57*, 1007. Blodgett, K. B.; Langmuir, I. *Phys. Rev.* **1937**, *51*, 964.

(3) Gaines, G. L., Jr. *Thin Solid Films* **1980**, *68*, 1. Honig, E. P. *J. Colloid Interface Sci.* **1973**, *43*, 66. Kopp, F.; Fringeli, U. P.; Mühlethaler, K.; Günthard, Hs. H. *Biophys. Struct. Mech.* **1975**, *1*, 75.

(4) Bigelow, W. C.; Pickett, D. L.; Zisman, W. A. *J. Colloid Sci.* **1946**, *1*, 513. Levine, O.; Zisman, W. A. *J. Phys. Chem.* **1957**, *61*, 1068. Bigelow, W. C.; Brockway, L. O. *J. Colloid Sci.* **1956**, *11*, 60. Bartell, L. S.; Ruch, R. J. *J. Phys. Chem.* **1956**, *60*, 1231; **1959**, *63*, 1045.

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