in 2 mL) was added a solution of Br_2 or Cl_2 in CCl_4 (1.05 mmol in 1 mL), causing the immediate formation of a solid. After 1 h at room temperature the solid was recovered as a highly hygroscopic, uncrystallizable material. The ^{13}C spectra were taken in D_2O solution. The respective picrates were obtained by metathesis with aqueous sodium picrate (see Table III).

***endo*-4-Hydroxy-*cis*-1-thioniabicyclo[3.3.0]octane (19)** was obtained as the chloride salt as follows. To an ethanol solution of the bis(pyranyl) derivatives **31** (0.69 g in 10 mL) was added aqueous 1 N HCl (11 mL) and the solution heated at reflux for 30 min. After neutralization with 1 N NaOH, the solution was concentrated under reduced pressure, and the aqueous residue was extracted with CH_2Cl_2 to remove any unreacted starting material. The aqueous phase was evaporated under reduced pressure and the residue extracted with MeOH to remove the inorganics. Evaporation of the solvent left 0.25 g (80%) of a viscous oil, whose ^{13}C spectrum (reported in Table I) showed it to be free of organic impurities.

***exo*-4-Hydroxy-*cis*-1-thioniabicyclo[3.3.0]octane (20)** was obtained as the triflate salt by treating *trans*-4,5-dihydroxythiocane (**27**) with trifluoromethanesulfonic acid in a procedure similar to that described for the parent cation **12**. The salt is a viscous uncrystallizable material; metathesis with hot aqueous sodium tetraphenylborate gave, after crystallization from H_2O/acetone, a crystalline solid (see Table III).

Attempted Transannular Cyclization of (*Z*)-4-Methylthiacyclooct-4-ene (9). Trifluoromethanesulfonic acid treatment of the title olefin for various lengths of time failed to produce the expected bicyclic 4-methyl derivatives. The material isolated after 2 h of reaction time was a sulfonium salt whose ^{13}C NMR spectrum (acetone-d_6) shows in the olefinic carbon region a singlet at δ 136.5 and a doublet at δ 126.7, indicative of the presence of the same $CCH{=}C(CH_3)C$ fragment present in the starting material. This structural feature finds support in the ^1H NMR spectrum which shows a low-field triplet of doublets (δ 5.62, 1 H, J = 8.0 and 1.0 Hz) which can be attributed to a single olefinic proton coupled to an allylic CH_3 group. The latter shows up as a narrow doublet (δ 1.81, 3 H, $J \simeq 1.0$ Hz). Further multiplet resonances are present at δ 3.8 (2 H), 3.4 (4 H), 2.9–2.5 (4 H), 2.2 (6 H), and 1.72 (6 H). Finally, and most revealing a CH_3 singlet is present at δ 1.26. The spectra are consistent with the dimeric product **32** (see Results and Discussion section). With progressively longer contact times, materials are produced whose NMR spectra become more and more complex and indicative of the presence of higher oligomers.

Registry No. 1, 64945-41-1; (±)-2, 66840-93-5; (±)-3, 66840-94-6; (±)-4, 73505-88-1; (±)-5, 73543-32-5; 6, 64945-38-6; (±)-7, 73543-33-6; (±)-8, 73543-34-7; 9, 73505-89-2; 10, 71411-34-2; 11, 73505-90-5; 12 triflate, 73505-92-7; 12 picrate, 73505-93-8; (±)-13 triflate, 73505-95-0; (±)-13 hexafluorophosphate, 73543-35-8; (±)-14 triflate, 73543-37-0; (±)-14 hexafluorophosphate, 73573-16-7; (±)-15 triflate, 73505-97-2; (±)-15 hexafluorophosphate, 73543-38-1; (±)-16 triflate, 73543-40-5; (±)-16 hexafluorophosphate, 73609-89-9; 17 triflate, 73505-99-4; 17 picrate, 73512-98-8; 18 triflate, 73506-01-1; 18 picrate, 73506-02-2; (±)-19 chloride, 73505-77-8; (±)-20 triflate, 73543-19-8; (±)-20 tetraphenylborate, 73609-88-8; (±)-21 bromide, 73505-78-9; (±)-21 picrate, 73543-21-2; (±)-22 bromide, 73543-22-3; (±)-22 picrate, 73573-13-4; (±)-23 chloride, 73505-79-0; (±)-23 picrate, 73543-24-5; (±)-24 chloride, 73543-25-6; (±)-24 picrate, 73573-15-6; 25, 73505-81-4; (±)-26, 73505-83-6; (±)-27, 73505-84-7; 28, 72050-57-8; (±)-*cis*-29, 73543-27-8; (±)-*trans*-29, 73543-29-0; (±)-*cis*-30, 73505-86-9; (±)-*trans*-30, 73543-31-4; (±)-31, 73505-87-0; 32, 73505-59-6; (*E*)-33, 73505-60-9; (*Z*)-33, 73505-61-0; 34, 73505-62-1; 35, 26551-55-3; (±)-(*E*)-36, 73543-16-5; (±)-(*Z*)-36, 73543-17-6; (±)-37, 73505-63-2; (±)-38, 73505-64-3; (±)-39, isomer 1, 73512-97-7; (±)-39, isomer 2, 73505-66-5; (±)-39, isomer 3, 73523-05-4; (±)-39, isomer 4, 73505-68-7; (±)-*cis*-40, 73505-70-1; (±)-trans-40, 73505-72-3; (±)-*cis*-41, 73505-74-5; (±)-*trans*-41, 73505-76-7; thietane, 287-27-4; crotyl bromide, 4784-77-4; 3,3-dimethylthietane, 13188-85-7; allyl bromide, 106-95-6; 2-methylallyl chloride, 1458-98-6; lithium diisopropylamide, 4111-54-0; 2-phenylethyl iodide, 17376-04-4.

Supplementary Material Available: Computed (force field) geometries, energies, and energy components for **1-t**, **1-c**, and **2–5**. (Table IV, bond distances; Table V, bond angles; Table VI, dihedral angles; Table VII, energies and energy components) (6 pages). Ordering information is given on any current masthead page.

Stereochemical Study on Nitro Tautomerization of Nitronate Adducts from Conjugate Addition of RMgX to a 4-Methoxy-1-nitronaphthalene System

Giuseppe Bartoli,* Marcella Bosco, and Graziano Baccolini

Istituto di Chimica Organica, Università, 40136 Bologna, Italy

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Addition of RMgX to 4-methoxy-1-nitronaphthalene (**1**) leads to formation of nitronate 1,4 adduct (**2**) together with lesser amounts of 1,6 addition product (**3**). On treatment with aqueous acetate–acetic acid buffer, **2** is converted into a nitronate anion which undergoes quick protonation at C-1 to give a mixture of *trans*- and *cis*-2-methyl-4-methoxy-1-nitro-1,2-dihydronaphthalene, with neat prevalence of the latter isomer. Conversion of kinetically favored cis compound into the more stable trans isomer occurs up to equilibrium, on prolonging times of the reaction. Prevailing formation of the less stable isomer is interpreted in terms of a sterically controlled approach of the proton to the carbon of the nitronate function of a nonplanar cyclohexadienic system in which prototropic attack must occur from the less hindered side. Conformational and configurational analyses based on interpretation of NMR spectra of reaction products showed the nitro group to exist preferentially "quasi-axial" in both cis and trans compounds. The large difference in stability between the two isomers can therefore be explained by the fact that the nitro and methyl groups are in an almost eclipsed reciprocal orientation in the cis isomer, whereas they are mutually "anti" oriented in the trans one. The influence of the size of the alkyl group on *aci*-nitro tautomerization and on cis–trans isomerization has been investigated: the conformational equilibrium of the nitronate anion is submitted to the steric effects of the alkyl substituent, which, moreover, strongly affect the isomerization process rate.

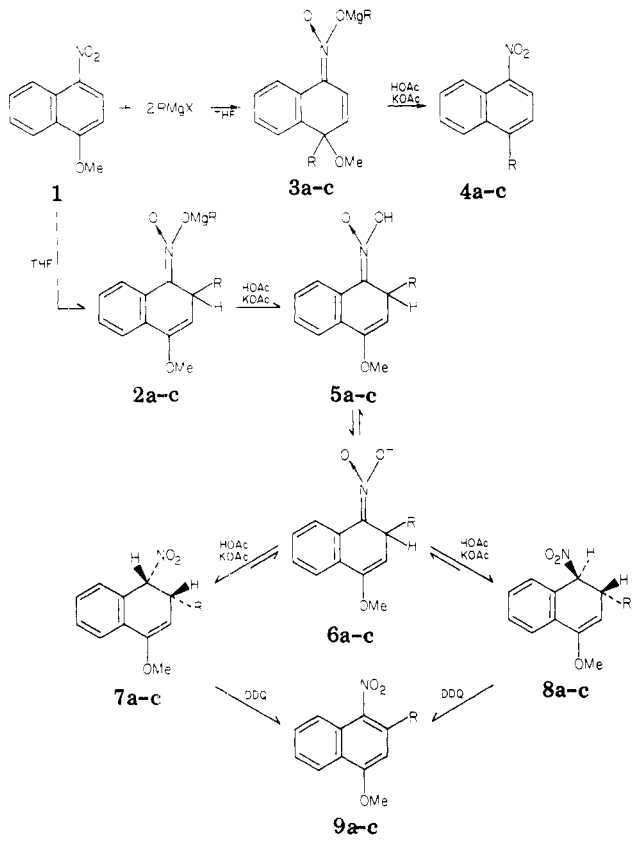
Nitronate adducts from conjugate addition of RMgX to nitroarenic systems and their reactivity toward reducing[1] and oxidizing agents[2] and toward Lewis acids[3] have been reported in previous papers.

(1) G. Bartoli, A. Medici, G. Rosini, and D. Tavernari, *Synthesis*, 6, 436 (1978).

(2) G. Bartoli, M. Bosco, and G. Baccolini, *J. Org. Chem.*, **45**, 522 (1980).

0022-3263/80/1945-2649$01.00/0

Scheme I[a]



[a] a, CH_3; b, $PhCH_2CH_2$; c, $PhCH_2$.

The overall results are in part at variance with well-established reactivity patterns reported in the literature for such classes of compounds. For instance, treatment of these adducts with concentrated hydrochloric acid gives aromatic nitroso compounds,[3] whereas nitronates are generally known to undergo other decomposition pathways in aqueous HCl, i.e., Nef reaction and reduction to oximes.[4] Another example is offered by the reactivity toward potassium permanganate[2] in basic medium, where conversion into aromatic nitro compounds rather than to carbonyl derivatives[5] has been found. The above discrepancies could be accounted for by the fact that these adducts can be easily converted into aromatic derivatives, owing to their cyclohexadienic structures. On the other hand, when the particular nature of adducts prevents the aromatization process, the usual reactivity can be observed.[6]

One of the most important reactions of aci compounds is the tautomerization[7] to nitro derivatives at medium acidic pH values. It would appear to be of interest, therefore, to ascertain whether analogous reaction paths might occur in nitronate adducts derived from reactions of nitroarenic systems with Grignard reagents; moreover, the particular geometry of nitro compounds, which could be formed in these cases, should imply interesting stereochemistry.

4-Methoxy-1-nitronaphthalene (1) was chosen to start these studies, since, from previous results,[8] almost exclusive attack at the C_2 position by the entering alkyl group of RMgX would be expected to take place.

Table I. Products and Yields (Percent) of Reactions between RMgX and 4-Methoxy-1-nitronaphthalene under Various Quenching Conditions

quenching	R = CH_3,[c] 7a and 8a	R = $PhCH_2$-CH_2,[d] 7b and 8b	R = Ph-CH_2,[e] 7c and 8c
KOAc-HOAc[a]	76	68	69
dilute H_2SO_4[b]	55	50	45
CH_3COOH[b]	63	53	52

[a] After 1 h of reaction. [b] With immediate removal of the products. [c] Only trace amounts of 4a in all cases. [d] Yield of 4b was 5% in all cases. [e] Yield of 4c was 5% in all cases.

Table II. Relative Amounts[a] of *trans*- and *cis*-2-Alkyl-4-methoxy-1-nitro-1,2-dihydronaphthalenes at Various Reaction Times from Decomposition of Nitronate Adducts in Acetate Buffer at 25 °C

	% trans		
time, h	R = CH_3	R = Ph-CH_2CH_2	R = $PhCH_2$
0[b]	20	16	13
1	24	26	20
5	30	34	35
24	42	55	64
48	50	74	86
∞	90	94	98
$t_{1/2}$, h	55	24	16
trans/cis[c]	9	15	49

[a] Calculated from relative intensities of H-1 and H-3 resonances in the ^1H NMR spectra of the product of the reaction. [b] From quenching of the THF nitronate solution with dilute H_2SO_4, followed by immediate removal of products. [c] At equilibrium.

Results

After 1 mol of 4-methoxy-1-nitronaphthalene (1) was allowed to react with 2 mol of CH_3MgX in THF at room temperature for a few minutes, treatment with aqueous acetic acid–potassium acetate buffer for 1 h gave a mixture of *cis*- and *trans*-4-methoxy-2-methyl-1-nitro-1,2-dihydronaphthalenes (**7a** and **8a**, respectively) and trace amounts of 4-methyl-1-nitronaphthalene (Scheme I). Yields are listed in Table I.

^1H NMR analysis of the isomer mixture showed the presence of larger amounts of the cis compound, the cis/trans ratio being 3. The relative yield of trans with respect to cis isomer was found to increase with increasing reaction times; however, isomerization did not go to completion, a constant 90:10 ratio of trans to cis isomer being observed after 20 days. Extents of isomerization at various times are reported in Table II.

Experiments carried out with $PhCH_2CH_2MgBr$ and $PhCH_2MgBr$ gave analogous results (see Table II). However, larger amounts of methoxy-substitution products (**4**) were obtained (see Table I).

Isomerization experiments can be performed in shorter time by dissolving a mixture rich in the cis isomer in methanol in the presence of trace amounts of triethylamine. The observed maximum extents of isomerization are identical with those from buffer reactions.

Experiments were carried out in order to obtain a mixture as rich as possible in the cis isomer. For this

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(4) W. E. Noland and R. Libers, *Tetrahedron Suppl.*, 23 (1963); W. E. Noland, M. S. Baker, and H. I. Freeman, *J. Am. Chem. Soc.*, 78, 2233 (1956).
(5) H. Shechter and F. T. Williams, *J. Org. Chem.*, 27, 1699 (1962).
(6) G. Bartoli, M. Bosco, and G. Pezzi, *J. Org. Chem.*, 43, 2932 (1978).
(7) A. T. Nielsen, "The Chemistry of the Nitro and Nitroso Group", H. Feuer, Ed., Interscience, New York, 1969, Part I, p 349.
(8) G. Bartoli, M. Bosco, A. Melandri, and A. C. Boicelli, *J. Org. Chem.*, 44, 2087 (1979).

Table III. ^{1}H NMR Data of *cis*- and *trans*-2-Alkyl-4-methoxy-1-nitro-1,2-dihydronaphthalenes in $CDCl_3$ at 30 °C

	chemical shift,[a] ppm							
compd	H_1	H_2	H_3	OMe	CH_3	Ph-CH_2CH_2	Ph-CH_2CH_2	$PhCH_AH_B$
7a	5.44	3.14	4.62	3.74	1.32			
8a	5.32	3.52	4.93	3.71	1.10			
7b	5.46[b]	3.00	4.70	3.72		2.00	2.90	
8b	5.32	3.38	4.96	3.68		1.64	2.70	
7c	5.40[b]	3.34	4.74	3.71				2.7-3.14
8c	5.20[b]	3.87	4.93	3.76				2.4 (H_A) and 2.76 (H_B)[c]

[a] In all compounds aromatic hydrogens resonate in the region between δ 7.0 and 7.80. Values at 100 MHz from Me_4Si as reference. [b] Approximate values from decoupling experiments. [c] The $PhCH_AH_B$ and H_2 hydrogens form an ABX system, which can be approximately analyzed as an AMX system.

Table IV. $J_{1,2}$ and $J_{2,3}$ values (Hertz) of *cis*- and *trans*-2-Alkyl-4-methoxy-1-nitro-1,2-dihydronaphthalenes[a]

compd	$J_{1,2}$	$J_{2,3}$
7a	6.0	2.2
8a	4.2	5.6
7b	5.7	2.2
8b	2.7	6.0
7c	5.3	2.0
8c	2.4	6.0

[a] Other J values are as follows: 7a, J_{2,CH_3} = 7.2 Hz; 8a, J_{2,CH_3} = 7.2 Hz; 8c, $J_{A,B}$ = 13.5, $J_{A,2}$ = 9.0, $J_{B,2}$ = 7.0 Hz. The $PhCH_2CH_2$ system in compounds 7a and 8b and the $PhCH_2$ system in compound 7c give second-order spectra, and thus reliable J values cannot be calculated even with the aid of computer-assisted procedures.

purpose, the isomerization rate was decreased by decomposing the nitronate at lower pH's. Decomposition of **2a–c** with either dilute acetic acid or dilute H_2SO_4 (1%) to a bromocresol green end point, followed by immediate removal of products, gave identical results. Relative cis and trans amounts obtained from these reactions are reported in Table II. These values can be assumed to be close to the initial cis–trans proportion before the isomerization process starts. Under these conditions lower yields of both isomers were obtained (see Table I). Since the rate of nitro formation decreases with decreasing pH,[9] these findings are very likely due to incomplete tautomerization. However, our attempts to isolate nitronic acids **5a–c** by treating THF solutions of **2** with sulfuric acid[10] at pH <3 were unsuccessful. Under these conditions intractable mixtures were always obtained.

Finally, each of the mixtures of **7a–c** and **8a–c** can be quantitatively converted into the corresponding aromatic nitro compounds **9a–c** with DDQ in boiling dry benzene.

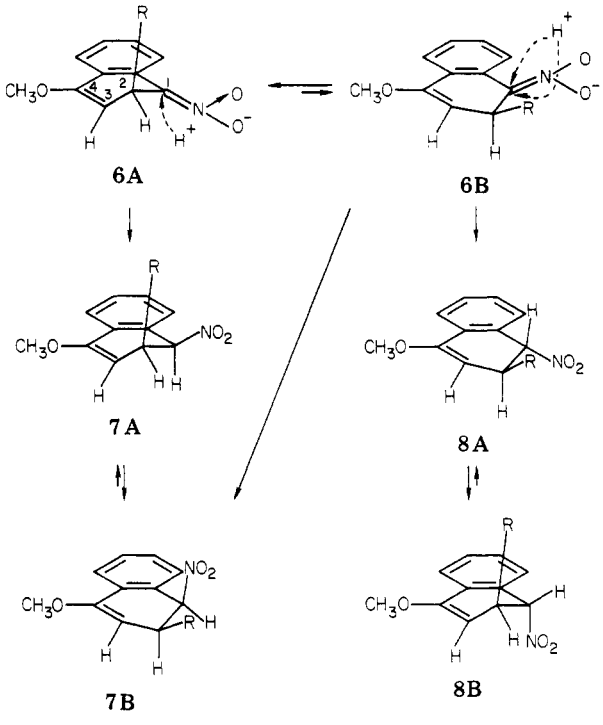
Characterization of the Products. 4-Alkyl-1-nitronaphthalenes. Compounds **4a–c** were identified by common analytical procedures.

Compound **4a** was identical with a sample of 4-methyl-1-nitronaphthalene prepared by an independent route.[11]

Unknowns **4b** and **4c** showed spectroscopic characteristics similar to those of **4a**. Particularly in the ^{1}H NMR spectra of all three products, hydrogen in position 2 resonates at δ 8.06 as a doublet (part of an AB system with J_{AB} = 8 Hz).

***cis*- and *trans*-2-Alkyl-4-methoxy-1-nitro-1,2-dihydronaphthalenes.** Owing to the impossibility of isolating pure cis or trans isomers (see Experimental Section), spectroscopic investigations were always carried out on

Scheme II[a]



[a] R = CH_3; $PhCH_2CH_2$; $PhCH_2$.

mixtures of the two isomers. IR spectra showed the presence of characteristic stretching bands of the aliphatic nitro group at ca. 1560 and 1350 cm^{-1}. ^{1}H NMR spectra were consistent with the proposed dihydronaphthalenic structures. Chemical shift values for **7a–c** and **8a–c** are reported in Table III, while $J_{1,2}$ and $J_{2,3}$ values are listed in Table IV. For all investigated compounds, assignments of all protons were made on the basis of their chemical shift and with the aid of decoupling techniques, with the exception of the H-1 and H-3 hydrogens, determination of which required experiments with deuterated reagents. Since H-1 is the only proton which arises from the reaction medium, nitronate adducts were decomposed with a CH_3COOK–CH_3COOD in D_2O buffer. ^{1}H NMR analysis of the resulting reaction products showed that the hydrogen at ca. δ 5.4 was replaced by deuterium, thus indicating that this proton was the H-1 hydrogen. An additional feature of the NMR spectrum of the mixture of **7a** and **8a**, in which the presence of an aliphatic methyl group was evidenced by signals at δ 1.32 and 1.10, respectively, allowed us to unambiguously assign to these compounds, and consequently to **7b,c** and **8b,c**, a 1,2-dihydronaphthalenic structure.

Owing to the nonplanarity of dihydronaphthalenic systems and to the consequent possibility of substituents

(9) H. Feuer and A. T. Nielsen, *Tetrahedron Suppl.*, 60 (1963).
(10) A. Hantzsch and O. W. Schultze, *Chem. Ber.*, **29**, 699 (1896); M. I. Konowalow, *ibid.*, **29**, 2193 (1896).
(11) Lesser, *Justus Liebigs Ann. Chem.*, **402**, 11 (1914).

at positions 1 and 2 assuming pseudoaxial or pseudoequatorial orientation (see Scheme II) a configurational and conformational analysis of structures **7a–c** and **8a–c** was necessary. Assignments of cis and trans configurations were made on the basis of measured values of $J_{1,2}$ and $J_{2,3}$ and confirmed by comparison with the following coupling constant values reported by Katritzky[12] for a series of 1,2-dihydronaphthalenes: $J_{1e,2e}$ = 2 Hz, $J_{1a,2a}$ = 16 Hz, $J_{1a,2e}$ = $J_{1e,2a}$ = 6.4–7.2 Hz, $J_{2a,3}$ = 2–3 Hz, $J_{2e,3}$ = 6.6 Hz.[13,14]

In compounds **7a–c**, values of $J_{1,2}$ fell within the range of 5–6 Hz, in good agreement with axial–equatorial or equatorial–axial coupling, while $J_{2,3}$ was in the range of 2.2–2 Hz, consistent with the coupling of the ethylenic proton to a vicinal axial proton.

Therefore, a cis structure was to be assigned to these compounds, in which the nitro group is almost exclusively in the axial position and the alkyl group in the equatorial position (**7B**). This assertion is supported by conclusions reported by Katritzky[12] on the preferentially pseudoaxial position assumed by bulky substituents at the 1-position of 1,2-dihydronaphthalenes.

Furthermore, a linear decrease of $J_{1,2}$ is observed in going from **7a** to **7c**, according to the expected greater distortion of the molecule, resulting from increasing steric hindrance between the axial nitro group and the equatorial substituents, as the bulkiness of the alkyl group increases.

Trans structure **8B** was assigned to compounds **8a–c**, in which the nitro group and the alkyl substituent are each preferentially in the axial position: in fact, measured values of coupling constants $J_{1,2}$ and $J_{2,3}$ are in good agreement with values estimated by Katritzky for a $J_{1e,2e}$ and a $J_{2e,3}$, respectively.

A small discrepancy is observed in the case of compound **8a** for which a $J_{1,2}$ of 4.2 Hz and a $J_{2,3}$ of 5.6 Hz were measured, and it can be explained in terms of some importance assumed in the conformational equilibrium of the molecule by a conformer in which the nitro and alkyl group exist in an equatorial position (**8A**), when the substituent at C-2 is moderate in size (methyl group).

2-Alkyl-4-methoxy-1-nitronaphthalenes. Compounds **7a–c** and **8a–c** were converted into **9a–c** in order to have further confirmation of the 2-alkyl-1,2-dihydronaphthalenic structures of **7** and **8**. Compound **9a** was identified by comparison with an authentic sample prepared from an independent route.[2] Compounds **9b** and **9c** showed spectroscopic characteristics quite identical with **9a**. Particularly in the ^{1}H NMR spectra of all three products, the hydrogen at position 3 resonates at ca. δ 6.5 as a singlet.

Discussion

All reaction products arise from conjugate addition of RMgX to nitroarenic systems. From a comparison between the overall yields of ortho and para alkylation compounds, 1,4 addition appears to be largely favored over 1,6 addition. These findings confirm our previous statements[8] that attacks at unsubstituted positions are strongly privileged.

A small increase in para alkylation product is observed on going from methyl to $PhCH_2CH_2$ and $PhCH_2$ groups; this trend can be attributed to some weak steric hindrance[15,16] of the ortho nitro group toward the entering alkyl group. Analogous weak effects have been observed in previous instances.[6]

The overall results strongly support the reaction mechanism outlined in Scheme I.

Interaction between RMgX and **1** gives nitronate adducts **2** and **3**. Addition of buffer decomposes **3** to **4** and **2** to nitronic acid **5**. In such a feebly acidic medium, **5** can be considered extensively ionized.[7] Thus a complete and rapid[17] tautomerization occurs via C-protonation at the nitronate function to give larger amounts of kinetically favored cis isomer. Slow reequilibration of cis into the more stable trans compound takes place subsequently. The fact that isomerization rates decrease at lower pH's confirms that this process occurs substantially via nitronate **6**.

Kinetic Preference for the Cis Compound. Preferential formation of the less stable isomer has been generally observed in systems[18–20] in which an electrophilic reagent attacks the nucleophilic center of an exocyclic double bond having a bulky vicinal group. In *aci*-nitro tautomerization reactions, examples of this behavior have been reported for the cyclohexane system[21] and for certain steroids.[22] In all cases, kinetically favored formation of the cis compound was attributed to the steric control of prototropic attack in a transition state which closely resembles the reactant compound.

In nonplanar cyclohexadienic nitronate **6**, the alkyl group may assume a quasi-axial (**6A**) or quasi-equatorial (**6B**) orientation (Scheme II). C-Protonation at the nitronate function of **6A** is expected to preferentially occur from the less hindered axial direction,[23] leading to cis compound **7B** via its less stable conformer **7A**. On the other hand, in conformer **6B**, the steric hindrance exerted by the C-2 axial hydrogen toward an equatorial approach is too little to direct the proton to enter preferentially from the axial side and hence to lead to trans compound **8B** via its less stable conformer **8A**: very likely, the proton cannot discriminate between an axial and an equatorial direction of attack, and the protonation pathway at this conformer must be such as to lead to both cis and trans compounds (**7B** and **8B**) with only a slight prevalence of the latter.

Kinetic preference for the cis compound formation, therefore, must essentially depend on the extent of the shift to the left of equilibrium between **6A** and **6B**. Even with a moderately sized alkyl substituent such as a methyl group, a preference of the C-2 substituent for axial orientation must be expected, so as to minimize its interaction with the oxygen of the nitronate function ($A^{(1,3)}$ strain).[24] Moreover, the relative stability of the **6A** conformer must

(12) M. J. Cook, A. H. Katritzky, F. C. Pennington, and B. M. Semple, *J. Chem. Soc. B*, 523 (1969).

(13) The reliability of this comparison lies in the fact that the nitro group has been found not to exert an appreciable lowering effect on vicinal coupling constants in cyclohexanic systems, in spite of its strong electron-withdrawing power.[14]

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(17) See ref 7, p 354.

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(20) H. E. Zimmerman and T. W. Cutshall, *J. Am. Chem. Soc.*, **81**, 4305 (1959); H. E. Zimmerman, *J. Org. Chem.*, **20**, 449 (1955); H. E. Zimmerman and J. Giallombardo, *J. Am. Chem. Soc.*, **78**, 6259 (1956); H. E. Zimmerman, *ibid.*, **79**, 6554 (1957).

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(22) A. Bowers, M. B. Sanchez, and H. J. Ringold, *J. Am. Chem. Soc.*, 81, 3702 (1959); A. Bowers, L. C. Ibanez, and H. J. Ringold, *ibid.*, **81**, 3707 (1959).

(23) S. K. Malhotra and F. J. Johnson, *J. Am. Chem. Soc.*, **87**, 5493 (1965).

(24) S. K. Malhotra and F. J. Johnson, *J. Am. Chem. Soc.*, **87**, 5492 (1965).

increase with increasing size of alkyl substituent. In fact a constantly increasing kinetic preference for the cis compound on going from a methyl to a benzyl group is evidenced by the percentages reported in Table II.

Cis–Trans Isomerization. Though isomerization of cis into the more stable trans compounds generally requires basic conditions, in the present system this process occurs in an acetate buffer medium, owing to the strongly acidic nature of H-1. Even with the moderately sized methyl group, a large difference in stability (1.3 kcal/mol) between the cis and trans isomers is observed.

In a cyclohexadienic system like **6**, owing to the small distortion[25] of the ring, the quasi-axial nitro and the quasi-equatorial alkyl groups are almost eclipsed, so that they sterically interact. The increase in the trans/cis ratio at equilibrium on going from a methyl to a benzyl group supports this interpretation. In addition, the half-time of isomerization, approximatively calculated from semiquantitative studies and reported in Table II, follows the order $PhCH_2 > PhCH_2CH_2 > CH_3$, as expected from stability differences through the series of alkyl groups.

Experimental Section

IR and mass spectra were recorded with a Perkin-Elmer 257 and a JEOL-100 instrument, respectively.

^1H NMR spectra were recorded with a Varian 100-MHz spectrophotometer (tetramethylsilane as internal standard).

THF was purified as previously described;[3] 4-methoxy-1-nitronaphthalene was a commercial product (EGA Chemie).

Preparation of THF Nitronate Solution. A 6.6-mL sample of a 3 N solution of RMgX in THF was added dropwise to a solution in the same solvent (30 mL) of 2 g of **1** (9.8×10^{-3} mol) at 20 °C under nitrogen. After few minutes the reaction goes to completion. This solution must be immediately used.

Decomposition of Nitronates with Aqueous Acetate Acetic Acid Buffer. The above-prepared THF solution of nitronate was poured into a buffer mixture, prepared by dissolving 20 g of potassium acetate and 5 mL of glacial acetic acid in 50 mL of water at room temperature under nitrogen. The reaction was stirred for 1 h and then extracted with CH_2Cl_2. The organic layer was washed once with a saturated aqueous solution of $NaHCO_3$ and several times with water, dried, and evaporated at reduced pressure. The residue was submitted to chromatographic separation on a silica gel column (cyclohexane–ethyl acetate, 19:1, as eluent) to give **4** and a mixture of **7** and **8**. Yields are reported in Table I. Our attempts to separate **7** and **8** through various chromatographic methods were unsuccessful. The relative amounts of **7** and **8** in their mixtures were detected by quantitative ^1H NMR analysis. IR spectra (film) of these mixtures (oils) show ν_{NO_2} at ca. 1560 and ca. 1350 cm^{-1}. The elemental analyses are as follows.

Mixture of **7a** and **8a**: calcd for $C_{12}H_{13}NO_3$: C, 65.74; H, 5.98; N, 6.39. Found: C, 65.51; H, 5.88; N, 6.43.

7b and **8b**: calcd for $C_{19}H_{19}NO_3$: C, 73.76; H, 6.19; N, 4.53. Found: C, 73.81; H, 6.15; N, 4.53.

7c and **8c**: calcd for $C_{18}H_{17}NO_3$: C, 73.20; H, 5.80; N, 4.74. Found: C, 73.23; H, 5.81; N, 4.80. The ^1H NMR data for these compounds are reported in Tables I and II. The data for compounds **4a–c** are as follows.

4a: mp 69–70 °C (lit.[11] mp 70–71 °C); mass spectrum, *m/e* 187 ($M^{+\cdot}$).

4b: mp 86–88 °C (from ethanol); ^1H NMR ($CDCl_3$) δ 2.98–3.58 (4 H, A_2B_2 system, CH_2CH_2), 7.0–7.4 (6 H, m, Ph and H-3), 7.5–7.73, 8.16 and 8.6 (2 H, 1 H and 1 H, m, H-5, H-6, H-7, and H-8), 8.06 (1 H, d, H-2, $J_{2,3}$ = 8 Hz); mass spectrum, *m/e* 277 ($M^{+\cdot}$). Anal. Calcd for $C_{18}H_{15}NO_2$: C, 77.96; H, 5.45; N, 5.05. Found: C, 78.01; H, 5.49; N, 5.10.

4c: mp 54–55 °C (from hexane); ^1H NMR ($CDCl_3$) δ 4.42 (2 H, s, CH_2), 7.0–7.4 (6 H, m, Ph and H-3), 7.45–7.66, 8.10, and 8.56 (2 H, 1 H and 1 H, m, H-5, H-6, H-7, and H-8), 8.06 (1 H, d, H-2, $J_{2,3}$ = 8 Hz); mass spectrum, *m/e* 263 ($M^{+\cdot}$). Anal. Calcd for $C_{17}H_{13}NO_2$: C, 77.35; H, 4.98; N, 5.32. Found: C, 77.42; H, 5.01; N, 5.36.

Semiquantitative studies of Table II were performed by drawing samples from energically stirred mixtures at appropriate times. The samples were diluted with water and extracted with CH_2Cl_2. The organic layers were washed with aqueous $NaHCO_3$ and several times with water, dried, and evaporated at reduced pressure. The residues were dissolved in the minimum amount of $CDCl_3$. These solutions were submitted to quantitative ^1H NMR analysis. Cis and trans percentages were calculated from the relative intensities of the H-1 and H-3 hydrogens. The presence of compound **4** and trace amounts of byproducts do not interfere with these measurements. It has been found that washing with aqueous $NaHCO_3$ does not appreciably change the isomerization proportions.

Decomposition of Nitronates at Lower pH Values. The above-prepared solution of nitronate was poured into a solution of 10 mL of glacial acetic acid in 50 mL of water. The reaction mixture was immediately extracted with CH_2Cl_2. The above-described workup gave a residue, which was submitted to quantitative ^1H NMR analysis.

Identical results were obtained when dilute H_2SO_4 (1%) was used to decompose the nitronate solution to a bromocresol green end point. In some experiments, the residue was chromatographed on a silica gel column by using an appropriate hexane–ethyl acetate eluent mixture. The yields obtained are reported in Table I.

Isomerization of Cis and Trans Mixtures with Triethylamine. The mixtures of **7** and **8** from the acetic acid experiments were dissolved at room temperature in methanol containing trace amounts of triethylamine. Isomerizations to the equilibrium values of Table II are complete after ca. 4 days for R = CH_3, ca. 3 days for R = $PhCH_2CH_2$, and ca. 2 days for R = $PhCH_2$.

Reactions of Mixtures of 7 and 8 with DDQ. Any mixture of **7a–c** and **8a–c** was quantitatively converted into the corresponding aromatic nitro compounds **9a–c** by treatment with a slight excess of DDQ in refluxing dry benzene for 8 h.

9b: mp 122 °C; ^1H NMR ($CDCl_3$) δ 3.06 (4 H, s, CH_2CH_2), 3.92 (3 H, s, OMe), 6.38 (1 H, s, H-3), 7.10–7.40 (5 H, m, Ph), 7.48–7.84 and 8.26 (4 H, m, H-5, H-6, H-7, and H-8). Anal. Calcd for $C_{19}H_{17}NO_3$: C, 74.25; H, 5.58; N, 4.56. Found: C, 74.34; H, 5.61; N, 4.59.

9c: mp 108–110 °C; ^1H NMR ($CDCl_3$) δ 3.98 (3 H, s, OMe), 4.16 (2 H, s, CH_2), 6.52 (1 H, s, H-3), 7.16–7.40 (5 H, s, Ph), 7.46–7.90 and 8.28 (4 H, m, H-5, H-6, H-7, and H-8). Anal. Calcd for $C_{18}H_{15}NO_3$: C, 73.70; H, 5.15; N, 4.78. Found: C, 73.80; H, 5.18; N, 4.80.

Data for compound **9a** have been previously described.[2]

Registry No. 1, 4900-63-4; **4a**, 880-93-3; **4b**, 73323-52-1; **4c**, 73323-53-2; **7a**, 73323-54-3; **7b**, 73323-55-4; **7c**, 73323-56-5; **8a**, 73323-57-6; **8b**, 73323-58-7; **8c**, 73323-59-8; **9a**, 72207-00-2; **9b**, 73323-60-1; **9c**, 73323-61-2; 2-bromo-1-phenylethane, 103-63-9; phenylmethyl bromide, 100-39-0.

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