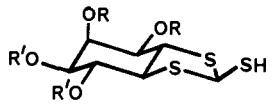
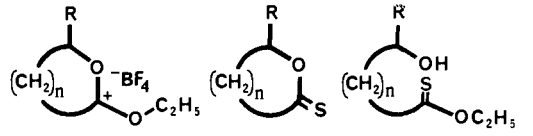


[21] R=R′ = Ac

[22] $R_2 = R_2' = Me_2C$

18-crown-6, −78 °C) led to the exclusive cleavage of the endocyclic C–O bonds to give **12a** and **13a**, respectively.[22-24]



R	n			
Me	2	27	28	29
Et	3	30	31	32
H	4	33	34	35

These results clearly prove that the breakdown of hemiorthothiol intermediates [3] and [4], in each of which there are two leaving (alkoxy) groups of identical intrinsic leaving group abilities (except for orientation of nonbonded electron pairs), is subject to stereoelectronic control (Deslongchamps effect), despite a counteracting entropy term.[25] It is highly probable that, under aprotic conditions, a similar stereoelectronic effect is operative in the cleavage of hemiortho esters of the type $RC(OH)(OR)_2$. We are currently pursuing our studies in that direction.

Acknowledgment. We thank the Research Corporation, the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Biomedical Research Support Program (BRS 6 Grant RR 7150), Division of Research Resources, National Institutes of Health, for financial support. We are also grateful to Professors G. Posner and R. H. Schlessinger for the details of their lactone α-alkylation procedures.

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(21) Lactonium salt **8** was prepared from *trans*-2,3-tetramethylene-δ-valerolactone (**14b**) by treatment with (i) LDA/THF (−78 °C, 0.5 h), (ii) MeI/HMPT (−42 °C, 3 h), (iii) LDA/THF (−78 °C, 0.5 h), (iv) MeI/HMPT (−42 °C, 3 h), (v) $Et_3O^+BF_4^-/CH_2Cl_2$ (27 °C, 3 h), (vi) NaOMe/MeOH–*i*-PrOH (−78 °C, 1 h), (vii) $BF_3{\cdot}Et_2O/Et_2O$ (−78 °C, 15 min); overall yield 17.5%.

(22) In view of the minute amounts of the kinetic products formed at −78 °C (**12a** and **13a**) and their marked propensity to undergo cyclization (**12a** → **14a**; **13a** → **15a**), we could not isolate and characterize them directly. But, when a sample of **7** was treated with NaSH in CD_3CN, rapid scanning in the δ 4.0–5.0 range revealed a characteristic quartet ($-C(=S)OCH_2CH_3$) at 4.50 ppm, *at the same time* that an aliquot of the NMR sample showed an intense $PdCl_2$-positive spot on TLC (R_f 0.55). Subsequent TLC analysis showed this spot to grow fainter in favor of another thiono compound (R_f 0.75). Correlation of the R_f values of fully characterized compounds **29**, **32**, **35** (R_f's 0.53 ± 0.02) and **28**, **31**, **34** (R_f's 0.76 ± 0.02) from the sulfhydrolysis of **27**, **30**, and **33** further substantiate the structural assignments of **12a** and **13a** (R_f's 0.53 and 0.55, respectively) and **14a** and **15a** (R_f's 0.78 and 0.77, respectively). As the temperature was raised, the spots with R_f's 0.53 and 0.55 gradually grew fainter while those with R_f's 0.78 and 0.77 intensified. All the R_f's above were determined on Merck precoated TLC silica gel 60 F-254 by eluting with $CHCl_3$–CH_3CN 5:1 v/v. Further, **15a** was isolated and its ^1H NMR spectrum revealed characteristically shifted signals ($CDCl_3$) for the diastereotopic geminal methyl groups (δ 1.28, 1.48) as compared with those of **15b** (δ 1.16, 1.28).

(23) On the TLC plates, minute amounts of thionolactones **14a** and **15a** were observed in the respective mixtures. However, control experiments with chromatographically pure **32** indicated that upon rechromatography on silica gel, a small amount of thionolactone **31** was formed. If anything, the cyclizations of **12a** and **13a** to give **14a** and **15a**, respectively, ought to be more facile than that of **32** to **31**; hence, the minute amounts of **14a** and **15a** in the original mixtures are, in all likelihood, artifacts of the TLC experiment.

(24) Interestingly, the sulfhydrolysis of **30** at −78 °C, under conditions identical with those for **7** and **8**, also revealed *exclusive* cleavage of the endocyclic C–O bond to give **32**; the latter gradually rearranged to give a mixture of **31** and **32**. The sulfhydrolysis of **30**, at −40 °C, on the other hand, gave an 80:20 (**32**/**31**) mixture; at 0 °C, the ratio was 53:47.

(25) At a standard state of 1 M, $\Delta S°$ for a typical reaction in which one molecule of reactant fragments into two species would be +35 gibbs and the corresponding $\Delta G°$ would be −10.5 kcal/mol (see: Jencks, W. P. *Adv. Enzymol.* **1975**, *43*, 276). Hence, the cleavage of the *exocyclic* C–O bond in each of [**3**] and [**4**] should be favored entropically by part of the 10.5 kcal/mol depending on the relative extent of cleavage in the respective transition states. If one disregards this entropy term completely and assumes a ratio of rate constants of 100:1 ($k_{[3]\rightarrow 12a}/k_{[3]\rightarrow 14a}$ or $k_{[4]\rightarrow 13a}/k_{[4]\rightarrow 15a}$), the *lower* limit for the stereoelectronic factor is conservatively estimated at 2.7 kcal/mol at −78 °C.

[20.10]-, [22.10]-, and [26.10]Betweenanenes, Conformationally Flexible Bicyclic Alkenes: Synthesis, Chemistry, and Optical Resolution

Sir:

In 1977 we described the synthesis of [10.10]betweenanene (**13**, $n = 12$), a novel fused-ring trans bicyclic alkene.[1] The bridging arrangement of the two rings was found to block additions to the buried double bond, resulting in dramatic reactivity differences between the trans (**13**, $n = 12$) and cis (**12**, $n = 12$) isomers.[1-3] We now wish to record the synthesis of [20.10]-, [22.10]-, and [26.10]betweenanenes (**13a–c**) by a new route of general applicability and some preliminary chemical studies on these conformationally flexible olefins, including the optical resolution and absolute configuration of the [26.10] and [22.10] homologues.

Our interest in the aforementioned betweenanenes was stimulated by the possibility that the larger ring might be capable of rotation, jump rope fashion, around the smaller ring, thereby exposing the double bond to external reagents (see Scheme I, structure **13**). An examination of space-filling models led us to believe that the [24.10] system (**13**, $n = 26$) could undergo such isomerism. The synthesis of the relevant olefins is outlined in Scheme I.[4]

Diketones **2** and **3**, obtained via cuprous iodide promoted addition[5] of ω-undecenylmagnesium bromide and ω-tridecenylmagnesium bromide,[6] respectively, to dodecandioyl chloride (**1**), yielded trienes **4** and **5** upon McMurry cyclization with the $TiCl_3$/Li reagent.[7] Hydroboration–oxidation[8] gave the diols **6** and **9** whose further conversion to dialdehydes **7** and **10** was effected with the Corey–Suggs reagent.[9] Dialdehyde **8** was secured via oxidation of triene **4** with osmium tetroxide to the bis(glycol) which was cleaved with periodic acid.[10] Cyclization of the foregoing dialdehydes with $TiCl_3$/Li[7] led to the dienes **11a–c** as mixtures (cis–trans) of disubstituted double bond isomers (mainly the trans isomer, $\nu = 965$ cm^{-1}).[11] Selective hydrogenation over Pt cleanly afforded the cis bicyclic olefins **12a–c**. Photolysis in xylene–cyclohexane (1:6) with a 450-W medium-pressure mercury lamp effected partial conversion to the trans isomers (**13a**/**12a** = 1.1, **13b**/**12b** = 1.6, **13c**/**12c** = 1.3)[3,12] which

(1) Marshall, J. A.; Lewellyn, M. E. *J. Am. Chem. Soc.* **1977**, *99*, 3508–3510. Marshall, J. A.; Chung, K.-H. *J. Org. Chem.* **1979**, *44*, 1566–1567.

(2) Marshall, J. A. *Acc. Chem. Res.* **1980**, *13*, 213–218.

(3) Nakazaki, M.; Yamamoto, K.; Yanagi, J. *J. Am. Chem. Soc.* **1979**, *101*, 147–151.

(4) Satisfactory spectral and analytical data were obtained for all new compounds.

(5) Dubois, J.-E.; Boussu, M.; Liou, C. *Tetrahedron Lett.* **1971**, 829–832.

(6) The bromide was prepared by addition of ω-undecenylmagnesium bromide to ethylene oxide and subsequent treatment of the resulting alcohol with *N*-bromosuccinimide and triphenylphosphine in benzene according to Schweizer et al. (*J. Org. Chem.* **1969**, *34*, 212–215).

(7) McMurry, J. E.; Fleming, M. P.; Kees, K. L.; Krepski, L. P. *J. Org. Chem.* **1978**, *43*, 3255–3266.

(8) Brown, H. C.; Subba Rao, B. C. *J. Am. Chem. Soc.* **1969**, *81*, 6423–6427.

(9) Corey, E. J.; Suggs, J. W. *Tetrahedron Lett.* **1975**, 2647–2650.

(10) Lemieux, R. U.; von Rudloff, E. *Can. J. Chem.* **1955**, 1701–1703.

(11) Nakanishi, K.; Solomon, P. H. "Infrared Absorption Spectroscopy", 2nd ed.; Holden-Day: San Francisco, CA, 1977, p 17.

(12) Hammond, G. S.; Saltiel, J.; Turro, N. J. *J. Am. Chem. Soc.* **1964**, *86*, 3197–3217.

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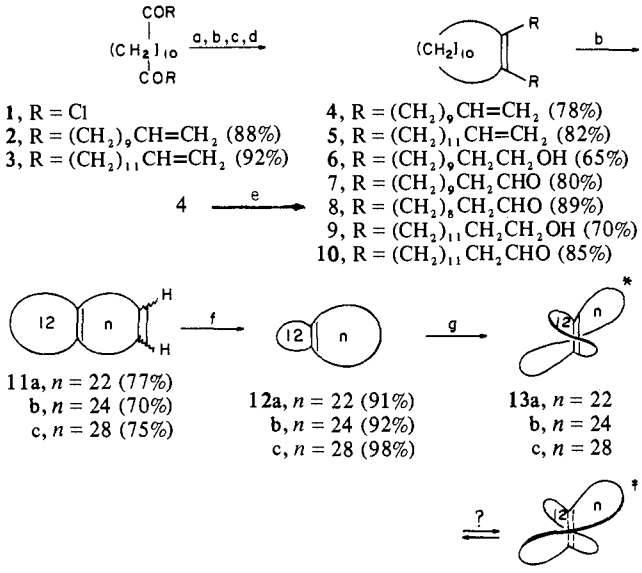
Scheme I[a]



[a] (a) RMgBr, Et_2O, CuI, −78 °C → 0 °C. (b) $TiCl_3$, Li, DME, Δ, 20 h of addition time. (c) $(Sia)_2BH$, THF; H_2O_2, NaOH. (d) $CrO_3 \cdot Py_2$, CH_2Cl_2. (e) OsO_4, C_5H_5N; $NaHSO_3$, H_2O; $NaIO_4$, dioxane, H_2O. (f) H_2/Pt-C. (g) $h\nu$, xylene, cyclohexane (92–94% material recovery). *The double bond is between the two rings; the smaller ring is above. †The double bond is beneath both rings; the larger ring is above.

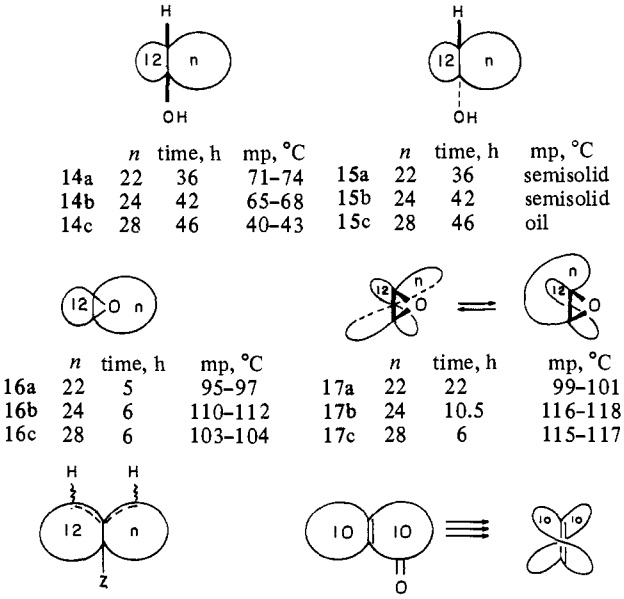
were conveniently separated by chromatography on silver nitrate impregnated silica gel (10–15%). The faster moving trans isomers (**13**) were eluted with hexane; the cis isomers required ether as the eluant.

Both the cis (**12a–c**) and trans (**13a–c**) bicyclic olefins underwent hydroboration with excess (tenfold) BH_3 in THF to give the expected alcohols **14a–c** and **15a–c** after oxidation with alkaline hydrogen peroxide.[8] Reaction times under standardized conditions are given in Scheme II.[13a] Surprisingly, the hydroboration rate seems more affected by ring *size* than by ring stereochemistry.

Epoxidation, on the other hand, showed the expected steric dependence. Reaction with excess *m*-chloroperoxybenzoic acid ($NaHCO_3$ buffer) in methylene chloride afforded the epoxides **16a–c** and **17a–c**. Reaction times[13a] and melting point data are given in Scheme II. Here the largest ring betweenanene, **13c**, showed reactivity comparable to that of the cis bicyclics **12a–c** while the smaller [20.10]betweenanene was significantly slower. We have previously shown that the cis [10.10]bicyclic olefin **12** (n = 12) reacts very rapidly (~1 min for complete reaction) with *m*-chloroperoxybenzoic acid,[13b] while the trans isomer **13** (n = 12) is recovered unchanged after three weeks exposure to the peroxy acid.[1]

Both the cis and trans [26.10]olefins (**12c** and **13c**) undergo photosensitized oxygenation[14] to give similar mixtures (double bond isomers) of allylic alcohols **18** after treatment with lithium aluminum hydride to reduce the initially formed hydroperoxide. The former reaction was complete within 1 h whereas the latter required 6 h. [10.10]Betweenanene (**13**, n = 12) was recovered unchanged after 20 h. Isomerization of the cis and trans [26.10]bicyclic olefins **12c** and **13c** could be effected with methanesulfonic acid in acetic acid,[15] iodine in dioxane,[16] or KAPA in 1,3-propanediamine.[17] All procedures gave rise to mixtures containing principally trisubstituted alkenes **19**[15] at relative rates of roughly 2:1 in favor of the cis isomer **12c**.

Scheme II



	n	time, h	mp, °C
14a	22	36	71–74
14b	24	42	65–68
14c	28	46	40–43

	n	time, h	mp, °C
15a	22	36	semisolid
15b	24	42	semisolid
15c	28	46	oil

	n	time, h	mp, °C
16a	22	5	95–97
16b	24	6	110–112
16c	28	6	103–104

	n	time, h	mp, °C
17a	22	22	99–101
17b	24	10.5	116–118
17c	28	6	115–117

18, n = 26, Z = OH
19, n = 26, Z = H
20, n = 12, Z = H

21 **22**

Nakazaki and co-workers recently obtained the first optically active betweenanene, "(−)-(*R*)-D_2-bicyclo[8.8.0]octadec-1(10)-ene" (**22**), through photoisomerization of the bicyclic enone **21** in an optically active solvent.[18] An optical purity of 0.5–1% was estimated by comparison of the rotation with that of (−)-*trans*-cyclooctene. We have found that both [26.10]- and [22.10]-betweenanene (**13c** and **13b**) undergo asymmetric epoxidation upon treatment with (+)-monoperoxycamphoric acid in chloroform.[19] If the reaction is quenched at 50% conversion (30 equiv of peroxy acid, 7.5 h of reaction time), optically active olefin **13c**, $[\alpha]^{24}_D$ − 24.7° (*c* 3.31, hexane), and **13b**, $[\alpha]^{22}_D$ −32.4° (*c* 3.32, hexane), can be isolated through chromatography on silica gel. These olefins showed a negative Cotton effect at 195 nm indicative of the *R* configuration[20] as pictured in Scheme I.[21] An enantiomeric excess of 6.0% and 7.6% can be estimated for **13c** and **13b** based on shifts in the ^{13}C NMR spectra of the hydroboration products, alcohols **15c** and **15b**, after addition of chiral shift reagent, Eu(facam)$_3$.[22a] The carbinyl carbons (δ 69.39 and 69.42) were thereby split into two closely spaced peaks with relative areas of 35:31 and 127:109, respectively (Δδ = 3.77 and 3.74, ΔΔδ = 0.27 and 0.24).[22b] The same splittings were observed with the racemic alcohols but the peak areas were 1:1, as expected.

The aforementioned experiments illustrate the remarkable reactivity differences between the smaller ring betweenanenes, such as [10.10], and the larger (jump rope) homologues. Of course, the observed reactions may not actually require a full 180° turn of the larger ring (see Scheme I). Indeed the more flexible rings may be able to expose the double bond without even turning

(13) (a) The reaction progress was monitored by thin-layer chromatography (silica gel) at periodic intervals until starting olefin could no longer be detected. (b) Reaction times for acyclic tetrasubstituted alkenes are also less than 1 min under these conditions. Thus, the large ring cycloalkenes **12a–c** and **13a–c** are surprisingly unreactive in comparison to acyclic or smaller ring olefins.

(14) Marshall, J. A.; Hochstetler, A. R. *J. Org. Chem.* **1966**, *31*, 1020–1025.

(15) Marshall, J. A.; Black, T. H.; Shone, R. L. *Tetrahedron Lett.* **1979**, 4737–4740.

(16) (a) Signaigo, F. K.; Cramer, P. L. *J. Am. Chem. Soc.* **1933**, *53*, 3327–3333. (b) Golden, D. M.; Egger, K. W.; Benson, S. W. *Ibid.* **1964**, *86*, 5416–5420.

(17) Brown, C. A.; Yamashita, A. *J. Am. Chem. Soc.* **1975**, *97*, 891–892.

(18) Nakazaki, M.; Yamamoto, K.; Maeda, M. *J. Chem. Soc., Chem. Commun.* **1980**, 294–295.

(19) Pirkle, W. H.; Rinaldi, P. L. *J. Org. Chem.* **1977**, *42*, 2080–2082.

(20) Scott, A. I.; Wrixon, A. D. *Tetrahedron* **1970**, *26*, 3695–3715.

(21) The rules for assigning absolute configuration to *trans*-cycloalkenes are given in: Cahn, R. S.; Ingold, C. K.; Prelog, V. *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 385–416. See p 402.

(22) (a) Facam is 3-(trifluoromethylhydroxymethylene)-*d*-camphorato. See: Kime, K. A.; Sievers, R. E. *Aldrichim. Acta* **1977**, *10*, 54–62. (b) Fraser, R. R.; Stothers, J. B.; Tan, C. T. *J. Magn. Reson.* **1973**, *10*, 95–97.

past the allylic centers of the smaller ring. Further studies will be directed at this point. Interestingly, none of the three "jump rope" betweenanenes **13a–c** gives rise to a colored charge-transfer complex with tetracyanoethylene whereas the cis counterparts **12a–c** form deeply colored complexes.[23] Thus, in even the largest, most flexible betweenanene, **13c**, the double bond is not readily accessible to a bulky reagent.

(23) Merrifield, R. E.; Phillips, W. D. *J. Am. Chem. Soc.* **1958**, *80*, 2778–2782.

(24) Department of Chemistry, University of South Carolina, Columbia, SC 29208.

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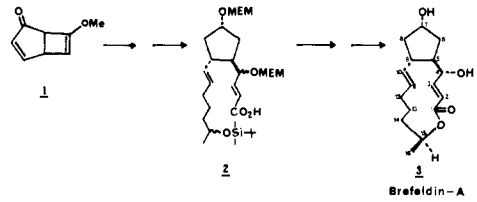
Received July 10, 1980

An Efficient Total Synthesis of (±)-Brefeldin-A[1]

Sir:

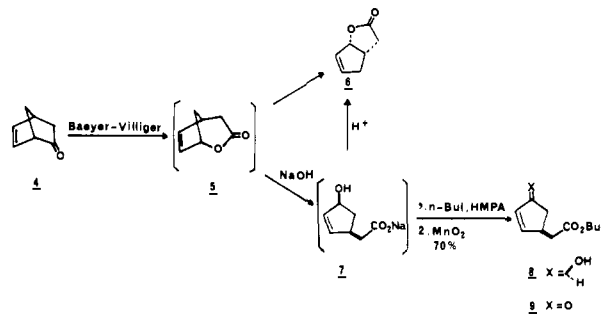
The unusually broad spectrum of biological activity exhibited by brefeldin-A (**3**)[2] combined with its structural resemblance to the prostaglandins has engendered a rather impressive synthetic effort to date in a number of laboratories.[3] In 1977 we reported[3b] a formal total synthesis of this fungal metabolite consisting of a high-yield conversion of the α-tropolone methyl ether photoproduct **1** to the monocyclic intermediate **2**, which had earlier[3a] been



transformed to racemic brefeldin-A. In this communication, we report a different total synthesis of this natural product that is substantially simpler, shorter, and more efficient than our original approach. The salient features of this synthesis include (a) ready access to an alternative Michael acceptor (replacing **1**), the "correct" enantiomer of which can be obtained through chiral induction as well as by resolution, (b) a streamlined construction of the problematic C-1 to C-4 portion of the molecule, and (c) an effective combination of protecting groups that permits easy differentiation at the C-1, -4, -7, and -15 functions (while still affording stereocontrol at C-4[3a–d]) and simplifies both chromatographic purifications and spectral analyses.

In reconsidering our earlier approach, we felt an important new objective to be a simple means of obtaining large amounts of a cyclopentenone that could be used as the Michael acceptor of the C-10 to C-16 portion of brefeldin-A and ultimately secured in the correct optically active form. We had already found that 6-heptyn-2-one is reduced with baker's yeast to (*S*)-(+)-6-heptyn-2-ol (to be used for the C-10 to C-16 portion) in up to 53% yield (5–10-g scale) and with virtually complete enantioselectivity.

Norbornenone (**4**) thus appeared to be an excellent starting



material—obtainable in optically active form[4–6] and, in principle, easily converted to a 4-[(carbalkoxy)methyl]cyclopentenone.[6a] Under the usual Baeyer–Villiger conditions, the product initially formed from norbornenone, lactone **5**, rearranged very readily to give the unwanted lactone **6**;[7] however, by using H_2O_2–NaOH in H_2O–Et_2O,[6b] lactone **5** could be intercepted to produce its hydroxy acid salt **7**, which in turn could be directly alkylated with excess *n*-butyl iodide in HMPA[8] at room temperature to afford the hydroxy ester **8** (racemic series). Allylic oxidation of **8** with manganese dioxide in chloroform then provided the desired enone ester **9** in 70% overall yield on large-scale runs.

Stereoselective conjugate addition to this cyclopentenone of the C-10 to C-16 carbon unit was carried out at −78 °C in THF by using the mixed cuprate **10**[3a,b] derived from the trans[9] vinyllithium reagent and (1-pentynyl)copper in the presence of 2 equiv of hexamethylphosphorous triamide[10] to give the trans adduct **11** in 72% yield after purification (Scheme I). A minor amount of the corresponding 5,9-cis product was also obtained (~4% yield). Reduction of the trans product **11** with L-Selectride in THF at −78 °C produced an ~2.7:1 mixture of the C-7 α- and β-alcohols,[11] from which the pure α-alcohol **12** could be conveniently separated in 65% yield from **11** through treatment with a catalytic amount of *p*-TsOH in refluxing toluene, followed by filtration over silica gel.[12] The C-7 hydroxyl group in **12** was then protected as the methyl ether (MeI, Ag_2O, CH_3CN, reflux,[14] 93%), which proved to be a very satisfactory alternative to the previously employed methoxyethoxymethyl and methoxymethyl C-7 hydroxyl protecting groups.[3a–d]

An improved sequence[15] for the construction of the requisite

(1) This synthesis was presented May 9, 1980, at SECO 17, Bordeaux, France.

(2) Singleton, V. L.; Bohonos, N.; Ullstrup, A. J. *Nature (London)* **1958**, *181*, 1072. Härri, E.; Loeffler, W.; Sigg, H. P.; Stähelin, H.; Tamm, Ch. *Helv. Chim. Acta* **1963**, *46*, 1235. Betina, V.; Nemec, P.; Kovâč, S.; Kjaer, A.; Shapiro, R. H. *Acta Chem. Scand.* **1965**, *19*, 519. Weber, H. P.; Hauser, D.; Sigg, H. P. *Helv. Chim. Acta* **1971**, *54*, 2763 and references cited. For the biological effects of brefeldin-A, see footnotes 2–4 in ref 3c.

(3) (a) Corey, E. J.; Wollenberg, R. H. *Tetrahedron Lett.* **1976**, 4701, 4705. Corey, E. J.; Wollenberg, R. H.; Williams, D. R. *Ibid.* **1977**, 2243. (b) Baudouy, R.; Crabbé, P.; Greene, A. E.; Le Drian, C.; Orr, A. F. *Ibid.* **1977**, 2973. (c) Bartlett, P. A.; Green, F. R., III *J. Am. Chem. Soc.* **1978**, *100*, 4858. (d) Kitahara, T.; Mori, K.; Matsui, M. *Tetrahedron Lett.* **1979**, 3021. For other approaches, see: (e) Curran, D. P.; Scholtz, D. *Monatsh. Chem.* **1977**, *108*, 1401. (f) Livinghouse, T.; Stevens, R. V. *J. Chem. Soc., Chem. Commun.* **1978**, 754.

(4) Asymmetric induction in hydroboration: (a) Mislow, K.; Berger, J. G. *J. Am. Chem. Soc.* **1962**, *84*, 1956. (b) Brown, H. C.; Yoon, N. M. *Isr. J. Chem.* **1976**, *15*, 12. In Diels–Alder: (c) Sauer, J.; Kredel, J. *Tetrahedron Lett.* **1966**, 6359. (d) Corey, E. J.; Ensley, H. E. *J. Am. Chem. Soc.* **1975**, *97*, 6909 and references cited.

(5) Resolution: Berson, J. A.; Walia, J. S.; Remanick, A.; Suzuki, S.; Reynolds-Warnoff, P.; Willner, D. *J. Am. Chem. Soc.* **1961**, *83*, 3986. Reference 4d.

(6) See also: (a) Corey, E. J.; Schaaf, T. K.; Huber, W.; Koelliker, U.; Weinshenker, N. M. *J. Am. Chem. Soc.* **1970**, *92*, 397. (b) Weinshenker, N. W.; Stephenson, R. *J. Org. Chem.* **1972**, *37*, 3741.

(7) Meinwald, J.; Seidel, M. C.; Cadoff, B. C. *J. Am. Chem. Soc.* **1958**, *80*, 6303. The free acid corresponding to **7** was also very unstable, rearranging to **6**. See: Grieco, P. A.; Yokoyama, Y.; Withers, G. P.; Okuniewicz, F. J.; Wang, C.-L. J. *J. Org. Chem.* **1978**, *43*, 4178. See, however, ref 6.

(8) Shaw, J. E.; Kunerth, D. C.; Sherry, J. J. *Tetrahedron Lett.* **1973**, 689. The *n*-butyl ester was found to be the most satisfactory of the esters synthesized (Me, Et, *i*-Pr, *n*-Bu) in terms of ease of purification and degree of stereoselectivity in the subsequent conjugate addition reaction.

(9) Collins, P. W.; Jung, C. J.; Gasiecki, A.; Pappo, R. *Tetrahedron Lett.* **1978**, 3187.

(10) Corey, E. J.; Beames, D. J. *J. Am. Chem. Soc.* **1972**, *94*, 7210.

(11) This mixture of alcohols could not be resolved into more than one spot on analytical TLC plates.

(12) The lactonized β-alcohol thus obtained (24% yield) could be converted to the α-alcohol **12** in 40% overall yield by successive treatment as follows: NaOH; CH_2N_2; DEAD, Ph_3P, AcOH;[13] NaOH, *n*-BuI, HMPA,[8] thus raising the yield of **12** from **11** to 75%.

(13) See ref 3c and references cited.

(14) See: Finch, N.; Fitt, J. J.; Hsu, I. H. S. *J. Org. Chem.* **1975**, *40*, 206 and references cited.

(15) Greene, A. E.; Le Drian, C.; Crabbé, P. *J. Org. Chem.* **1980**, *45*, 2713.

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