Table II. Ratio of Quantum Yields at Various Wavelengths

λ, nm	$\Phi(P_3 \rightarrow Pro_3)/\Phi(Pro_3 \rightarrow P_3)$	$\Phi(P_3 \rightarrow L_3)/\Phi(L_3 \rightarrow P_3)$	$\Phi(P_3 \rightarrow T_3)/\Phi(T_3 \rightarrow P_3)$
295.0	0.11	0.12	3.86
297.5	0.12	0.16	3.79
300.0	0.11	0.17	3.28
302.5	0.11	0.19	2.43
305.0	0.22	0.32	2.65

Table III. Calculated Quantum Yields

λ, nm	$\Phi(P_3 \rightarrow Pro_3)$	$\Phi(P_3 \rightarrow L_3)$	$\Phi(P_3 \rightarrow T_3)$
254	(0.014)[a]	(0.04)[a]	(0.41)[a]
295.0	0.04	0.06	0.43
297.5	0.04	0.06	0.42
300.0	0.04	0.08	0.36
302.5	0.04 (0.02)[a]	0.09 (0.09)[a]	0.27 (0.29)[a]
305.0	0.08	0.18	0.29

[a] Experimental value; see ref 23, p 27.

view of the reported finding of 295 nm as the most effective wavelength, our attention was focused in the 295–305 nm region. Each irradiation was carried out to the establishment of the quasi-photostationary state consisting of Pro_3, P_3, L_3, and T_3. The results are given in Table I.[21]

The ratio of the quantum yields for the various interconversions, after correction for the molar extinction coefficients at the various wavelengths,[22] are given in Table II. A more quantitative evaluation, given in Table III,[24] for the actual changes in the individual quantum yields of P_3 to Pro_3 and P_3 to L_3 can be obtained by using the conclusion of the Leiden group[18] that the quantum yields for the ring-opening reactions, Pro_3 to P_3 and L_3 to P_3, do not exhibit any wavelength effects. Furthermore, the reported quantum yields for the conversion of P_3 to T_3 at 254 and 302.5 nm,[23] when taken in conjunction with our experimental determination of the quantum yield ratios, indicate that the quantum yield for T_3 to P_3 is similar at the two wavelengths, 0.10 at 254 nm and 0.12 at 302.5 nm. Following the same reasoning used for the ring opening reactions,[18] it can be concluded that the quantum yield for T_3 to P_3 is virtually wavelength independent. The calculated quantum yields for P_3 to T_3 are given in Table III, with an average value of 0.11 for the quantum yield for T_3 to P_3.

The dramatic changes in quantum yields for the ring-closure reactions with the narrow wavelength range of 302.5–305.0 nm do not seem likely to be due to a rapid change in the molar extinction coefficients of the specific conformers of P_3 leading to Pro_3 and L_3, the so-called c(−)Zc and c(+)Zc conformers.[23] A doubling of the coefficient value of both conformers within a 2.5-nm range would be required, and such seems improbable since the molar extinction coefficient of P_3, itself, is decreasing by 29%. Thus, these results indicate that excited-state properties are involved in the wavelength effects found in the photochemical ring closure of previtamin D_3; the nature of this involvement is currently being studied.

On the other hand, the change in the molar extinction coefficient with wavelength of the P_3 conformer that is involved in the isomerization to T_3, i.e., the tZc conformer, could readily account for the changes in the P_3 to T_3 quantum yield, and excited-state properties need not be involved in this isomerization process.

Registry No. P_3, 1173-13-3; Pro_3, 434-16-2; L_3, 5226-01-7; T_3, 17592-07-3.

(21) The results given are based upon triplicate experiments; the error on the lower quasi-photostationary state concentrations was 10% while the maximum error on the higher concentrations was less than 4%.

(22) The molar extinction coefficients at various wavelengths are reported by Phillips (Phillips, R. B. Ph.D. Thesis, University of California, Berkeley, CA, 1982). Errors in molar extinction coefficients were ±2% of value used in calculation.

(23) Gielen, J. W. J. Ph.D. Thesis, Leiden, Netherlands, 1981.

(24) The overall error limits in the calculated quantum yields is 12%.

Bicyclo[2.2.1]heptanes in Organic Synthesis. Total Synthesis of the 16-Membered Ring Macrolide Tylonolide Hemiacetal: Synthesis and Coupling of the C(3)–C(9) and C(11)–C(17) Fragments

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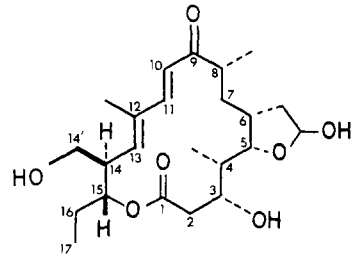
Received May 28, 1982

Tylosin,[1] a structurally complex 16-membered ring macrolide antibiotic that is presently used therapeutically[2] and sold commercially as its tartrate under the name Tylan[3] for the treatment of chronic respiratory disease in chickens, has been the focus of several synthetic investigations.[4] Efforts on the synthetic front have recently culminated in carbohydrate-based total syntheses of *O*-mycinosyltylonolide hemiacetal[4d] and the C(14′) O-tritylated derivative of tylonolide *O*-methylhemiacetal.[4c]

Our strategy for the construction of tylonolide hemiacetal (**1**)



1

centered around the use of the chiral bicyclo[2.2.1]heptenol **4**, whose carbon framework permits elaboration of the seven-carbon C(3)–C(9) fragment **3** and the seven carbon C(11)–C(17) fragment **2**. We detail below the synthesis of the key intermediates **2** and **3** in optically active form and the elaboration of the 16-membered ring of tylonolide hemiacetal.

The left-hand fragment **2** was prepared as outlined in Scheme I. The known bicyclo[2.2.1]heptane derivative **4**,[5] $[\alpha]_D$ −122.8° (*c* 2.50, $CHCl_3$), was benzylated and subjected to acid-catalyzed removal of the ketal to provide in 87% overall yield ketone **5**. Baeyer–Villiger oxidation of **5** and subsequent treatment of the crude hydroxy acid with boron trifluoride etherate gave rise (89%) to bicyclic lactone **6**, $[\alpha]_D$ +204.8° (*c* 7.11, $CHCl_3$). Sequential reduction of the lactone and the carbon–carbon double bond afforded the corresponding diol whose primary hydroxyl was smoothly transformed[6] (70% overall) to the primary selenide **7** without any complications due to the presence of the secondary hydroxyl. The transformation of selenide **7** into cyclopentanol **8** ($[\alpha]_D$ +47.4° (*c* 1.26, $CHCl_3$), mp 43–44 °C) was achieved in a straightforward fashion in very high yield. Collins oxidation

(1) Hamill, R. L.; Haney, M. E., Jr.; Stamper, M.; Wiley, P. F. *Antibiot. Chemother.* (*Washington, D.C.*) **1961**, *11*, 328. Omura, S.; Matsubara, H.; Nakagawa, A.; Furosoki, A.; Matsumoto, T. *J. Antibiot.* **1980**, *33*, 915. Omura, S.; Matsubara, H.; Nakagawa, A.; Furosoki, A.; Matsumoto, T. *J. Antibiot.* **1980**, *33*, 915. Omura, S.; Matsubara, H.; Nakagawa, A.; Furosoki, A.; Matsumoto, T. *J. Antibiot.* **1980**, *33*, 915.

(2) McGuire, J. M.; Bonieces, W. S.; Higgins, C. E.; Hoehn, M. M.; Stark, W. M.; Westhead, J.; Wolfe, R. N. *Antibiot. Chemother.* (*Washington, D.C*) **1961**, *11*, 320.

(3) Tylan is available from Elanco Products Co., a division of Eli Lilly and Company.

(4) (a) Masamune, S.; Hayase, Y.; Chan, W. K.; Sobczak, R. L. *J. Am. Chem. Soc.* **1976**, *98*, 7874. (b) Nagel, A. A.; Vincent, L. A. *J. Org. Chem.* **1979**, *44*, 2050. (c) Tatsuta, K.; Amemaya, Y.; Kanemura, Y.; Kinoshita, M. *Tetrahedron Lett.* **1981**, *22*, 3997. (d) Nicolaou, K. C.; Pavia, M. R.; Seitz, S. P. *J. Am. Chem. Soc.* **1982**, *104*, 2027. (e) Lu, L. D.-L. *Tetrahedron Lett.* **1982**, *23*, 1867.

(5) Grieco, P. A.; Ohfune, Y.; Yokoyama, Y.; Owens, W. *J. Am. Chem. Soc.* **1979**, *101*, 4749.

(6) Grieco, P. A.; Gilman, S.; Nishizawa, M. *J. Org. Chem.* **1976**, *41*, 1485. See also: Grieco, P. A.; Takigawa, T.; Schillinger, W. S. *Ibid.* **1980**, *45*, 2247.

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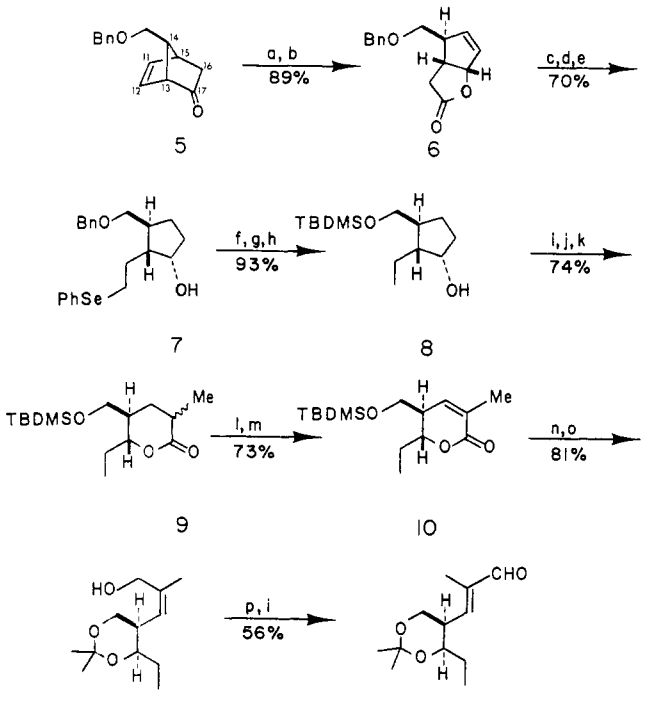
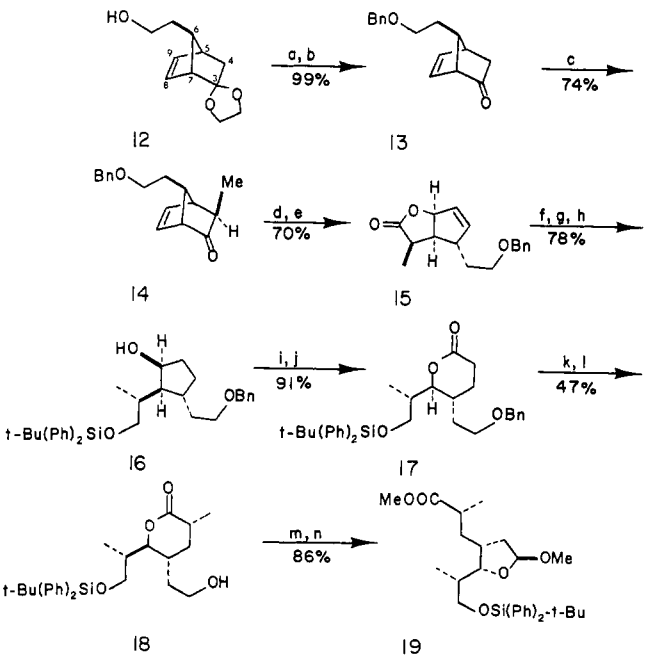
Scheme I. Preparation of the C(11)–C(17) Fragment 2[a]

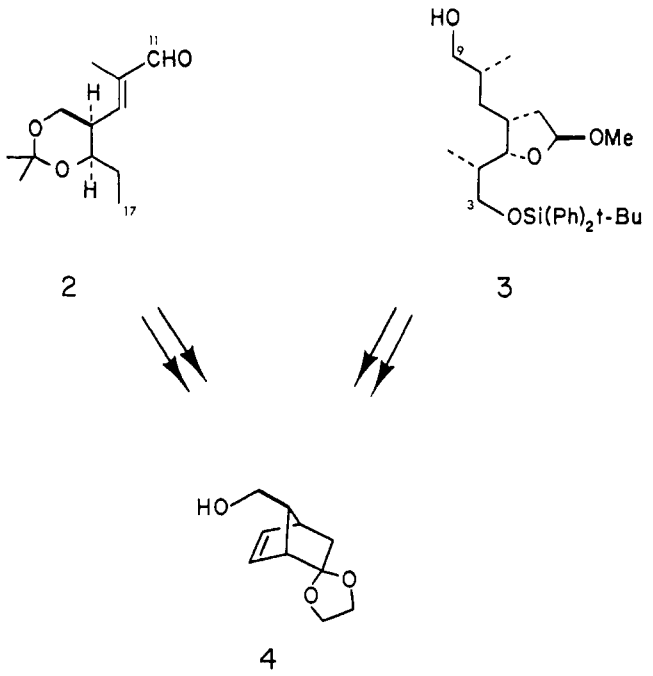


[a] 30% H_2O_2, 10% NaOH, CH_3OH–H_2O–THF (1:1:1), ~5 °C. [b] BF_3·Et_2O, CH_2Cl_2, 0 °C. [c] $LiAlH_4$, Et_2O, 0 °C. [d] $NaBH_4$, $NiCl_2$·$6H_2O$, CH_3OH, 0 °C. [e] PhSeCN, Bu_3P, THF, −23 °C. [f] Bu_3SnH, PhMe, AIBN, 105 °C. [g] H_2, 10% Pd/C, EtOAc. [h] *t*-Bu(Me)$_2$SiCl, imidazole, DMF. [i] CrO_3·2Py, CH_2Cl_2, 0 °C. [j] MCPBA, $NaHCO_3$, CH_2Cl_2, 0 °C. [k] LDA, THF, −78 °C; MeI. [l] LDA, THF, −78 °C; PhSeCl. [m] 30% H_2O_2, THF, 0 °C. [n] $LiAlH(OMe)_3$, THF, 0 °C. [o] Acetone, CSA, $CuSO_4$. [p] BuLi, THF, *p*-MeC_6H_4SCl; silica gel.

Scheme II. Preparation of the C(3)–C(9) Fragment 19[a]



[a] NaH, PhH–Me_2SO, BnCl, 50 °C. [b] 10% HCl, THF. [c] LDA, THF, −78 °C; MeI. [d] 30% H_2O_2, 10% NaOH, MeOH–THF–HOH (1:1:1), ~5 °C. [e] BF_3·Et_2O, CH_2Cl_2. [f] $LiAlH_4$, Et_2O, 0 °C. [g] $NaBH_4$, $NiCl_2$·$6H_2O$, 0 °C. [h] *t*-Bu(Ph)$_2$SiCl, CH_2Cl_2, Et_3N, DMAP, 0 °C. [i] CrO_3·2Py, CH_2Cl_2, 0 °C (10 min) → 25 °C (30 min). [j] MCPBA, CH_2Cl_2, $NaHCO_3$, $[(Me)_3CC_6H_2(Me)OH]_2S$, 0 °C. [k] LDA, THF, −78 °C; MeI, −78 → −40 °C. [l] H_2, Pd–C, EtOH. [m] CrO_3·2Py, CH_2Cl_2. [n] TsOH, MeOH.



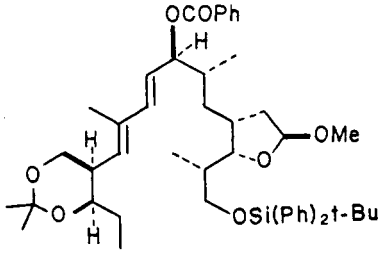
of **8** and subsequent treatment with *m*-chloroperbenzoic acid generated the corresponding δ-lactone, which was directly methylated via the lactone enolate giving rise to **9** in 74% overall yield.

Selenenylation and subsequent oxidation and elimination of benzeneselenenic acid provided the unsaturated lactone **10**, $[\alpha]_D$ +77.9° (*c* 0.95, $CHCl_3$). Reduction of **10** proceeded with simultaneous cleavage of the silyl ether, affording the corresponding triol which upon treatment with acetone and camphorsulfonic acid in the presence of anhydrous copper sulfate furnished allylic alcohol **11**, $[\alpha]_D$ −37.5° (*c* 0.84, $CHCl_3$), with the incorrect geometry about the C(12)–C(13) olefinic linkage. Olefin inversion was efficiently achieved via application of a sulfenate–sulfoxide–sulfenate interconversion.[7] The desired *E*-allylic alcohol upon oxidation produced the very sensitive aldehyde **2**, $[\alpha]_D$ −63.7° (*c* 2.70, $CHCl_3$), which constitutes the C(11)–C(17) segment of tylonolide hemiacetal.

With the construction of the C(11)–C(17) fragment accomplished, we proceeded to elaborate the chiral bicyclo[2.2.1]heptene **4** into **3**, which represents the C(3)–C(9) fragment of tylonolide hemiacetal. Scheme II illustrates the sequence of events that led from **4** to **3**. The starting alcohol **4** was transformed into alcohol **12**, $[\alpha]_D$ −101.3° (*c* 1.40, $CHCl_3$), via a four-step sequence [(1) TsCl, Py; (2) NaCN, Me_2SO, 100 °C; (3) 40% aqueous KOH, $HOCH_2CH_2OH$, 130 °C; (4) $LiAlH_4$, THF] in 90% overall yield. Benzylation and subsequent deketalization gave rise to bicyclo[2.2.1]heptenone **13**, $[\alpha]_D$ −424° (*c* 1.73, $CHCl_3$), which upon alkylation with methyl iodide provided (74%) ketone **14**, $[\alpha]_D$ −341° (*c* 1.26, $CHCl_3$), as the sole product. That alkylation had occurred exclusively from the exo face was clearly evident from examination of the 220-MHz NMR spectrum of **14**, which revealed the *endo* proton as a quartet (J = 7.0 Hz) centered at δ 1.91.[8] Baeyer–Villiger oxidation of ketone **14** with basic hydrogen peroxide generated the corresponding hydroxy acid which smoothly rearranged to bicyclic lactone **15**, $[\alpha]_D$ +153° (*c* 1.09, $CHCl_3$). Transformation of **15** into δ-lactone **17**, $[\alpha]_D$ +46.0° (*c* 1.0, $CHCl_3$), was achieved in straightforward fashion via the intermediacy of cyclopentanol **16**, $[\alpha]_D$ +22.0° (*c* 1.34, $CHCl_3$). Methylation of the lactone enolate derived from **17** provided in 93% yield a 1:1 mixture of monomethylated lactones. Without separation, the mixture of benzyl ethers was subjected to hydrogenolysis, giving rise to near quantitative yield of **18**, $[\alpha]_D$ +47.0° (*c* 2.10, $CHCl_3$), and the corresponding epimeric com-

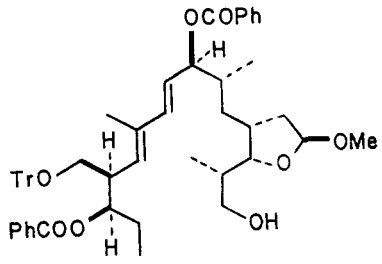
(7) Evans, D. A.; Andrews, G. C. *Acc. Chem. Res.* **1974**, *7*, 147.
(8) Cf.: Marshall, J. L.; Walter, S. R. *J. Am. Chem. Soc.* **1974**, *96*, 6538.

Scheme III



24

a, b, c, d
66%



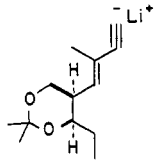
25

[a] PPTS, MeOH. [b] TrCl, Et_3N, DMAP, CH_2Cl_2. [c] PhCOCl, py, DMAP. [d] Bu_4NF, THF.

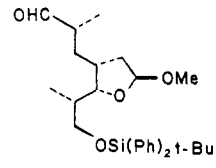
pound in a 1:1 ratio, which could be efficiently separated on a 10-μm porasil column by using 1:2 ethyl acetate–hexane (α = 1.3).

Completion of the synthesis of the C(3)–C(9) fragment involved oxidation of **18** to the corresponding aldehyde which upon exposure to methanol in the presence of acid gave way to ester **19**, $[\alpha]_D$ +31.6° (*c* 0.92, $CHCl_3$), in 86% yield. Reduction ($LiAlH_4$, Et_2O, 0 °C) of the ester unit provided in 95% yield the intact C(3)–C(9) fragment **3**, $[\alpha]_D$ +40.4° (*c* 1.01, $CHCl_3$).

The availability of the C(11)–C(17) and C(3)–C(9) fragments **2** and **3** in enantiomerically pure form permits completion of the total synthesis of tylonolide hemiacetal. The coupling of fragments **2** and **3** was achieved in 75% yield by condensation of the lithium acetylide **20** [prepared in 65% overall yield from aldehyde **2** by

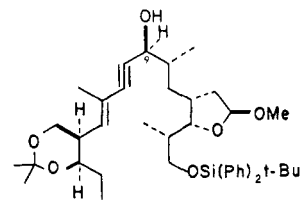


20

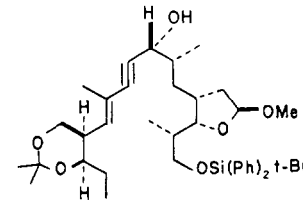


21

a three-step process:[9] (1) Ph_3P, CBr_4, CH_2Cl_2, Na_2CO_3; (2) acetone, CSA, $CuSO_4$;[10] (3) BuLi (2.03 equiv), THF, −78 °C], with the aldehyde **21** derived from **3** by Collins oxidation (CrO_3·2Py, CH_2Cl_2, 0 °C, 1 h, 95% yield). There was obtained a 1:1 mixture of the C(3)–C(17) acyclic adducts **22** [R_f 0.40, 1:1 ether–hexane, three developments; $[\alpha]_D$ +2.52° (*c* 0.72, $CHCl_3$)] and **23** [R_f 0.28; $[\alpha]_D$ −7.29° (*c* 0.80, $CHCl_3$)], which were separated by column chromatography on silica gel. Both **22** and **23** have independently been converted into tylonolide hemiacetal; however, for brevity, only the transformation of enantiomerically pure **22** into **1** will be detailed. Reduction ($LiAlH_4$, THF, 5 °C) of the C(10)–C(11) acetylenic linkage in **22** and subsequent benzoylation (PhCOCl, DMAP, Py) of the C(9) β-hydroxyl gave



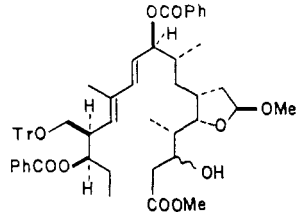
22



23

(73% overall) substrate **24** (Scheme III), $[\alpha]_D$ +35.5° (*c* 1.85, $CHCl_3$), possessing the all-trans arrangement of double bonds.

With the C(3)–C(17) fragment **24** available in chiral form as an enantiomerically pure substance, we concentrated our efforts on completing the construction of the C(1)–C(17) acyclic seco acid **27** (R = H), which would set the stage for the final assembly



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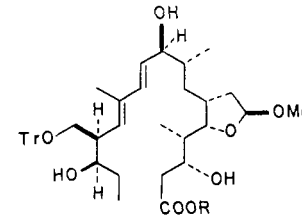
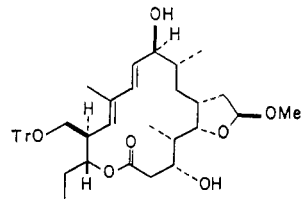


27

of the 16-membered macrolide ring. Toward this end, substrate **24** was transformed, as outlined in Scheme III, into the acylic primary alcohol **25**, $[\alpha]_D$ +67.4° (*c* 1.38, $CHCl_3$).

Collins oxidation (0 °C) of **25** followed by reaction with lithio methyl acetate in THF at −78 °C (10 min) provided in 65% yield **26** as a 1:1 mixture about C(3). β-Hydroxy ester **26** upon treatment with sodium methoxide in methanol afforded (93%) ester **27** (R = Me, R_f 0.30, ether) and the corresponding C(3) epimeric β-hydroxy ester (R_f 0.39), which were separated by preparative TLC. The spectral properties of **27** (R = Me), $[\alpha]_D$ +39.5° (*c* 0.81, $CHCl_3$), were identical in all respects with a sample of **27** (R = Me), $[\alpha]_D$ +43.0° (*c* 1.00, $CHCl_3$), synthesized previously in our laboratory from natural tylosin.[11]

Assembly of the 16-membered macrolide ring of tylonolide hemiacetal was achieved as follows. Hydrolysis [1 N NaOH–MeOH (1:4), 60 °C, 2 h] of **27** (R = Me) provided seco acid **27** (R = H), which was converted into the corresponding 2-pyridinethiol ester[12] by treatment of **27** (R = H) with 2,2′-dipyridyl disulfide and triphenylphosphine in THF. Subsequent thermolysis[13] (PhMe, reflux, 24 h) provided in 19% overall yield from **27** (R = Me) macrolide **28**, mp 180–181 °C, $[\alpha]_D$ +75.3° (*c* 1.00,



28

$CHCl_3$). Allylic oxidation (MnO_2, CH_2Cl_2, 3 h) followed by treatment with aqueous acetic acid in tetrahydrofuran (1:1:3) gave after purification an 80% yield of synthetic (+)-tylonolide hemiacetal **1**, mp 102.5–103.5 °C (CH_2Cl_2–hexane) (lit.[14] mp 103–105

(9) Cf.: Corey, E. J.; Fuchs, P. L. *Tetrahedron Lett.* **1972**, 2769.

(10) The use of acetone–camphorsulfonic acid in this reaction sequence is necessitated by the fact that during the isolation of the 1,1-dibromo olefin from the reaction of aldehyde **2** with Ph_3P/CBr_4, one encounters loss of the acetonide group.

(11) Grieco, P. A.; Inanaga, J.; Lin, N.-H. *J. Org. Chem.*, in press.

(12) Mukaiyama, T.; Araki, M.; Takei, H. *J. Am. Chem. Soc.* **1973**, *95*, 4763.

(13) Corey, E. J.; Nicolaou, K. C. *J. Am. Chem. Soc.* **1974**, *96*, 5614.

(14) Miyano, K.; Nakagawa, A.; Omura, S. *Chem. Pharm. Bull.* **1982**, *30*, 97.

°C), $[\alpha]_D$ 30.4° (*c* 0.55, $CHCl_3$), which was identical in all respects with an authentic sample prepared in our laboratory by degradation of tylosin.[11,15]

Acknowledgment. This research was supported by a Public Health Research Grant from the National Institute of Allergy and Infectious Diseases (AI 17410). The 360-MHz NMR instrument (Nicolet) used in the above studies was purchased in part through funds provided by the National Science Foundation (Grant No. CHE-81-05004). We are grateful to Dr. Tats Matsuoka (Lilly Research Laboratories) and Dr. Arthur Nagel (Pfizer Central Research) for generous gifts of tylosin.

Supplementary Material Available: Spectral and analytical data for **1–3**, **5–8**, **10–19**, **22**, **24**, **25**, **27** (R = Me), and **28** (7 pages). Ordering information is given on any current masthead page.

(15) Assigned structures are fully supported by IR, NMR, and combustion analysis.

Application of Rapid-Scan Fourier Transform Infrared Spectroscopy To Characterize the Monodentate Intermediate in the Photochemical Formation of Tetracarbonyl(4,4′-dialkyl-2,2′-bipyridine)metal from Hexacarbonylmetal

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Received May 24, 1982

We report direct infrared spectral evidence establishing that the photochemical formation of $M(CO)_4(4,4'\text{-}R_2\text{-}2,2'\text{-bpy})$ (M = Cr, Mo, W; R = CH_3, $n\text{-}C_{19}H_{39}$; bpy = bipyridine) from $M(CO)_6$ occurs via $M(CO)_5(4,4'\text{-}R_2\text{-}2,2'\text{-bpy})$, where the potentially bidentate ligand is coordinated in a monodentate fashion (eq 1–3). This study was stimulated by the observation that

$$M(CO)_6 \underset{\Delta}{\overset{h\nu}{\rightleftharpoons}} M(CO)_5 + CO \quad (1)$$

$$M(CO)_5 + 4,4'\text{-}R_2\text{-}2,2'\text{-bpy} \xrightarrow{\Delta,\ \text{fast}} M(CO)_5(4,4'\text{-}R_2\text{-}2,2'\text{-bpy}) \quad (2)$$

$$M(CO)_5(4,4'\text{-}R_2\text{-}2,2'\text{-bpy}) \xrightarrow{\Delta,\ k_3} M(CO)_4(4,4'\text{-}R_2\text{-}2,2'\text{-bpy}) + CO \quad (3)$$

$M(CO)_4L$ (L = bidentate ligand) could be generated in a one-photon process. The use of rapid-scan Fourier transform infrared (FT IR) spectroscopy, a complement to time-resolved Raman spectroscopy,[1] provides definitive, molecular specific characterization not typically obtained in the study of light-induced reactions monitored in the UV–vis region of the spectrum.

It is established that near-UV irradiation of $M(CO)_6$ (M = Cr, Mo, W) results in efficient ($\Phi > 0.1$) dissociative loss of CO, eq 1,[2] forming a 16-valence-electron $M(CO)_5$, which reacts readily with solvent to form a weakly bound solvent complex that can rapidly react with two-electron donor ligands such as pyridine with a second-order rate constant of $\sim 2 \times 10^6$ s^{-1}.[2b,c,e] Figure 1a shows the FT IR spectral changes observed within 5 s after ~2-s irradiation of a 0.5 mM $W(CO)_6$ solution in methylcyclohexane containing 0.3 mM 2-phenylpyridine and ~1 mM CO.[3] The negative peak at 1981 cm^{-1} corresponds to the disappearance of $W(CO)_6$, and positive peaks at 2070, 1930, and 1911 cm^{-1} correspond to the appearance of $W(CO)_5$(2-phenylpyridine). Nearly the same spectrum is observed for authentic samples of $W(CO)_5$(py) (py = pyridine) (Table I). Figure 1b shows that similar FT IR spectral changes occur within 5 s after a 2-s irradiation of 0.5 mM $W(CO)_6$ in methylcyclohexane containing 8.7 mM $4,4'\text{-}(n\text{-}C_{19}H_{39})_2\text{-}2,2'\text{-bpy}$[4] and ~1 mM CO, consistent with the formation of $W(CO)_5(4,4'\text{-}(n\text{-}C_{19}H_{39})_2\text{-}2,2'\text{-bpy})$ (2066, 1925, 1909 cm^{-1}), where only one nitrogen is coordinated, since

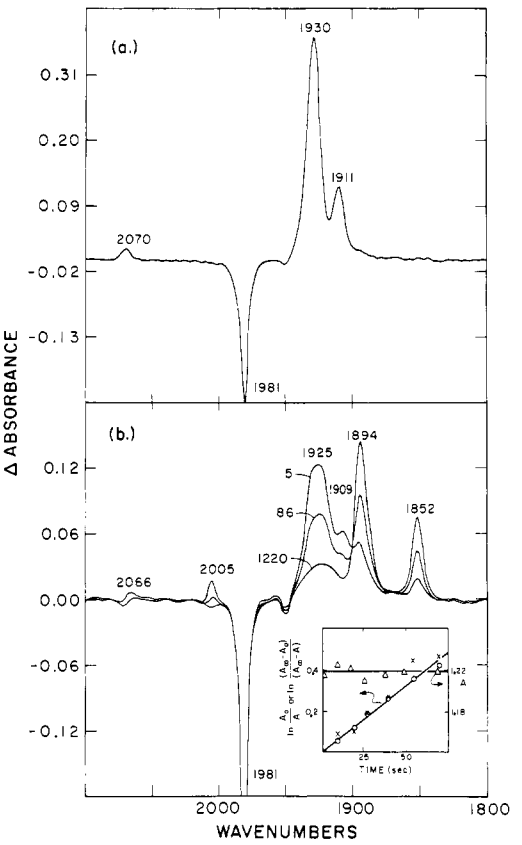

Figure 1. Infrared spectral changes resulting from irradiation of $W(CO)_6$. (a) Difference infrared spectrum obtained within 5 s after irradiation with a 200-W high-pressure Hg lamp of a 0.5 mM $W(CO)_6$ solution containing 6.3 mM 2-phenylpyridine, showing the disappearance of $W(CO)_6$ as a negative peak at 1981 cm^{-1} and appearance of $W(CO)_5$(2-phenylpyridine) as positive at 2070, 1930, and 1911 cm^{-1}. (b) Difference infrared spectra 5, 86, and 1220 s after irradiation with a 200-W high-pressure Hg lamp of a 0.5 mM $W(CO)_6$ solution containing 8.7 mM $4,4'\text{-}(n\text{-}C_{19}H_{39})_2\text{-}2,2'\text{-bpy}$. Inset shows time-dependent behavior of peaks at 1981 cm^{-1} corresponding to $W(CO)_6$ (Δ), 1925 cm^{-1} corresponding to $W(CO)_5(4,4'\text{-}n\text{-}C_{19}H_{39})_2\text{-}2,2'\text{-bpy}$) (○), and 1894 cm^{-1} corresponding to $W(CO)_4(4,4'\text{-}(n\text{-}C_{19}H_{39})_2\text{-}2,2'\text{-bpy})$ (×). The remaining absorbance at 1925 cm^{-1} after 1220 s is attributed to a monodentate ligand impurity. The presence of this peak is accounted for in the kinetic analysis.

(1) Cf., for example: (a) Hub, W.; Schneider, S.; Dorr, F. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 323. (b) Atkinson, G. H.; Dosser, L. R. *J. Chem. Phys.* **1980**, *72*, 2195; (c) Beck, S. M.; Brus, L. E. *J. Am. Chem. Soc.* **1981**, *103*, 2495; (d) Dallinger, R. F.; Farquharson, S.; Woodruff, W. H.; Rogers, M. A. *Ibid.* **1981**, *103*, 7433; (e) Hub, W.; Schneider, S.; Dorr, F.; Simpson, J. T.; Oxman, J. D.; Lewis, F. D. *Ibid.* **1982**, *104*, 2044.

(2) (a) Geoffroy, G. L.; Wrighton, M. S. "Organometallic Photochemistry"; Academic Press: New York, 1979, Wrighton, M. S. *Chem. Rev.* **1974**, *74*, 401; (b) Lees, A. J.; Adamson, A. W. *Inorg. Chem.* **1981**, *20*, 4381; (c) Tyler, D. R.; Petrylak, D. P. *J. Organomet. Chem.* **1981**, *212*, 389; (d) Perutz, R. N.; Turner, J. J. *J. Am. Chem. Soc.* **1975**, *97*, 4791; (e) Bonneau, R.; Kelly, J. M. *Ibid.* **1980**, *102*, 1220.

(3) All reactions were carried out in deoxygenated, olefin-free methylcyclohexane solvent. Generally, solutions were 1 mM in CO to allow in situ monitoring of the importance of $M(CO)_5S \rightarrow M(CO)_6$ during the short time scale experiments. Samples were loaded into 0.1-mm path length cells under CO. Irradiation of the sample in the cell was carried out for a brief period at 298 K, and the sample was transferred as rapidly as possible to the Nicolet 7199 FT IR to record FT IR spectra every ~0.2 s to follow the reaction.

(4) Obtained as a gift from S. J. Valenty (lab notebook no. 10900-50-2) of General Electric Research and Development Center, Schenectady, NY. The long alkyl chain derivative was used since $M(CO)_4(2,2'\text{-bpy})$ precipitates upon formation in alkane solvents.

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