space limiting the sizes of the product molecules.

Molecular shape-selective catalysis was first reported by Weisz and Frilette in 1960.[8] With zeolite A, which has a pore opening of ~5 Å in diameter, straight-chain molecules such as normal paraffins, normal olefins, straight-chain primary alcohols, etc., were selectively converted in the presence of their branched isomers. The latter, because their molecular dimensions exceeded those of the catalyst's pore openings, could not enter the zeolite and react. Similarly, only straight-chain molecules small enough to diffuse out of the zeolite appeared as products.

ZSM-5 has pore openings made of 10-membered oxygen rings[2] with dimensions intermediate between the 8- and 12-membered rings in zeolite A and faujasite, respectively. The fact that ZSM-5 sorbs monocyclic hydrocarbons and excludes molecules with critical dimensions larger than that of 1,3,5-trimethylbenzene[9] suggests the possibility of shape-selective reactions among aromatic molecules.

Although all three xylene isomers can enter the pore of ZSM-5, diffusion measurements indicate that the diffusivity of *p*-xylene is $>10^3$ times faster than that of *o*- and *m*-xylenes. With the regular ZSM-5 crystals, which are $<0.5\ \mu$m in size, the isomer distribution of C_8 aromatics produced catalytically from the alkylation of toluene with methanol and the disproportionation of toluene showed essentially an equilibrium distribution of the xylene product composed of 54% meta, 23% ortho, and 23% para at 500 °C.[10] When the crystal size of ZSM-5 was increased to 3 μm, the diffusional path length was increased, and *p*-xylene was produced in excess of its equilibrium yield as shown by the data in Table I.

The diffusional characteristics of ZSM-5 could be modified even more significantly by treatment with a variety of chemical reagents. With these chemically modified zeolites we have achieved para selectivity as high as 97% for the toluene alkylation reaction. Similarly, high para selectivity has been achieved in the toluene disproportionation reaction to produce benzene and *p*-xylene as the principal products.

Selected results summarized in Table II show 88–97% concentrations of the para isomer in the xylene product. Modification with phosphorus was made by impregnating the zeolite crystals with aqueous phosphoric acid. Elemental analysis showed that 8.5% phosphorus was present. The magnesium-modified catalyst was prepared by impregnating with aqueous magnesium acetate and had a magnesium content of ~11% by weight. It is proposed that these chemical treatments function in part by reducing the pore openings and channel dimensions of the ZSM-5 crystals, favoring the formation of the para isomer and permitting it and small molecules to diffuse out of the catalyst at a rapid rate.

These results provide the basis for the development of a new class of stereospecific catalytic processes for the production of para-substituted aromatic hydrocarbons of importance to the petrochemical industry. *p*-Xylene, for example, with an annual production capacity exceeding 5 billion pounds in the United States, is oxidized to terephthalic acid, a major component of polyester fibers. Presently, *p*-xylene is produced by isomerizing a C_8 aromatic concentrate to an equilibrium mixture of xylene isomers, separating a portion of the para isomer from the mixture, and recycling the remaining ortho/meta rich stream back through the isomerization step to reach equilibrium again, etc. The process is complex and costly. Direct production of the desired para isomer offers a potentially simpler process.

Acknowledgment. We thank A. B. Schwartz and his coworkers, for supplying the zeolite samples used in this study, and also acknowledge contributions made to various phases of the above work by S. A. Butter, C. Chu, R. H. Daniels, J. M. Ross, B. Weinstein, and L. B. Young.

References and Notes

(1) Argauer, R. J.; Landolt, G. R. U.S. Patent 3 702 886, 1972.
(2) Kokotailo, G. T.; Lawton, S. L.; Olson, D. M.; Meier, W. M. *Nature (London)* **1978**, *272*, 437.
(3) Venuto, P. B.; Hamilton, L. A.; Landis, P. S.; Wise, J. J. *J. Catal.* **1966**, *4*, 81.
(4) Venuto, P. B.; Hamilton, L. A.; Landis, P. S. *J. Catal.* **1966**, *5*, 484.
(5) Yashima, T.; Ahmad, H.; Yamazaki, K.; Katsuta, M.; Hara, N. *J. Catal.* **1970**, *16*, 273.
(6) Kaeding, W. W.; Jurewicz, A. J.; Butter, S. A. U.S. Patent 3 894 107, 1975.
(7) Chang, C. D.; Silvestri, A. J. *J. Catal.* **1977**, *47*, 249.
(8) Weisz, P. B.; Frilette, V. J. *J. Phys. Chem.* **1960**, *64*, 382.
(9) Chen, N. Y.; Garwood, W. E. *J. Catal.* **1978**, *52*, 453.
(10) Taylor, J. W.; Wagman, D. D.; Williams, M. G.; Pitzer, K. S.; Rossini, F. D. *J. Res. Natl. Bur. Stand. U.S.A.* **1946**, *37*, 95.

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Received April 2, 1979

Intriguing Aspects of 1,2-Dialkyldimolybdenum and -ditungsten (M≡M) Chemistry

Sir:

Both historically[1] and commercially[2] σ-alkyl complexes have played a prominent role in the development of mononuclear organo transition metal chemistry. Our syntheses[3] of *anti*-1,2-dichlorotetradimethylamido compounds, $M_2Cl_2(NMe_2)_4$ (M≡M, M = Mo, W), affords the opportunity of attempting to prepare 1,2-dialkyltetradimethylamido compounds by use of the general metathetic reaction

$$M_2Cl_2(NMe_2)_4 + 2LiR \xrightarrow[-78\ °C]{\text{toluene}} M_2R_2(NMe_2)_4 + 2LiCl \qquad (1)$$

Compounds of the form $M_2R_2(NMe_2)_4$ allow an investigation of the reactivity patterns of σ-alkyl groups bonded to the simplest of metal clusters, namely dimetal centers. We here report our extended[4] syntheses of compounds of the general formula $M_2R_2(NMe_2)_4$ and, in particular, describe their reactivity patterns toward carbon dioxide and *tert*-butyl alcohol with special attention being given to the labeled compounds $M_2(CH_2CD_3)_2(NMe_2)_4$.

From reaction 1 we have obtained $M_2R_2(NMe_2)_2$ compounds for both M = Mo and M = W where R = CH_3, CH_2CH_3, CH_2CD_3, $CH_2CH_2CH_2CH_3$, $CH(CH_3)_2$, CH_2CMe_3, CH_2SiMe_3, and CMe_3.[5] Purification of these compounds followed the following general procedure: (1) the reaction mixture was warmed slowly to room temperature whereupon the solvent was stripped; (2) hexane was added and the solution was filtered using a medium frit with standard Schlenk techniques; (3) the hexane solvent was again stripped and the residue was purified by sublimation (80–100 °C, 10^{-6} cm Hg) to give yellow-orange (M = Mo) or orange-red solids (M = W). When R = *n*-butyl, the compounds were liquids at room temperature and were purified by vacuum distillation.

In all cases the ^1H NMR spectra of the $M_2R_2(NMe_2)_4$ compounds obtained in toluene-d_8 solution at −60 °C (100 or

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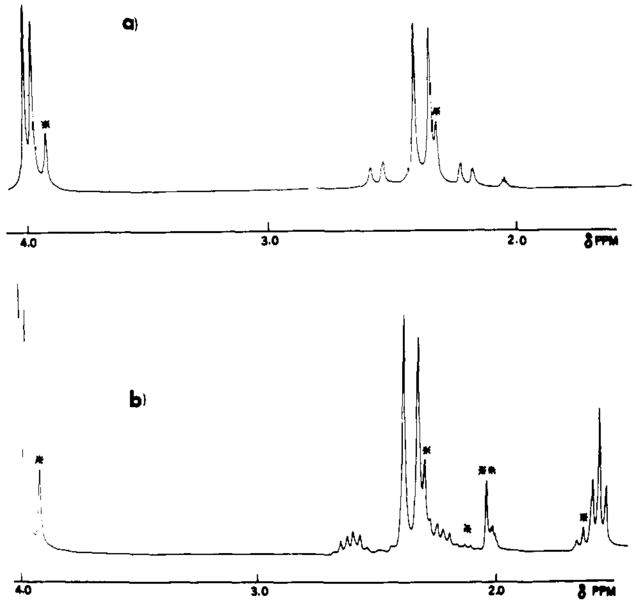

Figure 1. ^1H NMR spectra recorded at 270 MHz, −61 °C in toluene-d_8 of (a) *, anti and gauche, $Mo_2(CH_2CD_3)_2(NMe_2)_4$, and (b) *, anti and gauche, $Mo_2(CH_2CH_3)_2(NMe_2)_4$. ** represents residual protonated toluene.

270 MHz) showed a mixture of anti and gauche 1,2-dialkyl rotamers. The gauche rotamer was always the predominent rotamer and, rather interestingly, as the bulk of the alkyl group increases $CH_3 \rightarrow CH_2CMe_3$ so the predominance of the gauche rotamer increases.[6] At −60 °C rotations about M-N bonds are restricted leading to proximal and distal *N*-methyl resonances.[7] A mixture of *anti*- and *gauche*-$M_2R_2(NMe_2)_4$ should have a total of three proximal and three distal *N*-methyl resonances.[8]

The thermal stability of these compounds is quite remarkable and the stability of the isopropyl and *tert*-butyl compounds[9] with respect to isomerization to *n*-propyl and isobutyl ligands, respectively, implies that β-hydrogen elimination is either kinetically or thermodynamically not favorable. This is also implied by our observation that, when $LiCH_2CD_3$[10] is used in reaction 1, the resultant 1,2-diethyl compounds retain their ^2H atoms exclusively in the β position: $M_2(CH_2CD_3)_2(NMe_2)_4$. Figures 1a and 1b compare the ^1H NMR spectra of the labeled, CH_2CD_3-containing compound and the protio compound, respectively.

In hydrocarbon solutions *all* of the above compounds react with CO_2 to give selective insertion into the metal-nitrogen bond.[11] The β-elimination stabilized alkyls of *both* molybdenum and tungsten react according to

$$M_2R_2(NMe_2)_4 + CO_2 \text{ (excess)} \rightarrow M_2R_2(O_2CNMe_2)_4 \quad (2)$$

In this reaction the M-M triple bond is retained.[12] However, rather interestingly, the non-β-hydrogen elimination stabilized alkyls of dimolybdenum and ditungsten react quite differently. The molybdenum compounds react according to

$$\underset{(M\equiv M)}{Mo_2(R)_2(NMe_2)_4} + CO_2 \text{ (excess)} \rightarrow \underset{(M\equiv M)}{Mo_2(O_2CNMe_2)_4} + R\text{—}H + \text{1-alkene} \quad (3)$$

Reaction of the labeled compound $Mo_2(CH_2CD_3)_2(NMe_2)_4$ with CO_2 in benzene in a sealed NMR tube led to the specific formation of $CD_2{=}CH_2$ and CH_2DCD_3 as determined by ^2H NMR. See Figure 2a. The ^2H spectrum of the ethylene, $CD_2{=}CH_2$, showed the predicted splitting based on the ^1H-^1H couplings reported for ethylene and the known magnitudes of the gyromagnetic ratios of ^1H and ^2H.[14] As a further check, we purchased[15] $CD_2{=}CH_2$, *trans*-$CHD{=}CHD$, and *cis*-$CHD{=}CHD$ and recorded their ^2H spectrum in benzene; the observed splittings agreed well with those predicted[14] and thus confirmed unequivocally the formation of exclusively[16] $CD_2{=}CH_2$ in reaction 3 for R = CH_2CD_3. To check the ^2H spectrum of CH_2DCD_3 in benzene, we prepared a sample by the addition of D_2O to a solid sample of $LiCH_2CD_3$ using a vacuum manifold followed by condensation into an NMR tube. The ^2H spectrum of the gaseous products showed the same pattern for CH_2DCD_3 and, moreover, revealed that some ethylene, specifically $CD_2{=}CH_2$, is formed when D_2O is added to anhydrous $LiCH_2CD_3$ in a vacuum manifold.[17]

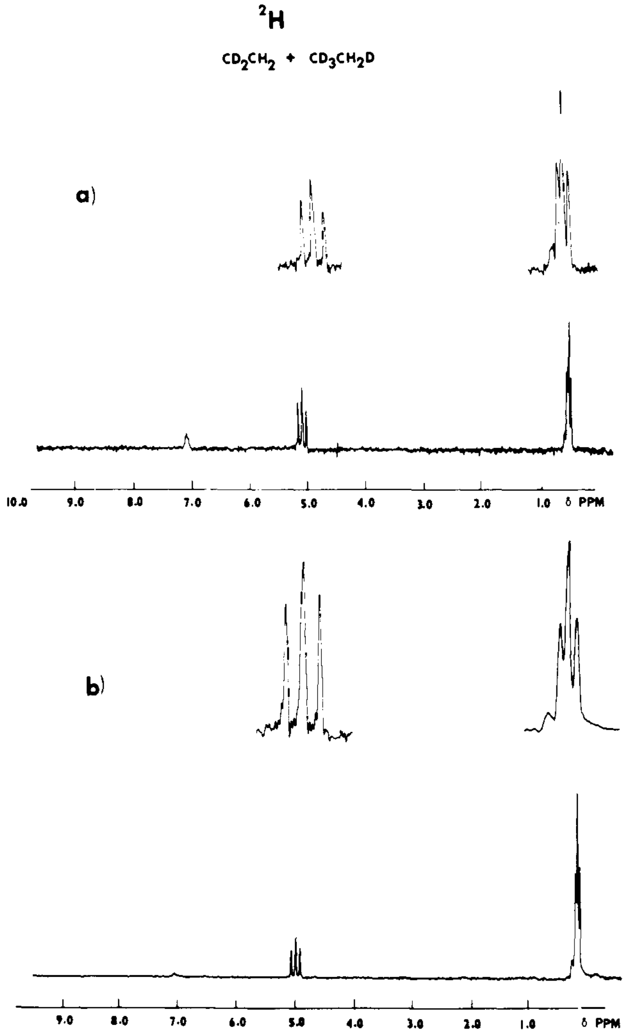

Figure 2. ^2H NMR spectra recorded at 16 °C and 33.77 MHz of the gases formed in the reactions of (a) CO_2 with $Mo_2(CH_2CD_3)_2(NMe_2)_4$ and (b) D_2O with $LiCH_2CD_3$. Both spectra were recorded in benzene. The scale expansions shown in a and b are not the same.

In a separate experiment, a mixture of $Mo_2(CH_2CH_3)_2(NMe_2)_4$ and $Mo_2(CH_2CD_3)_2(NMe_2)_4$ in benzene was reacted with CO_2 in a sealed NMR tube. The ^2H NMR spectrum was identical with that shown in Figure 2a. Thus, within the limits of NMR detection, CH_2DCD_3 was the only deuterated ethane present.[16]

When CO_2 is added to a hydrocarbon solution of $W_2(C_2H_5)_2(NMe_2)_4$, a green-blue tungsten containing precipitate is formed and *only* ethane is evolved. Using the labeled $W_2(CH_2CD_3)_2(NMe_2)_4$, the ethane appears by ^2H NMR spectroscopy to be predominantly CH_3CD_3. The fate of the ethylene and the nature of tungsten compounds are presently unknown.

Reactions of these $M_2R_2(NMe_2)_4$ compounds with alcohols are dependent on the nature of (i) the alkyl group R, (ii) the alcohol, and (iii) the metal, Mo or W. For example, $M_2(CH_3)_2(NMe_2)_2$ compounds (M = Mo, W) both react with *tert*-butyl alcohol to give $M_2(CH_3)_2(OBu^t)_4$ compounds. However, addition of Pr^iOH to $Mo_2(CH_3)_2(NMe_2)_4$ yields $Mo_2(OPr^i)_6$ ($M{\equiv}M$) and CH_4 (2 equiv). The analogous reaction involving $W_2(CH_3)_2(NMe_2)_4$ has not yet been carried out, but it is known that attempts to prepare $W_2(OPr^i)_6$ have led to $W_4(\mu\text{-}H)_2(OPr^i)_{14}$.[18] The reaction of $Mo_2(C_2H_5)_2(NMe_2)_4$ with Bu^tOH yielded $Mo_2Et(OBu^t)_5$ and ethane.[4b] Using the labeled compound $Mo_2(CH_2CD_3)_2(NMe_2)_4$, we find that addition of Bu^tOH causes the exclusive[16] elimination of CH_2DCD_3. The resulting ethyl ligand in $Mo_2(C_2H_3D_2)(OBu^t)_5$ contains a statistical distribution of deuteriums on the α and β carbons, namely integration indicates that $\alpha{:}\beta = 2{:}3$.

The purpose of this communication is to draw attention to the intriguing chemistry associated with alkyl groups coordinated to the dimolybdenum or ditungsten ($M{\equiv}M$) centers. (1) In $M_2R_2(NMe_2)_4$ compounds, β-hydrogen elimination is either kinetically or thermodynamically not favorable. (2) Addition of CO_2 to $Mo_2(CH_2CH_3)_2(NMe_2)_4$ ($M{\equiv}M$) leads to formation of $Mo_2(O_2CNMe_2)_4$ ($M{\equiv}M$) by an intramolecular mechanism. It seems likely that this involves an initial irreversible β-hydrogen elimination which is then followed by C–H reductive elimination. However, it is not known at what step during CO_2 insertion that this process occurs, nor is it known whether C–H reductive elimination occurs across the M—M triple bond, $H—M{\equiv}M—Et \rightarrow M{\equiv}M + Et—H$, or via an oxidative addition–reductive elimination process at one metal center, $M^{II}{\equiv}M^{IV}(H)(Et) \rightarrow M^{II}{\equiv}M^{II} + Et—H$. (3) That $W_2(C_2H_5)_2(NMe_2)_4$ should react so differently with CO_2 is also fascinating, and once again points to the elusive nature of $W_2(O_2CX)_4$ ($M{\equiv}M$) compounds.[19] (4) Addition of Bu^tOH to $Mo_2(CH_2CD_3)_2(NMe_2)_4$ which leads to $Mo_2(C_2H_3D_2)(OBu^t)_5$ and CH_2DCD_3 implies that alcoholysis, as with CO_2 insertion (2 above), once again facilitates an irreversible β-hydrogen process which is then followed by C–D reductive elimination. This further implies that formation of the σ-ethyl ligand arises from $CH_2{=}CD_2$ and $Bu^tO—H$. The statistical distribution of H/D atoms over the α and β carbons in the σ-ethyl ligand thus formed is consistent with a then reversible β-hydrogen elimination process favoring the coordinated ethyl ligand:

$$M—H + C_2H_4 \rightleftharpoons M—C_2H_5$$

While all these observations raise intriguing mechanistic questions which cannot be answered at this time, we do note that our observations have at least one parallel with mononuclear transition metal alkyl chemistry: reductive elimination involving C—H bond formation is more facile than reductive elimination involving C—C bond formation.[20]

Acknowledgments. We thank the Office of Naval Research for support of this work. The ^1H NMR spectrum shown in Figure 1a was obtained through the courtesy of Mr. Dean Katahira at Yale University. Mass spectral data were kindly obtained for us by Mr. Peter Cook and Professor D. C. Bradley at Queen Mary College, London.

References and Notes

(1) (a) G. Wilkinson, *Science*, **185**, 109 (1974); (b) M. F. Lappert, P. J. Davidson, and R. Pearce, *Acc. Chem. Res.*, **7**, 209 (1974); (c) R. R. Schrock and G. W. Parshall, *Chem. Rev.*, **76**, 243 (1976).
(2) J. K. Kochi in "Organometallic Mechanisms and Catalysis", Academic Press, New York, 1978.
(3) M. Akiyama, M. H. Chisholm, F. A. Cotton, M. W. Extine, and C. A. Murillo, *Inorg. Chem.*, **16**, 2407 (1977).
(4) (a) The preparation and structure of $Mo_2(CH_3)_2(NMe_2)_4$ has been reported: M. H. Chisholm, F. A. Cotton, M. W. Extine, and C. A. Murillo, *Inorg. Chem.*, **17**, 2338 (1978). (b) The preparation and reactivity of $Mo_2(C_2H_5)_2(NMe_2)_4$ was previously reported: M. H. Chisholm, D. A. Haitko, and C. A. Murillo, *J. Am. Chem..Soc.*, **100**, 6262 (1978).
(5) Satisfactory analytical data have been obtained. All compounds showed molecular ions in the mass spectrometer, $M_2R_2(NMe_2)_4^+$, and we thank Professor D. C. Bradley and Mr. Peter Cook at Queen Mary College for kindly obtaining these valuable spectra for us. This collaboration was promoted by a NATO grant to D.C.B. and M.H.C.
(6) We have no rationale for this observation; our intuition would have suggested the opposite trend.
(7) For an assignment of proximal and distal *N*-Me resonances, see M. H. Chisholm, F. A. Cotton, B. A. Frenz, W. W. Reichert, L. W. Shive, and B. R. Stults, *J. Am. Chem. Soc.*, **98**, 4469 (1976).
(8) For a detailed discussion, see the variable-temperature ^{13}C NMR studies carried out on $W_2(CH_3)_2(NEt_2)_4$: M. H. Chisholm, F. A. Cotton, M. W. Extine, M. Millar, and B. R. Stults, *Inorg. Chem.*, **15**, 2244 (1976).
(9) *tert*-Butyl transition metal complexes (and to a lesser extent isopropyl complexes) are relatively rare. See ref 2. The reversible β-H elimination from an alkyl metal complex *without* attendant reductive elimination of alkane was elegantly studied in alkyl gold(III) chemistry. The isomerization of *trans-tert*-butyldimethyl(triphenylphosphine)gold(III) proceeds spontaneously at 25 °C in ethereal solution to produce the *trans*-isobutyldimethyl(triphenylphosphine)gold(III) complex in *quantitative* yield. See A. Tamaki and J. K. Kochi, *J. Chem. Soc. Chem. Commun.*, 423 (1973).
(10) Prepared from the reaction between CD_3CH_2Br and Li shot in hexane and purified by sublimation at 65 °C, 10^{-6} cmHg. CD_3CH_2Br was obtained from Merck Sharp & Dohme.
(11) The mechanism of this insertion has been shown to proceed via an amine catalyzed sequence: M. H. Chisholm and M. W. Extine, *J. Am. Chem. Soc.*, **99**, 792 (1977).
(12) All these compounds show molecular ions in the mass spectrometer and are believed to be directly analogous to the structurally characterized diethylcarbamato analogue $W_2(CH_3)_2(O_2CNEt_2)_4$: M. H. Chisholm, F. A. Cotton, M. W. Extine, and B. R. Stults, *Inorg. Chem.*, **16**, 603 (1977).
(13) $Mo_2(O_2CNMe_2)_4$ is formed as a fine yellow precipitate in this reaction. It shows a strong molecular ion $Mo_2(O_2CNMe_2)_4^+$ and a doubly charged molecular ion $Mo_2(O_2CNMe_2)_4.^{2+}$ In all respects it appears like $Mo_2(O_2CR)_4$ compounds for which scores have been structurally characterized and all of which contain a Mo–Mo quadruple bond.
(14) From R. M. Lynden-Bell and N. Sheppard, *Proc. R. Soc. A.*, **269**, 1385 (1965): for ethylene $J_{cis}(^1H{-}^1H) = +11.7$, $J_{trans}(^1H{-}^1H) = 19.1$, and $J_{gem}(^1H{-}^1H) = +2.5$ Hz; $\gamma(^1H) = 2.675 \times 10^4$ radians/(s·G), $\gamma_{^2H} = 4.107 \times 10^3$ radians/s·G. Using this data it was possible to calculate the splittings of $CD_2{=}CH_2$, *trans*-CHD=CHD and *cis*-CHD=CHD. The calculated splittings were obtained by using the program entitled NMRCAL, a part of the Nicolet-80 system. For each of the isomeric dideuterioethylenes a centered three-line pattern was observed with the only apparent distinguishing characteristic being the separation between the outer lines. The calculated vs. observed splittings in hertz for each dideuterioethylene are as follows: 1,1-dideuterioethylene, 4.8 (4.8); 1,2-*cis*-dideuterioethylene, 3.3 (3.3); and *trans*-1,2-dideuterioethylene, 2.2 (2.2).
(15) From Merck Sharp & Dohme.
(16) By exclusively, we mean within the limits of NMR detection which is at least 95%.
(17) Alkyllithium and alkylaluminum compounds are well known to undergo β-H elimination under thermolysis[2] but we are not aware of anyone reporting the formation of ethylene upon the addition of water. It quite possibly is formed under our conditions because $LiCH_2CD_3$ is present in excess as D_2O is added and therefore thermolysis is a competitive reaction owing to local heating effects which accompany hydrolysis. See also B. J. Wakefield in "The Chemistry of Organolithium Compounds", Pergamon Press, Elmsford, N.Y., and Oxford, 1974, Chapter 15.
(18) M. Akiyama, D. Little, M. H. Chisholm, D. A. Haitko, F. A. Cotton, and M. W. Extine, *J. Am. Chem. Soc.*, **101**, 2504 (1979).
(19) A. Bino, F. A. Cotton, Z. Dosi, S. Koch, H. Kuepers, M. Millar, and J. C. Sekutowski, *Inorg. Chem.*, **17**, 3245 (1978).
(20) J. R. Norton, *Acc. Chem. Res.*, **12**, 139 (1979), and references therein.

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Received April 20, 1979

Stereospecific Total Synthesis of *dl*-Austamide

Sir:

Austamide (**1**) is a toxic metabolite of *Aspergillus ustus* whose isolation and structure elucidation was described by Steyn in 1971.[1] Herein we report the first stereospecific total synthesis of *dl*-austamide.

Austamide contains elements of great synthetic difficulty, possessing two labile enamide functionalities as well as the delicate ψ-indoxyl chromophore. In addition, it is necessary to control the relative stereochemistry of two asymmetric centers, one of which is located at a spiro ring junction. Our synthetic strategy is outlined in Scheme I. The cornerstone of

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