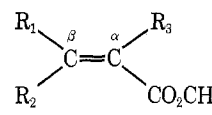
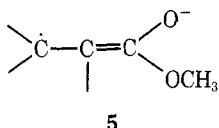


Table II
Calculated Electron Densities in Acrylate Esters



R ₁ , R ₂	R ₃	α	β
H, H	H	4.0448	3.9498
H, H	CH ₃	4.0408	3.9643
CH ₃ , H	H	4.0738	3.9163
CH ₃ , H	CH ₃	4.0638	3.9319
CH ₃ , CH ₃	H	4.1101	3.8973
CH ₃ , CH ₃	CH ₃	4.0910	3.9180



V¹¹), electron transfer in this system appears to be highly unlikely.¹⁰

Experimental Section

The procedures for the reactions of acrylates with alkali diphenylmethides are so similar that only one is given in detail. Variations are indicated in the Discussion or in Table I, as are physical constants.¹²

Reactions of Acrylic Esters with Alkali Diphenylmethides.
Methyl 2,3,3-Trimethyl-4,4-diphenylbutanoate. Sodium diphenylmethide was prepared by addition of 16.8 g (0.1 mol) of diphenylmethane in 50 ml of ether to 0.1 mol of sodium amide in liquid ammonia, prepared from 2.3 g (0.1 g-atom) of sodium and a small amount of anhydrous ferric chloride in 250 ml of liquid ammonia. The resulting deep orange solution was stirred for 10 min and 12.8 g (0.1 mol) of methyl trimethylacrylate in 25 ml of ether

was added during 10 min. To the resulting green solution was added 6 g of ammonium chloride. The ammonia was replaced by ether and the mixture was stirred with 250 ml of 0.1 *N* hydrochloric acid. The aqueous layer was separated and extracted with 100 ml of ether, and the combined ether solutions were dried over sodium sulfate and concentrated to give 28 g of a pale yellow liquid. Distillation afforded 6 g of starting materials [bp 70–200°/(1 mm)] and 22 g of methyl 2,3,3-trimethyl-4,4-diphenylbutanoate, bp 170° (0.8 mm). A solution of 4 g of the ester was dissolved in 20 ml of cold concentrated sulfuric acid, and the orange solution was stirred for 5 min and poured onto ice. Recrystallization from petroleum ether afforded 1.5 g (40%) of 4-phenyl-2,3,3-trimethyl-1-tetralone, mp 137°.

Acknowledgement. The authors wish to thank Dr. H. A. Kuska, who provided the CNDO/2 programs from QCEP and assisted in their use.

Registry No.—Sodium diphenylmethide, 5152-68-1; 2-methyl-4,4-diphenylbutyric acid, 57090-82-1; 3,3-dimethyl-4,4-diphenylbutanoic acid, 57090-83-2; 2,3,3-trimethyl-4-phenyl-1-tetralone, 57090-84-3; diphenylmethane, 101-81-5; sodium amide, 7782-92-5.

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Oxidative Addition of Sodium and Zinc Arenesulfonates to Derivatives of Diazenedicarboxylic Acid^{1,2}

John E. Herweh* and Richard M. Fantazier

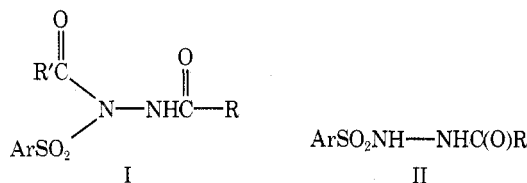
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1,2-Diazenedicarboxamide (DDA), a number of substituted diazenedicarboxamides, and diethyl diazenedicarboxylate react with the sodium and zinc salts of *p*-toluene- and benzenesulfonic acids in Me₂SO or DMF to give addition products (I) and/or addition-elimination products (II). With DDA and the *N,N*-disubstituted derivatives, the trisubstituted diazene (I) is unstable under alkaline conditions generated and undergoes elimination. The resulting products, sulfonyldiazene-carboxamides (II), are formed in high yield. DDA also undergoes oxidative addition with sodium arenesulfonates in aqueous media and subsequent elimination to give II in nearly quantitative yield. Symmetrically substituted diazenedicarboxamides, exemplified by *N,N'*-diethyl-1,2-diazenedicarboxamide and *N,N'*-diphenyl-1,2-diazenedicarboxamide, react with arenesulfonate salts in Me₂SO to yield a mixture of I and II. The latter may result from elimination of an isocyanate from I under alkaline conditions. Tetrasubstituted diazenedicarboxamides, such as *N,N,N',N'*-tetramethyl-1,2-diazenedicarboxamide (TMDDA), and diazenedicarboxylates, such as diethyl diazenedicarboxylate (DEDD), afford only the trisubstituted product (I), the latter or its anion being stable under basic conditions.

α -Carbonyl diazenes may be characterized as oxidants by virtue of their tendency to act as strong electron acceptors. Oxidation may result in the formation of addition products involving a diazene and substrate.³ The currently described reaction of α -carbonyl diazenes with salts of arenesulfonic

acids to give products possessing the general structures I and II may be placed in this category. The oxidation of arenesulfonic acids by diphenyldiazene (azobenzene) and certain substituted analogues has been reported,^{4,5} the reaction proceeding by addition of the acid across the diazene



linkage to give sulfonyldiazanes. The reaction of sulfonic acids or their salts with α -carbonyl diazenes is relatively unexplored.

Messinger⁶ recently reported the preparation of several trisubstituted diazenes (I) by the addition of benzene- or *p*-toluenesulfonic acid to either ethoxy or morpholino derivatives of diazenedicarboxylic acid. We have examined the reaction of several zinc and sodium arenesulfonates with a number of diazenedicarboxylic acid derivatives in some detail and we are presenting here these results and some information bearing on the mechanisms of the reaction.

Results

Reaction of 1,2-Diazenedicarboxamide (DDA) with Salts of Arenesulfonic Acids. When DDA and either the zinc or sodium salt of arenesulfonic acids are combined in equivalent amounts in Me_2SO solution⁷ at room temperature, a rapid reaction occurs, to yield the corresponding sulfonyldiazanecarboxamides (II, R = NH_2) in high yield. NMR analysis of freshly combined $\text{Me}_2\text{SO}-d_6$ solutions of DDA and zinc bis(*p*-toluenesulfinate) (1) (2:1 mole ratio) confirmed the rapidity of the reaction; signals due to DDA and sulfinate were absent after several minutes. Following the mixing of reactants, NMR signals appear, some of which are coincident with those of the sulfonyldiazanecarboxamide (2) ultimately isolated, while others are presumably associated with some labile intermediate or adduct. In time, these latter absorptions disappear,⁸ and those characteristic of the major reaction product, *p*-toluenesulfonyldiazanecarboxamide (2), predominate.

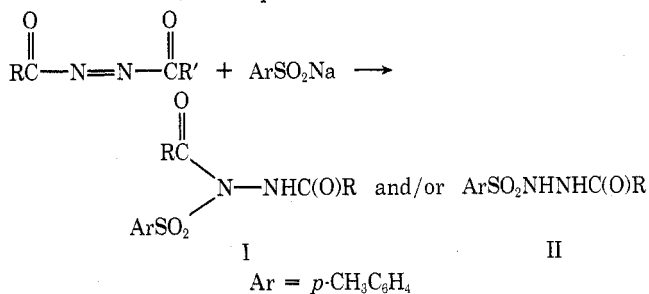
In one case, the free sulfonic acid, *p*-acetamidobenzenesulfonic acid, was used in place of the corresponding salt. In Me_2SO , no apparent reaction occurred; however, adding the reaction mixture to water several hours after mixing resulted in the precipitation of a white, gelatinous solid. The product (87.5% yield) was formulated as 1-*p*-acetamidobenzenesulfonyl-1,2-diazenedicarboxamide (4) on the basis of its elemental analysis, molecular weight, and NMR spectrum (Table III) (see Experimental Section). 4 is converted to *p*-acetamidobenzenesulfonyldiazanecarboxamide (5) (77% conversion) by consecutive treatments with aqueous base and acid.

Monitoring the reaction of DDA with *p*-acetamidobenzenesulfonic acid in $\text{Me}_2\text{SO}-d_6$ by NMR confirmed the qualitative observation that essentially no immediate reaction occurs. The NMR spectrum simply consists of a composite of absorptions due to the reactants. After ca. 20 hr, however, the spectrum was again recorded and exhibited absorptions that were comparable to those of the isolated product 4. After ca. 6 days, the reaction mixture remained unchanged, as determined by NMR.

To broaden the scope of reaction conditions, a suspension of DDA in water and the water-soluble sodium benzene- or *p*-toluenesulfonates was allowed to react. The corresponding sulfonyldiazanecarboxamides 2 and 3 were obtained in near quantitative yields.

Reaction of Substituted Diazenedicarboxamides with Salts of Sulfonic Acids. A number of substituted diazenedicarboxamides were allowed to react with sodium *p*-toluenesulfinate in Me_2SO . In the case of *N,N'*-diethyl-1,2-diazenedicarboxamide (DEDDA), an immediate reac-

Table I
Reaction Products from Substituted DDA's and Sodium *p*-Toluenesulfinate^a



R'	R	Product type	% yield	Mp, °C
EtNH	EtNH	II (6)	39	199–200 dec ^b
Me ₂ N	Me ₂ N	I (8)	77	197–198 dec ^c
H ₂ N	Ph ₂ N	II (9)	98	186–188 dec ^d
PhNH	PhNH	I (11)	33	180–182.5 dec
		II (10)	27	210–211 dec

^a Satisfactory elemental analyses and molecular weight determinations were recorded for all compounds. ^b Recrystallized from chloroform. ^c Recrystallization from carbon tetrachloride–chloroform (4:1). ^d Recrystallized from absolute alcohol.

Table II
NMR Data and Assignments for Sulfonyldiazanecarboxamides (II)^a

$$\begin{array}{c} \text{O} \\ \parallel \\ \text{ArSO}_2\text{NH}_B-\text{NH}_A\text{CR} \\ \text{II} \end{array}$$

Compd	Chemical shifts, ppm, δ		
	H _A	H _B	R
3	7.91 (s)	9.50 (s)	NH ₂ , 5.92 (s)
2	7.91 (s)	9.42 (s)	NH ₂ , 5.95 (s)
6	7.85 (s)	9.36 (s)	NH _F Et: H _F , 6.28 (t, $J = 5.0$ Hz); CH ₂ , 2.95 (q, $J = 7.0$ Hz); CH ₃ , 0.90 (t, $J = 7.0$ Hz)
9	8.55 (s)	9.40 (s)	NPh ₂ , 7.2 (m)
5	8.00 (s)	9.37 (s)	NH ₂ , 6.0 (s)
10	8.53	9.60	NH _F Ph: H 8.34 (s), Ph, ca. 7.2 (m)

^a Solvent: $\text{Me}_2\text{SO}-d_6$.

tion occurred upon combining solutions of DEDDA and sulfinate. A 39% yield of 1-*p*-toluenesulfonyl-*N*-ethyl-2-diazenecarboxamide (6) was obtained (Table I).

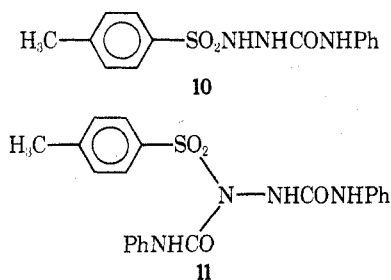
The facility with which the reaction of DEDDA and sodium *p*-toluenesulfinate proceeds was substantiated by NMR. NMR spectra obtained directly after combining DEDDA with zinc bis(*p*-toluenesulfinate) (1) in $\text{Me}_2\text{SO}-d_6$ may be interpreted as showing the presence of an adduct, namely, 1-*p*-toluenesulfonyl-*N,N'*-diethyl-1,2-diazenedicarboxamide (7) (Table III). After ca. 24 hr, the NMR spectrum of the reaction mixture showed a diminution in the intensity of absorptions attributed to 7, and the emergence of absorptions coincident with those of *p*-toluenesulfonyl-*N*-ethyl-2-diazenecarboxamide (6), the isolated product (Tables I and II). In addition to 6 and the postulated adduct 7, an absorption at δ 5.78 (ill-defined triplet attributed to NH adjacent to ethyl group) and the complexity of absorptions in the regions ca. δ 1.0 and 3.0 attributed to the methylene and methyl protons of the ethyl groups suggested the presence of a third component. The composition of the reaction mixture continued to change with time; after

ca. 6 days, both 6 and the unknown third component were present in greater amounts.

When *N,N,N',N'*-tetramethyl-1,2-diazenedicarboxamide (TMDDA) was allowed to react with sodium *p*-toluenesulfinate, the characteristic color was not dissipated. Work-up of the reaction mixture in a manner similar to that utilized for the reaction product from DEDDA gave 1-*p*-toluenesulfonyl-*N,N,N',N'*-tetramethyl-1,2-diazenedicarboxamide (8) in 77% yield (Table I). When the reaction was repeated with zinc bis(*p*-toluenesulfinate) (1) in $\text{Me}_2\text{SO}-d_6$ using a 2:1 mole ratio of the α -carbonyl diazene compound to sulfinate, NMR absorptions indicated the relatively rapid formation of a single component. The NMR absorptions⁹ attributed to this reaction product were comparable to those exhibited by the trisubstituted diazene derivative (8) (Tables I and III) previously identified.

Variable results were obtained when a series of *N*-phenyl substituted diazenedicarboxamides were allowed to react with sodium *p*-toluenesulfinate in Me_2SO at room temperature. With unsymmetrical *N,N*-diphenyl-2-diazenedicarboxamide, an immediate reaction occurred; work-up of the reaction mixture gave a nearly quantitative yield of 1-*p*-toluenesulfonyl-*N,N*-diphenyl-2-diazanecarboxamide (9) (Table I). The relative rapidity of the reaction and the formation of the sulfonyldiazanecarboxamide (9) as the major reaction product was confirmed by following the reaction by NMR.

Reaction of *N,N*-diphenyl-1,2-diazenedicarboxamide with the sulfinate gave a mixture of two products. Identification of the products as 1-*p*-toluenesulfonyl-*N*-phenyl-2-diazanecarboxamide (10) and 1-*p*-toluenesulfonyl-*N,N'*-diphenyl-1,2-diazanecarboxamide (11) was made on the basis of elemental analysis and NMR spectral data.



N,N,N',N'-Tetraphenyl-1,2-diazenedicarboxamide, which is sparingly soluble in Me_2SO at room temperature, failed to undergo significant reaction with the sulfinate under typical reaction conditions; 88% was recovered.

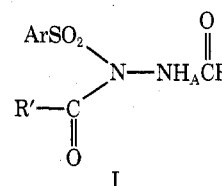
Miscellaneous Reactions of Some Diazenes with Sulfonic Acids and Their Salts. Diethyl diazenedicarboxylate (DEDD) reacted readily with zinc bis(benzenesulfinate) (12) in Me_2SO to give 1-benzenesulfonyl diethyl-1,2-diazanedicarboxylate (13) in high yield.

Diphenyldiazene and bis(2-cyano-2-propyl)diazene (BMPD) were also allowed to react with sodium *p*-toluenesulfinate under typical reaction conditions. In neither case was there any evidence for oxidative addition; 96% of the diphenyldiazene and 89% of the BMPD were recovered.

Sodium formaldehyde sulfoxylate reacts immediately with DDA in Me_2SO at room temperature to give a precipitate of 1,2-diazanedicarboxamide in 78% yield. Reaction of aminoiminomethanesulfonic acid with DDA in Me_2SO also failed to give an isolable addition product. Instead, 47% of the starting DDA was reduced to 1,2-diazanedicarboxamide and of the remaining starting material, 90% was recovered.

Kinetic Results. The rate of disappearance of DDA in the presence of an equivalent amount of sodium benzen-

Table III
NMR Data and Assignments for
Trisubstituted Diazenes (I)^a



Compd	Chemical shifts, ppm, δ		
	H _A	R'	R
8	9.0 (s)	NMe ₂ , 2.92 (s)	NMe ₂ , 2.78 (s)
13	10.46 (s)	OEt: OCH ₂ , 4.1 (m); ^b CH ₃ , 1.15 (m)	OEt: see R'
4	8.94 (s)	NH ₂ , 6.88 (s)	NH ₂ , 6.22 (s)
7	8.87 (s)	NH _F Et: H _F , ca. 7.4; ^c CH ₂ , ca. 3.19 (q), <i>J</i> = 6.5 Hz; CH ₃ , 1.07 (t), <i>J</i> = 6.5 Hz	NH _F Et: H _F , 6.5 (t) <i>J</i> = 5.0 Hz; CH ₂ , ca. 3.02 (q), <i>J</i> = 6.5 Hz; CH ₃ , 0.94 (t), <i>J</i> = 6.5 Hz
11	8.68	PhNH _E : H _E , 10.04 (s); Ph, ca. 7.4 (m)	PhNH _F : H _F , 10.6 (s); Ph, ca. 7.2 (m)

^a Solvent: $\text{Me}_2\text{SO}-d_6$. ^b Methylene and methyl protons appear as multiplets due to overlap of signals. ^c Signal appeared as a broad, poorly defined triplet.

Table IV
Rate Data for the Disappearance of 0.015 M DDA
in the Presence of Selected Benzenesulfinate^a

Benzenesulfinate ^d	Temp, °C	2nd order rate const, l. mol ⁻¹ min ⁻¹	Half-life, min
Sodium ^c	-25.0	19.5	3.4
Sodium ^c	-19.5	26.8	2.5
Sodium ^c	-15.5	30.3	2.2
Sodium ^c	-5.0	47.8	1.4
Sodium + water (0.06 M)	-14.5	30.1	2.2
Sodium + water (0.06 M)	-9.5	39.6	1.7
Sodium + Zn(OAc) ₂ ·2H ₂ O (0.00375 M)	-32.0	^b	5.9
Sodium + Zn(OAc) ₂ ·2H ₂ O (0.015 M)	-25.0	^b	2.7
Sodium + Zn(OAc) ₂ ·2H ₂ O (0.06 M)	-25.5	^b	0.7
Sodium + Zn(OAc) ₂ ·2H ₂ O (0.125 M)	-22.5	^b	0.6
Zinc (0.0075 M)	-30.0	^b	~0.2
Zinc (0.0075 M)	-22.5	^b	<0.2
Zinc (0.0075 M) + NaOCN (0.015 M)	-20.0	21.9	2.8

^a Unless noted otherwise, all experiments were conducted in dry DMF. ^b These experiments did not yield straight-line plots. Half-lives were taken directly from concentration-time data. ^c An Arrhenius plot for this reaction yielded an activation energy of 5.1 ± 0.3 kcal/mol. ^d Sodium salt (0.015 M) in all cases.

esulfinate in dry DMF was determined at low temperatures (see Experimental Section). Plots of $1/(\text{DDA})$ vs. time were linear over 3-4 half-lives, consistent with straightforward second-order kinetics. Pertinent rate data are included in Table IV. These data yielded a straight-line Arrhenius plot giving an activation energy of 5.1 ± 0.3 kcal/mol. Added water has virtually no effect on the reaction rate (Table IV).

The addition of zinc acetate dihydrate accelerates the

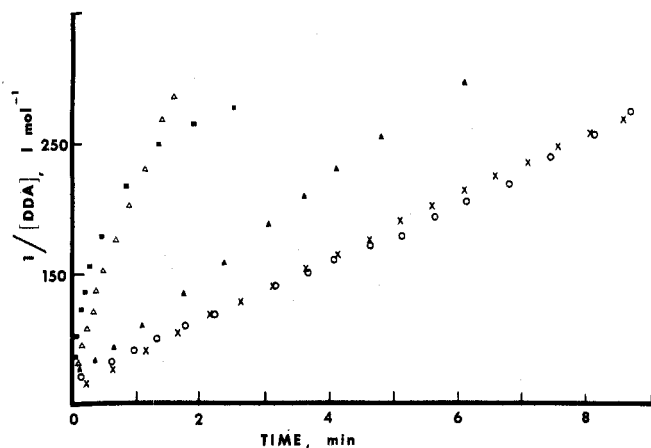


Figure 1. Comparative second-order kinetic plots for the disappearance of 0.015 M DDA: x, 0.015 M PhSO_2Na , -22.0° ; o, 0.0075 M $\text{Zn}(\text{PhSO}_2)_2$ + 0.015 M NaOCN , -20.0° ; \blacktriangle , 0.015 M PhSO_2Na + 0.015 M $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$, -20.5° ; \triangle , 0.015 M PhSO_2Na + 0.125 M $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$, -20.5° ; \blacksquare , 0.0075 M $\text{Zn}(\text{PhSO}_2)_2$, 22.5° .

rate of disappearance of DDA in the presence of sodium benzenesulfinate. As the initial concentration of zinc is increased, the rate of DDA disappearance increases. However, the resulting second-order kinetic plots are not linear. Rate constants were not calculated for these, but half-lives were determined and these are shown in Table IV. Representative second-order plots are shown in Figure 1. Very rapid reactions occur between DDA and zinc bis(benzenesulfinate) in DMF. These did not yield straight-line second-order kinetic plots (See Figure 1). At all temperatures above -30° , the half-life was too short to determine precisely. It was less than 0.2 min at -22.5° (Table IV).

The addition of 1 equiv (with respect to benzenesulfinate) of sodium or potassium cyanate to zinc bis(benzenesulfinate) effectively eliminates the accelerating action of the zinc salt and yields a kinetic plot for the disappearance of DDA that is nearly identical with that obtained with sodium benzenesulfinate alone. This is shown in Table IV and Figure 1.

Discussion

The reaction of arenesulfinate salts with DDA in Me_2SO may be interpreted as involving addition of a nucleophile, the arenesulfinate anion, to the electrophilic diazene linkage to form the substituted diazane anion (III) (Scheme I).

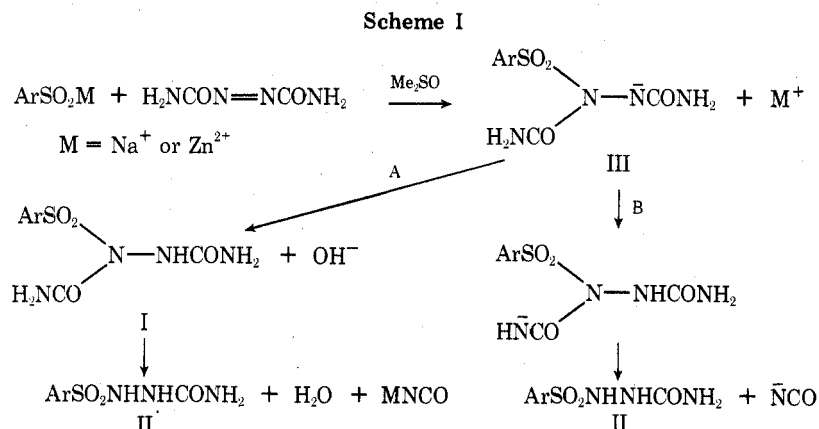
thereby enhancing the basicity of the reaction medium (Scheme I). Under conditions of relative high basicity I may be expected to eliminate cyanate to give the sulfonyldiazanecarboxamide (II, $\text{R} = \text{NH}_2$) and the cyanate of the metal cation present. Diazanetriscarboxamide is known to undergo rapid elimination of isocyanic acid in basic media to give 1,2-diazanedicarboxamide and a cyanate.¹¹

Alternatively, one may assume that moisture is not involved in the initial stages of the reaction and that the substituted diazane anion (III) simply undergoes a series of rearrangements resulting in the loss of cyanate and formation of the sulfonyldiazanecarboxamide (I) (Scheme I, path B). In the case of DDA and its reaction with sodium benzenesulfinate in DMF, water was found to have no effect on the rate of DDA disappearance (Table IV).

The relative ease with which the reaction proceeds in an aqueous medium, even though the system is heterogeneous (DDA is insoluble in water), may be taken as support for the participation of small amounts of water under homogeneous reaction conditions in Me_2SO .

Further evidence that small amounts of water may be involved in the reaction scheme arises from NMR studies of the reaction of TMDDA with anhydrous zinc bis(*p*-toluenesulfinate) (1). The NMR spectrum indicated the formation of the trisubstituted diazane derivative (8) directly. Since TMDDA does not possess any labile hydrogens, one can reasonably assume that the required NH proton in 8 was furnished by water. In the case of TMDDA a stoichiometric amount of water would be necessary to bring about complete formation of 8, contrary to the proposed reaction course involving DDA (Scheme I, path A). The formation of a trisubstituted diazane (I) as a reaction intermediate probably occurs in all cases involving reactions of diazenedicarboxamides with arenesulfonates. In those instances where the diazene compound bears a formamoyl group, the trisubstituted diazane derivative (I, $\text{R}' = \text{NH}_2$; $\text{R} = \text{NH}_2$ or NR_2) is relatively unstable and eliminates cyanate to give the sulfonyldiazanecarboxamide (II, $\text{R} = \text{NR}_2$ or NH_2). The relatively high basicity of the medium, enhanced as described above, probably contributes to the instability of I. In the one case where the free arenesulfonic acid (reaction involving *p*-acetamidobenzenesulfonic acid) was used, I was isolable. The latter readily lost the elements of isocyanic acid upon attempted purification by dissolution in aqueous base followed by acidification.

The kinetic studies provide additional support for the primary steps in Scheme I. The uncomplicated second-



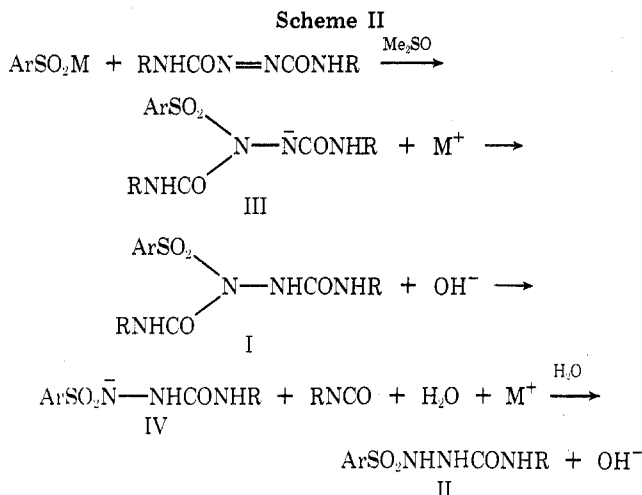
The reaction is facilitated by solvation of the particular metal cation of the sulfinate salt by Me_2SO . If traces of moisture¹⁰ are present, III may be converted to the 1-arenesulfinate-1,2-diazanedicarboxamide (I, $\text{R} = \text{R}' = \text{NH}_2$),

order kinetics observed for the reaction of sodium benzenesulfinate with DDA is consistent with a simple addition step. The reaction is rapid and its activation energy is exceptionally low.¹²

Zinc bis(benzenesulfinate) reacts with DDA at a considerably greater rate than that of the sodium salt. The rate of disappearance of DDA in the presence of sodium benzenesulfinate is accelerated by the addition of zinc acetate. These results are consistent with a catalytic effect by zinc. However, the apparent catalytic effect is not typical in that equivalent rather than trace amounts are required. If zinc ion is a catalyst for the addition of benzenesulfinate to DDA, it was reasoned that during the course of the reaction, zinc must be rendered inactive. Cyanate is a by-product of the addition reaction. If cyanate reacts with zinc to form an unreactive species, then this would explain the observed behavior.

Sodium (or potassium) cyanate, when added to zinc bis(benzenesulfinate) before mixing with DDA, completely eliminates the accelerating action of the zinc and yields kinetic curves virtually identical with those obtained with sodium benzenesulfinate.

When both formamoyl groups of DDA are replaced by *N*-monosubstituted carbamoyl groups, a mixture of the trisubstituted diazanes (I, $R = R' = \text{NHR}$) and the sulfonyldiazanecarboxamide (II, $R = \text{NHR}$) may result (Scheme II). This reflects on the stability of the initially formed tri-



substituted diazane derivative (I, $R = R' = \text{NHR}$) under basic conditions. In the case of 1,2-diazenedicarboxamide bearing *N*-monosubstituted carbamoyl groups, the sulfonyldiazanecarboxamide may well exist as the anion (IV, $R' = \text{NHR}$), since the fragment leaving I is a neutral organic isocyanate rather than a cyanate ion as in Scheme I (path B). The isocyanate may react with water and ultimately give the corresponding urea. In view of this it can be seen that the requirements of these systems for water may be intermediate between those involving diazenes bearing formamoyl groups and those possessing complete *N,N* disubstitution.

The course of reaction for fully substituted diazenedicarboxamides, such as TMDDA, has been discussed to some extent. The initially formed anion may react with any water present to give the trisubstituted diazanes (I, $R = R' = \text{NR}_2$) when zinc is the counterion, as NMR evidence suggests. Conversely, when sodium is the counterion, as in the preparative procedure leading to 7, the oxidative coupling product exists as the anion and 7 is formed after addition of the reaction mixture to water followed by acidification.

In the case of the diazenedicarboxylates, specifically DEDD, and its reaction with zinc bis(benzenesulfinate) (12) the initially formed addition product may remain as

the salt after addition to water. Only upon acidification is I ($R = \text{OEt}$) obtained. The apparent stability of the trisubstituted diazane anion (III, $R = R' = \text{OEt}$) is evidenced by the isolation of I in high yield. Neither bis(2-cyano-2-propyl)diazene nor diphenyldiazene undergoes reaction with sodium *p*-toluenesulfinate. Obviously neither of these diazenes possesses electrophilicity comparable to the α -carbonyl diazenes discussed above.

The aliphatic derivatives, sodium formaldehyde sulfoxylate and aminoiminomethanesulfinic acid, failed to give any isolable products analogous to either I or II upon reaction with DDA. The reactions were only briefly studied. However, if the initial step is addition to form a trisubstituted diazane anion or neutral species as with the arenesulfonates it can only be concluded that the sulfinate moiety is eliminated rather than isocyanic acid to give 1,2-diazanedicarboxamide as a major product.

In the case of α -carbonyl diazenes and arenesulfonates, the mild conditions required, the rapidity of the reactions, and the generally high yields suggest that the process described offers an attractive alternate synthetic route to trisubstituted diazanes and sulfonyldiazanecarboxamides.

Experimental Section

General. Infrared spectra were recorded on a Perkin-Elmer 451 infrared spectrophotometer. NMR spectra were recorded on a Jeolco Model JNM-4H-100, 100 MHz (using Me_4Si as an internal standard). Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. Melting points were determined in open capillary tubes on a Mel-Temp apparatus and are uncorrected.

Materials. Diazenes. 1,2-Diazenedicarboxamide (DDA) was used as received from Aldrich Chemical Co. Diphenyldiazene and bis(2-cyano-2-propyl)diazene (BMPD) from Eastman Organic Chemicals were also used as received. *N,N'*-Diethyl-1,2-diazenedicarboxamide (DEDD) and *N,N,N',N'*-tetramethyl-1,2-diazenedicarboxamide (TMDDA) were prepared as reported previously;¹³ material melting at 135–137° dec and 111–113°, respectively, was used in this work. Diethyl diazenedicarboxylate (DEDD), bp 69–71° (0.8 mm), was prepared according to a reported procedure.¹⁴

N,N-Diphenyl-1,2-diazenedicarboxamide (mp 155–157° dec, recrystallized from chloroform-hexane) was obtained in 70% yield by the lead tetraacetate (LTA) oxidation of the corresponding 1,2-diazane;¹⁵ ir (KBr) 3370 (s), 3275 (m), 1745 (sh, s), 1725 (s), 1690 (s), 1585 (m), 1485 (s), and 1355 cm^{-1} (s); NMR ($\text{Me}_2\text{SO}-d_6$) δ 8.10 (s, 2 H, NH_2) and 7.44 ppm (s, 10 H, Ph).

Anal. Calcd for $\text{C}_{14}\text{H}_{12}\text{N}_4\text{O}_2$: C, 62.68; H, 4.51; N, 20.89. Found: C, 62.83; H, 4.46; N, 20.78.

N,N,N',N'-Tetraphenyl-1,2-diazenedicarboxamide was also prepared (67% yield) by the LTA oxidation of its 1,2-diazane analogue.¹⁶ One recrystallization from DMF gave analytically pure product: mp 217–218°; ir (KBr) 1720 (s), 1575 (w), 1485 (s), 1445 (w), 1340 (s), 1325 (s), and 1315 cm^{-1} (s).

Anal. Calcd for $\text{C}_{26}\text{H}_{20}\text{N}_4\text{O}_2$: C, 74.27; H, 4.80; N, 13.33. Found: C, 74.37; H, 4.80; N, 13.46.

N,N'-Diphenyl-1,2-diazenedicarboxamide, from the nitric acid oxidation of *N,N'*-diphenyl-1,2-diazanedicarboxamide,¹⁷ mp 174–174.5° (lit. 182–183°),¹⁸ was used in this study: ir (KBr) 3295 (m), 1725 (s), 1710 (s), 1590 (m), 1525 (s), 1515 (s), and 1440 cm^{-1} (s); NMR ($\text{Me}_2\text{SO}-d_6$) δ 11.51 (s, 2 H, NH) and 7.1–7.8 ppm (complex m, 10 H, Ph).

Sulfinic Acids and Their Salts. Sodium benzenesulfinate, sodium *p*-toluenesulfinate, and *p*-acetamidobenzenesulfinic acid were used as received from Aldrich Chemical Co. Similarly, aminoiminomethanesulfinic acid (Eastman Organic Chemicals) and sodium formaldehyde sulfoxylate (Nopco Chemical Co.) were used as received. Zinc bis(benzenesulfinate) (12) and zinc bis(*p*-toluenesulfinate) (1) were prepared as their dihydrates in >80% yield by the addition of aqueous solutions of zinc acetate to the corresponding sodium sulfonates. The hydrated zinc bis(*p*-toluenesulfinate) (1a) and zinc bis(benzenesulfinate) (12a) were dried in vacuo at <40° in presence of P_2O_5 and gave analytically pure 1a and 12a, melting at 264–266 and 223–225°, respectively.

Anal. Calcd for $\text{C}_{14}\text{H}_{14}\text{O}_4\text{S}_2\text{Zn}\cdot 2\text{H}_2\text{O}$ (1a): C, 40.83; H, 4.41; S, 15.57; Zn, 15.88. Found: C, 41.10; H, 4.20; S, 15.75; Zn, 15.83.

Anal. Calcd for $C_{12}H_{10}O_4S_2Zn \cdot 2H_2O$ (12a): C, 37.56; H, 3.68; S, 16.71; Zn, 17.04. Found: C, 37.66; H, 3.69; S, 16.94; Zn, 17.02.

Upon drying the hydrated zinc bis(arenesulfonates) 1a and 12a at 110° (<0.1 mm) the corresponding analytically pure anhydrous salts were obtained, melting points were essentially unchanged: NMR (Me_2SO-d_6) (1) δ 7.46 (d, 4 H, adjacent to $-SO_2-$, $J = 8.0$ Hz), 7.16 (d, 4 H, adjacent to methyl, $J = 8.0$ Hz), and 2.31 (s, 6 H, $-CH_3$'s); NMR (Me_2SO-d_6) (12) 7.56 (m, 4 H, phenyl rings adjacent to $-SO_2-$) and 7.36 ppm (m, 6 H of Ph's).

Anal. Calcd for $C_{14}H_{14}O_4S_2Zn$ (1): C, 44.75; H, 3.76; S, 17.07; Zn, 17.40. Found: C, 44.77; H, 3.75; S, 17.19; Zn, 17.35.

Anal. Calcd for $C_{12}H_{10}O_4S_2Zn$ (12): C, 41.45; H, 2.90; S, 18.44; Zn, 18.80. Found: C, 41.45; H, 2.68; S, 18.35; Zn, 18.71.

General Procedure for Reaction of 1,2-Diazenedicarboxamide (DDA) with Metal Arenesulfonates in Me_2SO . 1,2-Diazenedicarboxamide (0.01 mol) and the metal arenesulfinate (0.005 or 0.01 mol depending on metal cation) were dissolved in a suitable amount of Me_2SO (typically 25 ml per 0.01 mol for both DDA and the sulfinate).¹⁹ When the two solutions were mixed, the yellow to orange color of DDA faded almost immediately. The color was usually completely discharged after several minutes. Typically, the reaction mixtures were left at room temperature overnight prior to work-up.²⁰

The relatively clear, colorless reaction mixtures were added to excess water (ca. 300 ml per 50 ml of reaction mixture) and cooled to ice-bath temperatures. The white solid precipitate was filtered, washed with fresh cold water, and dried in vacuo (in presence of P_2O_5).

Using either zinc or sodium salts of benzene- or *p*-toluenesulfonic acid (anhydrous or hydrated) as coreactants with DDA typically gave yields of the corresponding sulfonyl diazane carboxamides (2 or 3) in the range of 80–90%. The benzenesulfonyl diazane carboxamide (3) melts at 224–225° dec (lit.²¹ mp 218° dec) and the *p*-toluene analogue (2) at 232–234° dec (lit.²¹ mp 236° dec).

In one case, using zinc bis(*p*-toluenesulfinate) (1) as a reactant with DDA, a solution of silver nitrate (6% excess based on zinc salt) was added to the aqueous Me_2SO filtrate. A white solid precipitated immediately, the filtered and dried solid (100% yield when calculated as silver cyanate) gave ir absorptions (KBr) at 2150 (s), 1300 (m), 1210 (m), 637 (m), and 628 cm^{-1} (m).

The procedure followed when DMF was used as the solvent was identical with that described above.

Kinetic Studies. Solutions of DDA and sodium benzenesulfinate were prepared in dry DMF just before use. The initial concentration of each was 0.030 *M*. The 1:1 stoichiometry was verified by a photometric titration of a stock 0.03 *M* DDA solution in DMF with a similar solution of sodium benzenesulfinate. To aliquots of the DDA solution were added from a buret varying quantities of the sulfinate but maintaining an excess of DDA. After standing for 1 hr, the remaining DDA was determined spectrophotometrically.

In a typical kinetic experiment, 3 ml of 0.030 *M* DDA in DMF was pipetted into a modified 1-cm spectrophotometer cell which was fitted with a rubber serum cap. The cell was evacuated and placed in a Dewar flask containing methanol at the required temperature. The Dewar flask was strip silvered to provide an optical path for an analyzing light beam. A tungsten source and monochromator provided a beam of 419 nm (DDA maximum) light which passes through the cell and into a photomultiplier tube whose output was displayed on a strip-chart recorder. A syringe containing an equivalent quantity of sodium benzenesulfinate (3.0 ml, 0.03 *M*) solution was placed in the Dewar to equilibrate to the reaction temperature. The experiment was then started by injecting the sodium benzenesulfinate solution through the serum cap into the evacuated spectrophotometer cell. Mixing occurred rapidly and the decreasing DDA absorption was displayed on the recorder. The optical system was calibrated with known concentrations of DDA. Beer's law was followed over the concentration range employed. A plot of $1/[DDA]$ vs. time was linear over the duration of the measurements, typically 3–4 half lives.

In some later experiments, the procedure was modified to permit direct mixing of the reactants in a mixing head before entering the spectrophotometer cell. Each reactant was placed in a separate syringe and a syringe pump used to meter the solutions through heat-exchange coils and thence into a mixing chamber and finally directly into the cell. The total mixing time was approximately 5 sec. This modification assured more uniform temperature control, particularly at the lower limits (-30 to -20°).

General Procedure for Reaction of 1,2-Diazenedicarboxamide (DDA) with Metal Arenesulfonates in Water. A solution of sodium arenesulfinate (0.05 mol) in 50 ml of water was added

rapidly to a stirred suspension of DDA (0.05 mol) in 100 ml of water (containing 2 drops of Tween 85, a commercially available wetting agent). No apparent reaction occurred and the reaction mixture was quickly heated to 45–50°. The reaction mixture was maintained at 45–50° for a varied period of time (0.75–1.5 hr) until the suspended solid phase became white. After cooling to room temperature, the alkaline reaction mixture was neutralized and filtered and the filter cake was washed thoroughly with water and dried in vacuo (in presence of P_2O_5). The reaction products were identified as sulfonyldiazane carboxamides by elemental analysis, molecular weight, melting point, ir, and NMR spectra.

Benzenesulfonyldiazane carboxamide (3), mp 220–221° dec (92% yield), was obtained from DDA and sodium benzenesulfinate. The reaction product (2), mp 233–234.5° dec, 98% yield from sodium *p*-toluenesulfinate, was analyzed directly after drying in vacuo for 1.5 hr at 78°. Anal. Calcd for $C_9H_{11}N_3O_3S$ (2): C, 41.91; H, 4.84; N, 18.33; S, 13.99; mol wt, 229.3. Found: C, 42.06; H, 4.84; N, 18.28; S, 14.09; mol wt, 230 (determined in DMF by vapor phase osmometry).

In the case involving sodium *p*-toluenesulfinate, the basic aqueous filtrate obtained directly from the reaction product, *p*-toluenesulfonyldiazane carboxamide (2), was evaporated to dryness. The solid residue was mainly sodium cyanate as identified by ir (KBr): 2220 (s), 1300 (m), 1218 (m), and 623 cm^{-1} (m).

General Procedure for the Reaction of Substituted Diazenedicarboxamides with Sodium *p*-Toluenesulfinate. The substituted diazenedicarboxamides (0.01 mol), dissolved in 25 ml of Me_2SO , were combined with solutions of sodium *p*-toluenesulfinate (0.01 mol) in 25 ml of Me_2SO and the reaction mixtures were worked up in a manner similar to that described for DDA. Addition of the reaction mixtures to water gave weakly basic solutions. In the case of the *N,N'*-diethyl- and *N,N,N',N'*-tetramethyldiazenedicarboxamides the basic solutions remained clear, but solid reaction products precipitated upon acidification (see Table I). When added to water, reaction mixtures containing the substituted *N*-phenyl derivatives gave milky basic reaction mixtures; acidification gave the products shown in Table I.

In the case of *N,N'*-diphenyl-1,2-diazenedicarboxamide the crude reaction product consisting of 10 and 11 was resolved into its components by treatment with cold aqueous 5% sodium hydroxide. 1-*p*-Toluenesulfonyl-*N,N'*-diphenyl-1,2-diazenedicarboxamide (11) is insoluble in the cold alkali and can be purified by repeated recrystallization from benzene. The aqueous alkali solubles were acidified to precipitate 10; repeated recrystallization from acetic acid afforded analytically pure product (10).

Reaction of 1,2-Diazenedicarboxamide (DDA) with *p*-Acetamidobenzenesulfonic Acid. Solutions of DDA (2.32 g, 0.02 mol) in 50 ml of Me_2SO and *p*-acetamidobenzenesulfonic acid (3.98 g, 0.02 mol) in 25 ml of Me_2SO were combined. After several hours at room temperature, the clear, pale orange reaction mixture was added to 300 ml of water. The resulting clear, pale yellow solution was cooled to ice-bath temperatures and after ca. 0.5 hr, the mixture turned to a solid gelatinous mass.

The reaction mixture was filtered and the solid filter cake was washed consecutively with water, alcohol, and ether to give 5.5 g (87.5%) of crude 4, a white solid, mp 206–208° dec. A portion of the product (4) was recrystallized from glacial acetic acid to give analytically pure 4, mp 203–204.5° dec. Anal. Calcd for $C_{10}H_{13}N_5O_5S$ (4): C, 38.09; H, 4.15; N, 22.21; S, 10.17. Found: C, 38.16; H, 4.14; N, 22.17; S, 10.08. Still another portion (1.5 g) of the dried, crude reaction product (4) was dissolved in aqueous 10% sodium hydroxide. Acidification (3 *N* HCl) of the filtered, clear alkaline solution gave a crystalline white solid (1.0 g, 78%), mp 218–219° dec, that analyzed for *p*-acetamidobenzenesulfonyldiazane carboxamide (5). Anal. Calcd for $C_9H_{12}N_4O_4S$ (5): C, 39.70; H, 4.44; N, 20.58; S, 11.76; mol wt, 272.3. Found: C, 39.36; H, 4.93; N, 20.18; S, 11.85; mol wt, 281 (determined in DMF by vapor phase osmometry).

Reaction of Diethyl Diazenedicarboxylate with Zinc Bis(benzenesulfinate) (12). A solution of diethyl diazenedicarboxylate (DEDD, 3.48 g, 0.02 mol) in 25 ml of Me_2SO was combined with a solution of zinc bis(benzenesulfinate) (12, 3.47 g, 0.01 mol) in 50 ml of Me_2SO . The amber color of the diazene was immediately discharged and after several hours, the clear, colorless reaction mixture was added to 500 ml of water. A weakly alkaline mixture containing a finely divided white solid was filtered. The mixture was acidified and the water insoluble white solid was filtered. The washed and dried filter cake, 1-benzenesulfonyl diethyl-1,2-diazenedicarboxylate (13, 5.9 g, 93.5% yield) melted at 103–105°. One recrystallization from carbon tetrachloride gave analytically pure 13, mp 104–106°. Anal. Calcd for $C_{12}H_{16}N_2O_6S$ (13): C, 45.56; N,

5.10; N, 8.86; S, 10.14; mol wt, 316.3. Found: C, 45.55; H, 5.13; N, 8.78; S, 10.21; mol wt, 323 (determined in DMF by vapor phase osmometry).

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Registry No.—1, 24345-02-6; 2, 10396-10-8; 3, 10195-68-3; 4, 57049-47-5; 5, 10396-14-2; 6, 57049-48-6; 7, 57049-49-7; 8, 57049-50-0; 9, 57049-51-1; 10, 28744-07-2; 11, 57049-52-2; 12, 24308-84-7; 13, 57049-53-3; DDA, 123-77-3; sodium benzenesulfinate, 873-55-2; sodium *p*-toluenesulfinate, 824-79-3; sodium cyanate, 143-33-9; *N,N'*-diethyldiazenedicarboxamide, 18880-19-8; *N,N,N',N'*-tetramethyldiazenedicarboxamide, 10465-78-8; *N,N'*-diphenyl-1,2-diazenedicarboxamide, 17693-77-5; *N,N'*-diphenyl-1,2-diazenedicarboxamide, 57049-54-4; *p*-acetamidobenzenesulfonic acid, 710-24-7; diethyl diazenedicarboxylate, 1972-28-7.

References and Notes

- Presented in part at the International Symposium on Nucleophilic Substitution, Pocono Manor, Pa., April 13–18, 1975.
- The diazene derived nomenclature suggested for azo, hydrazo, etc., compounds by J. H. Fletcher, O. C. Dermer, and R. B. Fox, *Adv. Chem. Ser.*, No. 126, 246 (1974), is utilized in this paper. In accordance with the recommended nomenclature 1,1'-azobisformamide is referred to as 1,2-diazenedicarboxamide. The naming of other derivatives follows.
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- Although Me₂SO is the solvent of choice, DMF may also be used with similar results. In DMF as reaction solvent the rate of reaction may be reduced by cooling the reactants to ca. 5° prior to combining.
- After 16 hr absorptions attributed to reaction intermediates had disappeared.
- Absorptions attributed to the aromatic protons (A₂B₂ quartet) and the single NH proton were displaced ca. 0.7–0.8 ppm downfield from those in the isolated product 8. Similarly, absorptions assigned to the *N*-methyl and methyl arene protons were ca. 0.3–0.4 ppm downfield from their counterparts in 8.
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- N,N*-Diphenyl-1,2-diazanecarboxamide was obtained from the reaction of *N,N*-diphenyldiazanecarboxamide and isocyanic acid (from potassium cyanate and aqueous hydrochloric acid); material of mp 166–168° was used in this work.
- N,N,N',N'*-Tetra-phenyl-1,2-diazanecarboxamide was obtained (75.2% yield) from the reaction of diphenylcarbonyl chloride with diazane (triethylamine present as acid acceptor). Material of mp 213.5–217° (slow dec) was used in the current study.
- The diazane derivative (mp 246–247.5°, lit.¹⁸ mp 245°) was prepared 86% yield by treating phenyl isocyanate with diazane.
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- When the reaction was followed by NMR, indications were that the reaction was complete in ca. 1 hr and consequently work-up may be initiated sooner.
- (a) British Patent 896,497; *Chem. Abstr.*, 57, 11109 (1962); (b) U.S. Patent 3,152,176.

Thermal Decomposition of the Potassium Salts of Dinitroalkanes

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The potassium salts of phenyldinitromethane, 1,1-dinitroethane, and 1,1-dinitropropane decompose at 80° in DMF and other polar solvents in the presence of alkenes to yield Δ²-isoxazolines and potassium nitrate. When the alkene bears carboalkoxy groups, *cis* and *trans* isomeric alkenes yield only *trans* Δ²-isoxazolines. The *cis* isomer, 3-phenyl-4,5-dicarbethoxy-Δ²-isoxazoline, was found to isomerize to the more stable *trans* isomer under the conditions of the original thermal decomposition.

Torsell and Ryhage¹ have reported the thermal decomposition products of the potassium salts of polynitroalkanes to be mainly potassium nitrate and varying ratios of nitrous oxide and carbon dioxide with traces of other gases and potassium nitrite. They also reported ketene and a ketene dimer from the decomposition of potassium nitroethylnitronate in the mass spectrometer.

We report that in the presence of polar solvents such as dimethylformamide (DMF), dimethyl sulfoxide (Me₂SO), and dimethoxyethane the potassium salts of dinitroalkanes, 1, decompose at 80°C to yield carboxylic acids (more than 75%) and potassium nitrite (at least 95%). When an alkene intervenes under the same conditions, an isoxazoline and potassium nitrate are formed. We propose the nitrile oxide 4 as the immediate precursor of the isoxazoline 5. Intermediate 2 (or an electronically equivalent "nitrocar-

