see footnote 10). Since it is also known that racemization is several times faster in solvolyzing optically active 2-norbornyl brosylate than acid formation, it is clear that return occurs without the oxygens having fully equilibrated. This is in line with expectations derived from the work of Goering, for example, with the 1,2-dimethyl-2-norbornyl system.[11] It may also be noted that the final spectra show only the sulfonic acid and that no signal attributable to ethyl norbornyl ether can be seen, proving the absence of any *O*-acyl cleavage. Nor does any external return occur; enriched acid and natural abundance ester together in ethanol do not produce any hint of the presence of I or II.

In conclusion, we have detected and measured internal ion-pair return during solvolysis, in situ and without workup, and evaluated rate constants for both solvolysis of and oxygen scrambling in 2-norbornyl brosylate, the former in good agreement with known data. We believe that these experiments justify our claim that ^{17}O NMR is a rapid and convenient tool to detect return of pairs of ions and possibly of other species as well.[12]

Acknowledgment. We are pleased to acknowledge support by the donors of the Petroleum Research Fund, administered by the American Chemical Society, for this work. We also thank the NSF for its support to the Department in the form of Grant 8114412 to purchase the spectrometer.

Registry No. I, 85681-22-7; II, 85681-23-8; ^{17}O, 13968-48-4; $Pr(NO_3)_3$, 10361-80-5; O_2, 7782-44-7; 2-norbornyl brosylate, 4895-15-2; 2-norbornyl bromide, 29342-65-2; 2-norbornanol, 1632-68-4; europium chloride, 53801-49-3.

(10) The rate constant k_{ex} as recorded by most authors refers to the first-order approach to the equilibrium composition. It differs from k_I in the process

$$I \underset{k_{II}}{\overset{k_I}{\rightleftharpoons}} II$$

Here $k_I t = {}^2/_3 \ln (2 + 2r/(2 - r))$ (r = (II)/(I)).

(11) H. L. Goering and R. W. Thies, *J. Org. Chem.*, **40**, 925 (1975).

(12) it may be noted that in those cases where sulfonyl-^{17}O-labeled esters are adequate to the task at hand, the sulfonic acid liberated can be reused for the preparation of such esters with only the loss of one-third of its label.

Total Synthesis of (+)- and (-)-Tryptoquivaline G by Biomimetic Double Cyclization

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(+)-Tryptoquivaline G (**1**, Chart I) produced by *Aspergillus fumigatus*,[1] is one of several tryptoquivalines belonging to the tremorgic mycotoxin family. The novel structure was determined by chemical and physicochemical methods.[1] The first total synthesis was achieved by Buchi and co-workers,[2] who also established the absolute configuration. Subsequently, a formal synthesis of (±)-**1** was reported by Ban's group.[3]

We report here an abbreviated, facile biogenetic type total synthesis of (+)- and (-)-**1** by a different approach, utilizing the newly employed oxidative double cyclization of *N*-acyltryptophan precursor **10** (Chart II), which allowed an efficient formation of the unique ring system of **1** in one step.

Chart I

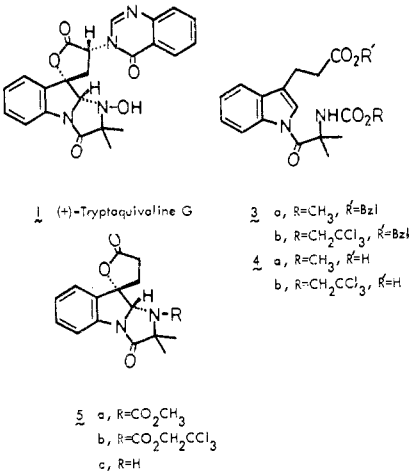
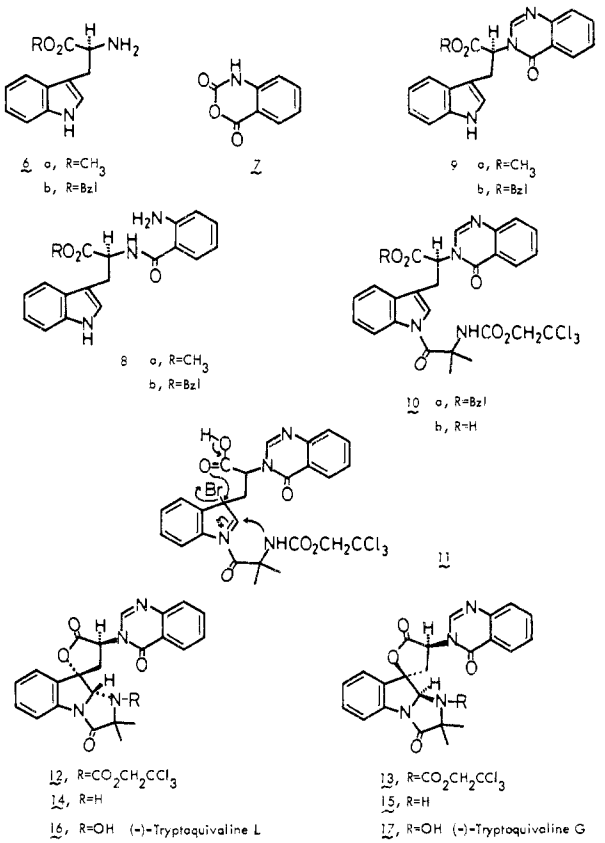


Chart II



From our studies on the bromination and oxidation of indoles[4] and also the results obtained by Witkop,[5] the formation of the imidazoindole spirolactone ring system could be envisaged as being derived from double cyclization of **10b** by bromination via **11**.

We first explored the acylation of indole nitrogen with amino acids as there is no established precedent for these reactions.[6]

Preliminary studies on the condensation of benzyl 3-indolepropionate with *N*-(methoxycarbonyl)- (**2a**) or *N*-[(trichloroethoxy)carbonyl]- (**2b**) methylalanine *p*-nitrophenyl esters in the presence of KF, 18-crown-6, and $EtN(i\text{-}Pr)_2$ in acetonitrile[7] led

(1) (a) Clardy, J.; Springer, J. P.; Buchi, G.; Mastuo, K.; Wrightman, R. J. *J. Am. Chem. Soc.* **1975**, *97*, 663-665. (b) Yamazaki, M.; Fujimoto, H.; Okuyama, E. *Tetrahedron Lett.* **1976**, 2861-2864. (c) Yamazaki, M.; Okuyama, E.; Maebayashi, Y. *Chem. Pharm. Bull.* **1979**, *27*, 1611-1617 and references therein.

(2) Buchi, G.; DeShong, P. R.; Katsumura, S.; Sugimura, Y. *J. Am. Chem. Soc.* **1979**, *101*, 5084-5086.

(3) Ohnuma, T.; Kimura, Y.; Ban, Y. *Tetrahedron Lett.* **1981**, *22*, 4969-4972.

(4) (a) Hino, T.; Nakagawa, M.; Wakatsuki, T.; Ogawa, K.; Yamada, S. *Tetrahedron* **1967**, *23*, 1441-1450. (b) Hino, T.; Nakamura, T.; Nakagawa, M. *Chem. Pharm. Bull.* **1975**, *23*, 2990-2997. (c) Hino, T.; Miura, H.; Murata, R.; Nakagawa, M. *Ibid.* **1978**, *26*, 3695-3703. (d) Nakagawa, M.; Kato, S.; Kataoka, S.; Hino, T. *J. Am. Chem. Soc.* **1979**, *101*, 3136-3137.

(5) Lawson, W. B.; Patchornik, A.; Witkop, B. *J. Am. Chem. Soc.* **1960**, *82*, 5918-5927.

(6) Preparation of 1-glycylindole and 1-glycylindoline were reported: Neklyudov, D. A.; Shchukina, L. A.; Suvorov, N. N. *Zh. Obshch. Khim.* **1967**, *37*, 797-800.

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to the formation of the N-acylated derivatives **3a** (84%) and **3b** (51%), which were debenzylated (H_2, Pd/C) to give **4a** and **4b**, respectively. Bromination of **4a** with NBS (2 equiv) in a refluxing solution of $CHCl_3$–CF_3CO_2H (10:1) gave **5a** (43%). The structure of **5a** was confirmed by spectroscopic means, and its stereochemistry was established by X-ray analysis, fortunately for our purposes, to have the cis configuration at the C–N and C–O bonds. The reaction of **4b** with NBS (2 equiv) in boiling solution of CH_2Cl_2–CF_3CO_2H (10:1) gave **5b** (29%), which was converted to **5c** (AcOH–Zn).[8]

With the imidazoindole spirolactone moiety corresponding to **1** in hand, we turned to the construction of the quinazolinone moiety. The reaction of L-tryptophan methyl ester (**6a**) and ethyl orthoformate with isatoic anhydride (**7**) in refluxing xylene for 3 h afforded quinazolinone derivative **9a** (25%).[9] An increase in the yield of **9a** was obtained when **6a** and **7** were converted to the amide **8a** (95%) by heating in benzene, which in turn was refluxed in benzene (3 h) with $(EtO)_3CH$ in the presence of a catalytic amount of TsOH to give **9a** (83%). Likewise, **9b** (79%) was obtained via **8b**.[2] Subsequent condensation of **10b** with **2b** in MeCN (KF, 18-crown-6, $EtN(i\text{-}Pr)_2$, 1 h) provided **10a** (42%).[10] Debenzylation of **10a** in $MeCO_2Et$ gave the key compound **10b** (94%). The stage was now set for the construction of **1** by oxidative double cyclization.

Addition of 3 mol of NBS[11] to a boiling solution of **10b** in CF_3CO_2H gave, presumably via intermediate **11**, a mixture of cyclization products of **12** and **13**. Upon reduction of the reaction mixture with Zn in AcOH, there were obtained **14** [21% from **10b**; mp 246–247 °C, $[\alpha]^{18}_D$ −183° (*c* 0.20)][12] and **15** (14%). The melting point and NMR spectrum of **14** were identical with those published by Buchi.[2] The total synthesis of **1** was now completed as follows. Oxidation of **14** with *m*-CPBA[2] in CH_2Cl_2 afforded the hydroxylamine **16** [mp 263–264 °C; $[\alpha]^{16}_D$ −217° (*c* 0.115)], which was identical (mp, NMR, IR, $[\alpha]_D$) with (−)-tryptoquivaline L (**16**) derived from natural tryptoquivaline G. Epimerization of **16** with *t*-BuLi in THF at −70 °C followed by addition of AcOH gave (+)-tryptoquivaline G (**1**). *m*-CPBA oxidation of **15** afforded (−)-tryptoquivaline G [**17**: mp 241–242.5 °C; $[\alpha]^{17}_D$ −148° (*c* 0.11)], whose IR and NMR spectra were superimposable with those of **1**. On the other hand, analogous series of reactions starting from D-tryptophan provided (+)-tryptoquivaline G [**1**: mp 241–242 °C; $[\alpha]^{15}_D$ +156° (*c* 0.21)][13] without the elaborate epimerization step the via 3′-epimer of **14** [mp 241–242 °C; $[\alpha]^{12}_D$ +100° (*c* 0.20)]. Chromatographic mobility and IR, mass, and NMR spectra of the synthetic **1** were indistinguishable from those of natural specimen.

These results implicate biosynthesis of tryptoquivalines by fungus.

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Supplementary Material Available: Spectral and physical data for compounds **4a**, **4b**, **5a**, **5b**, **5c**, **8a**, **8b**, **9a**, **9b**, and **10b** and the X-ray structure and crystal data along with various bond parameters of **5a** (14 pages). Ordering information is given on any current masthead page.

(7) Klausner, Y. S.; Chorev, M. *J. Chem. Soc., Perkin Trans. 1* **1977**, 627–631.

(8) Treatment of **5c** with $ClCO_2Me$ and K_2CO_3 in acetone provided **5a**, indicating that the stereochemistry of **5b** is also of cis configuration.

(9) Clark, R. H.; Wagner, E. C. *J. Org. Chem.* **1944**, *9*, 55–67.

(10) Prolonged reaction for the conversion of **8b** to **10a**, under these conditions, was accompanied with a partial racemization; about 25% racemization of **10a** occurred after 24 h.

(11) One equivalent of NBS was added three times in every 30 min (total 3 mol of NBS). When 3 equiv of NBS were added to a boiling solution of **10b** all at once, **15** (27.5%) was obtained as major product together with **14** (11%).

(12) All the $[\alpha]_D$ values were determined in acetone.

(13) The $[\alpha]^{12}_D$ value of natural tryptoquivaline G obtained by our hand is +154° (*c* 0.14, acetone).

Homogeneous Hydrogenolysis of Carbon Disulfide Catalyzed by a Molybdenum Dimer with Sulfido Ligands

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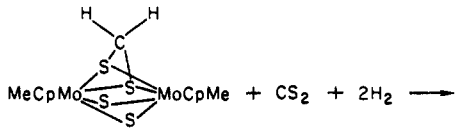
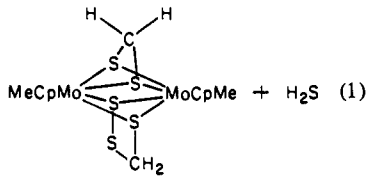
We have recently reported that molecular hydrogen reacts with bridging sulfido ligands in cyclopentadienylmolybdenum complexes to form hydrosulfido bridges.[2] The activation of hydrogen by the sulfido ligands in heterogeneous metal sulfide surfaces has been considered as a possible step in the mechanism of the commercially important hydrodesulfurization catalysts.[3,4] In order to determine whether the synthetic molybdenum complexes have value as potential models for the commercial catalysts, we have begun an investigation of the homogeneous hydrodesulfurization activity of these complexes. We report here a hydrogenolysis of carbon–sulfur bonds that is catalyzed by the Mo(IV) dimer $(CH_3C_5H_4MoS)_2S_2CH_2$ (**I**).[5] The reaction, which proceeds under the mild conditions of 75 °C and 2–3 atm of hydrogen, involves the initial conversion of carbon disulfide to hydrogen sulfide and thioformaldehyde. Although carbon disulfide has been reduced previously in homogeneous systems by its insertion into transition metal–hydride bonds,[6,7] no previous accounts of homogeneously catalyzed desulfurizations of this molecule have appeared.

The initial products of the hydrodesulfurization reaction are shown in eq 1. Hydrogen sulfide has been readily identified by



I



II

GC,[8] mass spectral, and NMR analysis. The reactive thioformaldehyde molecule is stabilized by its interaction with the bridging sulfur atoms in molybdenum complex **II**, an orange microcrystalline product that has been isolated and characterized.[9] NMR data are particularly relevant in the characterization of this complex. Resonances assigned to the two types of methylene groups in **II** are observed at 2.5 and 6.1 ppm in the ^1H spectrum

(1) Alfred P. Sloan Fellow, 1981–1983; Camille and Henry Dreyfus Teacher-Scholar, 1981–1986.

(2) Rakowski DuBois, M.; VanDerveer, M. C.; DuBois, D. L.; Haltiwanger, R. C.; Miller, W. K. *J. Am. Chem. Soc.* **1980**, *102*, 7456.

(3) (a) Massoth, F. C.; Kibby, C. L. *J. Catal.* **1977**, *47*, 300. (b) Massoth, F. E., *Ibid.* **1977**, *47*, 316.

(4) Kwart, H. C.; Schuit, G. C. A.; Gates, B. C. *J. Catal.* **1980**, *61*, 128.

(5) McKenna, M.; Miller, D. J.; Wright, L. L.; Tanner, L.; Haltiwanger, R. C.; Rakowski DuBois, M. *J. Am. Chem. Soc.*, in press.

(6) Adams, R. D.; Golembeski, N. M.; Selegue, J. P. *J. Am. Chem. Soc.* **1981**, *103*, 546.

(7) For a review of earlier insertion reactions of CS_2, see: Yaneff, P. V. *Coord. Chem. Rev.* **1977**, *23*, 183.

(8) Gas chromatographic identification of H_2S was achieved by using a 6-m Porapak N column from Varian in a Varian 920 instrument equipped with a thermal conductivity detector.

(9) Anal. Calcd for $C_{14}H_{18}S_5Mo_2$: C 31.23; H, 3.37; S, 29.77. Found: C, 31.32; H, 3.25; S, 29.90. ^1H NMR ($CDCl_3$) δ 1.94 (s, 6, CH_3), 2.50 (s, 2, S_2CH_2), 5.32 (m, 8, C_5H_4), 6.09 (s, 2, S_2CH_2); ^{13}C NMR ($CDCl_3$; results of off resonance decoupling included in parentheses) δ 15.70 (CH_3, q), 38.38 (S_2CH_2, t), 90.92 (S_2CH_2, t), 89.43, 94.37, 94.81 (Cp, d), 112.05 (Cp, s); IR (Nujol) 424 cm^{-1} (m, $\nu_{S\text{-}S}$); mass spectrum, 506 (P − S), 492 (P − CH_2S), 446 ($Cp_2Mo_2S_3$). Cyclic voltammetry in CH_3CN (0.1 M n-Bu_4NBF_4), scan rate = 100 mv/s: $E_{p/2}$ = +0.275 V vs. SCE, ΔE_p = 60 mV, $i_{pc}/i_{pa} \simeq 1$; $E_{p/2}$ = +0.835 V; ΔE_p = 70 mv, $i_{pc}/i_{pa} \simeq 1$. No reductions observed.

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