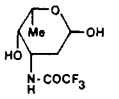
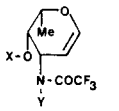
aklavinone nearly quantitatively.

The overall yield of aklavinone from bromojuglone was 34–41% counting two recycles of **11** and 18–22% not counting the recycles. Following the route exactly parallel with the one described for aklavinone, several aklavinone analogues have been synthesized. These results will be published elsewhere.[31]

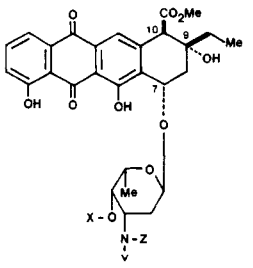
The glycosidation reaction of racemic aklavinone (**13**) and the *N*-methyl glycal **17**[10,32] (oil), prepared from *N*-(trifluoroacetyl)-



16

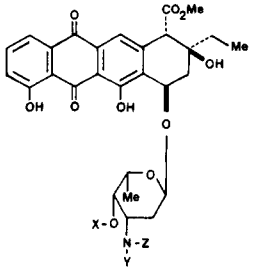


17 : X = $COC_6H_4NO_2$(p), Y = Me



18 : X = $COC_6H_4NO_2$(p), Y = Me, Z = $COCF_3$

20 : X = H, Y = Me, Z = H



19 : X = $COC_6H_4NO_2$(p), Y = Me, Z = $COCF_3$

daunosamine (**16**),[33-35] was smoothly effected in benzene containing a catalytic amount of *p*-toluenesulfonic acid monohydrate at 50 °C[36] to yield a mixture of mainly two products, chromatographic separation of which gave the glycosides **18**[10,37] (25–30% yield; mp 159–161 °C) and **19**[10,38] (25–30% yield; mp 158–161 °C). The NMR spectrum, in particular the spin–spin coupling constants and chemical shift of the anomeric proton, clearly indicated that both of the products were glycosides with the α-anomeric configuration. From the following experiments, the glycoside **18** was shown to be derived from aklavinone with the natural absolute configuration, while the glycoside **19** from aklavinone with the unnatural absolute configuration: (1) Acid hydrolysis of **18** (90% aqueous TFA/room temperature) yielded aklavinone with $[\alpha]_D$ +146°, whereas that of **19** yielded aklavinone with $[\alpha]_D$ −141°. The specific rotation of natural aklavinone[29] is known to be +158° in chloroform. (2) Glycosidation using aklavinone with the natural absolute configuration[29] gave only the glycoside **18** (mp, NMR, $[\alpha]_D$, TLC).

The stereoselectivity of the glycosidation was very high. This was most conclusively demonstrated by coupling aklavinone with the natural absolute configuration with the glycal **17**; NMR and TLC analysis of the reaction mixture indicated that several minor products were formed besides the desired glycoside **18** (80% isolated yield), but we were unable to isolate a large enough quantity of any one of the minor products to firmly assign a structure. However, the ratio of the α anomer to the β anomer, if any, was estimated to be better than 20:1.

Sodium methoxide treatment of **18** [$NaOCH_3$(excess)/CH_3OH/−20 °C/2 h] yielded *N*-demethylaklavin (**20**) along with a small amount (<5%, based on NMR analysis) of its C10 epimer; these conditions were crucial to the success of this transformation, since longer reaction time and/or higher reaction temperature led to the formation of as much as 35% of the C10 epimer (NMR and TLC analysis). The crude product was directly subjected to *N*-methylation by using the Borch procedure[39] (aqueous $CH_2O/NaBH_3CN$/AcOH/room temperature/1 h) to yield aklavin (**2**) in 70% overall yield from **18**. The synthetic substance was found to be identical with natural aklavin[40] on comparison of spectroscopic (NMR, IR, UV, $[\alpha]_D$) and TLC data.

Acknowledgment. Financial support from the National Cancer Institute, DHEW (Grant CA22215), is gratefully acknowledged.

(31) Sekizaki, H.; Hasan, I.; McNamara, J. M.; Kishi, Y., manuscript in preparation.

(32) Optically active *N*-trifluoroacetyldaunosamine (**16**)[33,34] was converted to the previously unknown glycal[10] [X = COC_6H_4-*p*-NO_2, Y = H in structure **17**; mp 152–153 °C] in 84% overall yield in 2 steps (i.e., (1) $ClCOC_6H_4$-*p*-NO_2/(dimethylamino)pyridine–pyridine/room temperature,[35] (2) 185 °C at 2.5 mmHg). N-methylation of this glycal under standard conditions (CH_3I/K_2CO_3/acetone/50 °C) afforded the *N*-methyl glycal **17**[10] [oil; NMR ($CDCl_3$): 1.29 (3 H, d, J = 6.6 Hz), 2.95 (3 H, q, J = 1.7 Hz), 4.67 (1 H, dt, J = 6.4, 2.0 Hz), 6.75 (1 H, dd, J = 6.4, 2.3 Hz) ppm; $[\alpha]_D$ −173° (*c* 1.12, $CHCl_3$)] in 92% yield.

(33) For the synthesis of daunosamine, see: (a) Marsh, J. P.; Mosher, C. W.; Acton, E. M.; Goodman, L. *Chem. Commun.* **1967**, 973. (b) Horton, D.; Weckerle, W. *Carbohydr. Res.* **1976**, *46*, 227. (c) Wong, C. M.; Ho, T.; Niemczura, W. P. *Can. J. Chem.* **1975**, *53*, 3144. (d) Yamaguchi, T.; Kojima, M. *Carbohydr. Res.* **1977**, *59*, 343. (e) Fronza, G.; Fuganti, C.; Grasselli, P. *J. Chem. Soc., Chem. Commun.* **1980**, 442. (f) Hauser, F. M.; Rhee, R. P. *J. Org. Chem.* **1981**, *46*, 227.

(34) We are indebted to Dr. M. R. Uskokovic, Hoffmann-La Roche, Inc., for a sample of this substance.

(35) The product at this stage is a known substance (see: Smith, T. H.; Fujiwara, A. N.; Lee, W. W.; Wu, H. Y.; Henry, D. W. *J. Org. Chem.* **1977**, *42*, 3653).

(36) Arcamone, F.; Bargiotti, A.; Cassinelli, G.; Redaelli, S.; Hanessian, S.; DiMarco, A.; Casazza, A. M.; Dasdia, T.; Necco, A.; Reggiani, P.; Supino, R. *J. Med. Chem.* **1976**, *19*, 733. We thank Professor Hanessian, University of Montreal, for various procedures of the glycosidation.

(37) NMR ($CDCl_3$): 1.11 (3 H, t, J = 7.1 Hz), 1.22 (3 H, d, J = 6.2 Hz), 2.87 (3 H, br s), 3.70 (3 H, s), 5.32 (1 H, br s), 5.59 (1 H, br s), 5.75 (1 H, br s) ppm; $[\alpha]_D$ − 50° (*c* 0.328, $CHCl_3$).

(38) NMR ($CDCl_3$): 1.10 (3 H, t, J = 7.1 Hz), 1.24 (3 H, d, J = 6.5 Hz), 2.85 (3 H, br s), 3.73 (3 H, s), 5.60 (3 H, br s) ppm; $[\alpha]_D$ −336° (*c* 0.147, $CHCl_3$).

(39) Borch, R. F.; Hassid, A. I. *J. Org. Chem.* **1972**, *37*, 1673.

(40) We are indebted to Dr. U. Weiss, National Institutes of Health, for a sample of natural aklavin.

Total Stereospecific Synthesis of (±)-Aklavinone

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Received March 5, 1981

The clinically important antitumor antibiotic aclacinomycin A (**1**), originally isolated from *Streptomyces galilaeus*,[1] exhibits inhibitory activity against leukemia L-1210 and P-388, sarcoma 180, 6C3HED lymphosarcoma, and other transplantable animal tumors.[2] Moreover, this anticancer agent shows less cardiotoxicity than either adriamycin or daunorubicin.[3] We wish to report the first total synthesis of (±)-aklavinone (**2**), the aglycon portion of aclacinomycin A, originally isolated by Ollis and co-workers as the naturally occurring (+) enantiomer.[4]

Reaction of 3-methoxyphthalic acid 1-methyl ester (**3**)[5] with 6-ethyl-5,6,7,8-tetrahydro-1-naphthol (**4**)[6] in the presence of

† Address correspondence to E. I. du Pont de Nemours, Inc., Central Research and Development Department, Experimental Station, Wilmington, DE 19898.

(1) Oki, T.; Matsuzawa, Y.; Yoshimoto, A.; Numata, K.; Kitamura, I.; Hori, S.; Takamatsu, A.; Umezawa, H.; Ishizuka, M.; Naganawa, H.; Suda, H.; Hamada, M.; Takeuchi, T., *J. Antibiot.* **1975**, *28*, 830–834.

(2) Hori, S.; Shirai, M.; Hirano, S.; Oki, T.; Inui, T.; Tsuka Goshi, S.; Ishizuka, M.; Takeuchi, T.; Umezawa, H. *Gann* **1977**, 685–690.

(3) Yamaki, H.; Suzuki, H.; Mishimura, T.; Tanaka, N. *J. Antibiot.* **1978**, *31*, 1149–1154. Misumi, M.; Yamaki, H.; Akiyama, T.; Tanaka, N. *J. Antibiot.* **1979**, *32*, 48–52.

(4) Gordon, J. J.; Jackman, L. M.; Ollis, W. D.; Sutherland, I. D. *Tetrahedron Lett.* **1960**, 28.

(5) Miller, D. G.: Trenbeath, S.; Sih, C. J. *Tetrahedron Lett.* **1976**, 1637–1640.

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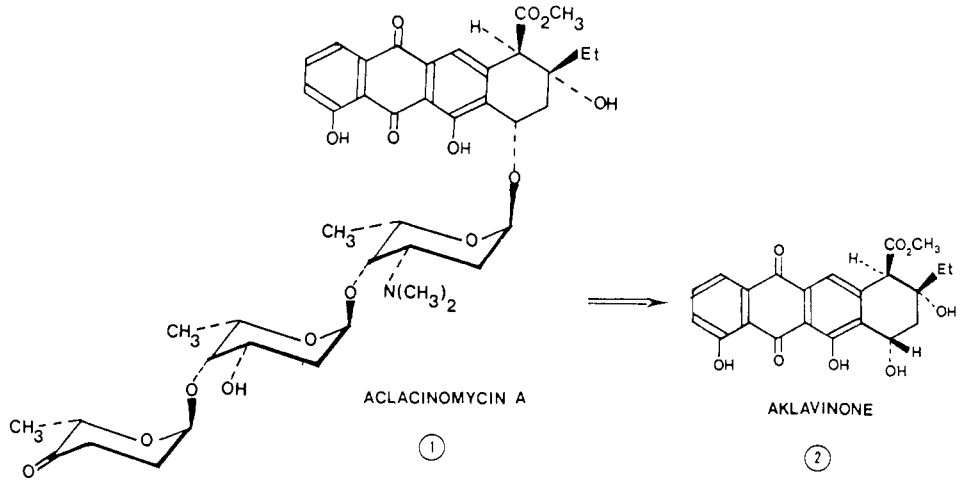
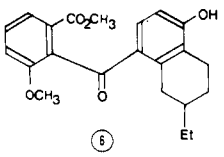
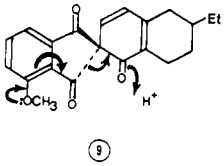


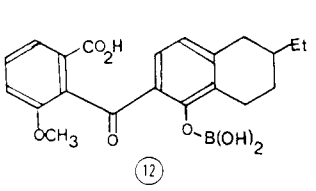
trifluoroacetic acid anhydride led to the aryl ester **5**,[17] mp 133–134 °C (Scheme I). Interestingly, at room temperature in boron trifluoride etherate, the aryl ester **5** underwent a Fries rearrangement to yield cleanly the *p*-benzophenone derivative **6**.[17] At

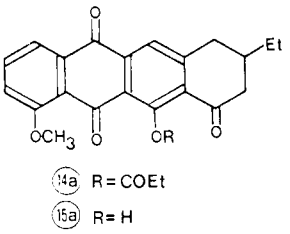




70 °C, the required ortho isomer **7**[17] was produced in a 1:1 ratio with **6** and at the reflux temperature of 126°, **5** rearranged entirely to the desired *o*-benzophenone **7**[7] without contamination by **6**. The compounds were readily differentiated by their proton NMR spectra, owing to the diagnostic chelated hydrogen present only in **7** at δ 13.5. Saponification of the *o*-benzophenone **7** yielded the desired acid **8**,[17] mp 181–182 °C.

Freidel–Crafts ring closure of **8** in hot polyphosphoric acid afforded exclusively the undesired anthracyclone **10**,[10] a product of a Hayashi-type rearrangement.[8] The dramatic ortho-directing property of the phenolic OH present in the acid **8** presumably forces the incipient acylium cation to yield the transient spiro intermediate **9**. This substance then fragments in a regiospecific manner, directed by the methoxy lone pair, to generate exclusively the regioisomeric acylium cation. Ring closure of this latter species leads to the sole formation of the undesired regioisomer **10**.[9] Treatment of the acid **8** with boric acid in concentrated sulfuric acid, however, afforded the desired regioisomer **11**,[17] mp 179–180 °C without a trace of the unwanted **10**. Presumably, the intermediate borate ester **12** deactivates the ortho-directing property of the phenol moiety enough to prevent the Hayashi rearrangement.[10a]





The tetracyclic species **11** was converted to the yellow propionate derivative **13**,[17] mp 143–144 °C, and then oxidized to the ketone **14**. Coproduction off the regioisomeric ketone **14a**,[17] mp 157–158 °C, occurred in this step; however, the mixture was easily separated by chromatography after hydrolysis to the phenolic derivatives, the yellow ketone **15**,[17] mp 224–225 °C dec, and the more polar orange-brown **15a**,[17] mp 219–220 °C. The desired product **15** was the major product favored over **15a** by a factor of 1.9, a result of the steric crowding around the position peri to the propionate group.[10b] Demethylation of **15** to the required orange diphenolic ketone **16**,[17] mp 203–204 °C; ^{1}H NMR ($CDCl_3$) δ 12.50 (1 H, s), 11.99 (1 H, s), 8.44 (1 H, s), 7.87 (1 H, m), 7.71 (1 H, m), 7.31 (1 H, m), 3.4–2.6 (2 H, m), 2.6–2.3 (2 H, m), 2.3–1.5 (3 H, m), 1.04 (3 H, t, J = 8 Hz), was uneventful.

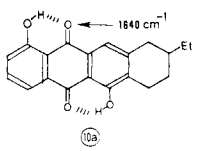
Introduction of the required extra carbon attached to C(10) in the key intermediate **16** was readily accomplished by treatment with trimethylsilyl cyanide to afford the *o*-silylated nitrile **17**[17] (Scheme II).[11] This intermediate was converted to the corresponding cyanohydrin **18**, which underwent dehydration to afford the cyano olefin **19**,[17] mp 227–228 °C. Treatment with basic hydrogen peroxide in methanol at room temperature epoxidized the double bond and simultaneously converted the nitrile to the carboxamide **20**,[17] mp 263–264 °C. The desired transformation of the carboxamido moiety to the required carbomethoxy function was problematical owing to the severe steric crowding in that portion of the molecule. However, treatment of **20** with the methyl Meerwwin's reagent afforded the imidate ester **21** in excellent yield. Hydrolysis of **21** in aqueous acid produced the expected[12]

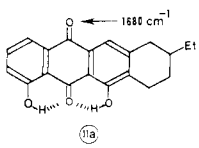
(6) Prepared from 5-methoxy-1-tetralone by (a) alkylation (potassium *tert*-butoxide, *tert*-butyl alcohol, EtI), (b) hydrogenation (H_2, Pd/C, HOAc/HCl), and (c) demethylation (48% HBr, 120 °C).

(7) Direct combination of **3** and **4** under a variety of conditions did not offer the regiochemical control that prior formation of the aryl ester **5** afforded.

(8) Hayashi, M. J. *J. Chem. Soc.* **1927**, 251. (b) *ibid.* **1930**, 1513, 1520. (c) Newman, M. S. *Acc. Chem. Res.* **1972**, *5*, 354. (d) Sih, C. H., *et al.*, *Tetrahedron Lett.* **1976**, 3385.

(9) The structures of the regioisomers **10** *vs.* **11** was determined by comparing the IR carbonyl frequencies of the tetrahydronaphthacenequinones **10a** and **11a**. The observed presence or absence of a nonchelated carbonyl band at 1680 cm^{-1} confirmed the assignments.

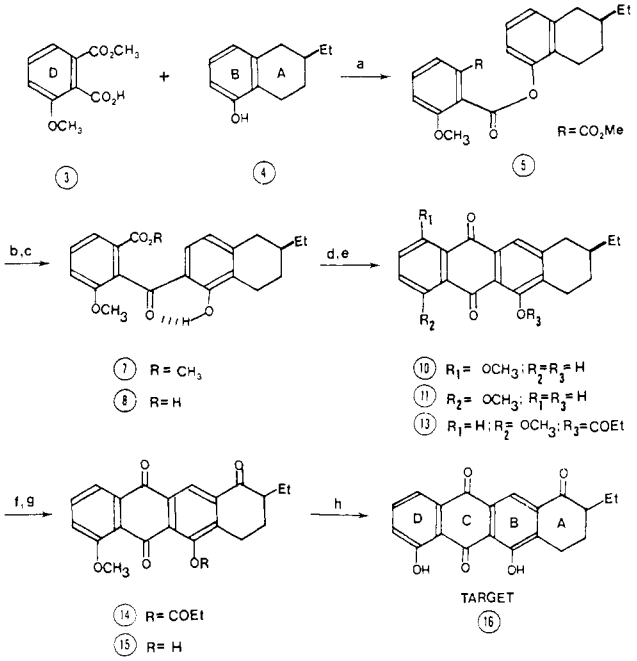




(10) (a) Such borate esters have been postulated as intermediates in the Bohn–Schmidt reaction, which affords an overall hydroxylation of an anthraquinone. See: Bohn, R. German Patent 46654, 1889. Schmidt, R. E. *Ibid.* 60855, 1891. Philips, M. *Chem. Rev.* **1929**, *6*, 168. (b) Oxidation of the acetate corresponding to **13** afforded a product ratio of 1.2, while the isobutyrate analogue yielded a ratio of 1.95. Difficulties in the formation of the isobutyrate analogue of **13** precluded its use, rendering the propionate **13** the substrate of choice.

(11) The formation of transient intermediates along the path to **17** could be detected by TLC and are believed to be adducts of Me_3SiCN and the aromatic carbonyls. The structure of **17** was assigned on thermodynamic grounds. See: Evans, D. A.; Hoffman, J. M.; Truesdale, L. K. *J. Am. Chem. Soc.* **1973**, *95*, 5822.

Scheme I[a]

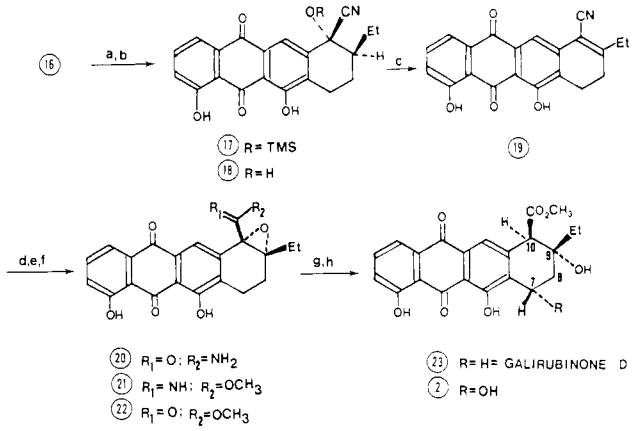


[a] (a) CF_3COOH, CH_2Cl_2 (3:2), Δ, 5 h (90%). (b) $BF_3 \cdot Et_2O$, Δ, 10 min (70%). (c) 1 N NaOH, CH_3OH, Δ, 0.75 h (100%). (d) $B(OH)_3$, concentrated H_2SO_4, 30% H_2SO_4 (fuming), 100 °C, 0.33 h (57%). (e) $(EtCO)_2O$, Py, 70 °C, 3 days (70%). (f) CrO_3, Ac_2O, HOAc, 6 °C, 3 h (43%). (g) 5% K_2CO_3, THF, Δ, 1.5 h (90%). (h) $AlCl_3$, CH_2Cl_2, 25 °C, 18 h (95%).

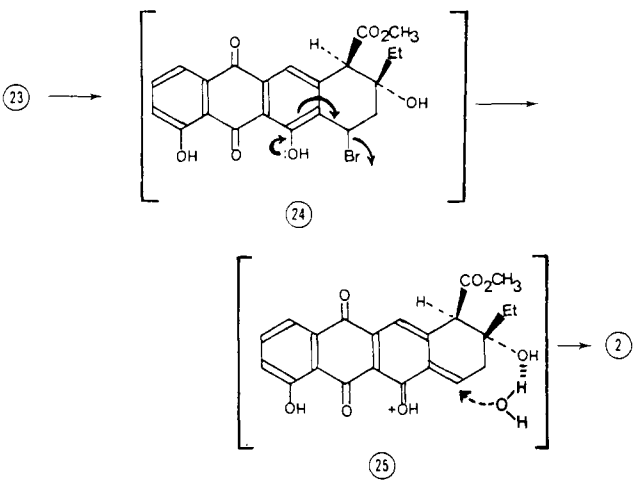
epoxy ester **22**[17], mp 229–230 °C; ^1H NMR ($CDCl_3$) δ 12.21 (1 H, s), 11.82 (1 H, s), 7.71 (1 H, m), 7.64 (1 H, m), 7.59 (1 H, m), 7.20 (1 H, m), 3.98 (3 H, s), 3.2–2.5 (2 H, m), 2.5–1.5 (4 H, m), 1.11 (3 H, t, J = 8 Hz), along with the amide **20**, obtained as the major product. Fortuately, the highly polar amide **20** was easily separated from the desired ester **22** by a simple chromatography and could then be recycled through **21**. The predominance of the amide is presumably a result of the severe steric interactions present in the expected tetrahedral intermediate which favors simple dealkylation of the imidate ester **21** rather than hydrolysis.[13]

Catalytic hydrogenation off the epoxy ester **22** yielded the β-hydroxy ester **23**,[17] mp 210–211 °C; ^1H NMR ($CDCl_3$) δ 12.50 (1 H, s), 12.09 (1 H, s), 7.82 (1 H, m), 7.66 (1 H, t, J = 8 Hz), 7.65 (1 H, s), 7.29 (1 H, m), 3.94 (1 H, Br s), 3.72 (3 H, s), 3.1–2.0 (4 H, m), 1.7–1.5 (2 H, m), 1.10 (3 H, t, J = 8 Hz), itself a natural product known as galirubinone D.[14] This key reduction was stereospecific and set up the desired trans relationship between the C(10) carbomethoxy group and the newly created C(9) alcohol. As expected, the epoxy ester was also reduced regiospecifically with rupture of only the benzylic carbon–oxygen bond. Interestingly, the hydrogenation failed entirely in ethanol but yielded **23** in ethanol/triethanolamine. The critical function of the added base is, we believe, to generate a quinone methide from a reduced anthraquinone intermediate which is then subsequently hydrogenated. Finally, the required introduction of the C(7)-alcohol function proceeded stereospecifically to afford the desired

Scheme II[a]



[a] Me_3SiCN, ZnI_2 (catalytic), CH_2Cl_2, 25 °C, 2 days (60%). (b) $KHSO_4$, CH_3OH, 25 °C, 0.25 h (100%). (c) $KHSO_4$, 130 °C, 0.25 h (66%). (d) 30% H_2O_2, 1 N NaOH, CH_3OH, 25 °C, 1.25 h (94%). (e) $(CH_3)_3OBF_4$, CH_2Cl_2, 25 °C, 4 h (80%). (f) 0.1 N H_2SO_4, THF, 45 °C, 60 h (30%). (g) H_2, $Pd/BaSO_4$, EtOH, $N(CH_2CH_2OH)_3$, 25 °C, 1.5 h (96%). (h) CCl_4/H_2O, NBS, AIBN (catalytic), Δ, 40 min; 10% K_2CO_3, THF, 25 °C, 0.33 h (70%).



1,3-*cis*-diol configuration at C(7) and C(9). This is in contrast to the well-documented experience in the total synthesis of adriamycinone[15] which generated predominantly the unwanted epi configuration at C(7) in the final step, a result which necessitated a tedious epimerization process. In our case, the initially formed C(7)-bromide **24** underwent solvolysis, possibly via the enone **25**, which was then hydrated from the less hindered α side to generate the target molecule (±)-aklavinone **2**,[17] mp 205–206 °C; ^1H NMR ($CDCl_3$) δ 12.75 (1 H, s), 11.96 (1H, s), 7.83 (1 H, m), 7.73 (1 H, s), 7.69 (1 H, *t*, J = 8 Hz), 7.31 (1 H, m), 5.39 (1 H, br s), 4.09 (1 H, s), 3.81 (1 H, s), 3.70 (3 H, s), 3.34 (1 H, br s), 2.6–2.2 (2 H, m), 1.8–1.5 (2 H, m), 1.09 (3 H, t, J = 8 Hz), possessing identical spectroscopic and TLC characteristics with an authentic sample of naturally occurring aklavinone.[16]

In summary, we have completed the first total synthesis of (±)-aklavinone (**2**), the aglycon portion of the anticancer agent

(12) Roberts, R. M.; DeWolfe, R. H. *J. Am. Chem. Soc.* **1954**, *76*, 2411–2414. DeWolfe, R. H.; Augustine, F. B. *J. Org. Chem.* **1965**, *30*, 699–702.

(13) Deslongchamps, P.; *Tetrahedron* **1975**, *31*, 2463–2490. Basic hydrolysis of the imidate ester **21** afforded the corresponding epoxy nitrile by a base catalyzed loss of methanol across the system.

(14) Eckardt, K.; Bradler, G. *Naturwissenschaften* **1965**, *52*, 539. Eckardt, K. *Chem. Ber.* **1967**, *100*, 2561. Our racemic synthetic sample had identical solution spectra and TLC behavior when compared to an authentic sample of galirubinone D (7-deoxyaklavinone) obtained by hydrogenolysis of natural aklavinone.

(15) Kende, A. S.; Tsay, Y.; Mills, J. E. *J. Am. Chem. Soc.* **1976**, *98*, 1967–1969. Smith, T. H.; Fujiwara, A. N.; Henry, D. W.; Lee, W. W. *Ibid.* **1976**, *38*, 1969–1971.

(16) Provided by the Department of Microbiology, Hoffmann-La Roche Inc., Nutley, NJ. Our synthetic sample of (±)-aklavinone was also shown to be identical with material synthesized via independent routes in the laboratories of Professor A. Kende (Rochester) and Professor Y. Kishi (Harvard). See accompanying communications.

(17) This substance gave satisfactory elemental analysis and spectroscopic data.

aclacinomycin A via a 17-step sequence that proceeds regioselectively and stereospecifically.

Acknowledgment. We express our gratitude to the staff of the Physical Chemistry Department of Hoffmann-La Roche for their determination of spectral and analytical data.

A Study of the Rate of Intervalence Electron Transfer Using Time Domain Reflectometry

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It is difficult to determine the rate of intervalence electron transfer for most mixed-valence compounds by using conventional spectroscopic techniques such as EPR, NMR, Mössbauer, and ESCA.[1] We report here the first successful use of the technique of time-domain reflectometry[2] (TDR) to obtain these kinetic data. This technique has two potential advantages over the techniques mentioned above. (1) It can obtain kinetic information over the frequency range 10^6–10^{10} Hz. Calculations based on the Hush theory[3] using the energy of the intervalence transfer band indicate that for most mixed-valence systems electron-transfer rates should fall within this frequency range at reasonable temperatures. This same range is often inaccessible with commonly used techniques. (2) The measurement involves a direct observation of the electron-transfer process. It is not subject to nuclear relaxation effects and other problems which inhibit the use of magnetic resonance techniques for many nuclei and/or electronic configurations. Thus, TDR should serve to complement existing techniques for studying electron-transfer phenomena.

Time-domain reflectometry measures the dielectric relaxation properties of a sample. TDR monitors the change in the dielectric constant, ϵ, as a function of time after the application of an electric field pulse as shown in Figure 1. For a typical Debye dielectric, this change can be described by

$$\epsilon(t) = \epsilon_\infty + (\epsilon_0 - \epsilon_\infty)(1 - e^{-t/\tau}) \quad (1)$$

When the electric field is applied, the sample is immediately polarized to give a dielectric constant corresponding to ϵ_∞. From this initial value, the dielectric constant continues to increase, exponentially approaching a value of ϵ_0 as the dipoles which exist in the sample have a chance to orient themselves with the applied field. The dielectric relaxation time, τ, is a measure of the rate at which the dipoles in the system can move to achieve this preferred orientation.

For solid mixed-valence compounds the "dipole motion" corresponds to an intervalence electron transfer between a pair of metal sites:

$$M_1^{Z+}—M_2^{(Z+1)+} \rightarrow M_1^{(Z+1)+}—M_2^{Z+} \quad (2)$$

Here, one electron transfer changes the population difference of the two states by two electrons. Thus, the actual rate of electron transfer is

$$K = 1/2\tau \quad (3)$$

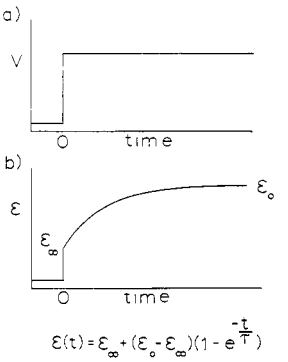

Figure 1. Dielectric relaxation in the time domain. (a) A representation of the external step voltage (or electric field) applied to a dielectric sample as a function of time. (b) A representation of the behavior of the dielectric constant as a function of time for the voltage pulse in (a).

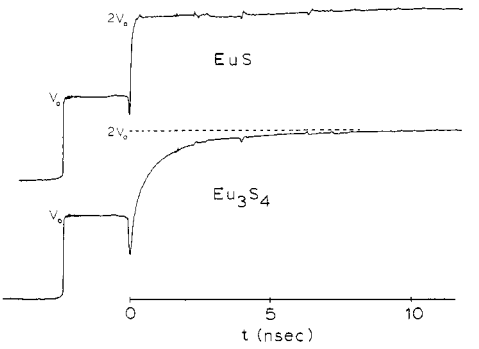

Figure 2. TDR spectra for europium sulfides. The top spectrum is the multiple-reflectance TDR spectrum obtained for EuS. The bottom TDR spectrum is that obtained for the mixed-valence Eu_3S_4.

We have monitored the dielectric relaxation behavior of a sample of europium sulfide powder, Eu_3S_4, by using a Hewlett-Packard time domain reflectometer.[4] In this device, a square wave voltage pulse, V_0, is propagated down a section of coaxial cable containing the sample. When this pulse encounters the surface of the sample, part of it is transmitted through the sample and part is reflected. Many such reflections eventually occur at both the front and back surfaces of the sample which represent impedence mismatches in the coaxial line. All reflected components of the pulse are eventually propogated back to the detector, and the total reflected signal, $R(t)$, is displayed on an oscilloscope. If the multiple-reflection sample-termination method developed by Cole[5] is used, the TDR data can be analyzed by the equation

$$\epsilon_\infty + (\epsilon_0 - \epsilon_\infty)(1 - e^{-[t-(1/2)T_r]/\tau}) + C_s/dC_c = \frac{c}{d}\int_0^t \frac{P(t')}{2V_0}\,dt' + \frac{c}{d}\int_0^t \frac{P(t')P(t-t')}{4V_0^2}\,dt' + \left(\frac{c}{d}\right)\left(\frac{T_r P(T_r)P(t)}{8V_0^2}\right) \quad t > T_r \quad (4)$$

where T_r is the rise time of the voltage pulse, C_s is stray end capacitance, C_c is coaxial line capacitance per unit length, d is the length of the sample-filled section of the line, c is the speed of light, and $P(t)$ is $V_0 - R(t)$.

Figure 2 shows TDR traces for Eu_3S_4 and EuS at room temperature. The initial voltage pulse, V_0, encounters the sample at $t = 0$. For EuS, no dielectric relaxation is observed. However, for the mixed-valence Eu_3S_4 sample, the reflected voltage is clearly indicative of dielectric relaxation on the TDR time scale. We attribute this dielectric relaxation to intervalence electron transfer between Eu(II) and Eu(III) sites in the sample. Analysis of the data indicates that this process has a dielectric relaxation time

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