J = 5.5, 10.9, 20.8 Hz), 6.19 (1 H, d, J = 2.5 Hz, OC(CH_2)=C*H*), 6.28 (1 H, dd, J = 2.5, 5.8 Hz, OCH=C*H*), 7.75 (1 H, d, J = 5.8 Hz, OC*H*=CHCO); exact mass calcd for $C_9H_{12}O_3$ 196.1099, found 196.1098; ^{13}C NMR ($CDCl_3$) δ 11.14, 23.33, 27.74, 31.15, 41.29, 64.23, 114.48, 116.43, 155.37, 170.44, 179.60; IR (film) 3450, 1685, 1590 cm^{-1}; $[\alpha]^{20}_D$ = -0.567 ($CHCl_3$, c = 4.06)] and 698 mg (24%) of enone **5** (HRMS calcd for $C_{11}H_{16}O_3$ 196.1099, found 196.1096).

General Procedure for the Conversion of Pyrones to Spiroketals. A 25-mL round-bottom flask equipped with a stir bar and stopper was charged with 20 mL of benzene, 1.0 mmol of pyrone, and 4 drops of trifluoroacetic acid. After stirring for 72 h, the reaction mixture was concentrated to provide the spiroketal-pyrone mixture. Chromatography (silica gel, 10% ethyl acetate in hexanes followed by 10% methanol in ethyl acetate) provided the pure spiroketal and recovered pyrone.

Dioxaspiro[5.5]undec-2-en-4-one (1). According to the general procedure above, 0.100 g (0.595 mmol) of valerolactone pyrone **30** provided 0.847 g (85%) of a 2.3:1 mixture of pyrone **30**-spiroketal **1**.

8(*R*),9(*S*)-Dimethyl-1,7-dioxaspiro[5.5]undec-2-en-4-one (4). According to the general procedure above, 0.053 g (0.29 mmol) of pyrone **31** provided 0.051 g (95%) of a 4:1 mixture of pyrone **31**-spiroketal **4**.

8(*R*)-Ethyl-1,7-dioxaspiro[5.5]undec-2-en-4-one (5). According to the general procedure above, 1.37 g (6.97 mmol) of pyrone **33** produced 0.788 g (58%) of enone **5** and 0.497 (36%) of recovered pyrone **33**.

8(*R*)-Isopropyl-9(*S*)-methyl-1,7-dioxaspiro[5.5]undec-2-en-4-one (6). According to the general procedure above, 1.00 g (4.46 mmol) of pyrone **32** provided 0.988 g (99%) of spiroketal **6**.

Enone 5 from Methoxyspiroketal 24 (BF_3·Et_2O). A 25-mL two-necked round-bottom flask equipped with a stir bar and nitrogen bubbler was charged with 0.083 g (0.36 mmol) of methoxyspiroketal **24** and 2 mL of CH_2Cl_2 and was cooled to 0 °C. To this solution was added 0.06 mL (0.4 mmol) of BF_3·Et_2O, and the reaction mixture was stirred for 5 min. The reaction was quenched with saturated NH_4Cl; the organic phase was dried over $MgSO_4$, concentrated, and chromatographed (25% ethyl acetate/75% hexanes) to yield 30 mg (44%) of enone **5** identical with that prepared above.

Enone 5 from Methoxyspiroketal 24 (Amberlyst). A suspension of 2 g of Amberlyst 15 in a solution of 966 mg (4.24 mmol) of spiroketal **24** and 50 mL of dichloromethane was heated to reflux for 16 h, then cooled, filtered, and concentrated. The residue was flash chromatographed (25% ethyl acetate in hexanes) to provide 484 mg (58%) of spiroketal **5** identical with that prepared above.

Acknowledgment. Financial support from the National Institutes of Health (AI-19544) as well as support from the Alfred P. sloan Foundation in the form of a fellowship to M.T.C. is gratefully acknowledged. We also thank Danute Bankaitis-Davis for technical assistance.

Registry No. **1**, 128777-42-4; **4**, 112320-64-6; **5**, 118418-86-3; **6**, 114066-16-9; **7**, 128683-62-5; **9**, 112320-60-2; **10**, 128683-63-6; **11**, 88400-10-6; **12**, 128777-43-5; **13**, 112320-62-4; **14**, 114066-14-7; **15**, 128683-64-7; **16**, 128777-44-6; **17**, 128683-65-8; **18**, 82467-25-2; **19**, 128777-45-7; **20**, 128777-46-8; **21**, 114066-15-8; **22**, 128777-47-9; **23**, 128777-48-0; **24**, 128777-49-1; **25**, 89036-08-8; **26**, 128683-66-9; **27**, 128683-67-0; **29**, 128683-68-1; **30**, 128683-69-2; **31**, 128683-70-5; **32**, 128683-71-6; **33**, 118418-87-4; MeOCH=CHCOCH$_3$, 4652-27-1; (*Z*)-MeOCH=CHC≡CH, 3685-19-6; δ-valerolactone, 542-28-9; (5*R*)-5-ethyltetrahydropyran-2-one, 118490-63-4; (5*S*,6*R*)-6-ethyl-5-methyltetrahydropyran-2-one, 114179-37-2; (5S,6*R*)-5,6-dihydro-6-ethyl-5-methyl-2*H*-pyran-2-one, 128683-72-7; sodioacetoacetaldehyde, 926-59-0; γ-butyrolactone, 96-48-0.

Supplementary Material Available: ^{13}C NMR and ^1H NMR spectra for key compounds (36 pages). Ordering information is given on any current masthead page.

Theoretical and Experimental Study on the Stereoselectivity of Michael Addition of Alkoxide Anion to Nitro Olefin

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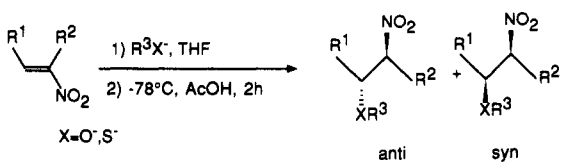
The Michael addition of alkoxide anions to nitro olefins is studied in terms of ab initio and MNDO molecular orbital calculations. We have also done experiments using nitro olefins with the same substituents calculated here. It is proposed that the stereoselectivity of the reaction is due to the endo alkoxy effect, which is structural, and the electronic effect in nitronate anion intermediates. The effect does not exist in intermediates of conjugate addition of simple alkyl group to nitro olefines. The difference depends on whether the atom in the γ-position possesses lone pair orbitals or not. High stereoselectivity was observed in the Michael addition to nitro olefins with the bulky substituents of the α-carbon. This is due to the difficulty in rotating the alkoxy fragment about the C_α-C_β axis.

Introduction

Michael addition is one of the most useful reactions in organic synthesis. Nitro olefins have been used as Michael acceptors because of their high electron deficiency.[1] For example, the reaction of thiols with nitro olefins proceeds smoothly in the presence of catalytic amounts of base to give corresponding β-nitro sulfides in quantitative yields. However, products of the method are usually mixtures of diastereoisomers, whose ratio is nearly 1:1. In order to control stereoselectivity of the Michael reaction with nitro olefin, several procedures have been developed and improved.[2,3] Recently, Ono and his co-workers also devel-

Scheme I



	1	2	3	4	5	6	7
R^1	H	H	Me	Me	Me	H	Me
R^2	H	Me	Me	Et	i-Pr	H	Me
R^3X	MeO	MeO	MeO	MeO	MeO	Et	$PhCH_2O$

(1) (a) *Houben-Weyl: Methoden der Organische Chemie*, 4th ed.; Muller, E., Ed.; George Thieme Verlag: Stuttgart, 1955; Part I, Vol. X. (b) Barrett, A. C. M.: Graboski, G. G. *Chem. Rev.* **1986**, *86*, 751.

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Table I. Geometrical Parameters[a] Optimized with ab Initio and Semiempirical Molecular Orbital Calculations.

	1a			2a			
parameters	6-31+G	3-21G	MNDO	3-21G	MNDO	11, 3-21G	12, 3-21G
C_α–C_β	1.484	1.486	1.487	1.500	1.494	1.518	1.505
C_α–N	1.296	1.297	1.391	1.293	1.392	1.495	1.261
N–O	1.317	1.335	1.237	1.339	1.238	1.238	1.421
C_β–O_γ	1.458	1.462	1.420	1.461	1.420	1.431	1.432
O_γ–C_δ	1.430	1.445	1.387	1.445	1.387	1.437	1.449
C_β–C_α–N	122.7	121.0	125.3	126.3	127.3	117.7	129.3
C_α–N–O	120.3	119.7	120.0	118.9	119.5	110.9	107.8
C_α–C_β–O	114.6	116.2	115.4	116.0	116.0	103.0	111.8
C_β–O_γ–C	116.2	112.8	121.7	116.1	121.6	114.9	114.3
H–C_β–C_α–N	180.4	180.1	177.9	180.5	180.0	−118.5	182.3
H–C_α–C_β–O_γ	81.1	85.9	73.1	84.7	65.2		
O–N–C_α–R^2	0.9	2.2	0.9	−2.2	−1.2	58.4	1.6
C_α–C_β–O_γ–C_δ	63.5	48.3	58.9	−37.0	−46.0	179.8	63.1

[a] Units for bond lengths and angles are angstroms and degrees, respectively.

oped a new method (Scheme I) which used kinetically controlled protonation to nitronate intermediates.[4] It is possible to obtain anti β-nitro sulfides and their analogues in yields more than 8 times greater than corresponding syn isomers. In the previous paper,[5] we used this procedure and obtained the result that the anti/syn ratios of products depend on the bulkiness of R^1 and R^2 and not on the bulkiness of nucleophiles for the system with thiolate anion. Eclipsed and perpendicular conformers were used to discuss the high anti selectivity of the reaction. A similar trend was observed in the reaction with alkoxide anions instead of thiolate ones. On the basis of these experiments, the perpendicular geometry was proposed for the geometry of intermediates.

Several theoretical studies have been performed in order to shed light on the stereoselectivity of addition to carbon–carbon double bonds. Houk and his co-workers used transition structures of intermediates constructed with chiral alkene and nitrile oxide.[6] In this case, the cyclic geometry in the transition structures determines stereoselectivity of products. The relative stability of eclipsed and perpendicular conformers are considered to determine stereoselectivity of the addition of electrophile, nucleophile, and radical to propene.[7] This appears to be also true for the Michael reaction that the product ratios depend on the bulkiness of substituents in both acceptors and nucleophiles.[8]

While perpendicular conformers are considered as intermediates in the addition of thiolate or alkoxide anions to nitroolefines (Scheme I), the bulkiness of the nucleophiles are not so important for the stereoselectivity. Moreover, the reaction proceeds without stereoselectivity when alkyl anion equivalents are used as nucleophiles. It

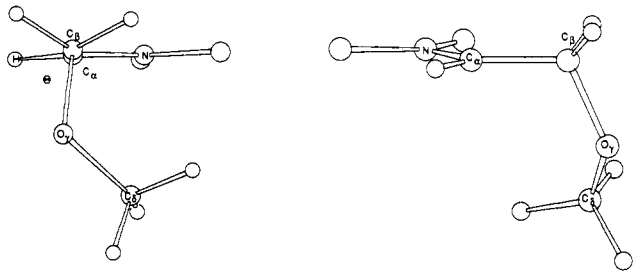


Figure 1. Optimized structure of the intermediate **1** with 6-31+G basis set. θ is the dihedral angle H–C_α–C_β–O_γ.

is unlikely that this is due to a difference between relative steric sizes of the alkyl and alkoxy groups. These features are restricted to the reaction of nitro olefins in comparison with other types of Michael reactions. Although there are interesting features of the Michael reaction with nitro olefins and thiolate or alkoxide anions, this reaction has not been examined in terms of molecular orbital (MO) calculations. It is, therefore, necessary to analyze the nature of the reaction so as to understand the mechanism and origin of the high anti selectivity of Scheme I. In this study, intermediates of the reaction were investigated by use of MO calculations. We also performed experiments with the same substituents calculated here.

Calculations and Experiments

Molecular Orbital Calculations. Ab initio MO calculations were performed for small molecules such as **1**, **2**, **11**, and **12** using the GAUSSIAN-82 program[9] at the Institute for Molecular Science. The 3-21G and 6-31+G basis sets[10] were used for geometry optimization with the energy gradient method. Although somewhat less reliable than the ab initio calculations, we used the MNDO[11] method for molecules with large substituents such as **3–7** in order to directly compare the calculation results with experimental data. **6** has an ethyl group instead of a methoxy group. Both **a** and **b** conformers of nitronate anion intermediates were taken into account in order to discuss the protonation path subsequent to the formation of the intermediate. The *aci*-nitro compound **11** and the nitro ether **12** were optimized for the same purpose. Since the

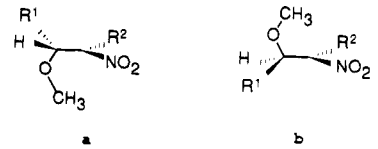
(2) Steves, R. W.; Mukaiyama, T. *Chem. Lett.* **1985**, 855.
(3) (a) Seebach, D.; Golinski, J. *Helv. Chim. Acta* **1981**, *64*, 1413. (b) Seebach, D.; Beck, A. K.; Mukhopadhyay, T.; Thomas, E. *Ibid.* **1982**, *65*, 1101. (c) Seebach, D.; Brook, M. A. *Ibid.* **1985**, *68*, 319.
(4) (a) Ono, N.; Kamimura, A.; Sasatani, H.; Kaji, A. *J. Org. Chem.* **1987**, *52*, 4133. (b) Ono, N.; Kamimura, A; Kawai, T.; Kaji, *J. Chem. Soc., Chem. Commun.* **1987**, 1550. (c) Kamimura, A.; Ono, N. *Tetrahedron Lett.* **1989**, *30*, 731.
(5) Kamimura, A.; Sasatani, H.; Hashimoto, T.; Kawai, T.; Hori, K.; Ono, N. *J. Org. Chem.* **1990**, *55*, 2437.
(6) (a) Houk, K. N.; Duh, H.; Wu, Y.; Moses, S. R. *J. Am. Chem. Soc.* **1986**, *108*, 2754. (b) Brown, F. K., Houk, K. N. *Ibid.* **1985**, *107*, 1971. (c) Houk, K. N.; Firestone, R. A.; Munchausen, L. L.; Mueller, P. H.; Arison, B. H.; Garcia, L. A. *Ibid.* **1985**, *107*, 7227. (d) Houk, K. N.; Morse, S. R.; Wu, Y.; Rondan, N. G.; Jager, V.; Schohe, R.; Fronczek, F. R. *Ibid.* **1984**, *06*, 3880.
(7) (a) Caramella, P.; Rondan, N. G.; Paddon-Row, M. N.; Houk, K. N. *J. Am. Chem. Soc.* **1981**, *103*, 2438. (b) Paddon-Row, N. M.; Rondan, N. G.; Houk, K. N. *Ibid.* **1982**, *104*, 7162.
(8) McGarvey, G. J.; Williams, J. M. *J. Am. Chem. Soc.* **1985**, *107*, 1435.
(9) (a) Binkley, J. S.; Frisch, M. J.; De Frees, D. J.; Raghanvachari, K.; Whiteside, R. A.; Schlegel, H. B.; Pople, J. A., 1982, GAUSSIAN-82; Department of Chemistry, Carnegie-Mellon University, Pittsburg, PA. (b) Koga, N., the IMS version of GAUSSIAN-82.
(10) (a) Hehre, W. J.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 4233. (b) Dill, J. D.; Pople, J. A. *Ibid.* **1975**, *62*, 2921.
(11) Dewer, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899.

Table II. Yields and Anti/Syn Ratios of Products of the Michael Addition of Alkoxy or Alkyl Groups to Nitro Olefins

run	intermediate	product	R^1	R^2	R^3	X	yield, %	anti/syn	ref
1	3	13	Me	Me	Me	O	46	85/15	a
2	4	14	Me	Et	Me	O	56	98/2	a
3	5	15	Me	i-Pr	Me	O	44	98/2	a
4	7	16	Me	Me	$PhCH_2$	O	73	91/9	b
5	8	17	$-(CH_2)_4-$		$PhCH_2O$	O	71	4/96[d]	b
6	9	18	Me	Me	Ph	CH_2	60	54/46	b
7	10	19	Ph	Me	CH_2=CH	CH_2	91	50/50	c

[a] This work. [b] Reference 5. [c] Reference 13. [d] In this case, the endo alkoxy effect leads the high syn selectivity.

relative stability of the molecules is related to the reaction mechanism, 6-31G*//3-21G energies were also calculated. Table I summarizes the ab initio and MNDO optimized geometrical parameters.



a b

The optimized structure of 1, obtained with the 6-31+G basis set, is displayed in Figure 1. Optimized bond lengths differ by less than 0.04 Å from those calculated with the 3-21G basis set. They are not much different from the MNDO results except for C–N and N–O lengths. Compared to the 6-31+G results, the MNDO calculation overestimates the C–N bond by 0.095 Å and underestimates the N–O bond by 0.08 Å. The difference of bond and dihedral angles are less than 5° between the 6-31+G and the 3-21G calculations except for the C_α–C_β–O_γ–C_δ dihedral angle. This difference is probably due to the presence of extra orbitals in the 6-31+G basis set. The set of diffuse orbitals in the 6-31+G basis set makes it possible to describe the hyperconjugation between the C_β–O_γ σ^* bond and the anionic orbital at C_α as well as the π-bonding in the anion fragment. The MNDO calculation also gave good agreement of angles with those from the 6-31+G calculation except for the two angles, C_β–O_γ–C, H–C_α–C_β–O_γ, which relate to the hyperconjugation.

According to the optimized geometrical parameters of the intermediate 1, C_α and C_β have sp^2 and sp^3 hybridization, respectively. It is, therefore, possible to consider two fragments, $C_\alpha R^2NO_2$ and $C_\beta HR^1OCH_3$, in the nitronate intermediates. We call them the anion and the alkoxy fragments, respectively. The dihedral angle H–C_α–C_β–O_γ (θ in Figure 1) is calculated to be 81.1°, indicating that 1 has almost a perpendicular conformation. This is the structure that we proposed for the intermediates of our reaction. The 3-21G level calculation shows that this feature is not changed by the introduction of a methyl group on R^1, i.e., θ's of 1 and 2 are calculated to be 85.9° and 84.7°, respectively. However, the MNDO calculation estimated these values to be 73.1° and 65.2°, respectively. It means that the MNDO method underestimates the hyperconjugation between the anion and the C–O σ^* orbitals.[12]

Another feature of the structure is that the methyl moiety in the methoxy group locates the syn position of the anion fragment about the C_β–O_γ axis. In spite of deficiencies in the basis set, optimized structures using the 3-21G basis set as well as MNDO method were similar to that from the 6-31+G basis set. As discussed below, the methoxy group plays an important role in the stereoselectivity of the reaction. Moreover, similar geometrical features were obtained for all intermediates calculated here. The MNDO calculations gave geometries in reasonable agreement with those obtained from ab inito calculations.

Experiment. In order to compare results of MO calculations with experiments, we tried to prepare the same compounds as calculated here. β-Nitro ethers were prepared by the reaction of alkoxide anions to nitro olefins and subsequent protonation at −78 °C (Scheme I). In this study, we used only methoxide anion (R^3 = Me) as the nucleofile. The results are summarized in Table II. The Michael addition of benzyl alcohol to nitro olefin proceeded in better yield than that of methanol (runs 1 and 4). Observed anti/syn selectivity is generally higher than 85/15. The stereochemistry of the products was determined by ^{13}C NMR in comparison with literature data.[4c] The best anti/syn selectivity is obtained when R^2 = isopropyl or ethyl (runs 2 and 3). The addition of alkoxide to a cyclic nitro olefin predominantly gave *cis*-β-nitro ether (run 5). These anti products were isomerized in the presence of catalytic amounts of triethylamine to give anti/syn mixture, whose ratio was generally 1:1. On the other hand, addition of simple alkyl group to nitro olefin took place with poor selectivity (runs 6 and 7[13]). As there is little difference between the relative steric bulk of alkyl and alkoxy groups, this observation is a distinct feature of the reaction. Little influences of counterions were observed in our reaction similar to the results of the previous paper.[5]

Results and Discussion

Geometries of Intermediates. The intermediates produced using out method (Scheme I) are nitronate anions formed from nitro olefins and alkoxide reagents.[5] We proposed the perpendicular conformation like **a** as the most feasible candidate for the geometry of the nitronate intermediate. This conformer always forms at the first step of the reaction. If protonation occurs anti to the methoxy group of the intermediate, then anti β-nitro ethers are formed. In fact, it is possible to control the stereoselectivity of the products when we use alkoxide anion as the nucleophile. Although this reasoning could also be applied to ethyl anion instead of methoxy anion in Scheme I, the alkyl anion equivalents show little stereoselectivity under the same reaction conditions. In order to investigate this difference, **1a** and **6a** were optimized using the MNDO method. The remarkable feature of **1a** is the endo conformation between the methyl moiety of the methoxy group and the anion fragment (Figure 1). As **7**, with a benzyloxy group, is also calculated to have this structural feature, the endo conformation is common in nitronate anions with an alkoxy group. As discussed above, the similar trend was obtained in geometries of 1 and 2 from the ab inito calculations.

(12) Glaser, R.; Streitwieser, A., Jr. *J. Mol. Struct. (Theochem)* **1988**, *163*, 19.

(13) (a) Pecunioso, A.; Menicagli, R. *J. Org. Chem.* **1989**, *54*, 2391. (b) Pecunioso, A.; Menicagli, R. *J. Org. Chem.* **1988**, *53*, 45. (c) Pecunioso, A.; Menicagli, R. *Tetrahedron* **1987**, *43*, 5411.

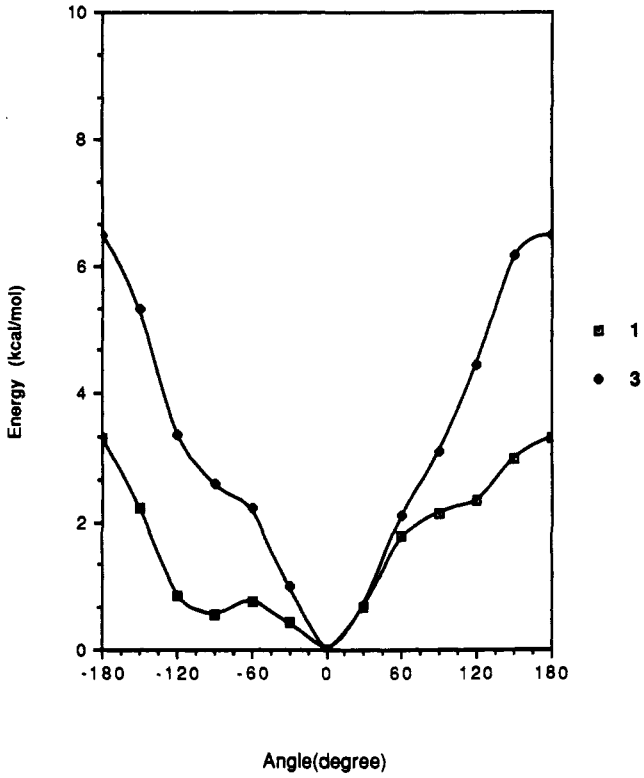
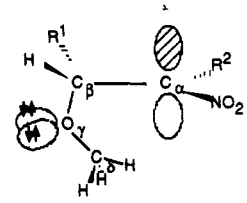


Figure 2. MNDO potential energy profiles of the rotation of the methyl moiety in the methoxy group about the C_β–C_γ bond. The rotation angle indicates change of the dihedral angle C_α–C_β–C_γ–O_δ from the optimized geometry.

The formation of a new C–O bond makes an anion orbital at C_α. The methoxy group has lone pair orbitals on oxygen atom at the γ-position. The methyl moiety of the



methoxy group lies beneath the C_α–C_β bond (Figure 1); in this conformation, repulsion between lone pair and the anion orbitals is minimized. The interaction between the anion orbital and the methyl moiety helps the preferable direction of the group. Figure 2 displays the MNDO energy profiles for the rotation of the methyl moiety about the C_β–O_γ axis. There is a potential minimum for **1a** around $\theta = -90°$ which corresponds to the angle for the exo conformation. This conformation has a higher energy by 0.5 kcal/mol than the endo conformation ($\theta - 0°$). The energy barrier of the process for **1a** is estimated to be less than 4 kcal/mol. On the other hand, **3a** with two methyl substituents on C_α and C_β does not have a minimum but a shoulder around −90°. The rotation of the methyl group needs more than 6 kcal/mol for the molecule. The temperature −78 °C in the quenching process freezes the rotation about the C_β–O_γ axis with such energy barrier. We call this structural and electronic feature the endo alkoxy effect.

As listed in Table II, anti/syn ratios for systems with R^2 = Et and i-Pr are 98/2 with 56 and 44% yields, respectively. Nitrocyclohexene **8** reacts with benzyl oxide anion and the ratio is 4/96 with 71% yield. When we used thiolate anion instead of alkoxide anion as a nucleophile, this value was 0/100.[5] In both cyclic cases, the endo alkoxy

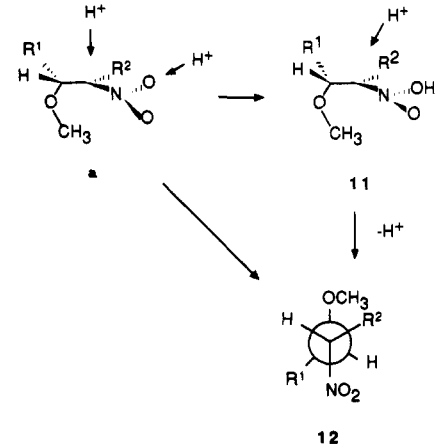
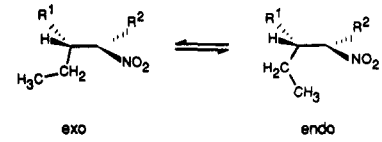


Figure 3. Feasible protonation pathways of the nitronate intermediate to the anti product.

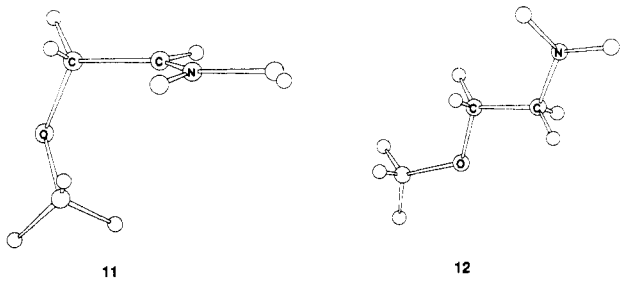
effect leads to cis isomers as the products. This effect can strongly control the stereoselectivity of the reaction. Therefore, anti isomers of products is likely to come from the conformer **a**.

On the other hand, the endo alkoxy effect does not apply to **6** because the γ-carbon atom has no lone pair orbitals. In the optimized geometry of ethyl intermediate **6**, the terminal methyl moiety and the anion fragment adopt an antiperiplanar conformation which is usually seen in alkyl chains. In this intermediate, rotation of the methyl group about the C_β–C_γ axis results in the endo conformation similar to **1**. MNDO calculations estimated that the exo



conformer is more stable by 0.5 kcal/mol than the endo conformer. It is not so difficult for protons to attack the position syn to the ethyl group in the exo conformer. The existence of the two conformers with little energy difference is important to determine the stereochemical outcome of the reaction even if the quenching process is done at temperatures as low as −78 °C. The reaction with alkyl anions and nitro olefins is not expected to proceed in a stereoselective way because of the absence of the endo alkoxy effect. We can expect only weak hyperconjugation between the anion at C_α and the C_β–C_γ σ^* orbitals for this molecule in comparison with nitronate intermediates.[16a] This electronic feature helps the formation of products without stereoselectivity. This is consistent with experimental results[5,13] that the anti/syn ratios for runs 6 and 7 are almost 50/50 as listed in Table II.

Protonation Pathway. It is possible to consider a protonation path in which a proton directly attacks C_α from the side anti to the methoxy group. If the endo alkoxy effect is strong enough to protect the side syn to the methoxy group from protons, this reaction for the **a** type of intermediates leads to formation of anti products. There is an alternative path via an *aci*-nitro compound[3b] such as **11** as shown in Figure 3. The isomerization of the intermediate leads to formation of the nitro compound **12**. Optimized structures of **11** and **12** using the 3-21G basis set are displayed in Figure 4. As **11** has a structural feature similar to that of the nitronate anion **1**, we can consider the endo alkoxy effect for the molecule and the methoxy group controls protonation to **11** and its analogues. Therefore, the effect is present whether or not the reaction proceeds via *aci*-nitro compounds.



11 12

Figure 4. Optimized structures of the *aci*-nitro intermediate **11** and nitro ether **12** using the 3-21G basis set.

The 6-31G*//3-21G energies were calculated to be −396.564 09 and −396.564 23 au[14] for **11** and **12**, respectively. According to energy difference between the two isomers (0.1 kcal/mol), we can expect both paths for the product. While syn and anti isomers of nitro compounds were obtained as the products of Scheme I, no trace of analogues of **11** was detected. There is no proof that *aci*-nitro compounds exist in the solution right after quenching with acetic acid. The solvent effect may relate to the observation. Even if *aci*-nitro compounds form, they gradually isomerize to the nitro ethers. On the other hand, there exist no paths for isomerizing from **12** to **11** or anything else under the reaction condition.[15] Therefore, only nitro compounds are obtained as the products of our experiment.

Substituent Effect. The first adducts of (*E*)-nitro olefins with methoxide anion are always the **a** conformers. The endo alkoxy effect is seen in all alkoxy intermediates calculated here. This effect controls the stereoselectivity of the reactions and major products are anti isomers. This explanation is consistent with our experiments. However, the ratio of the syn product is rather low in the case of R^2 = Me, i.e., the anti/syn ratio is 85/15, which is lower than those for isopropyl or ethyl (98/2). It may be reasonable that the anti selectivity of the reaction comes from the bulkiness of the substituents R^2 as well as the endo alkoxy effect. Bulkiness of R^2 equally prevents protons from approaching to both same and opposite sites of the alkoxy group. Therefore, we cannot explain lower selectivity found in the methyl system in comparison with those observed in the reaction with bulky groups.

As mentioned above, the **a** conformer with bulky substituents leads to anti products with more than 98% selectivity. Syn isomers is likely to be given from the **b** types of intermediates. It is necessary, therefore, to change the geometry of the intermediate from one to another in order to produce two geometrical isomers as the products. The **a** conformer changes its geometry to the **b** conformer through the rotation of the alkoxy fragment about the C_α–C_β axis. If this process is easy, anti/syn ratios of products are determined by thermodynamic stability of each conformer.

When we consider the relative stability of these intermediates, the steric repulsion between R^1 and R^2 groups in the **a** conformer should be compared with that between R^1 and NO_2 groups in the **b** conformer (Figure 5). As R^1 is a methyl group in the present case, the relative stability only depends on R^2. MNDO calculations estimated that all of **a** type intermediates are more stable than those of **b**. For example, **2a** and **5a** are more stable by 2.8 and 0.4 kcal/mol than **2b** and **5b**, respectively. The energy difference between **a** and **b** conformers of **2** is larger by 2.4 kcal/mol than that of **5**. The introduction of a bulky isopropyl group on C_α (**5**) results in decreasing the energy difference between the two conformers. According to the relative stability of the two conformers, the anti/syn ratio of the small substituent should be better than that of the large substituent. This expectation is opposite to the experimental results, i.e., the substitution with the bulky isopropyl and ethyl groups on C_α gives better stereoselectivity than that of the methyl group. It means that the difference of the thermodynamic stability between **a** and **b** conformers does not involve in stereoselectivity of the reaction.

If the rotation of the alkoxy fragment is not so easy, this process should relate to the stereoselectivity. Figure 6 displays the MNDO energy profiles of **1**, **2**, and **5** for the rotation about the C_α–C_β bond. In these calculations, all parameters were optimized except for the dihedral angle H–C_α–C_β–O_γ θ. The left and right sides of the figure are potential curves of the path A and B in Figure 5, respectively. The repulsion of R^1–NO_2 and CH_3O–R^2 groups

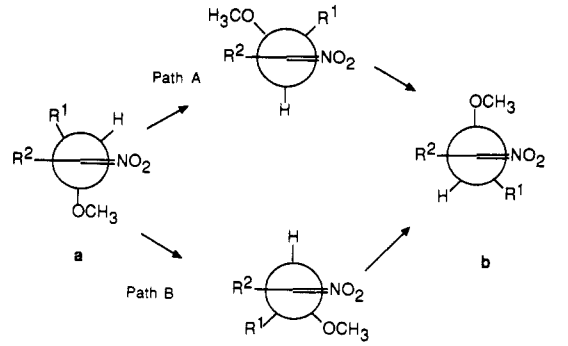


Figure 5. The rotation of the nitronate anion from the **a** to the **b** conformer.

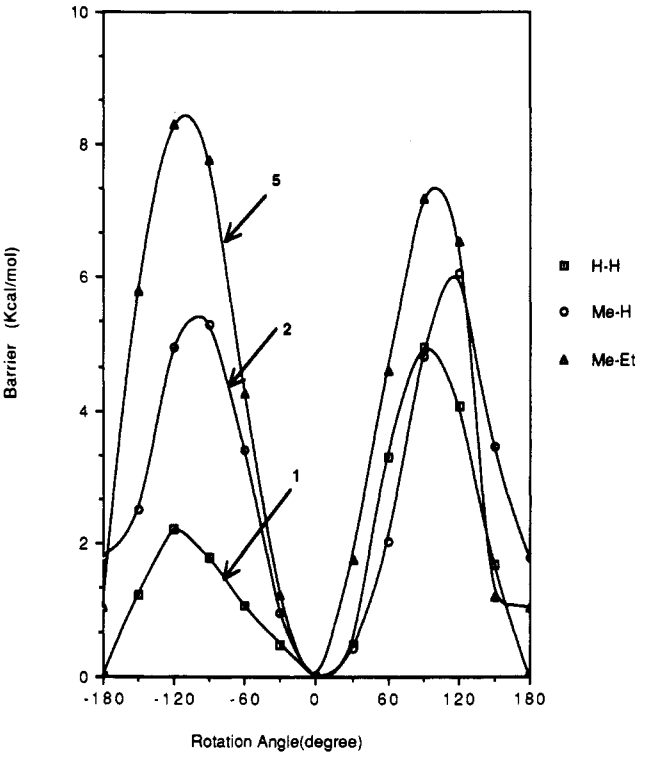


Figure 6. MNDO potential energy profiles of the rotation of the alkoxy fragment around the C_α–C_β bond. **1**, **2**, and **5** indicate potential curves for each intermediate. The rotation angle corresponds to an increase or decrease of the dihedral angle θ from the values in the optimized geometries.

(14) 3-21G energies of **11** and **12** are −394.325 68 and −394.324 74 au, respectively.

(15) Under the acidic condition we used for quenching process, we cannot consider deprotonation from Cα.

makes barrier for the path A. That of CH_3O–NO_2 as well as R^2–R^1 groups affects easiness of rotation for the path B. It is easily expected that **1** has the lowest barrier in the three molecules because both R^1 and R^2 are hydrogens. The methyl substitution on C_β (**2**) gives additional barrier by 2–3 kcal/mol to that for **1**. Because of having methyl and isopropyl groups, **5** has the highest energy barrier for the rotation. The energy height for the path B is lower than that for the path A for **5**. The conformer **b**, therefore, forms through the path B in the nitro olefins having bulky substitutents on R^1 and R^2.

The magnitude of the hyperconjugative interaction between the C_α anion and the C–O σ^* orbitals are largely related to the easiness of the process.[16] As discussed above, MNDO calculations underestimate the interaction. The energy barriers for th paths A and B are, probably, larger than those calculated with the semiempirical method. Unfortunately, the MNDO calculations could not describe the absolute difference of the barrier height between **3** and **4** or **5**, i.e., the intermediate with R^2 = Me is calculated to have a barrier similar to those for R^2 = Et and i-Pr. This is probably an artifact resulting from crude calculations. The smaller substituent is expected to give lower barrier than those for larger substituents seen in the relation between **1** and **2** of Figure 6. If this is true in the difference between **3** and **5**, we can expect that the anti/syn ratio of the methyl system is worse than that for the ethyl system. The anti/syn ratios for **3**, **4**, and **5** are 85/15, 98/2, and 98/2, respectively.

(16) (a) Apeloig, Y.; Rappoport, Z. *J. Am. Chem. Soc.* **1979**, *101*, 5095. (b) Avramovitch, B.; Weyerstahl, P.; Rappoport, Z. *Ibid.* **1987**, *109*, 6687. (c) Rappoport, Z.; Gazit, A. *Ibid.* **1987**, *109*, 6698. (d) Avramovitch, B.; Rappoport, Z. *Ibid.* **1988**, *110*, 911.

Experimental Section

Nitro olefins were prepared from dehydration of corresponding nitro alcohols. ^{1}H NMR spectra were recorded on Hitachi R-250H at 250 MHz. GLC analyses were carried out on Simadzu GC-8A.

Preparation of β-Nitro Ethers: *anti*-2-Methoxy-3-nitrobutane (13). To a solution of sodium methoxide, which was in situ generated from sodium hydride (60%, 606 mg) and methanol (1 mL), in THF (10 mL) was added 2-nitro-2-butene (525 mg, 5.2 mmol), and the resulting solution was stirred for 24 h at room temperature. The reaction mixture was cooled at −78 °C, and acetic acid was added (1 mL) and stirred for additional 1 h. Then the solution was poured into water, and the aqueous layer was extracted with ethyl acetate three times. The combined organic layer was washed with brine one time and dried over anhydrous Na_2SO_4. The solvent was removed in vacuo after filtration, and the residue was subjected to column chromatography (silica gel/hexane–ethyl acetate, 20:1) to give **13** in 46% yield (317 mg). The anti/syn ratio was determined by GLC analysis: ^{1}H NMR ($CDCl_3$) δ 1.22 (d, J = 6.1 Hz, 3 H), 1.53 (d, J = 6.7 Hz, 3 H), 3.36 (s, 3 H), 3.89 (dq, J = 4.9, 6.2 Hz, 1 H), 4.48 (dq, J = 4.8, 6.8 Hz, 1 H).

The other β-nitro ethers were prepared via the same procedure. The spectral data were as following. ***anti*-2-Methoxy-3-nitropentane (14):** ^{1}H NMR ($CDCl_3$) δ 0.98 (t, J = 7.4 Hz, 3 H), 1.22 (d, J = 6.1 Hz, 3 H), 1.88–2.09 (m, 2 H), 3.38 (s, 3 H), 3.64 (quint, J = 6.1 Hz, 1 H), 4.34 (ddd, J = 3.6 Hz, J = 6.1, 10.4 Hz, 1 H). ***anti*-2-Methoxy-4-methyl-3-nitropentane (15):** ^{1}H NMR ($CDCl_3$) δ 1.00 (d, J = 6.7 Hz, 6 H), 1.26 (d, J = 6.1 Hz, 3 H), 2.33 (m, J = 6.7 Hz, 1 H), 3.40 (s, 3 H), 3.71 (quint, J = 6.1 Hz, 1 H), 4.41 (dd, J = 6.1 Hz, J = 7.9 Hz, 1 H).

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Electrocatalytic Hydrogenation Using Precious Metal Microparticles in Redox-Active Polymer Films

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Glassy carbon felt electrodes have been modified by electrodeposition of poly(pyrrole–viologen) films (derived from *N,N'*-dialkyl-4,4'-bipyridinium salts), followed by electroprecipitation of precious metal (Pt, Pd, Rh, or Ru) microparticles. The resulting electrodes have been proved to be active for the electrocatalytic hydrogenation of conjugated enones (2-cyclohexen-1-one, cryptone, carvone, isophorone), styrene, and benzonitrile in aqueous media (pH 1). Despite low loadings of metal catalysts, high electric and products yields and a long term stability of these cathodes have been observed. The influence of the metal loading and the polymer structure on the catalytic efficiency as well as the selectivity obtained according to the metal catalyst used have been studied. Comparison with results previously reported for other catalytic cathodes like Pt/Pt, Pd/C, or Raney nickel electrodes proves the high efficiency of these metal microparticles within redox polymer film based electrodes.

Introduction

Electrocatalytic hydrogenation has never achieved the same success as catalytic hydrogenation even in the laboratory, despite the advantage of very mild conditions (room temperature and atmospheric pressure) normaly employed in electrochemical synthesis. In electrocatalytic hydrogenation, chemisorbed (active) hydrogen is formed directly at the electrode surface. Thus, the kinetic barrier for dissociation and mass transport of poorly soluble molecular hydrogen are bypassed and the reaction conditions are much milder than in regular catalytic hydrogenation. In comparison with conventional electrosynthesis, electrocatalytic hydrogenation offers selective and unusual

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