appear that with these highly reactive black slurries reaction is occurring mainly at the metal surface.[19]

One additional reaction that we carried out which further demonstrates the high reactivity of the nickel slurry is with triethyl phosphite. The highly reactive nickel powder was generated in the presence of triphenylphosphine; to this mixture, triethyl phosphite was added at −78 °C. After 10 min, the mixture was warmed to room temperature and stirred for 1 h. Workup of the reaction mixture yielded over 40% of the tetrakis(triethylphosphite)nickel(0) complex.[18]

The procedure is readily applied to other transition metals.

The reduction of $PdCl_2$ with potassium in the presence of triethylphosphine in THF yields a highly reactive black palladium slurry. Addition of pentafluorobromobenzene to the metal slurry produces a rapid reaction.[14] After 1 h the reaction was worked up, yielding 76% of the bromopentafluorophenylbis(triethylphosphine)palladium(II).[15,20] Addition of iodobenzene to the palladium slurry at room temperature for 1 h produced the new complex iodophenylbis(triethylphosphine)palladium(II) in 52% yield.[16]

$$Pd + 2Et_3P + C_6H_5I \longrightarrow \begin{matrix} PEt_3 \\ | \\ C_6H_5PdI \\ | \\ PEt_3 \end{matrix}$$

The reaction has been extended to unreactive halides. The exceptionally high reactivity of the slurries produced by this procedure is exemplified by the reaction of the palladium slurry with chlorobenzene to give the chlorophenylbis(triethylphosphine)palladium(II) in 54% yield based on the palladium halide used.

In a similar manner, highly reactive platinum slurries can be prepared by reduction of platinum halides in the presence of phosphines. The addition of pentafluorobromobenzene to the platinum slurry yielded the known *trans*-bromopentafluorophenylbis(triethylphosphine)platinum(II) in 40% yield, based on the platinum halide used. The reaction has been extended to other aryl halides.

In addition to Ni, Pd, and Pt, we have obtained preliminary evidence that reactive metal powders of Co, Fe, and Cr can be generated by this procedure.

The ability to generate highly reactive transition metal slurries with very simple apparatus will be of extensive value to synthetic inorganic, organic, and organometallic chemistry. We will report in the near future on additional chemistry of the nickel, palladium, and platinum slurries as well as the other transition metals mentioned.

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(11) Typical quantities are Et_3P (4.12 g), $NiCl_2$ (2.26 g), and K (1.26 g) in 30 mL of THF. The mixture was refluxed for 20 h and cooled to −78 °C whereupon C_6F_5Br (4.0 g) was slowly added. Stirring was maintained for 1 h and then the reaction was worked up. Yields are based upon $NiCl_2$.
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(14) Typical quantities are $PdCl_2$ (1.22 g), Et_3P (1.63 g), and K (0.53 g) and were mixed with 25 mL of THF. The mixture was refluxed for 20 h yielding the black metal slurry. The slurry was cooled to −78 °C and C_6F_5Br (1.7 g) was added. After 1 h, the reaction was warmed up to room temperature and worked up. Yields are based upon $PdCl_2$.
(15) All known complexes had identical melting point, IR, and NMR data with published results.
(16) The new complex had the correct IR, NMR, and analysis data.
(17) Alfred P. Sloan Fellow, author to whom correspondence should be sent, at North Dakota State University.
(18) In preliminary studies, the nickel powders have proven to be a good hydrogenation catalyst. Other catalytic studies with these metals are underway.
(19) Attempts to find any tetrakis(triethylphosphine)nickel(0) or tris(triethylphosphine)nickel(0) complexes in the reaction mixture have failed. However, it is clear that part of the nickel is in the form of Ni(II) or Ni(I) compounds.
(20) Up to 30% of the oxidative insertion products may be resulting from soluble Pd complexes. These complexes may include the tetrakis(triethylphosphine)Pd(0) and tris(triethylphosphine)Pd(0) complexes.

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Stereochemistry in Trivalent Nitrogen Compounds. 32. Torsional Barriers in Trinitrobenzenesulfenamides[1]

Sir:

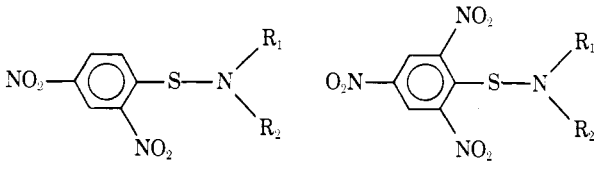
Sulfenamides[2] exhibit substantial barriers to torsion about the sulfur–nitrogen formal single bond.[3] The barriers are greatly increased when the substituent at the sulfenyl sulfur atom is electron withdrawing. The linear free energy correlation for a series of para-substituted benzenesulfenamides[3d] afforded a Hammett reaction constant of −2 and a comparison of the effect of meta and para substituents in the same system indicated that the effect was due to "throughresonance" of the aromatic π-system with an orbital on sulfur. As a result of this polar effect, the barriers in 2,4-dinitrobenzenesulfenamides were the highest which had yet been observed for torsion about N–S formal single bonds. It was of interest to examine the previously unknown 2,4,6-trinitrobenzenesulfenamides. If the barrier to stereomutation were raised by the third nitro group by an amount comparable to the effect of the first two, the sulfenamide configurational unit would have sufficient stereostability in some instances to permit isolation at room temperature of configuratively stable stereoisomers.

We now report the synthesis of a number of representative 2,4,6-trinitrobenzenesulfenamides whose barriers are in sharp variance with the high barriers expected. Instead, the barriers are considerably lower than those in the corresponding dinitrobenzenesulfenyl derivatives and are not much greater than the benzenesulfenyl analogues. Two examples serve to illustrate this point. The barrier in *N,N*-diisopropyl-2,4,6-trinitrobenzenesulfenamide, **2b,** 17.6 kcal/mol, is significantly lower than that in **1b,** 20.6 kcal/mol, and only somewhat higher than that in *N,N*-diisopropylbenzenesulfenamide, 14.3 kcal/mol. The sulfenylsulfonamide **2a** provides a more dramatic example. Figure 1 illustrates the change in barriers in this compound and four related compounds as a function of the number of nitro groups in the benzenesulfenyl residue. As in-

Table I[a]

Compound	Solvent	Obsd protons	$\Delta\nu$ (Hz)	T_c (°C)	$\Delta G_c^{\ddagger}$ (kcal/mol	K_{eq}[b]	Ref
1a	$C_6D_5CD_3$	$CH(CH_3)C_6H_5$	19.0	102.5	19.7	2.4	3c
2a	$CDCl_3$	$CH(CH_3)C_6H_5$	18.3	−4	13.8	0.9	*c*
		$C_6H_2(NO_2)_3$	15.1	−6	13.8		
1b	$C_6D_5CD_3$	$CH(CH_3)_2$	5.0	105	20.6		*c*
2b	$C_6D_5CD_3$	$CH(CH_3)_2$	12.7	62	17.6		*c*
1c	$C_6D_5CD_3$	$CH_2C_6H_5$	5.9 (J = 13.9)	57	16.5		3e
2c	$CDCl_3$	$CH_2C_6H_5$	22.8 (J = 12.4)	40	15.6		*c*
		$CH(CH_3)_2$	3.5	8	15.5		*c*
1d	$C_6D_5CD_3$/ C_2D_6SO	$CH_2C_6H_5$	23.5 (J = 14.5)	68	17.0		*c*
2d	$CDCl_3$	$CH_2C_6H_5$	25.8 (J = 15.3)	21	14.6		*c*
1e	$C_6D_5CD_3$	$CH(CH_3)_2$	18.4	115	20.1		3d
2e	$CDCl_3$	$CH(CH_3)_2$	4.2	−11	14.2		*c*
1f	$C_6D_5CD_3$	CH_2OCH_3[d]	10.7 (J = 9.8)	143	21.4		*c*
2f	$CDCl_3$	CH_2OCH_3[d]	33.0 (J = 10.0)	41	15.6		*c*

[a] All data were obtained on 2–4 mole % solutions at 60 MHz. [b] K refers to the intensity ratio of the higher field methyl doublet to the lower field doublet for **1a** and **2a** which exist as a mixture of diastereomers. The free energies of activation for these compounds refer to the conversion of the minor isomer to the major isomer. [c] This work. [d] The chemical shift difference between the diastereotopic geminal methyl groups was not large enough to permit measurement of the rate.



1 **2**

a, R_1 = $CHCH_3C_6H_5$; R_2 = p-$SO_2C_6H_4CH_3$ (p-toluenesulfonyl)
b, R_1 = R_2 = $CH(CH_3)_2$
c, R_1 = $CH_2C_6H_5$; R_2 = $CH(CH_3)_2$
d, R_1 = $CH_2C_6H_5$; R_2 = p-$SO_2C_6H_4CH_3$
e, R_1 = $CH(CH_3)_2$; R_2 = p-$SO_2C_6H_4CH_3$
f, R_1 = $C(CH_3)_2CH_2OCH_3$; R_2 = p-$SO_2C_6H_4CH_3$

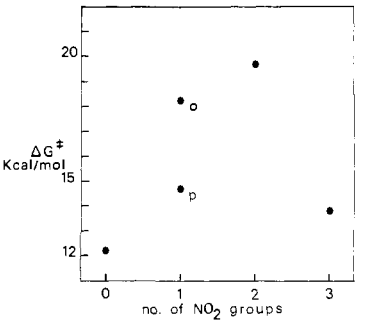
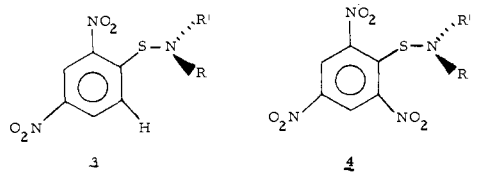


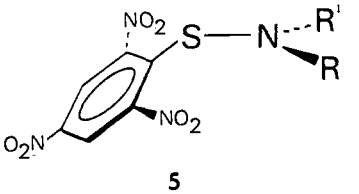
Figure 1. Torsional barriers in N-(1-phenylethyl)-N-arenesulfonylnitrobenzenesulfenamides as a function of the number of nitro groups in the sulfenyl phenyl ring. The two points for the mononitrobenzene sulfenamides refer to substitution at the ortho (o) and para (p) positions.

dicated, the barrier is significantly increased by the addition of either an ortho or para nitro group, further increased by the addition of a second nitro group, and dramatically decreased by the addition of the third nitro group. Further examples illustrating the decrease in barrier on the introduction of a third nitro group are given in Table I.

The introduction of the second ortho nitro group removes nearly completely the effect of the first two. Since linear free energy relationships[3d] indicate that the barrier enhancement is due to resonance, the effect of the third nitro group seems to be due to steric inhibition of resonance. This interpretation suggests that the conformation of the dinitrobenzenesulfenamides is one in which the plane of the dinitrophenyl ring lies within the CSN plane, **3**. Apparently, replacement of the ortho hydrogen with a larger nitro group would result in a structure, **4**, with substantial steric interaction between the nitro and NR′R moieties. If the steric destabilization is great enough, the conformation may be changed to one in which the plane of the nitrophenyl ring makes a substantial angle with the CSN plane, **5**. Such a change in the conformation of either the ground state or the transition state could account for the observed changes in free energies of activation.



3 **4**



5

If this explanation is correct, conformation **3** (or **4**) is the correct one for the resonance interation. Here the aromatic π system can conjugate with the nonbonding p orbital on sulfur but is perpendicular to the nitrogen lone-pair orbital. Our earlier conclusion[3d] that d-orbital conjugation was responsible for the barrier enhancement in nitrobenzenesulfenamides rested on the postulate that a sulfur d-orbital acted as a conjugating element through which the nitrogen lone-pair and the aromatic π-system could conjugate. The present findings, to-

gether with studies by Davis[6] and Kost,[7] cast doubt on our earlier conclusions and suggest that a different explanation be sought for the remarkable dependence[3] of sulfenamide torsional barriers on the electronegativity of the substituent at sulfenyl sulfur.[8]

References and Notes

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(8) (a) All new compounds reported here received satisfactory elemental analyses and had NMR spectra in accord with the assigned structures. The trinitrobenzenesulfenamides were prepared by reaction of trinitrobenzenesulfenyl chloride[6b] with the appropriate amine or the silver salt of the appropriate *N*-alkylsulfonamide. (b) G. Yamamoto and R. Raban, *J. Org. Chem*, **42**, 597 (1977).
(9) (a) A. P. Sloan Fellow, 1972–1976. (b) "Faculty of Science, University of Tokyo".

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A Spin Labeling Study of a Polysaccharide Support Matrix for Affinity Chromatography

Sir:

Although affinity chromatography is widely used for the separation and purification of a variety of biological molecules,[1] little information is available at the molecular level about the interactions upon which the technique depends, the microscopic structures of support materials, or the empirical observation that a "spacer arm" is sometimes required between the matrix and the immobilized ligand for maximum efficiency of separation.[2] The spacer, however, has been observed to confer upon the matrix a further binding selectivity independent of the immobilized ligand,[3] and hydrophobic chromatography[4] relies on this type of interaction.

We describe herein the use of the spin labeling technique[5] to investigate agarose,[6] a commonly used affinity chromatographic support matrix. Cyanogen bromide-activated agarose[6,7] was coupled to ω-aminocarboxylic acids, $H_2N(CH_2)_nCO_2H$, where n = 1, 3, 5, and 10, in 0.1 M bicarbonate buffer, pH 8.3, and each of these spacer–agarose conjugates was linked, after being washed free of unreacted amino acid, in the presence of 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride[8] (EDC), at pH 5, to each of the stable nitroxide radicals 4-amino-2,2,6,6-tetramethylpiperidino-1-oxy (**1**) and 3-amino-2,2,5,5-tetramethylpyrrolidino-1-oxy[9] (**2**). In addition the two nitroxides were coupled directly to the activated polysaccharide. Each labeled product was exhaustively washed on a sintered glass filter using bicarbonate (pH 8.3) and acetate (pH 4.0) buffers to remove noncovalently bound, adsorbed, spin label.[10]

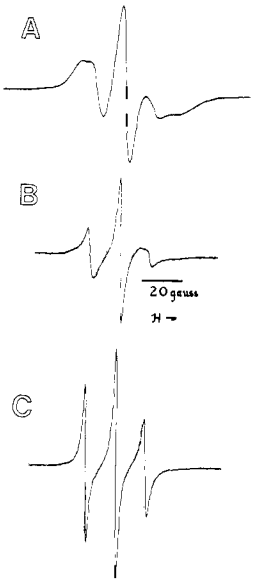
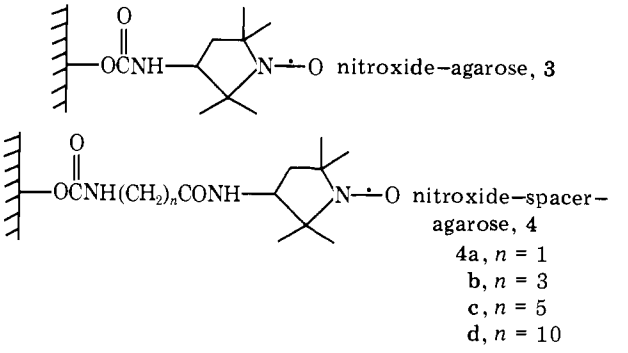


Figure 1. EPR spectra of: (A) compound **3**, (b) compound **4a** ($\tau = 1.4 \times 10^{-9}$ s), and (c) compound **4c** ($\tau = 4 \times 10^{-10}$ s), in aqueous suspension recorded at 28 °C on a Varian E-3 spectrometer.



The EPR spectra of the products[11] were found to become sharper with increasing n (Figure 1), and the rotational correlation times τ[12] of the nitroxide decrease, approaching a limiting value of 3×10^{-10} s at large n.[11] For $1 \leq n \leq 10$, i.e., in those cases where a spacer arm is present, the spectrum is characteristic of a "weakly immobilized" nitroxide moiety, while for directly bound label a "moderately immobile" spectrum is obtained, and two partially resolved spectral components are present. Both nitroxides gave similar results.

The increased freedom of rotational motion experienced by the nitroxide (ligand) in the presence of a spacer arm reflects its greater "availability" to the surrounding solution. Steric hindrance of the ligand by the support matrix has been suggested[13] as a factor tending to decrease binding efficiency of substrate in affinity chromatography in cases where the spacer is insufficiently long, and the quantitative (increase in τ) and qualitative (appearance of a second spectral component) changes in the spectra upon decreasing the length of the spacer and finally removing it completely corroborate this idea. It has also been found that the increase of the anchoring arm beyond a certain limiting length, typically corresponding to that of about an eight-atom chain, causes no further improvement in separation efficiency;[14] this is paralleled in our results by the approach of the correlation time of the nitroxide to a minimum value at about the same chain length.

The directly attached label appears to be present in two distinct environments characteristic of the support material.