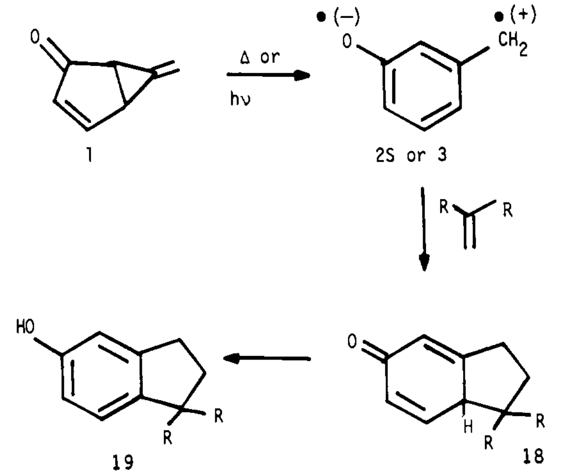
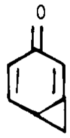
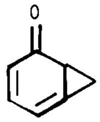
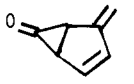
Scheme I



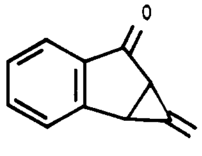
for the role of the intermediate might include the previously observed[1,3] triplet **2T**, but this seems unlikely in view of the normal Arrhenius preexponential term observed here. Violation of the spin prohibition in the reaction **1** → triplet **2T** should have resulted in a sharply diminished *A* factor.[6] Other formally possible candidates might be the ketones **13** and **14**, which are valency tautomers of **1**.

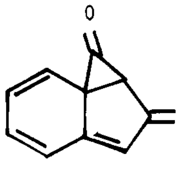

13


14


15

A perhaps more plausible candidate is the cyclopropanone **15**. Bond additivity calculations,[7] using the assumption of equal strain in **1** and **15**, suggest that the reaction **1** → **15** is nearly thermoneutral. That **15** indeed may be thermally accessible from **1** is strongly suggested by the observation that fulvene is a product of the pyrolysis of **1** under more drastic conditions (350 °C, 0.02 s, 10^{-4} torr).[8] However, if the methanolysis and cycloaddition of **1** proceed through **15** as an obligatory intermediate, the activation energy (E_a) for the corresponding reactions of the benzoenone **16** should be greater than that for **1** by the endothermicity of the cyclopropanone-forming step **16** → **17** ($\Delta H_r \sim 28$ kcal/mol). This would predict that **16** should react many orders of magnitude slower than **1**. In fact, however, we find the reaction of **16** with methanol at 105 °C gives 1-hydroxy-3-(methoxymethyl)naphthalene at a rate about 10 times *faster* than the methanolysis of **1**. Pending a basis for formal rejection of **13** and **14**, we consider the weight of evidence to favor a monocyclic singlet valency tautomer of **1**, either the singlet biradical **2** or the zwitterion **3**[9] as the reactive intermediate in the addition mechanism (Scheme I).


16


17

The addition reactions of the enone **1** are extraordinarily exothermic. With alcohols, **1** reacts to give *m*-hydroxybenzyl ethers,[1-3] a process that is exothermic by 72 kcal/mol.[7] This value is far greater than the exothermicity (ΔH_r) of addition of an alcohol to a simple olefin (31 kcal/mol) and comparable in magnitude to that of addition of an alcohol to a carbene (71 kcal/mol). In the cycloaddition of Scheme I, the overall ΔH_r is 89 kcal/mol, of which 69 kcal/mol is released in the actual cyclization to the ketonic precursor (**18**) of the phenolic indan (**19**). The overall energy yield is 50 kcal/mol greater than that in an archetypal Diels–Alder reaction. It is difficult to name any cycloaddition of a kinetically stable organic molecule that is nearly so exothermic.

Acknowledgment. We are grateful for the support of this work by the National Institutes of Health (GM 23375) and the National Science Foundation (CHE-8011399). We also thank the National Science Foundation for its support of the NSF Regional NMR Facility at Yale University (CHE-7916210).

Registry No. 1, 71946-85-5; 4, 82615-36-9; 5, 77366-77-9; 6, 82615-37-0; 7, 78-79-5; 8, 109-92-2; 9, 82615-38-1; 10, 82615-39-2; 11, 82621-38-3; 12, 82615-40-5; isobutylene, 115-11-7.

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(6) (a) Mazur, M. R.; Berson, J. A. *J. Am. Chem. Soc.* **1981**, *103*, 684. (b) Mazur, M. R.; Berson, J. A. *Ibid.* **1982**, *104*, 2217. (c) Rule, M.; Lazzara, M. G.; Berson, J. A. *Ibid.* **1979**, *101*, 7091. (d) Rule, M.; Mondo, J. A.; Berson J. A. *Ibid.* **1982**, *104*, 2209.

(7) (a) Estimated by using group contributions to heats of formation from Benson's tables (ref 7b). (b) Benson, S. W. "Thermochemical Kinetics", 2nd ed.; Wiley-Interscience: New York, 1976.

(8) Goodman, J.; Berson, J. A., unpublished results.

(9) (a) Although the rate constant k_r for methanolysis of **1** responds to the polarity of the solvent only weakly and in the direction opposite to that expected if charge separation were far advanced in the transition state (k_r in CH_3CN = $0.67k_r$ in benzene at 105 °C), a zwitterionic intermediate is not necessarily excluded. An "early" transition state is suggested by the observed E_a for **1**, 30 kcal/mol, which hardly differs from the E_a of about 28 kcal/mol found[10] for the unimolecular rearrangement of the ethylene ketal of **1** to that of **15**. Thus, the reaction of **1** shows little of the kinetic driving force potentially available from aromatization. (b) A zwitterionic intermediate is favored as the reactive species in the cycloadditions of cyclopropanones: Edelson, S. S.; Turro, N. J. *J. Am. Chem. Soc.* **1970**, *92*, 2770. (c) Intermediates related to **3** have been discussed in connection with other reactions: Leitich, J.; Wessely, F. *Monatsh. Chem.* **1964**, *95*, 129. Seiler, P.; Wirz, J. *Helv. Chim. Acta* **1972**, *55*, 2693. We are indebted to Professor Laren Tolbert, University of Kentucky, for calling the latter reference to our attention.

(10) Matlin, A. R.; Berson, J. A., unpublished work.

Photolysis of $Re_2(CO)_{10}$ in the Presence of Simple Olefins. Reactions of (μ-Hydrido)-(μ-alkenyl)-dirhenium Carbonyl Compounds

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Received June 7, 1982

UV photolysis of $M_2(CO)_{10}$, M = Mn or Re, in the presence of phosphine or phosphite ligands results in formation of the disubstituted dinuclear compounds 1,2-$M_2(CO)_8L_2$.[1] The reaction is believed to occur via thermal substitution of photogenerated $M(CO)_5\cdot$ radicals (eq 1–3). Substitution has also been effected

$$M_2(CO)_{10} \xrightarrow{h\nu} 2M(CO)_5\cdot \tag{1}$$

$$M(CO)_5\cdot \xrightarrow{L} M(CO)_4L\cdot + CO \tag{2}$$

$$2M(CO)_4L\cdot \rightarrow 1,2\text{-}M_2(CO)_8L_2 \tag{3}$$

by thermal means[2] or through use of Me_3NO.[3] It has recently been shown in these laboratories that 1,2-*dieq*-$Re_2(CO)_8(py)_2$ (py

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(1) (a) Wrighton, M. S.; Ginley, D. S. *J. Am. Chem. Soc.* **1975**, *97*, 2065. (b) Morse, D. L.; Wrighton, M. S. *Ibid.* **1976**, *98*, 3931. (c) Byers, B. H.; Brown, T. L. *Ibid.* **1975**, *97*, 947. (d) Kidd, D. R.; Brown, T. L. *Ibid.* **1978**, *100*, 4095.

(2) (a) Osborne, A. G.; Stiddard, M. H. B. *J. Chem. Soc.* **1964**, 634. (b) Jolly, P. W.; Stone, F. G. A. *Ibid.* **1965**, 5259.

(3) Koelle, U. *J. Organomet. Chem.* **1978**, *155*, 53.

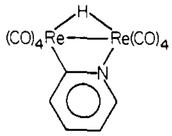
0002-7863/82/1504-4955$01.25/0

Table I. Spectroscopic Data for IIIa-c and IIIe

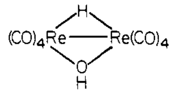
compd[a]	^{1}H NMR[b] (δ)	ν_{CO}, cm^{-1} [c]	m/e[d] (M$^+$)
IIIa	−14.42 (s, 1 H, μ-H), 6.51 (d, 1 H, H_2), 5.30 (dq, 1 H, H_1), 2.20 (d, 3 H, CH_3) $^3J_{H_1-H_2} = 15.9$, $^3J_{H_1-CH_3} = 5.4$ Hz	2114 (vw), 2083 (w), 2017 (s), 1994 (m), 1979 (ms), 1975 (sh), 1967 (m)	638
IIIb	−14.45 (s, 1 H, μ-H), 6.55 (d, 1 H, H_2), 5.36 (dt, 1 H, H_1), 2.29 (qd, 2 H, CH_2), 1.14 (t, 3 H, CH_3), $^3J_{H_1-H_2} = 16.1$, $^3J_{H_1-CH_2} = 5.2$, $^3J_{CH_2-CH_3} = 7.3$ Hz	2114 (vw), 2083 (w), 2017 (s), 1995 (m), 1979 (ms), 1976 (sh), 1967 (m)	652
IIIc	−14.44 (s, 1 H, μ-H), 6.51 (d, 1 H, H_2), 5.27 (dt, 1 H, H_1), 2.19 (td, 2 H, allyl CH_2), 1.4–1.6 (m, 4 H, CH_2CH_2), 0.96 (t, 3 H, CH_3), $^3J_{H_1-H_2} = 16.0$, $^3J_{H_1-CH_2} = 5.8$, $^3J_{H_1-CH_2} = 5.8$, $^3J_{CH_2-CH_3} = 7.3$	2114 (vw), 2083 (w), 2017 (s), 1994 (m), 1979 (ms), 1976 (sh), 1967 (m)	680
IIIe	−14.72 (s, 1 H, μ-H), 7.18 (dd, 1 H, H_2), 4.46 (dd, 1 H, H_1), 6.26 (dd, 1 H, H_3), $^3J_{H_1-H_2} = 17.2$, $^3J_{H_2-H_3} = 10.9$, $^3J_{H_1-H_3} = 2.9$ Hz	2117 (vw), 2085 (w), 2021 (s), 1998 (m), 1988 (m), 1978 (mw), 1970 (m)	624

[a] Satisfactory C, H analyses were obtained for all compounds. [b] 360 MHz, $CDCl_3$. [c] Hexane solution. [d] 70 eV electron impact, Re_2 372.

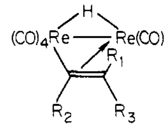
= pyridine) undergoes reaction in refluxing benzene to give (μ-H)$Re_2(CO)_8(\mu$-$C_5H_4N)$, I.[4] A similar species, II, is postulated



I



II



IIIa, $R_1 = R_2 = H$; $R_3 = CH_3$
b, $R_1 = R_2 = H$; $R_3 = C_2H_5$
c, $R_1 = R_2 = H$; $R_3 = n$-C_4H_7
d, $R_1 = H$; $R_2 = R_3 = CH_3$
e, $R_1 = R_2 = R_3 = H$
f, $R_1 = R_3 = H$; $R_2 = C_2H_5$

as an intermediate in the photochemical reaction of $Re_2(CO)_{10}$ with water.[5] A diaquo complex, *dieq*-1,2-$Re_2(CO)_8(H_2O)_2$, is believed to be the precursor to II. The diaquo and dipyridine compounds are proposed to react via thermal loss of L, with subsequent intramolecular oxidative addition (eq 4 and 5). This

$$1,2\text{-}Re_2(CO)_8L_2 \xrightarrow{\Delta} Re_2(CO)_8L + L \qquad L = py, H_2O \qquad (4)$$

$$Re_2(CO)_8L \rightarrow (\mu\text{-}H)Re_2(CO)_8(\mu\text{-}X) \qquad X = C_5H_4N, OH \qquad (5)$$

type of reactivity is presumably available to other disubstituted dinuclear compounds, provided that L is relatively labile and possesses a functionality (C–H, O–H, etc.) suitable for oxidative addition to the adjacent metal. We now report photochemical reactions of $Re_2(CO)_{10}$ with simple olefins, which we believe to occur by reaction pathways discussed above. We also report preliminary work on the reactivities of the photolysis products.

Room-temperature UV photolysis[6] of a hexane or toluene solution of $Re_2(CO)_{10}$ in the presence of excess 1-alkene results in formation of (μ-H)$Re_2(CO)_8(\mu$-(η^2-CH=CHR)), IIIa–c. Yields greater than 90% have been obtained by using propylene (1 atm), 1-butene (1 atm), and 1-hexene. The products, purified by column chromatography and sublimation, are light yellow oils at room temperature and air-stable in solution at 25 °C over a period of several hours. The proposed structure of III is based upon the spectroscopic data summarized in Table I. The alkenyl ligand bridges the two metals, forming a σ bond to one Re and a π bond to the other. The R group is trans to the Re–C σ bond, as evidenced by the magnitude of the coupling between the vinyl protons in the NMR spectrum (16 Hz). The bridging character of the hydride is inferred from its high-field NMR chemical shift, which is similar to those reported for bridging hydrides in rhenium carbonyl clusters.[7] The IR spectra in the carbonyl region are similar to that of the pyridyl-bridged complex I.[8] An X-ray crystal structure determination of I[9] reveals a characteristic Re–Re single-bond distance (3.20 Å) and a distorted octahedral geometry about each metal. These structural features are presumably also characteristic of III.

Formation of III is proposed to involve a 1,2-$Re_2(CO)_8(\eta^2$-olefin$)_2$ intermediate, formed via the mechanism discussed earlier. The two olefin ligands probably occupy equatorial positions. Dissociation of one olefin provides a site for oxidative addition of a vinylic C–H of the olefin coordinated to the adjacent Re. Terminal olefins are presumably constrained by steric requirements to add the C–H trans to the alkyl group.

The only precedents for the reactions observed are the thermal or photochemical reactions of simple olefins with osmium carbonyl clusters.[10] Photolyses of $Re_2(CO)_{10}$ in the presence of 1,3-butadiene,[11b] cycloheptatriene,[11a] or cyclooctatetraene[11b] lead to low yields of complex product mixes, none of which are analogous to III.

To examine the reactivity of internal olefins, we photolyzed $Re_2(CO)_{10}$ in the presence of 2-butene. Reaction with *cis*-2-butene (99%, 1 atm) results in the production of IIId,[12] but in 20% yield based upon reacted $Re_2(CO)_{10}$. The fate of the remaining Re has not been determined. Extended photolysis results in isomerization of IIId to the 1-butene product, IIIb. The only organometallic product of the photolysis of $Re_2(CO)_{10}$ with *trans*-2-butene (1 atm) is IIIb, probably resulting from the observed slow isomerization of *trans*-2-butene to 1-butene during reaction.

Room-temperature reaction of III with several nucleophiles results in the formation of 1,2-$Re_2(CO)_8L_2$ with liberation of alkene. For example, treatment of a toluene solution of IIIc with excess pyridine (0.1 M 20 equiv) yields quantitative production of *dieq*-1,2-$Re_2(CO)_8(py)_2$ and 1-hexene within 2–3 h. Similarly, conversion of IIIc to $Re_2(CO)_{10}$ is effected under 1 atm of CO (half-life 3–4 days).

Compounds IIIa–c all react with ethylene to give (μ-H)$Re_2(CO)_8(\mu$-(η^2-CH=CH_2)), IIIe, a pale yellow crystalline solid. This exchange of the alkenyl ligand occurs under mild conditions (25 °C, 1 atm of C_2H_4 over a toluene solution) and requires approximately 1 day. Similarly, dissolution of IIIe in neat 1-hexene results in quantitative production of IIIc within several hours.

Treatment of IIIb with phenyl acetylene (50 equiv, 0.2 M in heptane) gives a μ-hydrido, μ-alkynyl complex, (μ-H)Re_2-

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(4) Gard, D. R.; Brown, T. L. *Organometallics*, in press.

(5) Gard, D. R.; Brown, T. L. *J. Am. Chem. Soc.*, in press.

(6) Photochemical reactions were performed by using Pyrex-filtered sunlamp (GE, 275 W) radiation, which consists primarily of 366-nm wavelength.

(7) Humphries, A. P.; Kaesz, H. D. *Prog. Inorg. Chem.* **1979**, *25*, 145.

(8) IR spectrum of I: 2112 (vw), 2086 (w), 2015 (s), 2006 (m), 1994 (m), 1979 (w), 1960 (ms), 1958 (sh) cm^{-1} (hexane solution).

(9) Nubel, P. O.; Wilson, S. R.; Brown, T. L., to be submitted for publication.

(10) (a) Deeming, A. J.; Hasso, S.; Underhill, M. *J. Organomet. Chem.* **1974**, *80*, C53. (b) Keister, J. B.; Shapley, J. R. *Ibid.* **1975**, *85*, C29. (c) Johnson, B. F. G.; Kelland, J. W.; Lewis, J.; Rehani, S. K. *Ibid.* **1976**, *113*, C42.

(11) (a) Davis, R.; Ojo, I. A. O. *J. Organomet. Chem.* **1976**, *110*, C39. (b) Guggolz, E.; Oberdorfer, F.; Ziegler, M. L. *Z. Naturforsch., B* **1981**, *36B*, 1060.

(12) IIId: IR 2113 (vw), 2083 (w), 2016 (s), 1992 (s), 1978 (s), 1966 (m) cm^{-1} (hexane solution); ^{1}H NMR (360 MHz, CD_2Cl_2) δ −13.99 (s, 1 H, μ-H), 5.17 (q, 1 H, H_1), 2.99 (s, 3 H, Me_2), 2.04 (d, 3 H, Me_3), $^3J_{H_1-CH_3} = 5.8$ Hz.

$(CO)_8(\mu\text{-}(\mu^2\text{-}C{\equiv}CPh))$, as the major product.[13]

A very interesting and novel photochemical reaction pathway for III is seen in the photochemical reaction of $Re_2(CO)_{10}$ with ethylene. Although the major product of this photolysis is IIIe, we observe the formation of IIIb and IIIf[14] in 10–15% yield each. These 1-butenyl compounds are isomers that differ only in the mode of coordination of the 1-butenyl ligand. They apparently result from subsequent photochemical reaction of IIIe. Photolysis of a solution of IIIe under 1 atm of C_2H_4 produces approximately equal amounts of IIIb and IIIf. This reaction, which represents a dimerization of ethylene, is not observed in the thermal reactions of III with C_2H_4. The initial reaction process is probably photodissociation of CO from III, inasmuch as photolysis of IIIb in the presence of 1 equiv of pyridine yields a substituted compound, $(\mu\text{-}H)Re_2(CO)_7(\mu\text{-}(\eta^2\text{-}CH{=}CHC_2H_5))py$,[15] as the major product. Photodissociation of CO from IIIe would create a vacant site for coordination of an ethylene molecule, which could then undergo an insertion into the Re–H or Re–CH:CH_2 bond, followed by rearrangement to yield the butenyl products. It is noteworthy that IIIf is not produced to any appreciable extent (<1%) in the photolysis of $Re_2(CO)_{10}$ under a 1-butene atmosphere. Studies of the photochemical reactions of other derivatives of III with ethylene and other small molecules are in progress.

Acknowledgment. This research was sponsored by the National Science Foundation through Research Grant NSF CHE 81-19525. The authors are grateful to Kenneth S. Suslick for a helpful discussion.

Registry No. IIIa, 82638-69-5; IIIb, 82621-39-4; IIIc, 82621-40-7; IIId, 82621-41-8; IIIe, 82621-42-9; IIIf, 82621-43-0; $(\mu\text{-}H)Re_2(CO)_8(\pm\text{-}(\eta^2\text{-}CPh))$, 82621-44-1; $Re_2(CO)_{10}$, 14285-68-8; *dieg*-1,2-$Re_2(CO)_8(py)_2$, 67605-95-2; Re, 7440-15-5; propylene, 115-07-1; 1-butene, 106-98-9; 1-hexene, 592-41-6; *cis*-2-butene, 590-18-1; *trans*-2-butene, 624-64-6; phenyl acetylene, 536-74-3; ethylene, 74-85-1.

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(13) $(\mu\text{-}H)Re_2(CO)_8(\mu\text{-}(\eta^2\text{-}C{\equiv}CPh))$: IR 2119 (vw), 2094 (w), 2023 (s), 2002 (m), 1982 (ms) cm^{-1} (heptane solution); ^1H NMR (360 MHz, CD_2Cl_2) δ −13.01 (s, 1 H, μ-H), 7.57 (m, 2 H, α-H), 7.44 (m, 3 H, β- and γ-H); *m/e* (M^+) 698 (70 eV EIMS, Re_2 372).

(14) IIIf: ^1H NMR (90 MHz, $CDCl_3$) β −14.42 (s, 1 H, μ-H), 5.76 (d, 1 H, H_1 or H_3), 4.06 (d, 1 H, H_1 or H_3), 2.88 (q, 2 H, CH_2), 1.31 (t, 3 H, CH_3), $^3J_{H_1-H_3} = 2.2$ Hz, $^3J_{CH_2-CH_3} = 7.4$ Hz.

(15) Two isomers of this product are obtained.

Stereocontrolled Total Synthesis of (±)-Saframycin B

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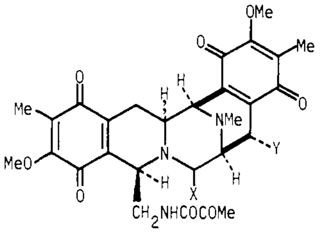
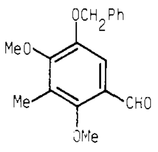
Received May 7, 1982

Saframycin B (**2**) was isolated as a satellite antibiotic from cultures of *Streptomyces lavendulae*, which is known to produce streptothricins.[1] Saframycin B and its congeners A (**1**), C(**3**), D, and E have been shown to be active against Gram-positive bacteria. Saframycins also exhibit antitumor activities, with saframycin A being particularly active.[1,2] The structure of saframycin B was elucidated by comparison of spectroscopic data with saframycin C, whose structure had been determined by X-ray crystallographic analysis.[3] Saframycin B represents a hitherto unknown class of compounds with bisquinone attached to a piperazine ring.[4] In this communication we report the first total synthesis of (±)-saframycin B.



1 X = CN, Y = H
2 X = Y = H
3 X = H, Y = OMe

The highly substituted benzaldehyde **4** was prepared from readily available 2,4-dimethoxy-3-methylbenzaldehyde[5] in seven steps [(1) 37% HCHO-H_2O, HCl, reflux; (2) NaOAc, AcOH, reflux; (3) *m*-CPBA, $CHCl_3$, reflux;[5] (4) Et_3N, MeOH, room temperature; (5) $PhCH_2Br$, K_2CO_3, DMF, 80 °C; (6) 3 N NaOH, MeOH, room temperature; (7) PCC, CH_2Cl_2, room temperature] in 76% overall yield. Addition of the carbanion of cinnamyl isocyanide, generated by 1.1 equiv of *n*-butyllithium at −78 °C, to the aldehyde **4** followed by esterification (PhCOCl, THF, −78 °C to room temperature) and hydration of the isocyanide (3 N HCl, THF, room temperature) gave a diastereomeric mixture (1:1) of the formamide **5** in 92% overall yield.[6] Upon basic hydrolysis



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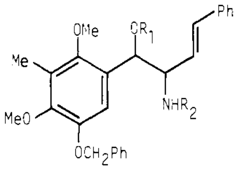
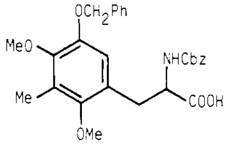


5 R_1 = COPh, R_2 = CHO
6 R_1 = R_2 = H



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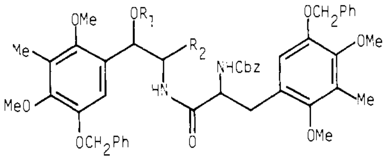
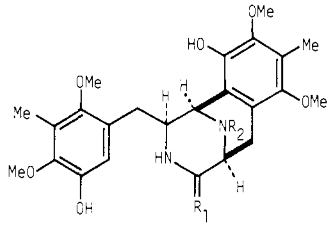


8 R_1 = H, R_2 = CH=CHPh
9 R_1 = COMe, R_2 = CH=CHPh
10 R_1 = COMe, R_2 = CHO



16 R_1 = O, R_2 = H
17 R_1 = O, R_2 = Me
18 R_1 = H_2, R_2 = Me

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(1) Arai, T.; Takahashi, K.; Kubo, A. *J. Antibiot.* **1977**, *30*, 1015.

(2) Arai, T.; Takahashi, K.; Ishiguro, K.; Mikami, T. *Gann* **1980**, *71*, 790.

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