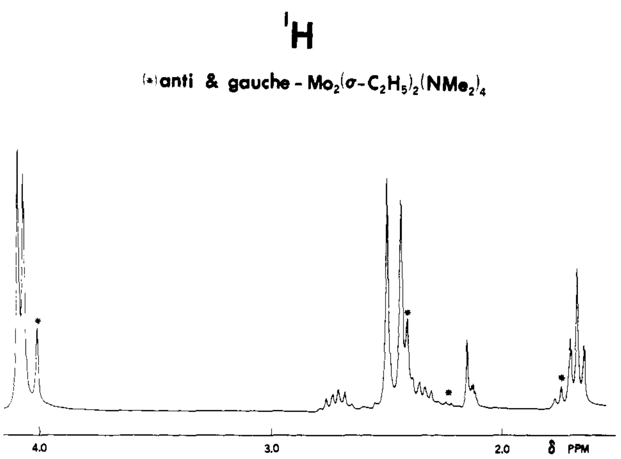

Figure 1. ^{1}H NMR spectrum of a mixture of anti and gauche $Et(Me_2N)_2Mo{\equiv}Mo(NMe_2)_2Et$ recorded in toluene-d_8 at −61 °C and 270 MHz.

ligand and two resonances in the ratio of 3:2 for the OBu^t groups.[8] This is consistent with an ethane-like molecule $(Bu^tO)_2(Et)Mo{\equiv}Mo(OBu^t)_3$ in which rotation about the $Mo{\equiv}Mo$ bond is rapid on the NMR time scale.[9]

$Mo_2Et_2(NMe_2)_4$ in toluene reacts rapidly with CO_2 ($\geq$4 equiv) to give a pale yellow finely divided precipitate. This compound has not been structurally characterized but is considered to be $Mo_2(O_2CNMe_2)_4$ and to have the dimolybdenum tetraacetate structure (M≣M)[10] on the following grounds: (i) analytical data,[11] (ii) infrared data,[12] and (iii) the appearance in the mass spectrum of a very strong ion corresponding to $Mo_2(O_2CNMe_2)_4{}^+$ (this is the ion of highest mass) and the doubly charged ion $Mo_2(O_2CNMe_2)_4{}^{2+}$. The compound is not appreciably soluble in hydrocarbon solvents, nor CD_2Cl_2, but is sparingly soluble in pyridine.[13]

In a sealed NMR tube reaction $Mo_2Et_2(NMe_2)_4$ in toluene-d_8 was reacted with CO_2 (>4 equiv). The finely divided precipitate was centrifuged to the top of the tube and the ^{1}H NMR spectrum of the clear, virtually colorless solution was recorded. The only proton signals observed corresponded to ethylene and ethane which were in the integral ratio of 4:6, respectively.[14] We conclude that the reaction between $Mo_2Et_2(NMe_2)_4$ and CO_2 proceeds stoichiometrically according to eq 1 and as such provides a model reaction for detailed studies of dinuclear reductive elimination.[15] A simple intramolecular mechanism involving an initial β-hydride elimination, $Et{-}Mo{\equiv}M{-}H + C_2H_4$, followed by C—H reductive elimination across the $Mo{\equiv}Mo$ bond, $Et{-}Mo{\equiv}Mo{-}H \rightarrow Et{-}H + Mo{≣}Mo$, satisfies all our observations.

In contrast to the above we find that $Mo_2Me_2(NMe_2)_4$ reacts with CO_2 according to eq 4.

$$Mo_2Me_2(NMe_2)_4 + 4CO_2 \rightarrow Mo_2Me_2(O_2CNMe_2)_4 \quad (4)$$

The compound $Mo_2Me_2(O_2CNMe_2)_4$[16] is of sufficient thermal stability to allow the detection of the molecular ion $Mo_2Me_2(O_2CNMe_2)_4{}^+$ in the mass spectrometer. In the solid state and in solution $Mo_2Me_2(O_2CNMe_2)_4$ is believed to share the $W_2Me_2(O_2CNEt_2)_4$ structure[17] which has a planar $C{-}W{\equiv}W{-}C$ unit with a C-W-W angle equal to 106°.

Acknowledgments. We thank the Office of Naval Research for support of this work and Professor D. C. Bradley, Queen Mary College, London, who through the auspices of a NATO Grant kindly provided mass spectral results.

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(4) For reductive elimination in mononuclear chemistry, see C. A. Tolman, *Chem. Soc. Rev.*, **1**, 357 (1972).

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(6) Found (calcd): C, 33.55 (33.79); H, 7.89 (8.04); N, 12.99 (13.15).

(7) See the structural and dynamic behavior of the related compound $W_2Me_2(NEt_2)_4$: M. H. Chisholm, F. A. Cotton, M. W. Extine, M. Millar, and B. R. Stults, *Inorg. Chem.*, **15**, 2244 (1976).

(8) Et group: $\delta(CH_2)$ 2.98, $\delta(CH_3)$ 1.78 (J_{HH} = 7.9 Hz). OBu^t groups at −76 °C: δ 1.60 and 1.56 in the integral ratio 3:2, respectively. Chemical shifts (δ) are given in parts per million downfield from Me_4Si.

(9) Accidental magnetic degeneracy could accout for the observed 3:2 spectrum (cf. predicted low-temperature limiting spectrum, 2:2:1).

(10) For a recent review of compounds containing M–N quadruple bonds, see F. A. Cotton, *Chem. Soc. Rev.*, **4**, 27 (1975). (b) The diethyl carbamate $Cr_2(O_2CNEt_2)_4{\cdot}(HNEt_2)_2$ has recently been structurally characterized and shown to have a Cr–Cr quadruple bond: M. H. Chisholm, F. A. Cotton, M. W. Extine, and D. C. Rideout, *Inorg. Chem.*, submitted for publication.

(11) Found (calcd): C, 26.23 (26.48); H, 4.25 (4.44); N, 10.09 (10.29).

(12) In particular the presence of a strong absorption at 1560 cm^{-1} assignable to $\nu(NCO_2)$ of a bridging bidentate carbamate ligand. See M. H. Chisholm and M. W. Extine, *J. Am. Chem. Soc.*, **99**, 782 (1977).

(13) ^{1}H NMR data recorded at 100 MHz, 25 °C in pyridine-d_5: $\delta(O_2CNMe_2)$ 2.93 ppm relative to Me_4Si.

(14) Found by weighing the traces 38–62. Any departure from the predicted ratio, 4:6, may be due to their differing solubilities or due to the inherent experimental error of weighing the cut traces.

(15) Labeling studies are planned in order to investigate (i) the reversibility of β-hydrogen elimination and (ii) the intra- vs. intermolecular nature of the reaction.

(16) Found (calcd): C, 29.50 (29.29); H, 5.14 (5.23); N, 9.65 (9.75).

(17) M. H. Chisholm, F.A. Cotton, M. W. Extine, and B. R. Stults, *Inorg. Chem.*, **16**, 603 (1977).

(18) Alfred P. Sloan Fellow, 1976–1978. Address correspondence to the Department of Chemistry, Indiana University, Bloomington, Ind. 47401.

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Stereoselective Total Synthesis of Racemic Kalafungin and Nanaomycin A

Sir:

Kalafungin (**1**)[1] and nanaomycins A (**2**)[2] and D (**1**)[3] are members of the naphthoquinone class of antibiotics, which also includes frenolicin[4] and griseusins A and B.[5] These natural products are potent antimicrobial agents, and the nanaomycins, in particular, have been shown[5] to be extremely active against mycoplasmas. In a recent publication,[6] Moore pointed out that these compounds have potential antineoplastic activity, as bioreduction may transform them into bisalkylating agents functioning similarly to the currently useful drug, mitomycin.[7] We wish to report the first total synthesis of kalafungin and of nanaomycins A and D.[8]

2-Allyl-5-methoxynaphthoquinone[9] was reduced with sodium hydrosulfite and alkylated with dimethyl sulfate and potassium hydroxide giving 2-allyl-1,4,5-trimethoxynaphthalene (**3**) (mp 37.5–39 °C)[10] in 70% yield (Scheme I). Osmium tetroxide-potassium chlorate[11] converted the allyl derivative into the corresponding diol, which was readily cleaved by periodate to give the aldehyde (**4**) (mp 80.5–92 °C)[10] in 80% overall yield. Titanium tetrachloride catalyzed reaction[12] of ketene ethyl *tert*-butyldimethylsilyl acetal with aldehyde **4** provided the hydroxy ester **5** in 50% yield. Oxidation of the dimethyl ether of the quinol was accomplished using ceric

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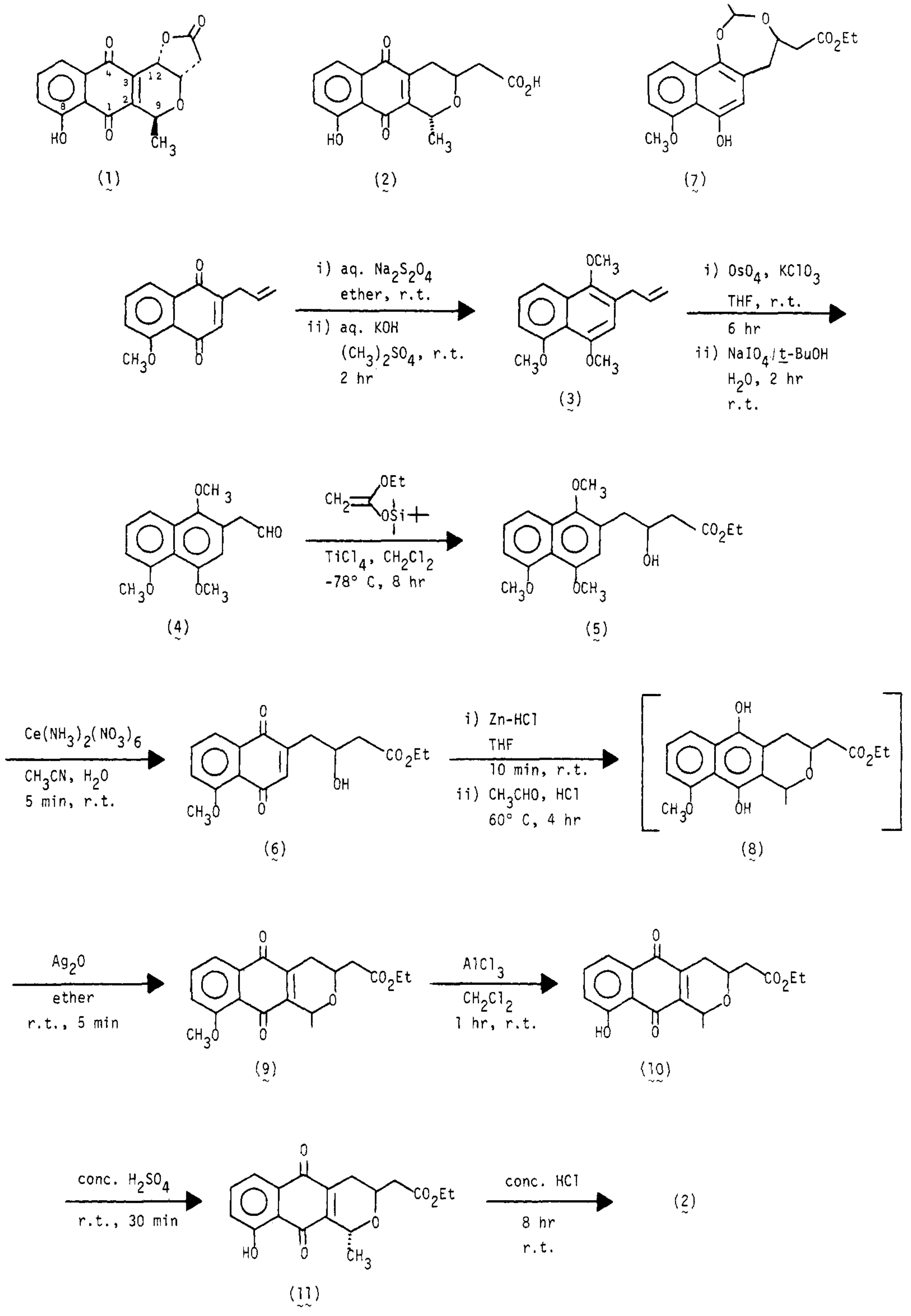
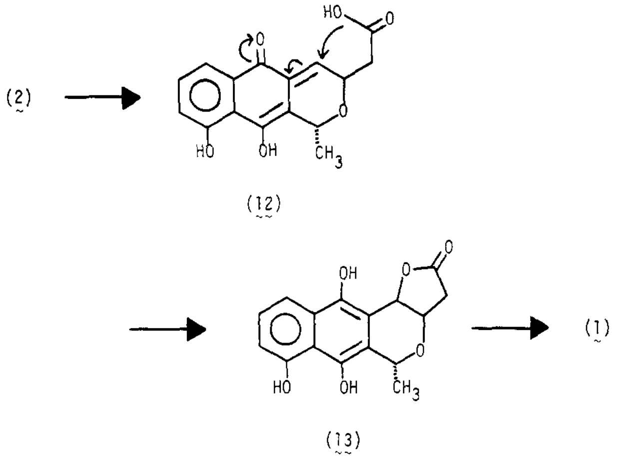
Scheme I



ammonium nitrate[13] furnishing the quinone **6** (mp 119.5–120.5 °C)[10] in 74% yield. Reduction of quinone **6** with zinc and hydrochloric acid gave the corresponding quinol, which, without purification, was treated with acetaldehyde and hydrochloric acid yielding an initial adduct. Based on NMR and mass spectral data,[14] as well as the fact that silver oxide oxidation of the adduct gave the starting quinone **6**, we concluded that this substance was the acetal **7**. Further treatment with acetaldehyde and hydrochloric acid led to the tricyclic product **8**,[8,9] which was oxidized quantitatively with silver oxide to the quinone **9** (mp 113–115 °C),[10] obtainable in 51% overall yield from the starting hydroxy ester **6**. The cis stereochemistry for the C_9 and C_{11} substituents of compound **9** was assigned on the basis of NMR studies.[15] Demethylation of the methyl ether **9** was achieved in 88% yield with aluminum chloride[16] giving the phenolic product **10** (mp 93–94 °C).[10] Concentrated sulfuric acid treatment caused epimerization at C_9 giving a 2:1 mixture[17] of the trans and cis isomers **11** and **10**, respectively, from which the pure trans isomer **11** (mp 134 °C)[10] was isolated by fractional recrystallization. By recycling of the mother liquor, **11** could be obtained in 70% yield from cis isomer **10**. Hydrolysis of the ethyl ester group was carried out in concentrated hydrochloric acid giving racemic nanaomycin A (**2**) (50%, mp 171–174 °C). Air oxidation of nanaomycin A has been reported to give nanaomycin D,[3] and indeed, treatment of our synthetic nanaomycin A with air in methanolic solution gave a racemic mixture of kalafungin and nanaomycin D (**1**)[3] (mp 135 °C dec). A plausible mechanism involves the quinone methide intermediate **12**[6] in the oxidative process. Intramolecular conjugate addition of the carboxylic acid into the enone would then give the quinol lactone **13**, which could be readily oxidized to give the quinone.



The IR, NMR, mass, and UV spectra, as well as the TLC behavior of the synthetic nanaomycin A and kalafungin–nanaomycin D, were indistinguishable from those of the respective natural products.[18]

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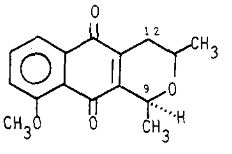
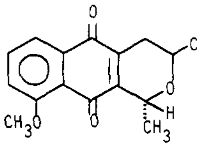


eleutherin



isoeleutherin

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Received May 17, 1978

Transverse Relaxation of Multiple Quantum Coherence in Nuclear Magnetic Resonance as a Probe of Molecular Motion

Sir:

The development of pulse techniques for observations of zero and multiple quantum (MQ) coherences in NMR[1-3] has opened new perspectives for relaxation studies of multilevel spin systems. Though not directly observable, MQ coherences may be stimulated by appropriately tailored pulses.[1-5] Their time evolution is characterized by a decay similar in kind to the transverse (T_2) decay of normal 1Q magnetizations, but the decay rates are quantitatively different. In combination with conventional longitudinal and transverse relaxation measurements, the MQ decay rates therefore provide a powerful tool for detailed studies of relaxation pathways and molecular dynamics. In this communication, we demonstrate the utility of double quantum line widths for the determination of spectral densities of motion in two single deuteron systems, $CDCl_3$ and $DC{\equiv}C{-}C{\equiv}N$, partially ordered in a nematic solvent.

The use of two-dimensional Fourier transform techniques[1,6,7] is essential for measurements of MQ decay rates in all but the very simplest[3,4] spin systems. After an initial excitation, the MQ coherences are allowed to evolve for a time t_1. The application of a "monitoring" pulse generates conventional (1Q) magnetizations with amplitudes which depend on the phases of the "invisible" coherences at $t = t_1$.[1,4] The free induction decay, which develops during the subsequent period t_2, yields the usual spectrum in a frequency domain F_2. A series of such spectra obtained at regular increments of t_1 may be subjected to a second Fourier transformation with respect to t_1. The modulation due to MQ coherences is thereby translated into resonance peaks in the frequency domain F_1.

The NMR spectrum of a single partially ordered deuteron consists[8] of two nondegenerate ($1 \rightarrow 0$ and $0 \rightarrow -1$) 1Q transitions at $\omega_0 \pm \omega_Q$. The double quantum (2Q) coherence of a simple three-level system may be readily excited[4] by a "soft" pulse applied at an offset $\Delta\omega$ from the center ω_0 of the doublet. Provided that $\Delta\omega \ll \omega_1 \ll \omega_Q$, the largest 2Q coherence is obtained for a pulse width $t_{p1} = \pi\omega_Q/2\omega_1{}^2$.[4] The monitoring pulse should ideally fulfill the condition $t_{p2} = \pi/2\omega_1$ with $\omega_1 \gg \omega_Q$. Alternatively, a weak ($\omega_1 \ll \omega_Q$) audiomodulated ($\omega_M \simeq \omega_Q$) monitoring pulse may be used.[9] Conditions for observation of the 2Q coherence for a single deuteron are not very stringent.[4] Any effect of spurious excitation of transverse 1Q magnetization by the first pulse may be suppressed by use of phase alternation.[5,10] Also, a monitoring pulse with $\omega_1 \simeq \omega_Q$ was found to be adequate.

An example of a two-dimensional spectrum of a liquid crystalline solution of DCCCN is shown in Figure 1. A section (540 Hz = 110 points) of the folded, phase corrected, 1Q

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