AD-A045 863 NORTH DAKOTA STATE UNIV FARGO F/G 11/6
CHEMISTRY AND TECHNOLOGY OF METAL POWDERS.(U)
OCT 77 R D RIEKE DAHC04-74-G-0182
UNCLASSIFIED ARO-11431.3-C NL

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Unclassified ARO 11431.3-C AND 14315.5-C

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

(18) **REPORT DOCUMENTATION PAGE**

READ INSTRUCTIONS BEFORE COMPLETING FORM

1. REPORT NUMBER (19) ARO, ARO ✓11431.3-C ~~and~~ 14315.5-C

2. GOVT ACCESSION NO. (12)

3. RECIPIENT'S CATALOG NUMBER

4. TITLE (and Subtitle) Chemistry and Technology of Metal Powders, (6)

5. TYPE OF REPORT & PERIOD COVERED (9) Final ~~Report~~, 1 Jun 74 - 14 Jun 77,

6. ~~PERFORMING ORG. REPORT NUMBER~~

7. AUTHOR(s) (10) Reuben D./ Rieke

8. CONTRACT OR GRANT NUMBER(s) (15) ✓DAHC04-74-G-0182, NC ✓DAAG29-76-G-0234 new

9. PERFORMING ORGANIZATION NAME AND ADDRESS

North Dakota State Unive~~rsity~~
Fargo, North Dakota 58102

10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS (12) 10 p.

11. CONTROLLING OFFICE NAME AND ADDRESS

U. S. Army Research Office
Post Office Box 12211
Research Triangle Park, NC 27709

12. REPORT DATE (11) Oct 77

13. NUMBER OF PAGES 8

14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)

15. SECURITY CLASS. (of this report) Unclassified

15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited.

DDC
RECEIVED
OCT 26 1977
F

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

The findings in this report are not to be construed as an official Department of the Army position, unless so designated by other authorized documents.

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Powder metals	Nickel
Reduction(chemistry)	Palladium
Reactivities	Cobalt
Chemical reactions	Platinum

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

We recently discovered in our laboratories a new process for the preparation of finely divided metal powders. Using this process we have prepared and made preliminary studies on a number of metal powders. The metals that were examined were found to exhibit far superior reactivity to that described in the literature for these metals or to that which ~~we have~~ found in ~~our~~ the laboratories using the standard metals and techniques. The basic process involves the reduction of a metal salt in an ethereal or hydrocarbon solvent under an argon atmosphere. The

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20. ABSTRACT CONTINUED

reductions in some cases are very exothermic and generally are complete within a few hours. The reduction produces fine black powders of the metal in question. The properties of the black metal powders are, in many cases, highly dependent on the solvent used, the reducing agent, the anion of the metal salt being reduced, the ration of reducing agent such as potassium to the metal salt being reduced, and the temperature at which the reduction is being carried out. The bulk of the effort was devoted to a study to determine if highly reactive transition metal powders could be prepared via this reduction procedure. The metals which were studied were nickel, palladium, cobalt and platinum.

FINAL REPORT

1. Author of Report: Reuben D. Rieke
2. North Dakota State University
3. Contract or Grant Number: DAAG29-76-G-0234
4. Period Covered by Report: June 1, 1974 - May 30, 1977
5. Results of Study:

We recently discovered in our laboratories a new process for the preparation of finely divided metal powders. Using this process we have prepared and made preliminary studies on a number of metal powders. The metals that were examined were found to exhibit far superior reactivity to that described in the literature for these metals or to that which we have found in our laboratories using the standard metals and techniques. It is the preparation of the highly reactive metal powders and a study of their chemistry that this research was aimed at.

The basic process involves the reduction of a metal salt in an ethereal or hydrocarbon solvent under an argon atmosphere. The reduction appears to be most conveniently carried out by using an alkali metal and a solvent whose boiling point exceeds the melting point of the alkali metal. The metal salt to be reduced must also be partially soluble in the solvent. The reductions in some cases are very exothermic and generally are complete within a few hours. In many cases, reduction times of less than one hour are required. The reduction produces fine black powders of the metal in question. The properties of the black metal powders are, in many cases, highly dependent on the solvent used, the reducing agent, the anion of the metal salt being reduced, the ratio of reducing agent such as potassium to the metal salt being reduced, and the temperature at which the reduction is being carried out. The reduction of the metal salt generates, in addition to the metal, one or more moles of alkali salt.

$$MX_n + nK \rightarrow M + nKX$$

It is quite clear that the simultaneous generation of the alkali salt is of importance in producing a highly reactive metal powder. Scanning electron microscope photographs along with elemental imaging by energy dispersive analysis clearly show that the black particles are composed of small crystallites of both the alkali salt and the metal. In some cases, these crystallites are of the order of size of microns and in other cases even less. Thus it would appear that one function of the alkali salt is to trap, in a certain sense, the small metal crystals and prevent them from conglomerating and growing into larger crystals and hence yielding smaller total surface area. It is also possible that in some cases the anions may be absorbed on the metal surface and help to activate the metal towards oxidative insertion. Using this reduction technique, we have been able to prepare several highly reactive main group metals.

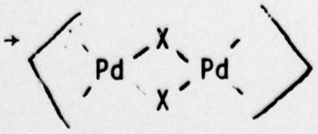
The bulk of the effort supported under this grant was a study to determine if highly reactive transition metal powders could be prepared via this reduction procedure. The metals which were studied were nickel, palladium, cobalt and platinum.

Our first efforts consisted of reduction of $NiCl_2$, NiI_2 or $PdCl_2$ with potassium in THF. We obtained finely divided black powder of the corresponding metal. These metal powders have shown high reactivity towards allyl halides and benzyl halide. The reactions proceeded rapidly at room temperature and yielded the products shown below:

$$Ni^* + CH_2 = CH - CH_2X \rightarrow \underset{\simeq 100\%}{[CH_2 = CH - CH_2]_2}$$

$$Ni^* + QCH_2X \rightarrow \underset{\simeq 100\%}{QCH_2 - CH_2 - Q}$$

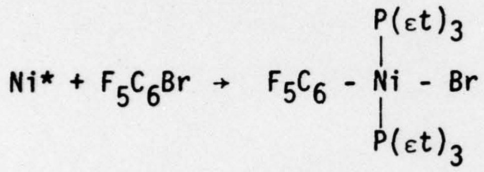
$$Pd^* + CH_2 = CH - CH_2X \rightarrow$$



$\simeq$ 95%

We have recently found that even more reactive Ni, Pd and Pt can be produced if the reduction is carried out in the presence of triethyl or triphenyl phosphine. Under these conditions the particle size of the metal is much smaller and the metal is much more reactive. For example, reduction of $NiCl_2$ with potassium in the presence of triethyl phosphine yielded black nickel (0) powders which reacted with pentafluorobromobenzene at -78°C.

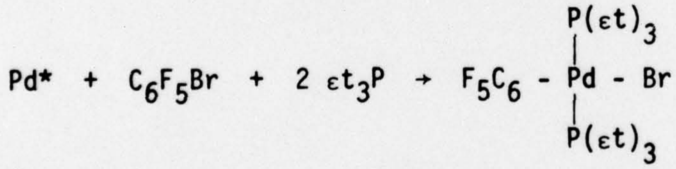
$$NiCl_2 + 2K + \varepsilon t_3P \rightarrow Ni^*$$



$$Ni^* + F_5C_6Br \rightarrow F_5C_6 - \underset{P(\varepsilon t)_3}{\overset{P(\varepsilon t)_3}{Ni}} - Br$$

The known compound bis(triethylphosphine) pentafluorophenyl nickel bromide was isolated in 60% yield. Carrying out the reduction in the presence of triphenyl phosphine the corresponding triphenyl phosphine complex was obtained in greater than 50% yield. The same reactions were found to result when Pd Cl_2 was reduced.

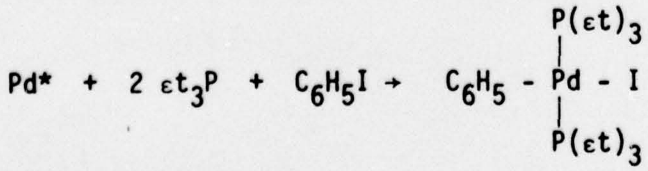
$$PdCl_2 + 2K + \varepsilon t_3P \rightarrow Pd^*$$



$$Pd^* + C_6F_5Br + 2\ \varepsilon t_3P \rightarrow F_5C_6 - \underset{P(\varepsilon t)_3}{\overset{P(\varepsilon t)_3}{Pd}} - Br$$

75% yield

Also, it was found that the palladium metal powder would react with iodobenzene to produce a new but somewhat unstable complex.



$$Pd^* + 2\ \varepsilon t_3P + C_6H_5I \rightarrow C_6H_5 - \underset{P(\varepsilon t)_3}{\overset{P(\varepsilon t)_3}{Pd}} - I$$

Highly reactive Pt powders have also been produced by this procedure. One reaction we have carried out is the oxidative insertion reaction with chlorobenzene.

The nickel, palladium and platinum slurries are much more reactive than the commercial powders. There are some indications that they might be more reactive than the corresponding metal slurry obtained from the cocondensation metal slurry technique. For example, our Ni slurries react rapidly with triethyl phosphite to give high yields ($\simeq$ 70%) of $(\varepsilon t_3P)_4$ Ni. We are in the process of exploring the full synthetic capabilities of these highly reactive metal powders.

Cobalt

We have completed several experiments with cobalt. Reduction of cobalt salts with potassium in THF produces a highly reactive black powder. The black powders have been found to undergo reaction with several different alkyl halides. It is assumed at this point that the reaction product results from oxidative insertion of the Co into the carbon halogen bond. We intend to fully characterize the reaction products and study the full extent of the use of the highly reactive cobalt powders in oxidative insertion reactions.

6. LIST OF MANUSCRIPTS SUBMITTED OR PUBLISHED UNDER ARO SPONSORSHIP DURING THIS PERIOD, INCLUDING JOURNAL REFERENCES:

(a) "Activated Metals. IX. A New Reformatsky Reagent Involving Activated Indium for the Preparation of β-Hydroxy Estes," Li-Chung Chao and R.D. Rieke, J. Org. Chem., 40, 2253 (1975).

(b) "Activated Metals. X. Direct Synthesis of Diphenylindium Iodide and Ditolylindium Iodide from Activated Indium Metal," Li-Chung Chao and R.D. Rieke, Syn. React. Inorg. Metal-Org. Chem., 5, 165 (1975).

(c) "Activated Metals. XI. An Improved Procedure for the Preparation of β-Hydroxy Esters Using Activated Zinc," R.D. Rieke and S.J. Uhm, Synthesis, 452 (1975).

(d) "Use of Activated Metals in Organic and Organometallic Synthesis," R.D. Rieke, Current Topics in Chemistry, 59, 1 (1975).

(e) "Preparation of Highly Reactive Transition Metal Powders. Oxidative Insertion of Nickel and Palladium Powders into Carbon - Halogen Bonds," R.D. Rieke, W. Wolf, N. Kujundzic and A. Kavaliunas, J. Amer. Chem. Soc., 99, 4159 (1977).

(f) "Use of Highly Reactive Metal Powders in Organic and Organometallic Synthesis," R.D. Rieke, Accounts of Chemical Research, 10, 0000 (1977).

(g) "Preparation and Reactions of Highly Reactive Magnesium Metal," R.D. Rieke, S.E. Bales and P.M. Hudnall, submitted to Organic Synthesis.

R. Rando, Department of Pharmacology, Harvard Medical School, Boston, Mass.

(28) Hydrogen removal has been shown to be at least partially rate determining in the reaction of MAO with substrates: B. Belleau and J. Moran, *Ann. N.Y. Acad. Sci.*, **107**, 822 (1963).

(29) The quaternary salts **10**, **11**, and **12** were prepared from the reaction of the corresponding unsaturated bromides or mesylate with trimethylamine.

(30) Solubilization of **10** in neutral deuterium oxide (25 °C) leads instantaneously (on the NMR time scale) to exchange of the terminal, acetylenic proton.

(31) The overwhelming preference for removal of propargyl vs. allylic protons is in accord with the much greater electron-withdrawing power of the ethynyl group than the vinyl group.[32-34]

(32) J. A. Landgrebe and R. H. Rynbrandt, *J. Org. Chem.*, **31**, 2585 (1966).

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(34) R. W. Taft, Jr., in "Steric Effects in Organic Chemistry", M. S. Newman, Ed., Wiley, New York, N.Y., 1956, p 619.

(35) That negative charge is more rapidly generated at a site adjacent to a triple bond than at an allylic site is also known from studies of base-catalyzed isomerizations of allenes and acetylenes: R. J. Bushby, *Quart. Rev.*, **24**, 585 (1970).

(36) (a) The strong preference for removal of a propargyl proton compared to an allyl proton stands in contrast to the ease of removing the corresponding hydrogen atoms. The most recently determined value for propargyl stabilization is 4.8 kcal/mol (R. Walsh, *Trans. Faraday Soc.*, **64**, 2085 (1971)), which is considerably smaller than the commonly quoted value of 12 kcal/mol for allylic stabilization (P. Nangia and S. W. Benson, *J. Am. Chem. Soc.*, **84**, 3411 (1962)).

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For examples of cycloaddition to allenes, see (a) W. T. Brady, J. D. Stockton, and A. D. Patel, *J. Org. Chem.*, **39**, 236 (1974); (b) W. R. Dolbier, Jr., and S.-H. Dai, *J. Am. Chem. Soc.*, **90**, 5030 (1968); (c). J. E. Baldwin and R. H. Fleming, *Fortsch. Chem. Forsch.*, **15**, 281 (1970).

A more complete account of the effect of substituents will be published in collaboration with Dr. A. Claesson of Uppsala University, Faculty of Pharmacy, Uppsala, Sweden, who has kindly furnished the terminally methylated derivatives of **4**.

(40) Private communication from Dr. R. P. Halliday, Norwich Pharmacal Co., Norwich, N.Y.

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Received November 15, 1977

Highly Reactive Transition Metal Powders. Oxidative Insertion of Nickel, Palladium, and Platinum Metal Powders into Aryl-Halide Bonds

Sir:

We have reported a new procedure for producing highly reactive metal powders.[1,2] This procedure consists of reduction of a metal salt from an ethereal or hydrocarbon solvent with an alkali metal. The primary consideration is that the metal salt in question be partially soluble in the solvent used. In most cases, the alkali metal used had a melting point lower than the boiling point of the solvent;[2] however, this is not necessary in all cases. In this paper we wish to report that, using a modification of this approach, highly reactive transition metal slurries can be prepared. Nickel, palladium, and platinum produced by this method are found to undergo oxidative insertion into C-X bonds and in some cases at relatively low temperatures.

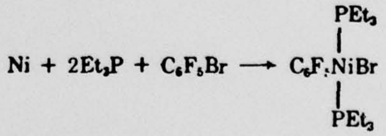
Oxidative addition of RX to transition metals has been observed using the metal atom or metal vaporization approach of Skell.[3,4] Klabunde has reported that nickel and palladium, when cocondensed with aryl halides, readily undergo oxidative insertion into the carbon-halogen bond.[5-8] Cocondensation of nickel or palladium with pentafluorobromobenzene and triethylphosphine gave good yields of the bromopentafluorobis(triethylphosphine)metal complex. The corresponding solution reaction of common commercial nickel powders or palladium powders with aryl halides has not been observed due to the poor reactivity of these and most other transition metals toward oxidative addition.

Initially we tried the standard approach of reduction of NiI_2, $NiBr_2$, or $NiCl_2$ with potassium in refluxing THF. Finely divided black nickel powders were obtained; however, they showed rather limited reactivity toward oxidative insertion into carbon-halogen bonds. Similar results were found with palladium.

We have demonstrated with several of the main group elements that the reactivity of the resulting metal is highly dependent on such factors as the solvent, reducing agent, anion, or in the case of some metals the presence of additional alkali salts.[2,9,10] In the case of the transition metals to be discussed in this paper, the presence of a triaryl- or trialkylphosphine during the reduction yields a highly reactive metal slurry. When triethylphosphine is added to NiI_2 in THF, the well known and highly soluble diiodobis(triethylphosphine)nickel(II) complex is formed. Addition of 2 mol of potassium to this mixture, and then heating at reflux, yields a very fine black metal slurry of nickel. The reduction time is very dependent upon the type of phosphine used. For example, when triethylphosphine or triphenylphosphine were used the reduction times were approximately 20 and 2 h, respectively.

The particle size of the black powder is much smaller than that resulting from the standard procedure without the presence of the triethylphosphine. Elemental imaging of the black nickel powder using energy dispersive analysis at a magnification of 5000 indicated that the distribution of nickel, potassium, and iodide is essentially random. When the reduction is completed, the precipitated KI is obtained in almost quantitative yields. These facts, coupled with the fact that the black metal slurry does not flash when added to water, strongly indicates that no potassium remains after the reduction and that the black slurry contains considerable nickel (0).

Not only is the particle size smaller when the reduction is carried out in the presence of the triethylphosphine but the reactivity of the metal toward oxidative additions is greatly enhanced. Upon the addition of pentafluorobromobenzene to the black nickel slurry produced[11] in the presence of triethylphosphine, a rapid reaction occurred yielding bromopentafluorophenylbis(triethylphosphine)nickel(II) in 60% yield.



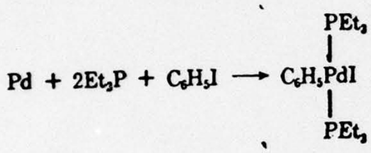
$$Ni + 2Et_3P + C_6F_5Br \longrightarrow C_6F_5\underset{\displaystyle PEt_3}{\overset{\displaystyle PEt_3}{Ni}}Br$$

Triphenylphosphine seems to have a similar effect. In fact, nickel slurries produced by reducing NiI_2 in the presence of triphenylphosphine are more reactive than those generated with the triethylphosphine procedure. Addition of pentafluorobromobenzene to the black nickel slurry at −78 °C resulted in an almost immediate reaction. Workup of the reaction yielded 46% of the bromopentafluorophenylbis(triphenylphosphine)nickel(II). Thus, the nickel generated by this method appears to be more reactive but the yield of the oxidative addition product was slightly less. These two sets of experiments suggest that the reaction was not occurring via oxidative addition of the tetrakis(triethylphosphine)nickel(0) or the tetrakis(triphenylphosphine)nickel(0) complexes. Parshall[12] and others[13] have shown that the tetrakis(triphenylphosphine)nickel(0) complex is less reactive than the tetrakis(triethylphosphine)nickel(0) complex in oxidative additions into aryl-halogen bonds. In several cases, reaction of the tetrakis(triphenylphosphine)nickel(0) complex with aryl halides often requires several hours of refluxing. Thus, it would 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]



$$\mathrm{Pd} + 2\mathrm{Et_3P} + \mathrm{C_6H_5I} \longrightarrow \mathrm{C_6H_5}\overset{\overset{\displaystyle \mathrm{PEt_3}}{|}}{\underset{\underset{\displaystyle \mathrm{PEt_3}}{|}}{\mathrm{Pd}}}\mathrm{I}$$

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.

Acknowledgment. Financial support of this investigation by the U.S. Army Research Office is gratefully acknowledged.

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(10) R. D. Rieke, K. Ofele, and E. O. Fischer, *J. Organomet. Chem.*, **78**, C19 (1974).
(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 $NiCl_2$.
(12) G. W. Parshall, *J. Am. Chem. Soc.*, 96, 2360 (1974).
(13) L. Cassar and A. Giarrusso, *Gazz. Chim. Ital.*, **103**, 793 (1973).
(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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Received January 24, 1977

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-