permit a reliable dissection of the overall salt effect into contributions of micropolarity and ion-exchange effects.

Experimental Section

Materials. 6-Nitrobenzisoxazole-3-carboxylic acid was prepared according to the methode of Borsche[9] and Lindemann and Cissee.[10] The product was crystallized from methanol; mp 149–159 °C (lit.[11] mp 167–169 °C, monohydrate). A phenol test[11] was negative. 1-Methyl-4-dodecylpyridinium iodide (**2**) was kindly provided by Dr. E. J. R. Sudhölter[12] (mp 112.5–113 °C, lit.[12] mp 112.5–113 °C). The salts used in all experiments were of the highest grade available (obtained from Baker or Merck AG) and were dried before use over P_2O_5 in vacuo at 100–150 °C for 24 h.

Kinetic Measurements. The formation of 2-cyano-5-nitrophenoxide from **1** was monitored at 30.0 °C by following the increase of the absorbance at 410 nm with a Beckmann Model 24 spectrophotometer equipped with a thermostated cell holder. The initial concentration of **1** was 1.2×10^{-4} M. All solutions contained 2×10^{-3} M of NaOH. For improvement of the reproducibility, a stream of nitrogen was led through the NaOH solution before **1** and **2** were added. In all cases satisfactory first-order kinetics were observed, the rate constants (obtained by Guggenheim's method) were reproducible to within 2%. Data plots in terms of eq 2 and 3 were analyzed by using an HP-25 programmable calculator.

Acknowledgment. We are much indebted to B. Eling for performing preliminary kinetic measurements.

Registry No. **1**, 42540-91-0; **2**, 62541-13-3.

Supplementary Material Available: Rate constants for decarboxylation of **1** as a function of the concentration of **2** (Table I) and as a function of the concentration of NaCl, NaBr, and NaI at a fixed concentration of **2** (11.5×10^{-3} M) (Table II) (2 pages). Ordering information is given on any current masthead page.

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New Synthesis of α,β-Unsaturated Aldehydes from Nitro Paraffins

Noboru Ono,* Hideyoshi Miyake, Rikuhei Tanikaga, and Aritsune Kaji

Department of Chemistry, Faculty of Science, Kyoto University, Kyoto 606, Japan

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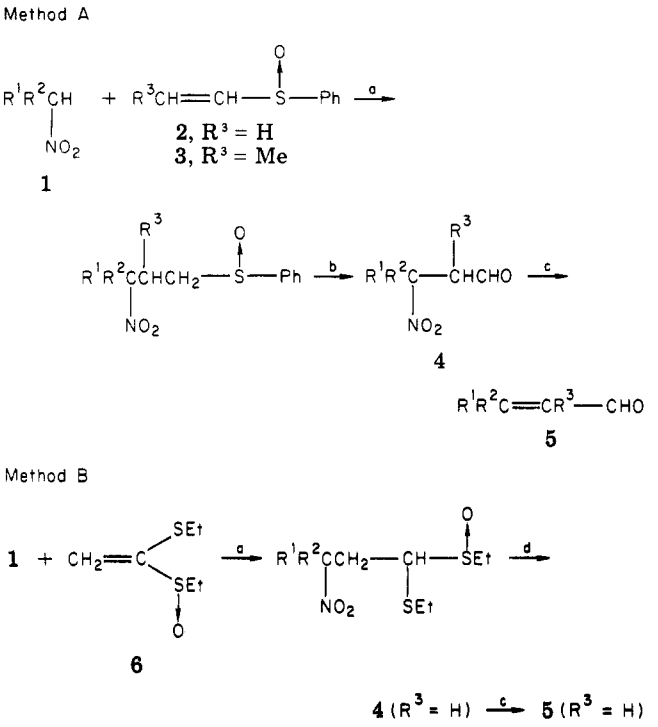
The nitro group has found extensive utility as an activating group in the formation of carbon–carbon bonds, but it generally fails to serve as a leaving group in substitution or elimination reactions by ionic processes.[1] In a special case, if electron-withdrawing groups exist at the β-position of the nitro function, elimination of nitrous acid takes place readily to give olefins in good yields.[2] So, if simple methods can be devised to convert nitro paraffins (**1**) to β-nitro aldehydes (**4**), a new synthetic method to get α,β-unsaturated aldehydes (**5**) from **1** is possible. In this paper we report the realization of this conversion via the Michael addition of **1** to α,β-unsaturated sulfoxides.

Scheme I[a]



[a] (a) DBU/CH_3CN, room temperature, 24–48 h; (b) $(CF_3CO)_2O$, aqueous $NaHCO_3$; (c) DBU/Et_2O, room temperature, 3 h; (d) $HClO_4$ (70%).

The methods are summarized in the generalized equations in Scheme I. As a sulfoxide, phenyl vinyl sulfoxide (**2**), phenyl 1-propenyl sulfoxide (**3**), or ketene diethyl dithioacetal *S*-monooxide (**6**) was employed.

The Michael addition of **1** to vinyl sulfoxides required 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as a base. The reaction was complete at room temperature in 24–48 h and gave the adduct in quantitative yields. Other bases such as triethylamine, potassium fluoride, and tetramethylguanidine were not so effective as DBU. The adduct was converted to **4** without purification by treatment with trifluoroacetic anhydride (TFAA) followed by hydrolysis with aqueous sodium hydrogen carbonate[3] (method A) or by acid hydrolysis[4] (method B). Elimination of nitrous acid from **4** resulted in the clean formation of **5** in good overall yields. The sulfoxides for method A are more readily obtained than those for method B. However, method B has the following merits. Hydrolysis to get **4** is very simple. Furthermore, the Michael addition of primary nitroalkanes to **6** gave the selective monoadduct, but that to **2** gave a mixture of the mono- and diadducts.

(1) The synthetic utility of aliphatic nitro compounds is well documented: (a) N. Kornblum, *Angew. Chem., Int. Ed. Engl.*, **14**, 734 (1975). (b) D. Seebach, E. W. Colvin, F. Lehr, and T. Weller, *Chimia*, **33**, 1 (1979). (c) N. Ono and A. Kaji, *Yuki Gosei Kagaku Kyokaishi*, **38**, 115 (1980). In these references some reactions use a nitro group as a leaving group. However, nitromethane or nitroethane reacts with p-$MeC_6H_4S^-$, a strong nucleophile, very slowly in DMF to give the substitution product in 80% or 3% yield, respectively. This suggests that nucleophilic substitution of R–NO_2 is very difficult: M. Benn and A. C. M. Meesters, *J. Chem. Soc., Chem. Commun.*, 579 (1977).

(2) (a) J. W. Patterson and J. E. McMurry, *J. Chem. Soc., Chem. Commun.*, 488 (1971). (b) N. Ono, H. Eto, R. Tamura, J. Hayami, A. Kaji, *Chem. Lett.*, 2371 (1976). (c) D. Seebach, M. S. Hoekstra, and G. Protschuk, *Angew. Chem., Int. Ed. Engl.*, **16**, 321 (1977). (d) S. Danishefsky, M. P. Prisbylla, and S. Hiner, *J. Am. Chem. Soc.*, **100**, 2918 (1978). (e) P. Bakuzis, M. L. F. Bakuzis, and T. F. Weingartner, *Tetrahedron Lett.*, 2371 (1978).
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(4) (a) J. L. Herrmann, G. R. Kieczykowski, R. F. Romanet, P. L. Wepplo, and R. H. Schlessinger, *Tetrahedron Lett.*, 4711 (1973). (b) J. L. Herrmann, G. R. Kieczykowski, R. F. Romanet, and R. H. Schlessinger, *ibid.*, 4715 (1973).

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Table I. Preparation of $R^1R^2C{=}CR^3CHO$ (5) from $R^1R^2CHNO_2$ (1) and α,β-Unsaturated Sulfoxides (2, 3, or 6)

R^1	R^2	R^3	method	yield of 5,[a] %	E/Z ratio[b]
Me	Me	H	B	63 (5a)	
Me	Et	H	A	59 (5b)	63/37
Me	Me_2CHCH_2	H	A	63 (5c)	64/36
Me	n-C_6H_{13}	H	B	65 (5d)	64/36
	$(CH_2)_4$	H	A	70 (5a)	
	$(CH_2)_4$	H	B	55 (5e)	
	$(CH_2)_5$	H	A	63 (5f)	
Me	CH_2CH_2COOMe	H	B	52 (3g)	65/35
cyclohexyl	H	H	B	66 (5h)	100/0
Me_2CH	H	H	B	82 (5i)	100/0
Me	Me	Me	A	55 (5j)	
Et	H	Me	A	52 (5k)	100/0

[a] Yields are based on nitroparaffins and they refer to pure and isolated products. [b] Determined by GLC and NMR.

Results are summarized in Table I. As nitro paraffins are available from various sources and the present methods consist of very simple procedures, they have some advantages over the conventional carbonyl olefination[5] which requires generally anhydrous conditions and strong bases like butyllithium.

Experimental Section

The α,β-unsaturated sulfoxides 2,[6] 3,[7] and 6[4] were prepared according to the literature methods. Phenyl vinyl sulfoxide (2): bp 119–120 °C (1.1 mmHg); NMR ($CDCl_3$) δ 5.88 (m, 1 H), 6.22 (m, 1 H), 6.72 (m, 1 H), 7.62 (m, 5 H). Phenyl 1-propenyl sulfoxide (3): bp 110–111 °C (0.3 mmHg); NMR ($CDCl_3$) δ 0.82 (d, 1.5 H), 1.08 (d, 1.5 H), 6.0–6.4 (m, 1 H), 7.5 (m, 5 H). This consists of about equal amounts of E and Z isomers. Ketene diethyl dithioacetal S-oxide (6): bp 88 °C (1 mmHg); NMR ($CDCl_3$) δ 1.08–1.44 (m, 6 H), 2.44–3.10 (m, 4 H), 5.92 (s, 1 H), 6.24 (s, 1 H). Nitro compounds 1 were prepared by the reaction of alkyl bromides with sodium nitrite,[8] condensation of the aldehydes with nitromethane or nitroethane,[9] or Michael addition of nitroethane to methyl acrylate.[10]

Method A. A solution of 1 (10 mmol), DBU (10 mmol), and 2 (10 mmol) in 10 mL of acetonitrile was kept at room temperature for 24 h. (The reaction mixture of 1 and 3 was kept for 48 h.) The reaction mixture was poured into water and extracted with diethyl ether. The ether layer was washed with 1 N aqueous HCl and dried over anhydrous magnesium sulfate. The residue after evaporation of the solvent was dissolved in 60 mL of acetonitrile containing 2,6-lutidine (20 mL). To this was added a solution of TFAA (20 mmol) in acetonitrile (20 mL) at 0 °C. After the reaction mixture was stirred at 0 °C for 10 min, an aqueous solution of sodium hydrogen carbonate (60 mmol, 60 mL of water) was added. Then the reaction mixture was stirred at room temperature for 4 h. The reaction mixture was extracted with diethyl ether, and the extract was washed with dilute hydrochloric acid and water. To the extract was added DBU (10 mmol), and the resulting mixture was stirred for 3 h at room temperature. The reaction mixture was poured into water, and the ether layer was washed with water and dilute hydrochloric acid and dried over anhydrous magnesium sulfate. The solvent was evaporated, and the residue was distilled with a Kugelrohr distillation apparatus to give compounds 5. The structures of compounds 5 were assigned by NMR, IR, or mass spectra. Some of them were converted to 2,4-dinitrophenylhydrazone (2,4-D), and the structures were assigned from them.

Method B. The Michael addition of 1 (10 mmol) to 6 (10 mmol) was carried out in the same way as in method A. The adduct was dissolved in 10 mL of acetonitrile and cooled to 0 °C. To this solution was added 70% $HClO_4$ (0.4 mL) with stirring, and the stirring was continued for 3 h at 0 °C. Then diethyl ether and 2% aqueous $NaHCO_3$ (100 mL) were added to the reaction mixture. The mixture was shaken carefully, and the ether layer was treated with DBU in the same way as in method A. Data used to assign the structures of 5 are summarized as follows.

5a: NMR (CCl_4) δ 1.99 (s, 3 H), 2.18 (s, 3 H), 5.80 (m, =CH, 1 H), 9.80 (d, CHO, 1 H); IR (neat) 1680 cm^{-1} (C=O); 2,4-D; mp 179–180 °C (lit.[11] mp 182–183 °C).

5b: NMR (CCl_4) δ 1.05 (t, 3 H), 2.0 (s, $CH_3C{=}C$, Z form), 2.2 (s, $CH_3C{=}C$, E), 2.2 (q, $CH_2{-}C{=}C$, E), 2.5 (q, $CH_2{-}C{=}C$, Z), 5.8 (m, =CH, 1 H), 9.98 (m, CHO, Z), 10.0 (d, CHO, E); IR (neat) 1680 cm^{-1} (C=O); 2,4-D; mp 176–181 °C. Anal. Calcd for $C_{12}H_{14}O_4N_4$: C, 51.80; H, 5.07; N, 20.13. Found: C, 51.86; H, 4.83; N, 20.25.

5c: NMR (CCl_4) δ 1.0 (m, 6 H), 1.8 (m, 1 H), 2.0 (s, $CH_3C{=}C$, Z form), 2.1 (d, $CH_2{-}C{=}C$, E), 2.2 (s, $CH_3C{=}C$, E), 2.5 (d, $CH_2{-}C{=}C$, Z), 5.8 (m, =CH, 1 H), 9.98 (d, CHO, Z), 10.0 (d, CHO, E); IR (neat) 1680 cm^{-1} (C=O); 2,4-D; mp 187–188 °C (lit.[11] mp 187–188 °C).

5d: NMR (CCl_4) δ 0.95 (m, 3 H), 1.4 (m, 11 H), 1.98 (s, $CH_3C{=}C$, Z), 2.18 (s, $CH_3C{=}C$, E), 2.20 (t, $CH_2{-}C{=}C$, E), 2.40 (t, $CH_2{-}C{=}C$, Z), 5.75 (m, =CH, 1 H), 9.72 (d, CHO, Z), 9.76 (d, CHO, E); IR (neat) 1680 cm^{-1} (C=O); mass spectrum, m/e 154 (M^+).

5e: NMR (CCl_4) δ 1.6–2.4 (m, 4 H), 2.4–3.0 (m, 4 H), 5.9 (m, =CH, 1 H), 9.74 (d, CHO, 1 H); IR (neat) 1680 cm^{-1}. These data are identical with those reported.[12] For the 2,4-D, mp 178 °C.

5f: NMR (CCl_4) δ 1.6–2.1 (m, 6 H), 2.2–3.0 (m, 4 H), 5.6 (m, =CH, 1 H), 9.90 (m, CHO, 1 H); IR (neat) 1680 cm^{-1} (C=O); 2,4-D; mp 202 °C (lit.[13] mp 201–202 °C).

5g: NMR (CCl_4) δ 2.12–2.32 (m, 4 H), 2.5 (s, 3 H), 3.65 (s, 3 H), 5.78 (d, =CH, 1 H), 9.91 (d, CHO, Z), 9.89 (d, CHO, E); IR (neat) 1720 cm^{-1} (COO), 1685 cm^{-1} (C=O); mass spectrum, m/e 156 (M^+).

5h: NMR (CCl_4) δ 1.6–2.0 (m, 11 H), 6.0 (m, =CH, 1 H), 6.75 (m, =CH, 1 H), 9.38 (d, CHO, 1 H); IR (neat) 1689 cm^{-1} (C=O); 2,4-D, mp 208–209 °C. Anal. Calcd for $C_{15}H_{18}N_4O_4$: C, 56.60; H, 5.70; N, 17.60. Found: C, 56.36; H, 5.59; N, 17.66.

5i: This aldehyde was isolated as the 2,4-D: mp 179–180 °C (lit.[14] mp 178 °C); NMR ($CDCl_3$) δ 1.09 (d, 6 H), 2.50 (m, 1 H), 6.21 (d, 1 H), 7.46 (d, 1 H), 7.6–8.5 (m, 3 H), 8.79 (d, 1 H), 8.96 (d, 1 H).

5j: NMR (CCl_4) δ 1.66 (s, 3 H), 1.98 (s, 3 H), 2.20 (s, 3 H), 9.98 (s, CHO, 1 H); IR (CCl_4) 1685 cm^{-1} (C=O); 2,4-D, mp 190–191 °C. Anal. Calcd for $C_{12}H_{14}O_4N_4$: C, 51.86; H, 5.07; N, 20.13. Found: C, 51.62; H, 4.99, N, 20.22.

5k: NMR (CCl_4) δ 1.10 (t, 3 H), 1.68 (s, 3 H), 2.38 (m, 2 H), 6.40 (m, =CH, 1 H), 9.24 (s, CHO, 1 H); IR (CCl_4) 1685 cm^{-1} (C=O). These data are identical with those reported[15] and show

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that **5k** consists of 100% *E* isomer.

Registry No. 1a, 79-46-9; **1b**, 600-24-8; **1c**, 66553-37-5; **1d**, 4609-91-0; **1e**, 2562-38-1; **1f**, 1122-60-7; **1g**, 10312-37-5; **1h**, 2625-30-1; **1i**, 625-74-1; **1k**, 108-03-2; **2**, 20451-53-0; (*E*)-**3**, 67652-99-7; (*Z*)-**3**, 67653-00-3; **5a**, 107-86-8; (*E*)-**5b**, 83436-87-7; (*Z*)-**5b**, 83436-90-2; **5b**-2,4-D_2, 3592-24-3; (*E*)-**5c**, 83436-88-8; (*Z*)-**5c**, 83436-89-9; (*E*)-**5d**, 82235-26-5; (*Z*)-**5d**, 82235-25-4; **5e**, 5623-82-5; **5f**, 1713-63-9; (*E*)-**5g**, 80998-56-7; (*Z*)-**5g**, 80998-57-8; (*E*)-**5h**, 37868-74-9; **5h**-2,4-D_2, 6556-91-8; (*E*)-**5i**-2,4-D_2, 19327-72-1; **5j**, 13153-14-5; **5j**-2,4-D_2, 33045-89-5; (*E*)-**5k**, 14250-96-5; **6**, 67209-90-9.

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Neutral Sugar Modifications of Macrolide Antibiotics. Diazo Phosphonate Mediated Intramolecular Cyclizations

J. R. Hauske,* M. Guadliana, and K. Desai

Pfizer Central Research, Groton, Connecticut 06340

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The ability to selectively elaborate the rather inaccessible C-3″ position of the cladinose moiety of the macrolide antibiotics erythromycin A (**1**) and 9-dihydroerythromycin A (**2**) is a challenging synthetic problem.[1a] The challenge stems from the inherent instability of the glycosidic linkage to typical dealkylation conditions. For example, the attempted demethylation of the cladinose moiety at the C-3″ position in compounds **1** or **2** by either Lewis acid or nucleophilic displacement conditions afforded only negligible quantities of the corresponding C-3″ carbinols (erythromycin C or 9-dihydroerythromycin C).[1b] Thus, we identified the fused ring derivative **5** as a useful synthetic target. Compound **5** may be viewed as a synthetic entry into C-3″-modified erythromycins, since oxidative cleavage of the resulting olefinic linkage would afford a potentially manipulatable α-hydroxy aldehyde derivative.

Our synthetic analysis of substrate **5** was based upon the hypothesis that it should be possible to carry out a controlled carbenoid insertion at the C-3″-methyl ether of the cladinose moiety. Since the macrolide presents a multitude of sites susceptible to carbenoid insertion, we chose to introduce a masked carbenoid functionality that would be preferably localized at a terminus proximate to the C-3″-methyl ether. We rationalized that, upon unmasking the carbenoid species, the favorable entropic driving force of an intramolecular cyclization would regioselectively direct the insertion to the relatively unactivated carbon–hydrogen center of the C-3″-methyl ether.

A reagent that is uniquely suited to the requirements of the proposed synthesis of **5** is the diazo phosphonate **4**.[2] For example, it is known[3] that the ylide derived from diazo phosphonate **4** nucleophilically adds to carbonyl centers in the presence of alcohols, affording a variety of substituted vinyl ethers. Although there are neither reports describing the implementation of this ylide in an intramolecular sense[4] nor the insertion of the latent carbenoid into an unactivated methyl ether carbon–hydrogen bond, it is not an unreasonable extension of the methodology. Therefore, our overall synthetic plan requires the addition of the diazo ylide derived from diazo phosphonate **4** to an appropriately substituted erythromycin precursor.

We selected 9-dihydroerythromycin A (**2**) as the macrolide substrate to attempt the synthesis of **5**, since **2** is inherently more stable than **1**.[5] Thus, intermediate **2** was converted in a straightforward manner to ketone **3** via Me_2SO–TFAA oxidizing conditions.[6] The oxidation is regiospecific for the C-4″ carbinol, and no C-9 oxidized material is isolated. Subsequent exposure of a dry tetrahydrofuran solution of ketone **3** and diazophosphonate **4** to potassium *tert*-butoxide affords carbohydrate modified derivative **5** as a crystalline material. The overall yield was 50% (Scheme I summarizes the overall sequence). The transformation of **3** to **5** is most interesting if one considers that when the reaction is carried out in the presence of a large excess of allyl alcohol,[7] *none* of the corresponding allyl vinyl ether resulting from intermolecular carbenoid insertion is observed.

Scheme II outlines our mechanistic proposal.[8] Although we have no unequivocal evidence, we believe that once the nucleophilic addition has occurred (**3** → **6**), the carbenoid moiety is unmasked and selectively inserts into the methyl ether carbon–hydrogen bond (formalized in **6** → **8**). Upon completion of the cyclization sequence, the olefin is formed by elimination (**8** → **5**) in the normal Emmons–Wadsworth fashion.

The utility of this carbenoid-mediated cyclization process may be far reaching since it allows one not only to homologate at a relatively unreactive center but also may allow formation of heterocycles[9] and fused heterocycles.

In summary, therefore, we have been able to synthesize the target erythromycin derivative **5** in 50% overall yield. The salient feature of the synthetic plan was a regioselective carbenoid insertion at a relatively unactivated carbon–hydrogen center, allowing facile ring closure.

Experimental Section

General Methods. NMR spectra were obtained on a Varian XL-100 or a Bruker 250-MHz spectrometer. Tetrahydrofuran

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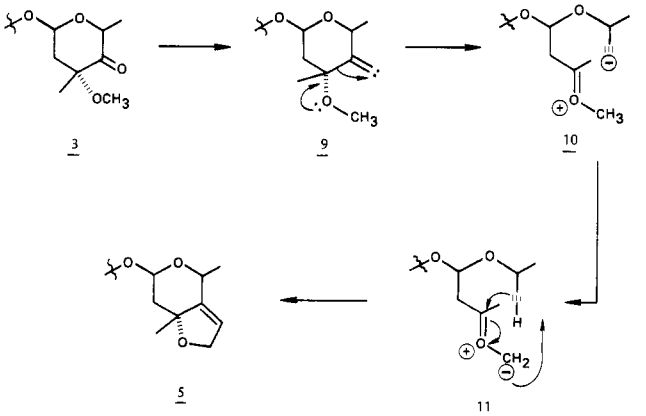
(8) An extremely interesting alternative mechanistic possibility was proposed by Professor Jack Baldwin during informal discussions. Professor Baldwin's scheme initially involves formation of a vinyl carbene (**9**), which rearranges to dipolar intermediate **11**. Intermediate **11** then



undergoes a dipolar cycloaddition to afford **5**. We thank Professor Baldwin for his contribution.

(9) It is interesting to note that addition of the diazoylide derived from **4** to *o*-methoxyacetophenone does *not* afford cyclized material; whereas similar treatment of 5-hydroxypentanal does result in the corresponding seven-membered cyclic enol ether.

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