O_2 were carried out for prolonged periods, ~5 h, with less than 50% loss of $[Q/QH_2]_{surf.}$. Since the reduction of O_2 is mass transport limited, fractional loss of $[Q/QH_2]_{surf.}$ need not lead to an equal fractional decline in observed current density. In such experiments we have determined $>10^6$ turnovers at >100 turnovers/s for the $[Q/QH_2]_{surf.}$ reagent without decline in current density. Concentrations of several millimolar H_2O_2 in pH 7.2 H_2O/electrolyte have been generated with >90% Coulombic efficiency. The $W/[Q/QH_2]_{surf.}$ electrodes are durable in deliberately prepared 0.1 M H_2O_2 pH 7.2 solutions and still efficiently reduce O_2 to H_2O_2 under these conditions for at least 30 min with <10% decline in current density.

The behavior of p-$WS_2/[Q/QH_2]_{surf.}$ photoelectrodes is consistent with the conclusion that H_2O_2 can be prepared by the visible light-driven reduction of O_2. Preliminary experiments show that the derivatized, but not naked, p-WS_2 can be used to reduce O_2 to H_2O_2 at an electrode potential of ~+0.2 V vs. SCE at pH 7.2 with a power conversion efficiency of ~2% for 632.8-nm, ~10 mW/cm^2 input energy. This represents significant improvement compared to an earlier study of a p-type Si-based[15] system for photoreduction of O_2 that required electrode potentials *negative*, not positive, of $E^{\circ\prime}(O_2/H_2O_2)$.

Acknowledgment. We thank Dow Chemical U.S. for support of this research.

Registry No. 1a, 83027-25-2; **1b**, 83027-26-3; **1b** hydroquinone derivative, 83027-28-5; WS_2, 12138-09-9; O_2, 7782-44-7; H_2O_2, 7722-84-1; Pt, 7440-06-4; W, 7440-33-7; BrPr, 106-94-5; $Br(CH_2)_3Si(OMe)_3$, 51826-90-5; 2-chloro-3-[[2-(dimethylamino)ethyl]amino]-1,4-naphthoquinone, 83027-27-4.

---

(15) Calabrese, G. S.; Wrighton, M. S. *J. Electrochem. Soc.* **1981**, *128*, 1014.

Diastereoselection in Intermolecular Nitrile Oxide Cycloaddition (NOC) Reactions: Confirmation of the "Anti-Periplanar Effect" through a Simple Synthesis of 2-Deoxy-D-ribose[†]

Alan P. Kozikowski* and Arun K. Ghosh

Department of Chemistry, University of Pittsburgh
Pittsburgh, Pennsylvania 15260

Received June 7, 1982

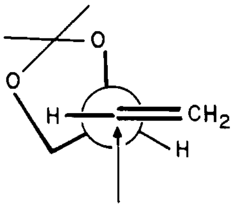
We have initiated recently a program to examine the extent to which an allylic asymmetric center can control diastereoface selection in both inter- and intramolecular additions of nitrile oxides to olefins.[1] While the extent of such diastereoselection appears to be relatively small when there is little to distinguish the allylic groups on a steric or electronic basis (except in intramolecular cyclizations where the allylic center is within the nonisoxazoline ring being formed),[2] we now report that an allylic oxygen substituent can, on the other hand, serve as a useful control element for achieving diastereoface selectivity in [3 + 2] cycloaddition reactions. We illustrate this new concept in stereocontrol through a simple synthesis of 2-deoxy-D-ribose.

Optically active (+)-(*S*)-isopropylidene-3-butene-1,2-diol, prepared from isopropylidene D-glyceraldehyde by reaction with methylenetriphenylphosphorane,[3] was reacted with (carboethoxy)formonitrile oxide[4] to afford an 80:20 mixture of diastereomeric cycloadducts. These products were separated by gravity chromatography, and the major isomer **3** (Scheme I) was heated with sodium hydroxide to effect the following transformations: (a) ester hydrolysis; (b) decarboxylative ring opening of the isoxazoline to a β-hydroxy nitrile; (c) hydrolysis of nitrile to carboxylate. Acidification and diazomethane treatment then yielded **4** (74% overall yield from **3**).[5] On converting this compound to its acetate and stirring with trifluoroacetic acid, the acetate of 2-deoxy-D-ribono-1,4-lactone (**5**) was formed (71%). The NMR of this compound was identical with that reported previously by Mukaiyama;[6] $[\alpha]^{24}_D = -12°$ (c 0.75, CH_2Cl_2); IR (thin film) 3450, 1785, 1740, 1240 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.07 (s, 3 H), 2.55 (dd, 1 H, J = 2.5, 18 Hz), 2.95 (dd, 1 H, J = 7, 18 Hz), 3.40–3.60 (m, 1 H), 3.85 (d, 2 H, J = 2.5 Hz), 4.40–4.60 (m, 1 H), 5.20–5.50 (m, 1 H); mass spectrum (15 eV), *m/e* 143, 84, 83, 53.

Trifluoroacetic acid treatment of **4** followed by bis(3-methyl-2-butyl)borane reduction of the intermediate lactone gave 2-deoxy-D-ribose (**7**).[6,7] The synthetic material was identical with authentic 2-deoxy-D-ribose by the standard criteria of comparison. Alternatively, the lactone **6** was silylated to give the crystalline bis(*tert*-butyldimethylsilyl) derivative **8** (mp 76 °C). Reduction of this product with Dibal gave the disilyl derivative **9** in 92% yield [$[\alpha]^{24}_D = +23.6°$ (after 8 h, c 0.096, MeOH)]. The 300-MHz ^1H NMR of **9** was identical with that obtained for the product generated by silylating authentic 2-deoxy-D-ribose and chromatographically separating out the disilyl derivative.

Additionally, it was observed that acetonitrile oxide reacted with **2** to deliver after N–O bond hydrogenolysis the erythro β-hydroxy ketone as the major product (^1H NMR ratio 88:12).[8] By reacting **2** with the nitrile oxide drived from the tetrahydropyranyl derivative of 2-nitroethanol[4] and then effecting both cleavage of the THP group and hydrogenolysis of the isoxazoline by Raney nickel/$AlCl_3$/MeOH/H_2O treatment, we generated nearly a single dihydroxy ketone (>94% by HPLC analysis).[9] Sodium periodate cleavage of this α-hydroxy ketone followed by diazomethane treatment yielded **4** as the major isomer. These studies thus reveal that the sense of the addition of a nitrile oxide to **2** is independent of the nature of the nitrile oxide employed.

One can rationalize the production of 2-deoxy-D-ribose as the major product of the above scheme through the following two factors: (a) cycloaddition occurs preferentially through a transition state resembling conformer A;[10] (b) addition of the nitrile oxide occurs anti to the C–O bond (the anti-periplanar effect).[11] This latter factor is due presumably to the minimization of secondary antibonding orbital interactions as predicted on a theoretical basis by the work of Houk et al. The explanation for such stereose-



A

[†] Dedicated to the memory of Dr. Anthony Ames.

(1) Kozikowski, A. P.; Chen, Y. Y. *J. Org. Chem.* **1981**, *46*, 5248. Kozikowski, A. P.; Stein, P. D. *J. Am. Chem. Soc.* **1982**, *104*, 4023.

(2) Kozikowski, A. P.; Chen, Y. Y. *Tetrahedron Lett.* **1982**, *23*, 2081.

(3) Crawford, R. J.; Lutener, S. B.; Cockcroft, R. D. *Can. J. Chem.* **1976**, *54*, 3364.

(4) Kozikowski, A. P.; Adamczyk, M. *J. Org. Chem.*, in press.

(5) The ^1H NMR of **4** has also been compared with the ^1H NMR of the product formed from the reaction of the anion of ethyl acetate with **1**, which is known to be an 85:15 mixture of diastereomers with **4** (ethyl ester) predominating. The ABX patterns of the α-methylene protons were identical.

(6) Murakami, M.; Mukaiyama, T. *Chem. Lett.* **1982**, 241.

(7) Nakaminami, G.; Shioi, S.; Sugiyama, Y.; Isemura, S.; Shibuya, M.; Nakagawa, M. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 2624.

(8) The structure of the major isomer was verified by hydrolyzing **4** to the corresponding β-hydroxy acid and reacting this compound with excess methyllithium. The ^1H NMR of the resulting β-hydroxy ketone matched that displayed by the major isomer present in the hydrogenolysis mixture of the isoxazolines prepared from **2** and acetonitrile oxide.

(9) Kozikowski, A. P.; Adamczyk, M. *Tetrahedron Lett.* **1982**, *23*, 3123.

(10) Karabatsos, G. J.; Fenoglio, D. J. *Top. Stereochem.* **1970**, *5*, 167.

(11) Caramella, P.; Rondan, N. G.; Paddon-Row, M. N.; Houk, K. N. *J. Am. Chem. Soc.* **1981**, *103*, 2438. For a related observation in a Diels–Alder reaction, see: Franck, R. W.; John, T. V.; Olejniczak, K.; Blount, J. F. *Ibid.* **1982**, *104*, 1106. The dominance of the anti-bonding effect of an allylic oxygen substituent was first suggested by Franck in this communication.

0002-7863/82/1504-5788$01.25/0

Scheme I

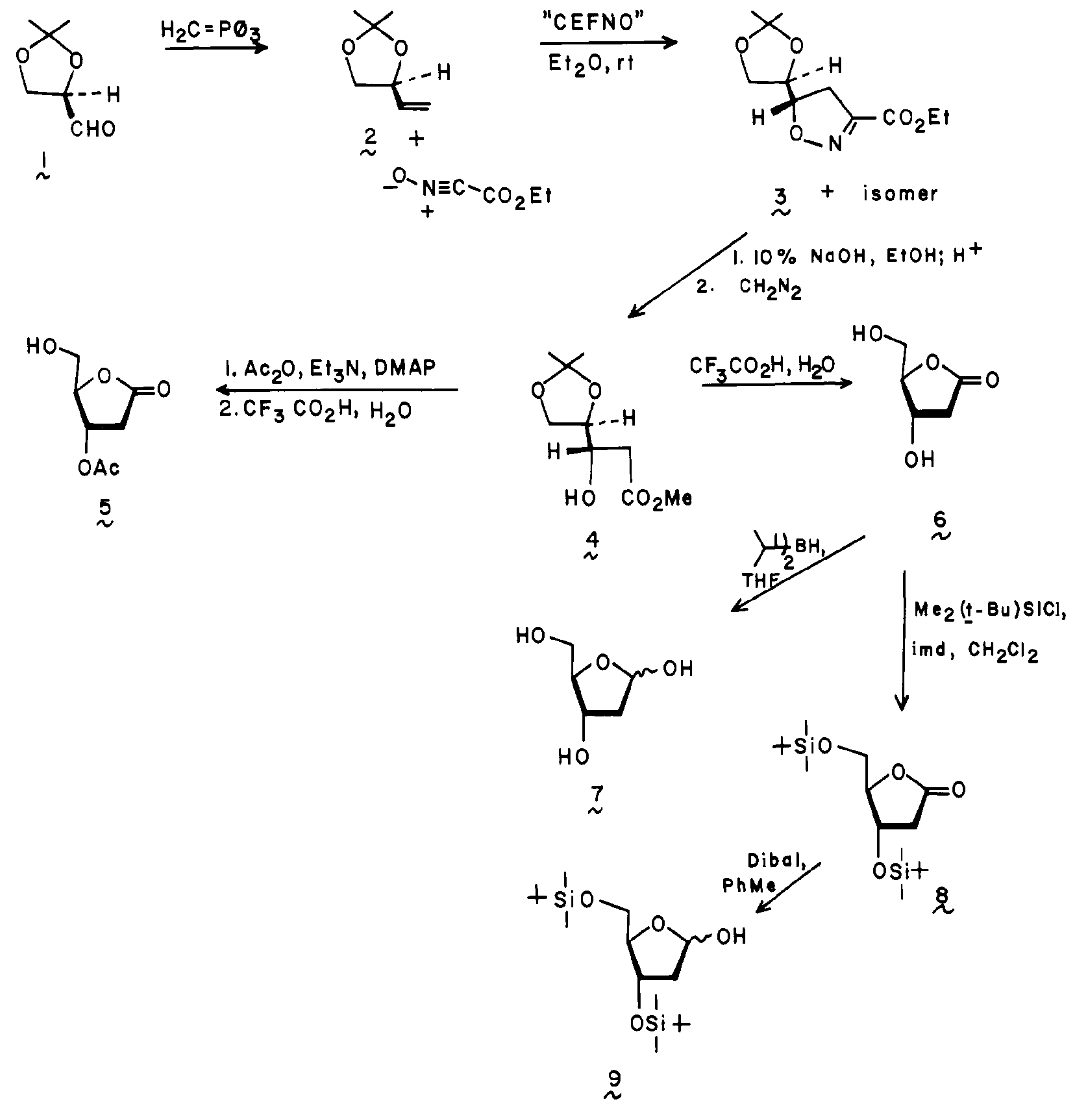
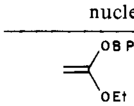
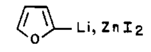
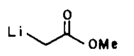
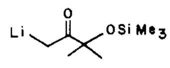
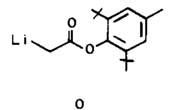
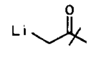


Table I. Aldol Stereoselection Observed in the Addition of Various Carbon Nucleophiles to **1**

nucleophile	erythro/threo, %	ref
	93/7 (+acetate >90:10)	6
	>95/<5	13
	85/15	14
	66/34	14
	66/34	14
	>95/<1	14

lection is, of course, related closely to that offered by Anh in support of the Felkin type transition state, i.e., the addition of a nuclephile to a carbonyl compound (bearing an α-asymmetric center) anti to the large group (the one having the lowest energy $\sigma^*_{C_2\text{-}X}$ orbital).[12]

For comparison with current aldol technology, we list in Table I the erythro/threo ratios observed for the reactions of **1** with various carbon nucleophiles.

In conclusion, we suggest that the anti-directing effect of an allylic oxygen should be very useful in cycloadding chiral or achiral nitrile oxides to chiral olefinic units so as to produce β-hydroxy carbonyl compounds (aldol fragments) in a stereopredictable fashion. A variety of molecular systems that can be constructed through applications of this stereochemical concept are now under study.[15]

Acknowledgment. We are indebted to the National Institutes of Health (HL-20579) and the Camille and Henry Dreyfus Foundation for support of this work. We are grateful to Professor Houk for helpful discussions.

---

(12) Anh, N. T. *Top. Curr. Chem.* **1980**, *88*, 145.

(13) Suzuki, K.; Yuki, Y.; Mukaiyama, T. *Chem. Lett.* **1981**, 1529.

(14) Heathcock, C. H.; Young, S. D.; Hagen, J. P.; Pirrung, M. C.; White, C. T.; VanDerveer, D. *J. Org. Chem.* **1980**, *45*, 3846.

(15) The reactions of nitrile oxides with 3-buten-2-ol and its derivatives are less selective than for **2**, except in the case where the hydroxyl group is protected as its *tert*-butyldimethylsilyl ether derivative. These results constitute unpublished observations by several groups: Kozikowski, A. P.; Ghosh, A. K.; Houk, K. N.; Moses, S., at the University of Pittsburgh, and Jäger, V. and co-workers at the University of Würzburg.