dried over Na_2SO_4. The ether solution was then concentrated to give an oil. Attempts at crystallizing this material led only to its partial destruction. The material was thus chromatographed on a 1 mm × 20 cm × 20 cm preparative silica gel TLC plate eluting with 30% EtOAc/hexane, providing 29.7 mg (74%) of product, which was homogenous by TLC (30% EtOAc/hexane) and GC (OV-17, 220 °C). The NMR and IR spectra of this material were identical with spectra obtained for material prepared from steroid **2**.

(b) From 3β-Acetoxy-20-methylpregn-20-en-5β-ol (2). With a procedure similar to the one described above, a 74% yield of rearranged material **15** was obtained from **2**: ^{1}H NMR δ 0.74 (d, 3, J = 7 Hz), 0.84 (d, 3, J = 7 Hz), 0.94 (s, 3), 0.96 (s, 3), 2.08 (s, 3), 5.24 (m, 1); IR 3650, 1740 cm^{-1}; exact mass calcd for $C_{24}H_{38}O_3$ m/e 374.28208, found m/e 374.28153.

17,20-Dimethyl-18-nor-17α-pregn-13-ene-3β,5β-diol (16): (a) Derived from 3β-Acetoxy-20-methylpregn-17(20)-en-5β-ol (1). An 18.9 mg (50.5 μmol) sample of **15**, prepared from **1** as described above, was dissolved in 2 mL of MeOH saturated with NH_3. After being stirred at room temperature overnight, the reaction mixture was partitioned between ether and water. The ether solution was washed with brine, dried over Na_2SO_4, and condensed under reduced pressure to give a residue, which was recrystallized from hexane to give 13.2 mg (79%) of the desired diol **16**, mp 181–185 °C. The NMR and IR spectra of this material were identical with those obtained for the sample of **16** prepared below. Anal. Calcd for $C_{22}H_{36}O_2$: C, 79.46; H, 10.91. Found: C, 79.25; H, 11.08.

(b) Derived from 3β-Acetoxy-20-methylpregn-20-en-5β-ol (2). With a procedure similar to the one described above, a sample of **15** derived from **2** was converted by NH_3/MeOH treatment to **16** in 65% chromatographed yield. Recrystallization from hexane provided a sample which had a mp 179–183 °C: ^{1}H NMR δ 0.73 (d, 3, J = 7 Hz), 0.84 (d, 3, J = 7 Hz), 0.92 (s, 3), 0.96 (s, 3), 2.86 (m, 2), 4.14 (m, 1); IR 3320 cm^{-1}. Anal. Calcd for $C_{22}H_{36}O_2$: C, 79.46; H, 10.91. Found: C, 79.53; H, 10.90.

A mixture of samples of diol **16** derived from sterols **1** and **2** had a melting point of 179–185 °C.

Acknowledgment. I am grateful to Professor E. E. van Tamelen for advice, encouragement, and financial support and to the Upjohn Co. for provision of a fellowship.

Reaction of $[Co(CN)_5]^{3-}$ with Alkenyl Halides in an Aprotic Medium

Louis S. Stuhl

Department of Chemistry, Brandeis University, Waltham, Massachusetts 02254

Received August 30, 1984

Activating aryl and vinyl halides toward substitution is one of the oldest uses of transition metals in organic synthesis.[1] Copper has been the metal of choice, but recently several methodologies, some catalytic in metal, have appeared based on nickel,[2] palladium,[3] or cobalt[4] chemistry.

Table I. Reactions of Haloalkenes with $Co(CN)_5^{3-}$

compd	T, °C	t, h	organic prods[a]	yield, %[b]
(*E*)-PhCH=CHBr	40	43	(*E*)-PhCH=CHCN	72
			(*Z*)-PhCh=CHCN	<3
(*Z*)-PhCh=CHBr (90% *Z*)	55	50	(*Z*)-PhCH=CHCN	43
			(*E*)-PhCH=CHCN	28
(*Z*)-PhCH=CHBr (>95% *Z*)	25	18	(*Z*)-PhCH=CHCN	47[c]
			(*E*)-PhCH=CHCN	16
			(*Z*)-PhCH=CHBr	37
(*Z*)-PhCH=CHCl	40	43	(*Z*)-PhCH=CHCN	32
			(*E*)-PhCH=CHCN	13
			(*Z*)-PhCH=CHCl	13
p-$CH_3OC_6H_4Br$	25	24	NR[d]	
$(CH_3)_2C$=CHCl	40	43	$(CH_3)_2C$=CH(CN)	68

[a] Identified by GC and ^{1}H NMR. [b] Determined by GC of ether extracts from aqueous workup unless otherwise indicated. [c] Determined by NMR of reaction mixture, normalized to 100%. [d] Also no reaction after heating 1 h at 60 °C.

Relatively little is known about the mechanisms of these reactions, and there has been some debate over the involvement of concerted exchanges versus organometallic intermediates[5] and between chain and nonchain one- vs. two-electron mechanisms.[6] In the case of the cobalt(II) catalyzed cyanide exchange with vinyl bromides, evidence has recently been presented for a mechanism involving a Co(I)/Co(III) catalytic couple and (σ-vinyl)cobalt cyanide intermediates.[7]

I now report that the reaction of $Co(CN)_5^{3-}$ with β-bromo styrene to give cinnamonitrile occurs under conditions where this mechanism cannot be operative. Reaction of $[(C_2H_5)_3(CH_3)N]_3Co(CN)_5$ with (*E*)-2-bromo-1-phenylethene (1:1 mol ratio) in acetonitrile proceeds slowly at room temperature and more rapidly at 40–80 °C to form a blue solution and solids. Workup with aqueous base and ether extraction gives (*E*)-3-phenylpropenenitrile (Table I). Although the starting cobalt complex is paramagnetic the reaction can be followed by ^{1}H NMR. No evidence for the buildup of an organocobalt intermediate is observed.

Reaction of $Co(CN)_5^{3-}$ with (*Z*)-2-bromo-1-phenylethene is not completely stereospecific: at 25 °C, a 3:1 ratio of (*Z*)- to (*E*)-3-phenylpropenenitrile results at ~60% conversion. At 55 °C, reaction is complete in under 48 h, giving a 71% yield of a 2.3:1 mixture of the *Z* and *E* nitriles (corrected for stereochemical purity of the starting material). Using a 2:1 ratio of $Co(CN)_5^{3-}$ to (*Z*)-2-bromo-1-phenylethene gives reduced stereospecificity and the foormation of significant amounts of (currently unidentified) additional products.

Under the conditions described herein, (*E*)-2-bromo-1-phenylethene is inert to $(C_2H_5)_3CH_3N^+CN^-$ in acetonitrile. Addition of $[(C_2H_5)_3(CH_3)N]_3Co(CN)_5$ to this halide–cyanide mixture does not catalyze the displacement reaction and in fact the presence of excess cyanide appears

(1) (a) Ullman reaction: Fanta, P. E. *Synthesis* **1974**, 9–21. (b) Ullman ether synthesis: Moroz, A. A.; Shvartaberg, M. S. *Russ. Chem. Rev. (Engl. Transl.)* **1974**, *43*, 679–689. (c) Rosenmund–von Braun reaction: Mowry, D. T. *Chem. Rev.* **1948**, *42*, 207–209. (d) Ester synthesis: Cohen, T.; Lewin, A. H. *J. Am. Chem. Soc.* **1966**, *88*, 4521–4522. (e) Application to vinyl halides: Cohen, T.; Poeth, T. *J. Am. Chem. Soc.* **1972**, *94*, 4363–4364. Lapouyade, R.; Daney, M.; Lapenue, M.; Bouas-Laurent, H. *Bull. Soc. Chim. Fr.* **1973**, 720–721.

(2) Some representative reports: Corey, E. J.; Hegedus, L. S. *J. Am. Chem. Soc.* **1969**, *91*, 1233–1234. Hashimoto, J.; Tsuruta, N.; Ryang, M.; Tsutsumi, S. *J. Org. Chem.* **1970**, *35*, 3748–3752. Semmelhack, M. F.; Helquist, P. M.; Jones, L. D. *J. Am. Chem. Soc.* **1971**, *93*, 5909–5310. Zembayashi, M.; Tamao, K.; Yoshida, J.; Kumada, M. *Tetrahedron Lett.* **1977**, 4089–4092. Tamao, K.; Sumitani, Y. K.; Zembayashi, A. F.; Kodama, S.; Nakajima, I.; Minato, A.; Kumada, M. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 1958–1969. Cramer, R.; Coulson, D. R. *J. Org. Chem.* **1975**, *40*, 2267–2273. Cassar, L. *J. Organomet. Chem.* **1973**, *54*, C57–C58.

(3) Inter alia: Yamaura, K.; Murahashi, S.-I. *Tetrahedron Lett.* **1977**, 4429–4430. Negishi, E.; Okukado, N.; King, A. O.; Van Horn, D. E.; Spiegel, B. I. *J. Am. Chem. Soc.* **1978**, *100*, 2254–2256. Takagi, K.; Okamoto, T.; Sakakibara, Y.; Oka, S. *Chem. Lett.* **1973**, 471–474. Heck, R. F. *Pure Appl. Chem.* **1978**, *50*, 691–701. Kim, J.-I. I.; Patel, B. A.; Heck, R. F. *J. Org. Chem.* **1981**, *46*, 1067–1073.

(4) (a) Dodd, D.; Johnson, M. D.; Meeks, B. S.; Titchmarsh, D. M.; Duong, K. N. V.; Gaudemer, A. *J. Chem. Soc., Perkin Trans. 2* **1976**, 1261–1267. (b) Funabiki, T.; Yoshida, S.; Tarama, K. *J. Chem. Soc., Chem. Commun.* **1978**, 1059–1061.

(5) Cohen, T.; Wood, J.; Dietz, A. G., Jr. *Tetrahedron Lett.* **1974**, 3555–3558.

(6) Kochi, J. K. "Organometallic Mechanisms and Catalysis"; Academic Press: New York, 1978; pp 168–173.

(7) Funabiki, T.; Hosomi, H.; Yoshida, I.; Tarama, K. *J. Am. Chem. Soc.* **1982**, *104*, 1560–1568.

0022-3263/85/1950-3934$01.50/0

to slow the reaction of the halide with $Co(CN)_5^{3-}$.

Characterization of the solids formed in these reactions has been thwarted by their instability and insolubility. On standing in an inert atmosphere, the initially blue solid formed in the reaction with (*E*)-1-bromo-2-phenylethene changes to a pale olive-green powder totally insoluble in all solvents examined. The blue solution remaining at the end of the reaction shows λ_{max} 611 nm, consistent with the $Co(CN)_2$ chromophore.[8] The blue solid has ν_{CN} 2105 cm^{-1}. The identities of the species formed from varying ratios of $Co(II)/CN^-$ and the difficulties involved in their characterizations have been discussed elsewhere.[9] Most likely the blue solid is a mixture of salts of $Co(CN)_4^{2-}$, $Co(CN)_3(MeCN)^-$, $Co(CN)_2(MeCN)_2$, and cyano-bridged polymers with the second of these predominating in solution. $Co(CN)_4^{2-}$ is not stable with the Et_3MeN^+ counterion.[10]

The mechanism proposed by Funabiki et al.[7] for cobalt-catalyzed cyanation of vinyl halides hinges on the conversion of $Co(CN)_5^{3-}$ to $HCo(CN)_5^{3-}$ followed by deprotonation to give a cobalt(I) species. Unlike their aqueous counterparts, solution of $(R_4N^+)_3Co(CN)_5^{3-}$ in anhydrous acetonitrile are quite stable in the absence of air and water and show no tendency to form $HCo(CN)_5^{3-}$ either by reaction with solvent or directly with H_2.[8,9] Thus the mechanism proposed for the aqueous solution reaction cannot be operative in acetonitrile. The aqueous reaction will proceed in the absence of added base, although as in acetonitrile the reaction is no longer catalytic. This suggests that a pathway not involving the $HCo(CN)_5^{3-}$ deprotonation may be accessible in water as well as in acetonitrile. We have so far been unable to reproduce the precipitate reported as forming in the base-free aqueous reaction[4] and so cannot compare it to that formed in acetonitrile.

The phenyl group of the 2-bromo-1-phenylethenes is not a requirement for reactivity with $Co(CN)_5^{3-}$. 1-Chloro-2-methylpropene reacts cleanly to form 3-methylbut-2-enenitrile. However, bromoethene, 2-bromopropene, and 2-bromo-3-phenylprop-2-enal, although quite rapidly consumed, do not give any other extractable organic products. (*Z*)-2-Chloro-1-phenylethene reacts similarly to but more slowly than its bromo analogue. Kinetic studies have not been attempted, but a qualitative reactivity ordering can be given: 1-chloro-2-methylpropene > (*Z*)-2-bromo-1-phenylethene > (*E*)-2-bromo-1-phenylethene > (*Z*)-2-chloro-1-phenylethene > *p*-bromoanisole (no reaction). This ordering is similar to that observed in the aqueous, catalytic system. As in the aqueous system, haloalkenes containing electron-withdrawing groups do not undergo the desired reaction. Thus, after 48 h at 40 °C, a 30% recovery of 3-chlorocyclohex-2-enone is found, with no volatile products detectable by GC. Bromomaleic anhydride reacts instantly with $(Et_3MeN^+)_3Co(CN)_5^{3-}$ to produce a dark red solution from which a red-black solid precipitates. This solid is still under study, but may be a π-complex of Co(I or II), since Funabiki et al. report such complexes as being deep red.[7,11]

Although the available data are meager for the purpose, and will probably remain so because of the intractable nature of the species involved, a referee has requested some discussion of possible mechanisms. Funabiki[7,12] has considered three distinct mechanisms for the aqueous alkaline Co–CN catalyst. A mechanism based on formation of a Co—H bond and its addition to the C=C bond of the vinyl halide (an addition–elimination mechanism) was rejected because of the observed high stereospecificity and the lack of deuterium incorporation into the product.

In the aprotic system, there is no obvious way in which a cobalt hydride could be formed. We have examined the Co(II)–CN system for evidence of hydride formation and have found it only in the otherwise very special case where Li^+ is the counterion in DMF solvent.[9] However, the possibility that a very small amount of a cobalt hydride is formed and is the reactive species in acetonitrile cannot be positively ruled out.

Funabiki excluded halogen abstraction/free radical pathways as being incompatible with the observed stereospecificity of the aqueous system. The lower stereospecificity of the aprotic conditions makes this type of mechanism quite plausible, particularly if coordination of the vinyl halide to cobalt prior to electron transfer/halide atom abstraction occurs. This would result in a coordinated vinyl radical, which might well have a reduced rate of isomerization. There is insufficient data in the literature on the configurational stability of substituted vinyl radicals, and none that I am aware of on π-complexed vinyl radicals, to enable judging the plausibility of this type of mechanism.

The mechanism that Funabiki favors for the aqueous system is one involving oxidative addition of the vinyl halide to a Co(I) species, most likely $Co(CN)_4^{3-}$, followed by reductive elimination of nitrile from the resulting vinylcyanocobalt(III) complex. This mechanism seems well supported for the aqueous system except for the lack of precedent for spontaneous reductive elimination from $RCo(CN)_5^{3-}$ complexes.[13] Funabiki has noted the possibility that the oxidative addition step could proceed either through a nucleophilic attack by Co(I) or through a radical nonchain (i.e., electron transfer) process, the latter being favored because of the observation that some aryl halides are reactive under the aqueous reaction conditions.[12] Very rapid trapping of the vinyl radical (which is a possibility) would be required to account for the observed high retention of configuration. An electron-transfer pathway would help explain the observed lack of stereospecificity in the cyanation of (*Z*)-2-bromo-2-butene as well as the formation of significant amounts of saturated nitriles in this case and with α-bromostyrene. Neither reduction products nor oligomerization products have been observed in the nonaqueous reaction, although some reduction products are observed under the aqueous conditions.

In the present nonaqueous system, the generation of Co(I) seems rather unlikely. A cobalt(I) species could arise via a disproportionation reaction.

$$2Co(CN)_5^{3-} \rightarrow Co(CN)_4^{3-} + Co(CN)_6^{3-}$$

A referee has pointed out that there is precedent for such a process in the reaction of $Co(CN)_5^{3-}$ with CO.[14] There is no evidence for spontaneous disproportionation of $(R_4N)_3Co(CN)_5$ compounds.[9] Attempts to prepare stable Co(I) cyanides in acetonitrile by reduction of Co(II) cyanides have produced only intractable solids with IR spectra consistent with the presence of cobalt in more than one oxidation state.[15] Electrochemical data suggest that

(8) White, D. A.; Solodar, A. J.; Baizer, M. M. *Inorg. Chem.* **1972**, *11*, 2160–2167.
(9) Carter, S. J.; Foxman, B. M.; Stuhl, L. S., submitted for publication.
(10) Carter, S. J.; Foxman, B. M.; Stuhl, L. S. *J. Am. Chem. Soc.* **1984**, *106*, 4265–4266.
(11) Funabiki, T. *J. Chem. Soc., Chem. Commun.* **1979**, 1116–1117.
(12) Funabiki, T.; Nakamura, H.; Yoshida, S. *J. Organomet. Chem.* **1983**, *243*, 95–100.
(13) Kwiatek, J.; Seyler, J. K. *J. Organomet. Chem.* **1965**, *3*, 433–437.
(14) Halpern, J.; Pribanic, M. *J. Am. Chem. Soc.* **1971**, *93*, 96–98.
(15) Carter, S. J.; Stuhl, L. S., manuscript in preparation.

(π-C_5H_5)$Co(CN)_2^{2-}$, a Co(I) complex that should have at least comparable stability to $Co(CN)_4^{3-}$, is unstable in acetonitrile on the cyclic voltametric time scale. Similar instability of low-valent cyanides in acetonitrile has been observed for other complexes.[16] It thus appears that cyanide has only limited ability to stabilize Co(I) in acetonitrile, and given the oxidizing power of Co(III) the disproportionation reaction above is probably thermodynamically unfavorable. A more interesting possibility is that coordination of the vinyl halide induces disproportionation. Electron-deficient alkenes are good ligands for low-valent cobalt.[17,18]

Thus it is not possible to choose from an abundance of possible reaction paths given the available evidence. There is evidence in both the aqueous and the acetonitrile reactions for π-coordination of the product nitriles, and coordination of the vinyl halides could well be important in one or both of the systems, but little is known about coordination of alkenes to Co(II) and even for Co(I) there are few well-characterized examples.[18]

Further mechanistic speculation concerning this reaction clearly is unwarranted at this time. The incomplete stereospecificity and lack of catalysis clearly distinguish our system from that of Funabiki et al., which appears to remain the method of choice for converting base-stable haloalkenes to α,β-unsaturated nitriles. The $(Et_3MeN)_3Co(CN)_5$ reaction may, however, be of value in organic synthesis when neither the aqueous base of the Funabiki reaction nor the high temperatures of the reaction with CuCN can be tolerated.

Experimental Section

General. All reactions were carried out in dry glassware under a nitrogen atmosphere. Acetonitrile was dried by distillation from P_4O_{10}. Dimethyl formamide (DMF) from Burdick and Jackson was stirred with activated 4-Å molecular sieves and filtered through a fine frit. Diethyl ether and THF for the preparation and purification of the cyanide salts were purified by distillation from sodium benzophenone. $(Et_3MeN)CN$,[19] (*E*)-C_6H_5CH=CHBr,[20] (*Z*)-C_6H_5CH=CHBr,[21] and (*Z*)-C_6H_5CH=$CHCl$[4a] were prepared and purified via literature procedures. Bromoethene, 2-bromopropene, 1-chloro-2-methylpropene, 2-bromo-3-phenylprop-2-enal, *p*-bromoanisole, and anhydrous $CoCl_2$ were commercial products. 1-Chloro-2-methylpropene was washed with Na_2SO_3 solution, filtered through activated alumina, and distilled. 2-Bromopropene was freshly distilled. Other halides were used as received.

Caution: Cyanides and nitriles should be assumed to be severe poisons and handled (wearing gloves) accordingly. No HCN should be produced in these reactions; however, safe laboratory practice requires that these reactions be carried out in a good fume hood or appropriately vented glovebox as a precaution against inadvertant HCN production.

Products, which are all known compounds, were identified by comparison with reported ^1H NMR data and also by GC comparison with authentic samples of those nitriles that were commercially available. Stereochemistry of the cinnamonitriles was assigned based on the reported ^1H NMR data.[4b] Quantitative analysis was by GC using the internal standard method. A 6 ft × $^1/_8$ in. 3% OV-210 on Chromosorb W column was used for halostyrene reaction analyses, a 6 ft × $^1/_8$ in. 1% SP-2100 on Carbopack B column was used for the 1-chloro-2-methylpropene reaction, and a 10% SP-2100 on Chromosorb W column was used for other analyses. Proton NMR was performed on a Varian EM-390 spectrometer. IR data were recorded on a Perkin-Elmer 683 spectrometer interfaced to a P-E 3500 Data Station.

$[(C_2H_5)_3(CH_3)N]_3[Co(CN)_5]$. A slight variant of the literature procedure for the synthesis of $[(C_2H_5)_4N][Co(CN)_5]$ was used.[8] A solution of $CoCl_2$ (1.04 g, 8.00 mmol) in 70 mL of DMF was slowly added to a stirred solution of $[(C_2H_5)_3(CH_3)N]CN$ (6.83 g, 4.0 mmol) in 250 mL of DMF. The flask holding the $CoCl_2$ solution was rinsed with 10 mL of DMF and the rinsings added to the reaction mixture, which was then stirred until its color stopped changing, ending as dark yellow. THF was added slowly with stirring until precipitation began, and the mixture was cooled to −35 °C. The yellow crystals that formed were collected by filtration and washed successively with 30 mL of a chilled 1:1 mixture of DMF and THF, 2 × 10 mL of THF, and 15 mL of ether. The product was recrystallized from a concentrated acetonitrile solution by addition of ether and cooling to −35 °C. After washing with chilled 1:1 acetonitrile–ether and then twice with ether, the solid was dried in vacuo for 1 h, to give $[(C_2H_5)_3(CH_3)N]_3Co(CN)_5$ (3.53 g, 82%) as opaque tan-yellow crystals. IR (mineral oil mull) 2070 cm^{-1}.

Reactions of $[(C_2H_5)_3(CH_3)N]_3[Co(CN)_5]$ with Haloalkenes. The reaction with (*E*)-PhCH=CHBr is given as a representative procedure. The bromostyrene (85 μL, 0.66 mmol) was added by syringe to 6.00 mL of a 0.100 M solution of $[(C_2H_5)_3(CH_3)N]_3Co(CN)_5$ in acetonitrile. Within 15 min the initially yellow solution became green. The reaction mixture was placed in a 40 °C oil bath. In 2.5 h the solution color was blue. Heating was continued for a total of 43 h. After cooling, the blue-green solution was opened to the air and poured into 10 mL of 0.1 M aqueous NaOH. The products were extracted with diethyl ether, and the dried ether solution was analyzed by GC. A 72% yield of (*E*)-cinnamonitrile was found, with no starting material and a trace of the *Z* nitrile. A nonaqueous workup, vacuum distillation without exposure of the reaction mixture to air, was used to isolate the products of the 1-chloro-2-methylpropene reaction.

Acknowledgment. This work was supported by the donors of the Petroleum Research Fund, administered by the American Chemical Society, and by the National Science Foundation under Grant CHE-8209006. I thank Prof. B. Snider for a gift of 3-chlorocyclohex-2-enone.

Registry No. $[(C_2H_5)_3(CH_3)N]_3[Co(CN)_5]$, 98087-79-7; (*E*)-PhCH=CHBr, 588-72-7; (*Z*)-PhCH=CHBr, 588-73-8; (*Z*)-PhCH=CHCl, 4604-28-8; *p*-$CH_3OC_6H_4Br$, 104-92-7; $(CH_3)_2C$=CHCl, 513-37-1; (*E*)-PhCH=CHCN, 1885-38-7; (*Z*)-PhCH=CHCN, 24840-05-9; $(CH_3)_2C$=CHCN, 4786-24-7; $[(C_2H_5)(CH_3)N]CN$, 69666-99-5; $CoCl_2$, 7646-79-9; bromoethene, 593-60-2; 2-bromopropene, 557-93-7; 3-chlorocyclohex-2-enone, 5682-75-7; bromomaleic anhydride, 5926-51-2; 2-bromo-3-phenylprop-2-enol, 5443-49-2.

(16) del Rosario, R.; Stuhl, L. S. *J. Am. Chem. Soc.* **1984**, *106*, 1160–1161.
(17) Agnes, G.; Bassi, I. W.; Benedicenti, C.; Intrito, R.; Calcaterra, M.; Santini, C. *J. Organomet. Chem.* **1977**, *129*, 401–413.
(18) Funabiki, T. *Rev. Inorg. Chem.* **1982**, *4*, 329–384.
(19) Kobler, H.; Munz, R.; Gasser, G. A.; Simchen, G. *Justus Liebigs Ann. Chem.* **1978**, 1937–1945.
(20) Dolby, L. J.; Wilkins, C.; Frey, T. G. *J. Org. Chem.* **1966**, *31*, 1110–1116.
(21) Cristol, S. J.; Norris, W. P. *J. Am. Chem. Soc.* **1953**, *75*, 2645–2646.

A New Dihydrobenz[*a*]anthraquinone Antitumor Antibiotic (PD 116740)

John H. Wilton, Daniel C. Cheney, Gerard C. Hokanson,* and James C. French

Warner-Lambert/Parke-Davis Pharmaceutical Research, Ann Arbor, Michigan 48105

He Cun-heng and Jon Clardy*

Department of Chemistry—Baker Laboratory, Cornell University, Ithaca, New York 14853

Received January 21, 1985

In the course of our anticancer drug discovery program, the fermentation broth of an as yet unidentified actinomycete isolate (WP 4669) was found to exhibit in vitro activity against L1210 lymphocytic leukemia and HCT-8

0022-3263/85/1950-3936$01.50/0