Finally, the air-stable, sublimable compounds IV were obtained by the reaction of I with $Mn(CO)_5Br$. For instance, compound IV (R = pz) was obtained as pale yellow, sublimable crystals, mp 213–215° (*Anal.* Calcd for $C_{15}H_{12}BMnN_8O_3$: C, 43.0; H, 2.87; N, 26.8; Mn, 13.2. Found: C, 42.8; H, 3.10; N, 26.9; Mn, 13.4). The infrared spectrum of this compound contained carbonyl bands at 2055 (s) and 1940 (vs) cm^{-1}. The nmr spectrum had a peak at τ 2.10 (which included the 3- or 5-H of the coordinated pyrazole moieties and the 3- and 5-H of the uncoordinated pyrazolyl group), a doublet (J = 2 cps), and ill-resolved triplets at τ 3.41 and 3.80 in a 5:3:1:3 ratio. Compound IV (R = H), mp 206–208°, was identified similarly.

The details of this work and the chemistry of transition metal poly(1-pyrazolyl)borates containing other ligands will be the subject of subsequent publications.

S. Trofimenko

Contribution No. 1332, Central Research Department
Experimental Station, E. I. du Pont de Nemours and Company
Wilmington, Delaware 19898

Received May 20, 1967

Acidities of Sulfones

Sir:

Using the method previously described[1] we have measured the pK_a's of a number of sulfones and find them to be much higher than commonly supposed (Table I).[2]

Table I. Acidities of Sulfones in Dimethyl Sulfoxide at 25°

Sulfone	pK_a[a]	Sulfone	pK_a
Methyl	28.5		>30
Methyl phenyl	27		
Ethyl phenyl	29		
Benzyl	22		>31
α-Methylbenzyl	23.5		
			>31

[a] *p*-Nitroaniline was used as the reference indicator.[1]

Examination of Table I reveals that: (1) methyl substitution for hydrogen causes an increase of 1.5 to 2 pK_a units [compare $(PhCH_2)_2SO_2$ with $(PhCHMe)_2SO_2$ and CH_3SO_2Ph with $MeCH_2SO_2Ph$]; (2) phenyl substitution causes a decrease of 6.5 pK_a units [compare $(CH_3)_2SO_2$ with $(PhCH_2)_2SO_2$]; and (3) substitution of a phenyl group for a methyl group at a β position causes a decrease of 1.5 pK_a units (compare $MeSO_2CH_3$ and $PhSO_2CH_3$). It is of interest to compare these effects with those observed in nitroalkanes, the only other oxygenated carbon acids for which equilibrium data are available. Here methyl substitution causes a decrease, rather than an increase, in pK_a (CH_3NO_2, 10.2; $MeCH_2NO_2$, 8.5; Me_2CHNO_2, 7.7).[3] Phenyl substitution causes a decrease in pK_a, as in the sulfone series, but of only 3.3 units, as compared to 6.5 units.[4] Substitution of a phenyl group for a methyl group at a β position appears to have relatively little effect ($MeCH_2CH_2NO_2$, pK_a = 8.98;[3b] $PhCH_2CH_2NO_2$, pK_a = 8.68).[5]

In attempting to rationalize these differences it is important to note that the oxygen acids (nitric and methanesulfonic) produced by substitution of NO_2 and CH_3SO_2, respectively, for H in HOH are of a comparable order of acidity,[6] whereas the corresponding carbon acids (nitromethane and methyl sulfone) produced by substitution of a nitro group for H of CH_4 differ in acidity by over 12 pK_a units.[7]

A variety of effects must be operating to make NO_2 and CH_3SO_2 of about equal effectiveness in promoting the acidity of oxygen acids, but of markedly unequal effectiveness in promoting the acidity of carbon acids. One of the most important of these is no doubt the degree of resonance stabilization in the corresponding conjugate bases. Whereas the conjugate bases in the oxygen series, NO_3^- and $CH_3SO_3^-$, each have three equivalent resonance contributors, the resonance contributors for $CH_2NO_2^-$ and for $CH_3SO_2CH_2^-$ are not equivalent. For $CH_2NO_2^-$ the $CH_2{=}NO_2^-$ contributor is highly important, not only because of the concentration of the negative charge on oxygen, but also because of the near equivalence of the C=N and N=O bond energies (147 and 145 kcal/mole, respectively). In contrast, the relatively poor conjugative stabilization provided by the 2p–3d overlap in the $[CH_3SO_2{=}CH_2]^-$ contributor makes it of much less importance than the other two contributors.[8]

If it is assumed that there is indeed a high degree of C=N bond character in the $CH_2NO_2^-$ nitronate ion, the progressive increase in acidity caused by substitution of methyl groups for hydrogen atoms in this ion can be understood in terms of a stabilizing influence analogous to that observed for C=C bonds. No such effect would be expected for the $CH_3SO_2CH_2^-$ ion.[9]

Phenyl substitution in $CH_2NO_2^-$ and $CH_3SO_2CH_2^-$ should cause an appreciable increase in stability. The much larger effect in the sulfone series is expected in

(1) E. C. Steiner and J. M. Gilbert, *J. Am. Chem. Soc.*, **87**, 382 (1965).

(2) (a) From an extrapolation based on the relationship of rates of proton abstraction and pK_a's of ketones, R. G. Pearson and R. L. Dillon, *ibid.*, **75**, 2439 (1953), estimated a pK_a of 23 for methyl sulfone. (b) See D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press Inc., New York, N. Y., 1965, for a discussion of the acidities of carbon acids.

(3) (a) D. Turnbull and S. Maron, *J. Am. Chem. Soc.*, **65**, 212 (1943); (b) G. W. Wheland and J. Farr, *ibid.*, **65**, 1433 (1943).

(4) V. Pihl, V. Timotheus, A. Pihl, and A. Talvik, "Organic Reactivity," Vol. II, No. 4, Tartu State University, Estonian SSR, 1965, p 24, give pK_a = 6.88 for $PhCH_2NO_2$.

(5) S. Hiidman, A. Pihl, and A. Talvik, ref 4, Vol. III, No. 8, 1966, p 65.

(6) R. P. Bell, "The Proton in Chemistry," Cornell University Press, Ithaca, N. Y., 1959, p 85.

(7) The difference is 18.3 units using the value for $CH_3SO_2CH_3$ of 28.5 (Table I) and 10.2 for CH_3NO_2,[3] but C. D. Ritchie and R. E. Uschold, *J. Am. Chem. Soc.*, **89**, 1721 (1967), have found that pK_a for CH_3NO_2 in DMSO is 15.9.

(8) Note that for CH_3COCH_3, which is intermediate in acidity between CH_3NO_2 and $CH_3SO_2CH_3$, the contribution of $^-OC(CH_3){=}CH_2$ is reduced relative to $O{=}C(CH_3)CH_2^-$ in that the bond energy for C=O (179) is considerably higher than that for C=C (146).

(9) Methyl substitution causes a decrease in the rate of proton abstraction by base from nitroalkanes [see S. H. Maron and V. K. La Mer, *J. Am. Chem. Soc.*, **60**, 2588 (1938)] and also from sulfones (J. M. Williams, Jr., Ph.D. Dissertation, Northwestern University, 1966). Nitroalkane acidities increase with methyl substitution *despite* this effect.[10] It is uncertain yet whether the decrease in acidities of sulfones on methyl substitution is caused entirely by this effect or whether methyl substitution also destabilizes the conjugate base and thereby causes it to react more rapidly in the reverse reaction.

(10) See H. M. Cardwell, *J. Chem. Soc.*, 2442 (1951), for a discussion.

view of the much higher basicity of the conjugate base.[11] The much larger effect in the sulfone series of substituting a phenyl group for a β-methyl group appears to be worthy of additional study.

Acknowledgment. This investigation was supported by Public Health Service Research Grant No. CA-07351 from the National Cancer Institute.

(11) Part of this larger difference may be due to a solvent effect.[7]

F. G. Bordwell, Robert H. Imes
Chemistry Department, Northwestern University
Evanston, Illinois 60201

E. C. Steiner
The Edgar C. Britton Laboratory, The Dow Chemical Company
Midland, Michigan
Received March 20, 1967

Steric Hindrance to the Formation of and Protonation of the Nitronate Ion from 2-Aryl-1-nitrocyclohexanes

Sir:

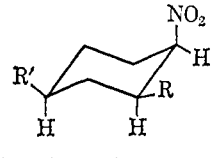
A study of the rates of nitronate ion formation from nitrocyclohexanes and related compounds (Table I) has revealed the presence of a sizable and unexpected steric effect of an equatorial 2-aryl substituent on an axial, *but not* an equatorial, hydrogen atom.

Table I. Rates of Nitronate Ion Formation from Nitroalkanes and Sodium Methoxide in Methanol at 25°

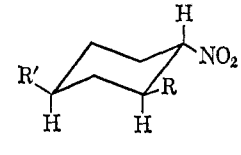
Compd	Nitroalkane	k, M^{-1} sec^{-1}	Relative rates	E_a[a]	ΔS^*
1	*cis*-4-*t*-Butyl-1-nitrocyclohexane[b]	1.0	220	16	−8
2	*cis*-2-*p*-Chlorophenyl-1-nitrocyclohexane[b]	1.9	410	16	−5
3	*cis*-2-*o*-Methylphenyl-1-nitrocyclohexane[b]	1.0	220	16	−7
4	*trans*-4-*t*-Butyl-1-nitrocyclohexane[b]	2.0×10^{-1}	44	16	−11
5	Nitrocyclohexane	3.3×10^{-1}	72		
6	2-Nitropropane	3.2×10^{-1}	70		
7	1-Phenyl-2-nitropropane	4.6×10^{-1}	100		
8	*trans*-2-*p*-Chlorophenyl-1-nitrocyclohexane[b]	9.3×10^{-3}	2.0	19	−6
9	*trans*-2-*o*-Methylphenyl-1-nitrocyclohexane[b]	4.6×10^{-3}	1.0	20	−5

[a] Calculated from measurements at two or more temperatures. [b] This sample was kindly furnished by Professor A. C. Huitric.

Examination of Table I shows that the rates of proton abstraction from *cis*-4-*t*-butyl-, *cis*-2-*p*-chlorophenyl-, and *cis*-2-*o*-methylphenyl-1-nitrocyclohexanes (**1**, **2**, and **3**, respectively) are all of a comparable order of magnitude.



1, R = H; R′ = *t*-Bu
2, R = *p*-ClC$_6$H$_4$; R′ = H
3, R = *o*-MeC$_6$H$_4$; R′ = H



4, R = H; R′ = *t*-Bu
8, R = *p*-ClC$_6$H$_4$; R′ = H
9, R = *o*-MeC$_6$H$_4$; R′ = H

trans-4-*t*-Butyl-1-nitrocyclohexane (**4**) reacts at a fivefold slower rate than the *cis* isomer, presumably because of the higher ground-state energy of the latter. The rate for nitrocyclohexane (**5**) is very close to that calculated from the Winstein–Holness equation,[1] using mole fraction values of 0.8 and 0.2 for the equatorial and axial conformers,[2] and the rate constants for **4** and **1** [relative rate = (0.8 × 44) + (0.2 × 220) = 79, *vs.* 72 observed].

Judging from the small rate effect of the β-aryl groups observed in **2** and **3** (compare with **1**) and the β-phenyl group in 1-phenyl-2-nitropropane (**7**) [compare with 2-nitropropane (**6**)], the inductive and steric effect of a β-aryl group on the rate of proton abstraction is normally small and accelerating. The 22-fold and 44-fold rate-*retarding* effects observed for the β-aryl groups in *trans*-2-*p*-chlorophenyl- and *trans*-2-*o*-methylphenyl-1-nitrocyclohexanes (**8** and **9**; compare with **4**) must, therefore, be attributed to the operation of a sizable steric effect. This is surprising since, in the perfect chair cyclohexane conformation, the (equatorial) β-aryl group in **8** or **9** has exactly the same skew relationship to the axial hydrogen atom as does the (axial) β-aryl group to the equatorial hydrogen atom in **2** or **3**. The most likely origin of this steric effect would appear to be the bending away from one another of the equatorial nitro and phenyl groups in **8** and **9**,[3] causing the cyclohexane ring to be deformed and allowing the aryl group to screen the axial hydrogen atom more effectively. (This is not possible in the *cis* isomers due to interference between the axial nitro group and the axial hydrogen atoms at C-3 and C-5.) This deformation must permit a considerable lowering of the ground-state energy of the *trans* isomer relative to the *cis* isomer, since introduction of a 2-phenyl substituent into nitrocyclohexane causes an apparent increase in the A value of the nitro group from 0.8 kcal/mole[2] to 2.7 kcal/mole.[4]

It follows that there must also be a sizable steric effect of an aryl group in the microscopic reverse of the proton-abstraction reaction. This requires that in the protonation of the nitronate ion derived from **2** (or **8**) or from **3** (or **9**) the proton enters preferentially into the equatorial position (equatorial:axial rate ratio = 205:1 for **2**:**8** and 220:1 for **3**:**9**). This reaction is not experimentally observable, since proton abstraction from the solvent by these nitronate ions is extremely slow. It has been observed, however, that in the closely related reaction, protonation of the nitronate ion from 2-phenyl-1-nitrocyclohexane under acidic conditions, the proton is delivered stereoselectively so as to give

(1) See E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, pp 234–239, for a discussion.

(2) W. F. Trager and A. C. Huitric, *J. Org. Chem.*, **30**, 3257 (1965).

(3) E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Interscience Publishers, Inc., New York, N. Y., 1965, p 127.

(4) H. E. Zimmerman and T. E. Nevins, *J. Am. Chem. Soc.*, **79**, 6559 (1957).