

acetalization of **10c** (using mesitaldehyde dimethyl acetal<sup>13</sup>), followed by introduction of a cyclic carbamate at C-9/C-11, furnished **12** [mp 260.5–262 °C,  $[\alpha]_D^{25} - 40.7^\circ$  (*c* 0.99, CHCl<sub>3</sub>)]. Carbamate **12** thus obtained was transformed by saponification<sup>14a</sup> and thioesterification<sup>14b</sup> to **11a**. Subjection of **11a** to Corey's method<sup>3a</sup> of lactonization (xylene, 140 °C) furnished **12** in 40% yield. However, under milder conditions (toluene, 110 °C), the yield of **12** increased to 70%.<sup>15</sup> These results substantiated the usefulness of our conclusions from the study of the structure/reactivity relationships pertaining to the lactonization reaction.

At this point it remained for us to develop an efficient preparation of **11a** from our synthetic intermediate **2** (Scheme I). To this end, **2** was transformed in 75% yield to the mesylate **13a** in four steps: (1) deprotection of the C-9 hydroxyl (with concomitant ester exchange at C-1), (2) selective phenoxyacetylation at C-3, (3) mesylation at C-9, and (4) deprotection<sup>16</sup> at C-3. Treatment of **13a** with LiN<sub>3</sub> furnished the inverted azide **13b** [ $R_1 = H$ ,  $R_2 = N_3$ ; mp 81–82 °C,  $[\alpha]_D^{25} + 19.7^\circ$  (*c* 2.2, CHCl<sub>3</sub>)] in 75% yield after chromatography.<sup>17</sup> Carbamate **13c** ( $R_1 = H$ ,  $R_2 = NHCO_2C_6H_4-p-NO_2$ ), derived from azide **13b**, was smoothly deprotected to furnish the hexaol **14a** contaminated with a minor byproduct.<sup>18</sup> Crude **14a** underwent selective cyclization to the 9,11-cyclic carbamate **14b** (mp 164.5–165.5 °C; 70% yield from **13b**), which was readily purified by chromatography. Acetalization<sup>13</sup> of **14b** under thermodynamically controlled conditions led to the desired **11b** ( $X = OCH_3$ ; 85% yield).<sup>19</sup> The thioester **11a** obtained from **11b** was identical to **11a**, derived from natural erythromycin (vide supra), and was lactonized in 70% yield to **12** [mp 260.5–262 °C,  $[\alpha]_D^{25} - 40.0^\circ$  (*c* 0.94, CHCl<sub>3</sub>)] by the previously established method.

With the intermediate lactone **12** in hand, we were ready to proceed with the conclusion of our synthesis of erythromycin, which is described in the following paper.<sup>9</sup>

**Acknowledgment.** We are indebted to Professor Yoshito Kishi for his help and encouragement and, in particular, for his acceptance of the role of principal investigator upon Professor Woodward's death. Financial assistance from the National Institutes of Health (GM04229) is gratefully acknowledged. Mass spectra were provided by the facility supported by the National Science Foundation (Grant CHE-7908590).

**Supplementary Material Available:** Physical properties (IR and <sup>1</sup>H NMR spectra, etc.) of selected synthetic intermediates (including **11a,b**, **12**, **13a–c**, and **14b**) and schemes used for the preparation of (1) lactones (**3cl**, **4bl–el**, **5al,bl**, **6bl**, **7al–dl**, **8al,bl**, and **9l**) from **10a** and **10b** and (2) thioesters **3b** and **6a** from **3cl** and **6bl**, respectively (13 pages). Ordering information is given on any current masthead page.

(12) It should be noted that the reported<sup>12a</sup> preparation of **10c** was subsequently shown<sup>12b</sup> to be incorrect: (a) Djokic, S.; Tamburasev, A. *Tetrahedron Lett.* 1967, 1645. (b) Massey, E. H.; Kitchell, B.; Martin, L. D.; Gerzon, K.; Murphy, H. W. *Ibid.* 1970, 157.

(13) Selective protection of the 1,3,4-triol was most effectively achieved via the mesitaldehyde acetal, even in cases where commonly used acetals failed.

(14) (a) The saponification method [NaOH in *t*-BuOH/EtOH (4/1)] employed was most effective in avoiding (i) epimerization at C-2 and (ii) formation of 12,13-epoxy acids when a free C-12 hydroxyl group was present. (b) Corey, E. J.; Clark, D. A. *Tetrahedron Lett.* 1979, 2875.

(15) The observed temperature effect can be explained mainly by the formation of byproducts only under the 140 °C conditions. The major byproduct, identified as the 2-*epi*-thioester (probably produced via a ketene), decomposed primarily to unidentified compounds under the 140 °C conditions and did not lactonize to give a 2-*epi*-lactone. The formation of such 2-*epi*-thioesters appears to be general under the 140 °C conditions and was also observed in other cases.

(16) The deprotection of the C-3 hydroxyl group is required; otherwise elimination leading to unsaturation at C-2/C-3 takes place under the subsequent displacement conditions.

(17) Unidentified elimination products were also formed in 20% yield. (18) This byproduct is probably the corresponding  $\delta$ -lactone of **14a**. It is the exclusive product under the usual acidic conditions used for such deprotections.

(19) Other acetals were also formed as minor products but were reequilibrated to **11b** after separation. The yield of **11b** is based on two such reequilibrations.

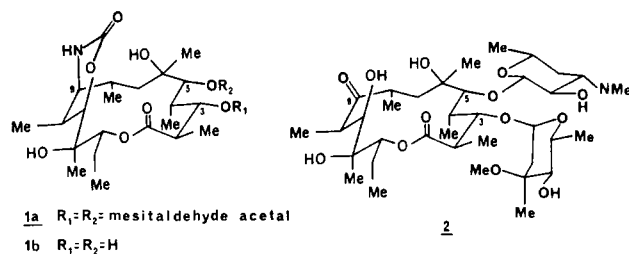
### Asymmetric Total Synthesis of Erythromycin. 3. Total Synthesis of Erythromycin

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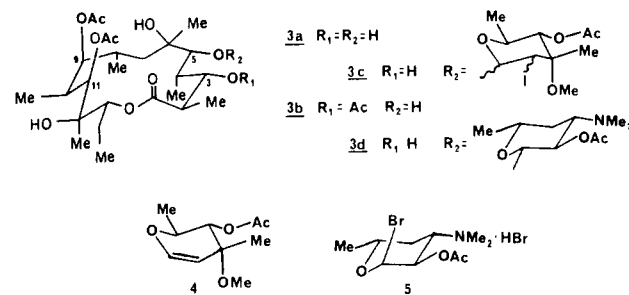
In the preceding paper<sup>1</sup> we described the preparation of the key lactone intermediate **1a** in optically active form. In this paper we report the synthesis of erythromycin (**2**) from **1a**. In essence,



this transformation involves the glycosidation of a suitable derivative of **1a** with L-cladinose and D-desosamine and the generation of the C-9 ketone functionality.

In planning our work we were aware that glycosidation, in particular, demanded highly specific operations, in terms of both site- and stereoselectivity: cladinose must be attached at the C-3 hydroxyl group with  $\alpha$ -anomeric stereochemistry and desosamine at C-5 with  $\beta$  stereochemistry. We felt that once appropriate solutions were available to the site-specific operations, the stereochemical control of the glycosidation reactions should be manageable. We, therefore, examined the relative reactivities of the C-3 and C-5 hydroxyl groups toward glycosidation; if there were a practical difference in reactivity, such an observation would naturally suggest a sequence of sugar attachment as well as minimize the need of protecting groups.

Initially we chose the lactone **3a**,<sup>2,3</sup> derived from natural er-



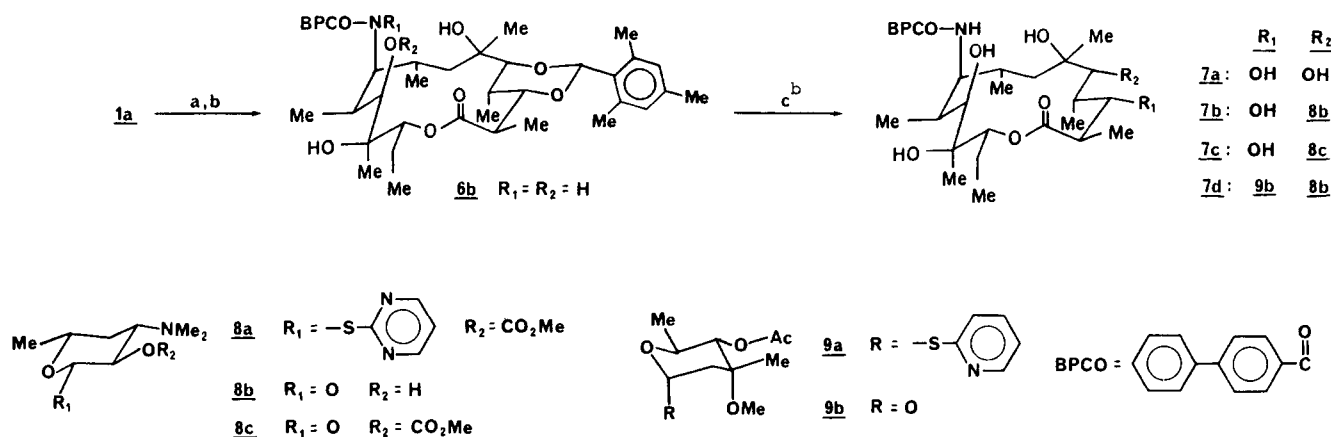
<sup>†</sup> Deceased July 8, 1979.

<sup>‡</sup> This manuscript was prepared by E.L., K.P.N., K.S., and D.E.W.

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(1) Woodward, R. B., et al. *J. Am. Chem. Soc.*, preceding paper in this issue.

(2) Diacetate **3a** was prepared by two independent routes—from (9*S*)-3'-de(dimethylamino)dihydroerythromycin<sup>2a</sup> via the sequence: Ac<sub>2</sub>O/DMAP/CH<sub>2</sub>Cl<sub>2</sub>, 25 °C; HCl/MeOH, 25 °C; and from (9*S*)-dihydroerythronolide A 3,5-mesitaldehyde acetal<sup>1</sup> in 90% yield via the sequence: Ac<sub>2</sub>O/DMAP/CH<sub>2</sub>Cl<sub>2</sub>, 25 °C; Conia's method (CF<sub>3</sub>COOH).<sup>2b</sup> (a) Jones, P. H.; Rowley, E. K. *J. Org. Chem.* 1968, 33, 665. (b) Huet, F.; Lechevallier, A.; Pellet, M.; Conia, J. M. *Synthesis* 1978, 63.

Scheme 1<sup>a</sup>

<sup>a</sup> (a) BPCOCl, Et<sub>3</sub>N, DMAP, CH<sub>2</sub>Cl<sub>2</sub>, room temperature; (b) aqueous NaOH, THF, *i*-PrOH, room temperature; (c) SiO<sub>2</sub>, aqueous CF<sub>3</sub>COOH, CH<sub>2</sub>Cl<sub>2</sub>, room temperature.<sup>2b</sup> <sup>b</sup> The conditions lead to 7a.

ythromycin,<sup>4</sup> to study the relative reactivities of the hydroxyl groups. We first investigated attachment of L-cladinose to **3a**, since greater reactivity of the C-3 vs. the C-5 hydroxyl group was suggested by predominant formation of the 3,9,11-triacetate **3b**<sup>5</sup> from **3a** upon acetylation (Ac<sub>2</sub>O/Py). However, glycosidation of **3a** with L-cladinal **4**<sup>6</sup> (3 equiv) under modified Tatsuta conditions<sup>7</sup> (3.1 equiv of *N*-iodosuccinimide in the presence of a radical scavenger<sup>7b</sup> in CH<sub>3</sub>CN at -30 → 25 °C) unexpectedly yielded the C-5 glycoside **3c**<sup>8</sup> as the predominant product (34% yield based on consumed **3a**; 47% conversion).<sup>9</sup> The greater reactivity at C-5 was further confirmed by the site-selective attachment of D-desosamine to **3a**. Thus glycosidation of **3a** using 5<sup>10a</sup> (5 equiv) under modified Koenigs-Knorr conditions<sup>10b,c</sup> (10 equiv of silver triflate, lutidine, CH<sub>2</sub>Cl<sub>2</sub>/THF at 25 °C) yielded a single isolable glycosidation product **3d**<sup>11</sup> (10% yield), the desired β-glycoside<sup>12</sup>

at C-5. These experiments suggested that the C-5 hydroxyl group would be more reactive toward glycosidation, and hence protection of only the C-9 and C-11 hydroxyl groups would be sufficient for our purposes.

In light of these observations we decided to first attach desosamine to a suitable derivative of our synthetic intermediate **1a**. The 9,11-protected **1b** (mp > 300 °C), readily available from **1a** by CF<sub>3</sub>COOH hydrolysis,<sup>2b</sup> appeared to be attractive in this regard, but insolubility in almost all solvents precluded its use. It therefore became necessary to first remove the cyclic carbamate (Scheme I). By acylation with *p*-phenylbenzoyl chloride,<sup>13</sup> carbamate **1a** was converted to **6a** (R<sub>1</sub> = R<sub>2</sub> = CO), hydrolysis of which afforded **6b** (70% yield<sup>14</sup> from **1a**). Deprotection of the C-3 and C-5 hydroxyl groups furnished the key glycosidation substrate **7a** in quantitative yield.

Glycosidation of **7a** employing D-desosamine **8a**<sup>15a,b</sup> (5 equiv) and silver triflate<sup>15c,d</sup> (6 equiv) in CH<sub>2</sub>Cl<sub>2</sub>/PhMe at 25 °C provided the expected β-glycoside **7b**<sup>12,16</sup> [mp 172–176 °C, [α]<sub>D</sub><sup>25</sup> -70.7° (*c* 0.63, CHCl<sub>3</sub>); 36% yield] after methanolysis.<sup>17a,b</sup> Furthermore, glycosidation of **7c**, derived from **7b** (ClCO<sub>2</sub>Me/CH<sub>2</sub>Cl<sub>2</sub>/aqueous NaHCO<sub>3</sub>), with L-cladinose **9a**<sup>18a</sup> (5.5 equiv) and Pb(ClO<sub>4</sub>)<sub>2</sub><sup>18b</sup> (6.5 equiv) in CH<sub>3</sub>CN at 25 °C, furnished after methanolysis<sup>17a</sup>

(3) In depicting **3a** and other lactones in this paper, we adopt the Perun-Celmer model as the conformation of the lactone system of erythromycin: (a) Celmer, W. D. *Pure Appl. Chem.* **1971**, *28*, 413. (b) Perun, T. J. In "Drug Action and Drug Resistance in Bacteria. 1. Macrolide Antibiotics and Lincomycin"; Mitsuhashi, S., Ed.; University Park Press: Baltimore, 1971; p 123.

(4) We are grateful to Dr. N. Neuss (Lilly Research Laboratories) for generously providing all of the natural erythromycin used in the present study.

(5) Relevant <sup>1</sup>H NMR (CDCl<sub>3</sub>) data for **3b**: δ 5.55 (H<sub>3</sub>, dd, *J* = 10.0, 4.0 Hz), 5.03 (1 H, d, *J* = 1.0 Hz), 4.80 (1 H, dd, *J* = 9.2, 3.6 Hz), 4.64 (1 H, dd, *J* = 9.6, 3.6 Hz).

(6) (a) Synthesis of L-cladinose: Lemal, D. M.; Pacht, P. D.; Woodward, R. B. *Tetrahedron* **1962**, *18*, 1275. (b) Cladinal **4** was prepared from 4-acetylcladinose<sup>7a</sup> in 88% yield by an improved sequence: 1-chloro-2,5-dioxophosphalan/(*i*-Pr)<sub>2</sub>NEt/ether, -40 → 25 °C; MeSO<sub>2</sub>N<sub>3</sub>, 25 °C. L-cladinose, used to prepare 4-acetylcladinose, was obtained quantitatively from natural erythromycin by glycolysis (continuous extraction: aqueous HCl/ether, reflux). For a less effective method, see: Wiley, P. F. *Methods Carbohydr. Chem.* **1962**, *1*, 264.

(7) (a) Tatsuta, K.; Fujimoto, K.; Kinoshita, M. *Carbohydr. Res.* **1977**, *54*, 85. (b) The use of butylidene-4,4'-bis-(6-*tert*-butyl-3-methylphenol) in a modified Tatsuta procedure significantly increased the yield of glycosidation. We thank Professor Y. Kishi for suggesting the use of radical scavengers and providing us with a number of such compounds.

(8) The assigned structure of **3c** is supported by the following observations: (a) <sup>1</sup>H NMR (CDCl<sub>3</sub>) signal δ 4.13 (br m) due to the proton attached to C-3 sharpened (dd, *J* = 7.5, 2.0 Hz) when D<sub>2</sub>O was added; (b) under forcing acetylation conditions (Ac<sub>2</sub>O/DMAP), only one additional acetate was introduced at C-3 of **3c**, indicating the absence of any other free secondary hydroxyl groups in **3c**.

(9) Two minor unidentified glycosides were also isolated in 7 and 2% yield (based on consumed **3a**).

(10) (a) Masamune, S.; Yamamoto, H.; Kamata, K.; Fukuzawa, A. *J. Am. Chem. Soc.* **1975**, *97*, 3513. (b) Hanessian, S.; Banoub, J. *Carbohydr. Res.* **1977**, *53*, C13. (c) It should be noted that the previously reported method (ref 10a) for attachment of **5** failed in the present case.

(11) The glycoside **3d** thus obtained was identical with an authentic sample prepared from (9*S*)-dihydroerythromycin (derived in 82% yield from **2** by reduction with NaBH<sub>4</sub>/alumina<sup>14a</sup>) via the sequence: Ac<sub>2</sub>O/DMAP/CH<sub>2</sub>Cl<sub>2</sub>, 25 °C; HCl/MeOH, 25 °C; AcCl/CH<sub>2</sub>Cl<sub>2</sub>/aqueous NaHCO<sub>3</sub>, 25 °C. (a) Santaniello, E.; Ponti, F.; Manzocchi, A. *Synthesis* **1978**, 891.

(12) The observed βanomeric stereochemistry was expected in view of the presence of a participating acyl group at the 2 position of the desosamine: see, for example, "Chemistry of the Glycosidic Bond"; Bochkov, Zaikov, Eds.; Pergamon Press: London, 1979.

(13) Scribner, R. M. *Tetrahedron Lett.* **1976**, 3853.

(14) Hydrolysis of **6a** afforded **6b** along with **1a** (3:2). The recovered **1a** was recycled twice to obtain the yield cited for **6b**.

(15) (a) Synthesis of D-desosamine: Richardson, A. C. *Proc. Chem. Soc.* **1963**, 131. (b) Thioglycoside **8a** was prepared in 63% yield from D-desosamine via the sequence: 2-mercaptopyrimidine/(NCO<sub>2</sub>Et)<sub>2</sub>/P(*n*-Bu)<sub>3</sub>/PhMe, -30 → 25 °C; ClCO<sub>2</sub>Me/CH<sub>2</sub>Cl<sub>2</sub>/aqueous NaHCO<sub>3</sub>, 25 °C. We are indebted to Drs. W. D. Celmer (Pfizer) and N. Neuss (Lilly Research Laboratories) for generously providing us with D-desosamine hydrochloride used in this study. (c) Among the metal salts [Hg(II), Cu(II), Ag(I) and Pb(II)] investigated, silver triflate was most effective. The glycosidation method used for **3a** → **3d** was less effective in the present case. See also ref 10c. (d) For similar glycosidation methods, see: (e) Mukaiyama, T.; Nakatsuka, T.; Shoda, S. *Chem. Lett.* **1979**, 487. (f) Hanessian, S.; Baquet, C.; Lehong, N. *Carbohydr. Res.* **1980**, *80*, C17.

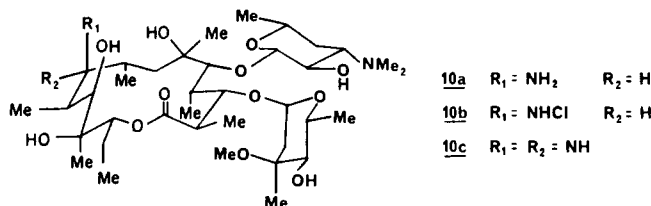
(16) The glycoside **7b**, obtained in the manner described, was identical with an authentic sample prepared from (9*S*)-erythromycylamine<sup>20</sup> via the sequence: HCl/MeOH, 25 °C; ClCO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>-*p*-Ph/Et<sub>3</sub>N/CH<sub>2</sub>Cl<sub>2</sub>/aqueous NaHCO<sub>3</sub>, 25 °C.

(17) (a) The methanolysis (Flynn, E. H.; Sigal, M. V., Jr.; Wiley, P. F.; Gerzon, K. *J. Am. Chem. Soc.* **1954**, *76*, 3121) facilitated isolation and purification of the products. (b) Three minor glycosides were also isolated in addition to **7b** in 13, 12, and 4% yield. (c) One minor glycoside was also isolated in addition to **7d** (1:3).

(18) (a) Cladinose **9a** (mp 149–151 °C) was prepared in 72% yield from 4-acetylcladinose (cf. ref 6b) by (2-Py-S)<sub>2</sub>/P(*n*-Bu)<sub>3</sub>/CH<sub>2</sub>Cl<sub>2</sub>, 0 °C. (b) Among the metal salts [Ag(I), Cu(II), and Pb(II)] studied, Pb(ClO<sub>4</sub>)<sub>2</sub> was best in terms of reaction yield, ease of workup, and purity of the product. The glycosidation method employed for **3a** → **3c** failed in the present case.

the glycoside **7d** (55% yield based on consumed **7b**; 37% conversion).<sup>17c</sup> The newly introduced anomeric stereochemistry of **7d** was shown to be of the desired  $\alpha$  configuration (vide infra). This stereochemical outcome can be attributed largely to participation by the solvent, CH<sub>3</sub>CN, which contributes to an overall double inversion during the course of the reaction.<sup>19</sup> These gratifying results enabled us to achieve site-selective introduction of both sugar moieties in a surprisingly simple manner, avoiding the extensive use of protecting groups.

Completion of the synthesis of erythromycin was carried out in the following manner. Simultaneous deprotection of both the C-4'' hydroxyl group of the cladinosyl moiety and the C-9 amino group in **7d** by Na-Hg/MeOH<sup>13</sup> furnished (9S)-erythromycylamine (**10a**) [mp 126-129 °C,  $[\alpha]_D^{25}$  -48.1° (c 0.59, CHCl<sub>3</sub>); 75% yield] which was found to be identical with an authentic



sample prepared from natural erythromycin by a known method.<sup>20</sup> Treatment of **10a** with *N*-chlorosuccinimide (1 equiv) in pyridine at 25 °C gave **10b** (mp 166-170 °C with partial melting at 130-134 °C), which was dehydrochlorinated by AgF in HMPA at 70 °C to yield erythromycinimine (**10c**).<sup>20a,b,21</sup> Hydrolysis of **10c** in water at 5 °C afforded the corresponding ketone (40% overall yield from **10a**), which was found to be identical with erythromycin (**2**) in all respects (<sup>1</sup>H NMR, mp, mmp,  $\alpha_D$ , mass, IR and chromatographic mobility).<sup>22</sup>

**Acknowledgment.** We are indebted to Professor Yoshito Kishi for his help and encouragement and, in particular, for his acceptance of the role of principal investigator upon Professor Woodward's death. Financial assistance from the National Institutes of Health (GM04229) is gratefully acknowledged. Mass spectra and FT-IR spectra were provided by the facilities supported by the National Science Foundation (Grants CHE-7908590 and CHE-7805150, respectively). The 250-MHz <sup>1</sup>H NMR spectra were measured by the facility supported by the National Science Foundation (Grant CHE-8019562) at the Massachusetts Institute of Technology.

**Supplementary Material Available:** Physical properties (IR and <sup>1</sup>H NMR spectra, etc.) of selected synthetic substances (including **2**, **6a,b**, **7a-d**, **8a**, **9a**, and **10a,b**) and scheme used for the synthesis of **2** from **3d** (16 pages). Ordering information is given on any current masthead page.

(19) For sterically demanding glycosidation substrates such as **7c**, pronounced participation by CH<sub>3</sub>CN was expected.<sup>19f</sup> The presumed intermediate nitrilium species was expected to have the  $\beta$  configuration, due to the "reverse anomeric effect": West, A. C.; Schuerch, C. *J. Am. Chem. Soc.* **1973**, *95*, 1333. Lemieux, R. U.; Morgan, A. R. *Can. J. Chem.* **1965**, *43*, 2205.

(20) (a) Wildsmith, E. *Tetrahedron Lett.* **1972**, 29. For other known methods, see: (b) Timms, G. H.; Wildsmith, E. *Ibid.* **1971**, 195. (c) Massey, E. H.; Kitchell, B.; Martin, L. D.; Gerzon, K.; Murphy, H. W. *Ibid.* **1970**, 157.

(21) Commonly used methods for oxidation of an amine were unsuccessful when applied to **10a**: (a) Kahr, K.; Berther, C. *Chem. Ber.* **1960**, *93*, 132. (b) Corey, E. J.; Achiwa, K. *J. Am. Chem. Soc.* **1969**, *91*, 1429. (c) Bachmann, W. E.; Cava, M. P.; Dreiding, A. S. *Ibid.* **1954**, *76*, 5554. Ruschig, H.; Fritsch, W.; Schmidt-Thomé, J.; Haede, W. *Chem. Ber.* **1955**, *88*, 883. (d) Bacon, R. G. R.; Hanna, W. J. W. *J. Chem. Soc.* **1965**, 4962. We attribute this failure in part to the hindrance caused by the hydroxyl groups at C-6 and C-11, which are close spatially to the C-9 amino group in **10a**. Thus treatment of **10a** with 3,5-di-*tert*-butyl-1,2-benzoquinone<sup>21b</sup> furnished the corresponding perhydro-1,3-oxazine at C-9/C-11 as a stable product.

(22) The glycoside **3d** (see text) has also been successfully converted to erythromycin: for the sequence employed see the supplementary material. This transformation constitutes another total synthesis of erythromycin, since **3a** (the precursor to **3d**) is derived from erythronolide A<sup>1,2</sup> and the synthesis of erythronolide A has been reported by Corey et al.; see ref 1e in the first paper in this series.

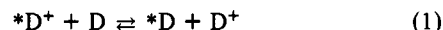
## Measurements of Degenerate Radical Ion-Neutral Molecule Electron Exchange by Microsecond Time-Resolved CIDNP. Determination of Relative Hyperfine Coupling Constants of Radical Cations of Chlorophylls and Derivatives<sup>1</sup>

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Chemically induced dynamic nuclear spin polarization (CIDNP) has been shown to be a good method to study photochemical electron transfer.<sup>2</sup> Electron transfer of an excited donor (D) or acceptor (A) molecule produces a geminate radical ion pair which may undergo a back-reaction leaving D and A in their ground states with polarized nuclear spins. It has been pointed out by one of us<sup>3</sup> that if the *only* reaction is electron transfer from D to A followed by back-transfer to regenerate ground states, it may be impossible to observe CIDNP unless the free paramagnetic ions have a relatively long life. This prediction arises directly from the radical pair theory of CIDNP which rigorously requires that at high field the nuclear polarization of the radicals undergoing geminate annihilation is of opposite sign and equal magnitude as that carried by the escaping free ions. If the free ions are converted to the same products as the geminate ions, no observable polarization results *unless* the free ions lose some of their polarization by relaxation, thus making the polarization generated in the geminate process dominant. The conversion of the polarized ions to polarized diamagnetic products can occur by ion annihilation and ion-neutral molecule electron exchange according to (1),



where the asterisks denote nuclear spin polarization. Since the concentration of the neutral molecules is often much higher than that of the ions, this is frequently the most important pathway and leads to failure to observe CIDNP.

In this communication, we wish to show that fast time-resolved CIDNP spectroscopy can get around this difficulty and give some information on electron exchange kinetics which are difficult to measure directly by other methods.<sup>4</sup> The basis for the success of the time-resolved method is the fact that geminate processes are complete in a fraction of a microsecond, while combination of free ions and/or exchange according to (1) may take tens or hundreds of microseconds depending on concentrations. Thus, if the magnetization is probed, say at 1  $\mu$ s after the radical ions have been generated by a laser flash, the polarization of products that is probed originates almost exclusively from geminate processes and has not yet been annihilated by the opposite polarization derived from the free ions.

The utility of the method is demonstrated by the photooxidation of chlorophyll and derivatives using quinone. The system had been studied by Roth and collaborators,<sup>5,6</sup> but they failed to observe any polarization of chlorophyll presumably because of rapid exchange according to (1).

Figure 1 shows the pigment polarizations obtainable when a dilute solution (<10<sup>-3</sup> M) of pigment containing 5  $\times$  10<sup>-3</sup> M

\* Argonne National Laboratory.

(1) Work performed under the auspices of the Division of Chemical Sciences, Office of Chemical Sciences, Office of Basic Energy Sciences of the U.S. Department of Energy.

(2) H. D. Roth, "Chemically Induced Magnetic Polarization"; L. T. Muus, P. W. Atkins, K. A. McLauchlan, and J. B. Peterson, Eds., D. Reidel, Dordrecht, Holland 1977, pp 35-76.

(3) G. L. Closs, *Chem. Phys. Lett.*, **32**, 277 (1975).

(4) G. L. Closs and R. J. Miller, *J. Am. Chem. Soc.*, **101**, 1639 (1979).

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