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).

Acknowledgment. We are grateful to Professor D. Swern, Temple University, for helpful suggestions in preparing this manuscript and to Messrs. W. Y. Whitmore and A. G. Geigley for recording the NMR spectra.

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*-acetamidobenzenesulfinic acid, 710-24-7; diethyl diazenedicarboxylate, 1972-28-7.

References and Notes

(1) Presented in part at the International Symposium on Nucleophilic Substitution, Pocono Manor, Pa., April 13–18, 1975.
(2) 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.
(3) E. Fahr and H. Lind, *Angew. Chem., Int. Ed. Engl.*, **5**, 372 (1966).
(4) A. Hantzsch and R. Glogauer, *Ber.*, **30**, 2555 (1897).
(5) W. Bradley and J. D. Hannon, *J. Chem. Soc.*, 2713 (1962).
(6) P. Messinger, *Arch. Pharm. (Weinheim Ger.)*, **307**, 348–355 (1974).
(7) Although Me_2SO 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.
(8) After 16 hr absorptions attributed to reaction intermediates had disappeared.
(9) Absorptions attributed to the aromatic protons (A_2B_2 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**.
(10) Water was not added purposely nor were any attempts made to exclude it. Me_2SO was usually stored over molecular sieves prior to use.
(11) J. E. Herweh and R. M. Fantazier, *J. Org. Chem.*, **38**, 2650 (1973).
(12) Alternately, the initial step in the reaction might be regarded as an electron-transfer (redox) process, $ArSO_2^- + DDA \rightleftarrows [ArSO_2\cdot + DDA\cdot^-]$. This interpretation does not alter the significant steps in Scheme I, and may be a better explanation for the observed rates.
(13) R. M. Fantazier and J. E. Herweh, *J. Am. Chem. Soc.*, **96**, 1187 (1974).
(14) J. C. Kauer, "Organic Syntheses", Collect. Vol. IV, Wiley, New York, N.Y., 1963, p 411.
(15) *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.
(16) *N,N,N',N'*-Tetraphenyl-1,2-diazanedicarboxamide was obtained (75.2% yield) from the reaction of diphenylcarbamoyl chloride with diazane (triethylamine present as acid acceptor). Material of mp 213.5–217° (slow dec) was used in the current study.
(17) The diazane derivative (mp 246–247.5°, lit.[18] mp 245°) was prepared 86% yield) by treating phenyl isocyanate with diazane.
(18) T. Curtius and W. Burkhardt, *J. Prakt. Chem.*, **58**, 227 (1898).
(19) Warming to 40–45° may be necessary to obtain solution of each reactant.
(20) 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.
(21) (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

Abdur Rahman and Leallyn B. Clapp*

Chemistry Department, Brown University, Providence, Rhode Island 02912

Received August 8, 1975

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 Δ^2-isoxazolines and potassium nitrate. When the alkene bears carboalkoxy groups, cis and trans isomeric alkenes yield only trans Δ^2-isoxazolines. The cis isomer, 3-phenyl-4,5-dicarbethoxy-Δ^2-isoxazoline, was found to isomerize to the more stable trans isomer under the conditions of the original thermal decomposition.

Torssell and Ryhage[1] 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 (Me_2SO), 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-

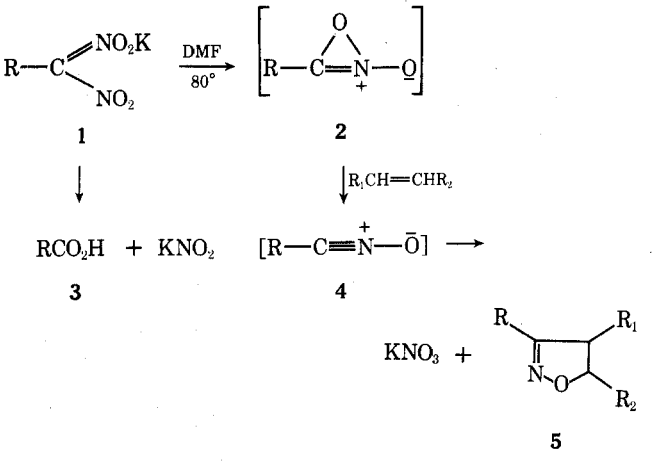
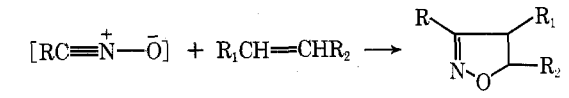


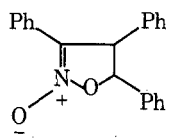
Table I
Formation of Δ^2-Isoxazolines by Thermal Decomposition of Potassium Salts of Dinitroalkanes with Various Dipolarophiles



Compd 5	R	R_1	R_2	Yield, %	Mp or bp, °C (mm)	J, Hz	δ, ppm C4H	δ, ppm C5H
a	Ph	CO_2Et	CO_2Et	52[a]	158–160 (0.2)	5.0	4.68	5.28
b	Ph	CO_2Me	CO_2Me	53[a,b]	50–51	5.0	4.75	5.35
c	Ph	H	OAc	70[b]	98–100	6.0[c], 2.0[d]	3.45	6.76
d	Ph	H	CO_2Et	39	150 (5)	8.5[c], 1.0[d]	3.5	5.01
e	Ph	H	OC_4H_9(n)	66	125–127 (1)		3.3	5.5
f	Ph	CO_2Et	Ph	40[a,e]	170–172 (0.8)	6.62	4.41	5.95
g	Ph	H	CH_2OEt	47	38–40		3.4	4.7
h	Et	H	OC_4H_9(n)	50[f]	75 (1)	6.0[c], 2.0[d]	2.78 2.51	5.12
i	Et	CO_2Et	CO_2Et	22[a]	75–77 (0.2)	6.0	4.4	5.18
j	Et	H	Ph	40[f]	135–137 (5)	6.2	3.2	5.3
k	Et	H	CO_2Et	55	125–127 (1)	8.5	3.79	5.46
l	Et	H	OAc	52[f]	36–38	6.0[c], 2.0[d]	2.9	5.75
m	Me	H	OC_4H_9(n)	60[f]	80–82 (3)	6.0[c], 3.0[d]	3.82	5.2
n	Me	CO_2Et	CO_2Et	26[f]	141–143 (3)	6.9	4.28	5.27
o	Me	H	CH_2OAc	50[f]	116–118 (3.5)		3.2	4.6
p	Me	H	OAc	55[f]	76–78	6.0[c], 2.5[d]	2.9	6.4
q	Me	H	Ph	51[f]	123–125 (3)	5.5	3.1	5.2
r	3-Methyl-4,5-diphenyl-Δ^2-oxadiazoline			10[f]	74–76			

[a] Trans isomer. [b] Reference 17. [c] Trans C4H. [d] Cis C4H. [e] F. Monforte and G. LoVecchio, *Gazz. Chim. Ital.*, **82**, 130 (1952); P. Grünanger, C. Gandini, and A. Quilico, *Rend. Ist. Lomb. Sci. Lett., Cl. Sci. Mat. Nat.*, **93A**, 467 (1959). [f] Reference 6. [g] Satisfactory analytical values (±0.3% for C, H, N) were reported for new compounds **5a–d,g–h**. Ed.

bene") should add an alkene to give an isoxazoline *N*-oxide but the known compound 3,4,5-triphenylisoxazoline *N*-oxide[2] (**6**) did not lose oxygen to potassium nitrite in DMF

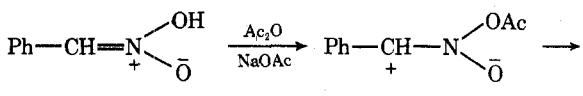


6

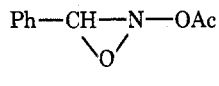
at 80° after 12 hr. Other reducing reagents, phosphorus trichloride,[3] sodium dithionite,[4] and zinc in acetic acid,[5] are known to remove such oxygens. We, therefore, exclude an isooxazoline *N*-oxide as the immediate precursor of **5**.

Benzhydroxamoyl chloride forms benzonitrile oxide in the presence of base at room temperature which dimerizes to diphenylfuroxane.[6] However, in DMF at 80° we obtained only benzoic acid from benzhydroxamoyl chloride. Diphenylfuroxane cannot have been the precursor of benzoic acid in this case because diphenylfuroxane is stable in DMF at 80°. No furoxanes were detected in the reactions in polar solvents at 80°. We conclude that **4** is the intermediate but 1,3-dipolar addition of the nitrile oxide to the alkene occurs faster than dimerization at the elevated temperature.

In related work, McKillop and Kobylecki[7] proposed the 1,3-dipolar intermediate, **7**, in the reaction of phenylnitromethane with acetic anhydride and sodium acetate.[8] Their



7



dipolar intermediate was highly selective, added only acetylenedicarboxylate to give an isoxazole, and did not lose acetic acid to give a nitrile oxide. Our proposed intermediate, **4**, was much less selective, as is known, and gave addition products with a number of less reactive dipolarophiles (Table I).

Since the results of the work of McKillop and Kobylecki differ from the present work, along with the stereochemical results (below), mutually exclusive intermediates, **4** and **7**, are warranted, as is suggested.

When the decomposition of the potassium salt of phenyldinitromethane was carried out at 80° in dimethylformamide in the presence of diethyl fumarate, a 52% yield of the Δ^2-isoxazoline **5a** was obtained. The NMR spectrum of the isoxazoline had peaks for protons at C4 (δ 4.68) and C5 (δ 5.28) corresponding to those reported[9] at C4 (δ 4.88) and C5 (δ 5.51) for the methyl ester **5b**.[10] The coupling constant for the trans protons (J = 5.0 Hz) was exactly that reported.[9]

When diethyl maleate was used as the trapping agent under the same conditions the more stable trans form **5a** was again obtained. To substantiate the isomerization, the cis 3-phenyl-Δ^2-isoxazoline was prepared by releasing benzonitrile oxide from benzhydroxamoyl chloride (Quilico's method[11]) at room temperature. Upon heating to 80° or within a few minutes upon standing at room temperature with a few drops of triethylamine the cis isoxazoline isomerized to the more stable trans form, **5a**.

By a similar procedure 3-phenyl-5-acetoxy-Δ^2-isoxazoline (**5c**) was obtained in 70% yield, mp 98–100° (lit.[10,12] 88–89°). The NMR spectrum for protons at C4 (δ 3.35, J = 2.0 Hz, and 3.45, J = 6.0 Hz) and at C5 (δ 6.75, doublet of doublets, J = 2.0 and 6.0 Hz) corresponded well with those calculated (δ 3.35, 3.38, and 6.81, respectively) for 3-phenylisoxazolines by Huisgen.[13] We obtained the lower melting point (as reported[10]) by Quilico's synthesis but recrystallization from carbon tetrachloride gave a higher

melting point. The melting point phenomenon appears to be a case of isomorphic crystals, since a third author has reported[14] the melting point 90–91°, remelting at 107–108°. Acetic acid was lost from **5c** at 160° to give 3-phenylisoxazole.[14]

Thermal decomposition of potassium 1-nitropropylnitronate in diethyl maleate in the presence of Me_2SO resulted in the isolation of *trans*-3-ethyl-4,5-dicarbethoxy-Δ^2-isoxazoline (**5i**). An identical product was obtained when propionitrile oxide, generated by Mukaiyama's method,[6] was added to diethyl maleate. The trans stereochemistry was assigned from the following argument on coupling constants. The coupling constants of C4 and C5 protons of a number of 3-phenyl-Δ^2-isoxazolines were reported[6] and it was shown that trans protons had J values in the range 4.4–6.6 Hz, whereas the cis protons had J values in the range 9.5–11.37 Hz. The coupling constant of C4 and C5 protons shown in the NMR spectrum of **5i** was 6.0 Hz, suggesting trans stereochemistry.

With vinyl acetate as the dipolarophile 3-ethyl-5-acetoxy-Δ^2-isoxazoline was prepared. On heating to 160° it also lost a molecule of acetic acid and was converted to 3-ethylisoxazole, a known compound.[6]

The 3-methyl-Δ^2-isoxazolines **5m–q** and the 1,2,4-oxadiazoline **5r** (Table I) were also obtained by the thermal decomposition of potassium nitroethylnitronate in vinyl *n*-butyl ether, diethyl maleate, allyl acetate, vinyl acetate, styrene, and benzalaniline, respectively, in the presence of DMF. The characterization of these compounds was made by their NMR and ir spectra and by synthesis of each from nitroethane. The compound 3-methyl-5-acetoxy-Δ^2-isoxazoline (**5p**) was also converted on heating (in 80% yield) to 3-methylisoxazole, a known compound.[14]

Thermal decomposition of potassium phenylnitromethylnitronate in DMF alone gave benzoic acid, polymeric material, and potassium nitrite, the latter identified through quantitative liberation of nitrogen gas from sulfamic acid.[15] The potassium salts of 1,1-dinitropropane and 1,1-dinitroethane gave propionic and acetic acids, respectively, under the same conditions. Whether the hydrogen came from the solvent, DMF, was not determined. Liu and Toriyama[16] reported that thermal decomposition of 3-chloro-3-phenylazirine in Me_2SO or dimethoxyethane gave benzoic acid.

Experimental Section

Melting points are corrected; boiling points are not corrected. *N,N*-Dimethylformamide (DMF) and dimethyl sulfoxide (Me_2SO) were dried over a molecular sieve, Linde type 3A (1/16 in.), before use. Instruments used were a Perkin-Elmer Model 257 infrared spectrophotometer and a Varian A-60A proton magnetic resonance spectrometer.

***trans*-3-Phenyl-4,5-dicarbethoxy-Δ^2-isoxazoline (5a). A. From Diethyl Fumarate.** Potassium phenylnitromethylnitronate (4.4 g, 0.02 mol) and 40 ml of diethyl fumarate was stirred with a magnetic stirrer in a 250-ml round-bottomed flask connected with a water condenser, protected from moisture with a calcium chloride guard tube and heated to 80°. *N,N*-Dimethylformamide was then added slowly until a clear solution was obtained (about 40 ml). After 2 hr a white precipitate of potassium nitrate started settling out but the stirring was continued for another 20 hr. The solution was filtered under suction and the precipitate of potassium nitrate (1.9 g, 94%) was washed with 10 ml of ether. The potassium nitrate gave the old brown ring test and failed to liberate nitrogen gas from sulfamic acid.[15] Washings and the filtrate were transferred to a separatory funnel and treated with 60 ml more of ether. The DMF was removed by washing three times with 30-ml portions of water. The ethereal layer was dried over anhydrous sodium sulfate and the ether evaporated on a rotary evaporator. The yellow solution was distilled under reduced pressure to remove diethyl fumarate and traces of DMF. *trans*-3-Phenyl-4,5-dicarbethoxy-Δ^2-isoxazoline was then collected at 158–160° (0.2 mm), yield 3.0 g (52%).

B. From Diethyl Maleate. A mixture of 2.2 g (0.01 mol) of potassium phenylnitromethylnitronate, 20 ml of diethyl maleate, and 20 ml of *N,N*-dimethylformamide was stirred at 80° in a 250-ml round-bottomed flask for 24 hr. A precipitate of potassium nitrate was obtained which was filtered. The solution was transferred to a separatory funnel and treated with 30 ml of ether, washed three times with 20-ml portions of water. The ethereal layer was dried over anhydrous sodium sulfate. Ether and diethyl maleate were removed by distillation under reduced pressure and the *trans*-3-phenyl-4,5-dicarbethoxy-Δ^2-isoxazoline was collected at 158–160° (0.2 mm). The NMR and ir spectra of the compound obtained using diethyl fumarate and diethyl maleate were identical, yield 1.48 g (50%).

C. By Isomerization of *cis*-3-Phenyl-4,5-dicarbethoxy-Δ^2-isoxazoline. Benzonitrile oxide was generated by Quilico's method[11] in the presence of diethyl maleate to give *cis*-3-phenyl-4,5-dicarbethoxy-Δ^2-isoxazoline. A sample of the reaction mixture was removed and its NMR spectrum verified the cis configuration for this method of synthesis: NMR ($CDCl_3$) C4 H δ 4.5, d, 1, J = 11.0 Hz; C5 H, 5.2, d, 1, J = 11.0 Hz.

The isolated cis isoxazoline was warmed on a hot plate until it changed color from light yellow to orange-yellow (15 min). The cis form was totally isomerized to the trans compound as determined by an NMR spectrum (Table I). The same result was obtained by treating the cis isoxazoline with a few drops of triethylamine at room temperature.[17]

3-Phenyl 5-Substituted Δ^2-Isoxazolines. Potassium phenylnitromethylnitronate (0.015 mol) was mixed with 40 ml of the monosubstituted volatile olefin (for **5c–e**) and stirred magnetically in a 150-ml round-bottomed flask at 70°. After 0.5 hr, 30 ml of DMF was slowly added through the condenser, and the stirring was continued for 24 hr. A white precipitate of potassium nitrate settled out during this time. A condenser set downward for distillation was connected and the olefin was stripped from the solution at reduced pressure. The residue was transferred to a separatory funnel, 50 ml of ether was added, and the solution was washed with three 30-ml portions of water. The ethereal layer was dried over anhydrous sodium sulfate. The yellow oil remaining after removal of the ether was distilled at reduced pressure.

The solid isoxazolines, **5b** and **5f**, were prepared in the same way and recrystallized from absolute methanol.

The 3-methyl-Δ^2-isoxazolines **5m–r** were prepared in an analogous manner. However, the reactions to prepare 3-ethyl-Δ^2-isoxazolines **5h–l** were carried out in Me_2SO because of the better solubility of potassium nitroethylnitronate in this solvent.

Attempted Deoxygenation of 3,4,5-Triphenyl-Δ^2-isoxazoline *N*-Oxide. One gram of 3,4,5-triphenyl-Δ^2-isoxazoline *N*-oxide[2] in 15 ml of dry DMF was allowed to react with 1 g of potassium nitrite at 80° with constant stirring for 12 hr. The potassium nitrite and DMF were washed out with water and the unreacted *N*-oxide was recovered quantitatively.[18]

Warning: It is unwise to use more than 0.02 mol of the potassium salts of dinitroalkanes in any new experiment as they are explosive. However, 1,1-dinitroethane and 1,1-dinitropropane were distilled as colorless liquids that have remained colorless in our laboratory for 22 years. Potassium 1-nitropropylnitronate was also stable in the bottle over the same period but potassium 1-nitroethylnitronate should only be prepared before use. The salts were prepared by the ter Meer reaction.[19]

Registry No.—**1** (R = Ph), 28198-51-8; **1** (R = Et), 33552-85-1; **1** (R = Me), 2517-91-1; *trans*-**5a**, 57065-93-7; *cis*-**5a**, 57065-94-8; **5b**, 17669-31-7; **5c**, 7064-07-5; **5d**, 50899-14-4; **5e**, 50899-19-9; **5f**, 17669-34-0; **5g**, 57065-95-9; **5h**, 57065-96-0; **5i**, 57065-97-1; **5j**, 55134-83-3; **5k**, 57065-98-2; **5l**, 57065-99-3; **5m**, 57066-00-9; **5n**, 57066-01-0; **5o**, 57066-02-1; **5p**, 7063-89-0; **5q**, 7064-06-4; **5r**, 18885-88-6; diethyl fumarate, 623-91-6; diethyl maleate, 141-05-9; vinyl *n*-butyl ether, 111-34-2; allyl acetate, 591-87-7; vinyl acetate, 108-05-4; styrene, 100-42-5; benzalaniline, 538-51-2; dimethyl fumarate, 624-49-7; ethyl acrylate, 140-88-5; ethyl cinnamate, 103-36-6; allyl ethyl ether, 557-31-3.

References and Notes

(1) K. Torssell and R. Ryhage, *Ark. Kemi*, **23**, 525 (1965).
(2) E. P. Kohler, *J. Am. Chem. Soc.*, **52**, 2038 (1930).
(3) F. T. Boyle and R. A. Y. Jones, *J. Chem. Soc., Perkin Trans. 1*, 167 (1973); M. Hamana, *J. Pharm. Soc. Jpn.*, **75**, 121 (1955); E. Ochiai, M. Ikehara, T. Kato, and N. Ikekawa, *ibid.*, **71**, 1385 (1951).

(4) J. P. Freeman and J. J. Cannon, *J. Heterocycl. Chem.*, **3**, 544 (1966).
(5) J. P. Freeman and J. J. Cannon, *J. Org. Chem.*, **34**, 194 (1969).
(6) T. Mukaiyama and T. Hoshino, *J. Am. Chem. Soc.*, **82**, 5339 (1960).
(7) A. McKillop and R. J. Kobylecki, *Tetrahedron*, **30**, 1365 (1974).
(8) F. R. Stermitz and D. W. Neiswander, *Tetrahedron*, **31**, 655 (1975); F. R. Stermitz and F. A. Norris, *J. Org. Chem.*, **35**, 527 (1970).
(9) M. C. Aversa, G. Cum, and M. Crisafulli, *Gazz. Chim. Ital.*, **98**, 42 (1968).
(10) A. Quilico and P. Grünanger, *Gazz. Chim. Ital.*, **85**, 1449 (1955).
(11) A. Quilico, G. Stagno d'Alcontres, and P. Grünanger, *Nature (London)*, **166**, 226 (1950).
(12) G. Stagno d'Alcontres and P. Grünanger, *Gazz. Chim. Ital.*, **80**, 741 (1950).
(13) R. Sustmann, R. Huisgen, and H. Huber, *Chem. Ber.*, **100**, 1802 (1967).
(14) R. G. Micetick, *Can. J. Chem.*, **48**, 467 (1970).
(15) L. B. Clapp, *J. Chem. Educ.*, **20**, 189 (1943).
(16) T. H. Liu and K. Toriyama, *Can. J. Chem.*, **50**, 3009 (1972).
(17) A. Quilico and P. Grünanger, *Gazz. Chim. Ital*, **85**, 1250 (1955).
(18) This experiment was taken from the M.S. Thesis of Miss Nazir Anjum, Punjab University, Lahore, Pakistan, 1975.
(19) E. ter Meer, *Justus Liebigs Ann. Chem.*, **181**, 4 (1876); L. F. Fieser and W. von E. Doering, *J. Am. Chem. Soc.*, **68**, 2252 (1946).

Iodonium Ylides. Reactions of Phenyldimedonyliodone with Several Thiocarbonyl Compounds. Evidence for Sulfur Ylide Intermediates

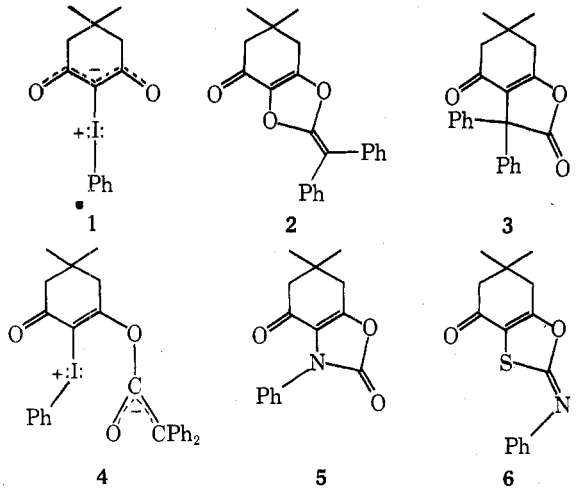
Gerald F. Koser* and Shwn-Meei Yu

Department of Chemistry, The University of Akron, Akron, Ohio 44325

Received July 14, 1975

When phenyldimedonyliodone (1) was allowed to react with phenyl isothiocyanate, the products were iodobenzene, 7 (8%), 8 (36%), and 9 (14%). Similar reaction of 1 with methyl isothiocyanate gave 7 (35%) and 9 (26%). The intermediacy of sulfur ylide 11, an analogous sulfur ylide from 1 and methyl isothiocyanate, and thiotrione 12 in those reactions seems to be indicated. An attempt to synthesize authentic 12 by treatment of 1 with hydrogen sulfide failed. However, compound 9 was isolated in 40% yield. Finally, when 1 was allowed to react with thiourea, the delocalized sulfur ylide 13 was obtained (67%).

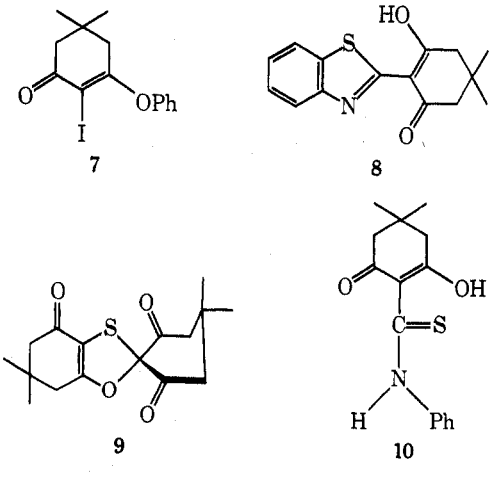
The formation of halonium ylides as reactive intermediates when certain carbenes are generated in the presence of organic halides is now a matter of record.[1-7] However, because of their instability, the halonium ylides have largely eluded isolation and study. Partially for that reason, we began an investigation of the chemical properties of phenyldimedonyliodone (1), a stable iodonium ylide which can be prepared by the condensation of dimedone with iodosobenzene diacetate.[8] Our first objective was to characterize the reactivity of 1 toward several electrophilic heterocumulenes, and we have already reported that 1 reacts with diphenylketene to afford ketene acetal 2 and lactone 3, presumably through the betaine 4, while phenyl isocyanate reacts with 1 to afford azalactone 5.[9] We now wish to report that the reaction of 1 with phenyl isothiocyanate takes a markedly different course, and, while we fully expected to obtain adduct 6, that compound was not isolated. In connection with this, the reactions of 1 with methyl isothiocyanate, hydrogen sulfide, and thiourea were also studied.



1 2 3 4 5 6

Results and Discussion

When phenyldimedonyliodone (1) and phenyl isothiocyanate were allowed to react in dichloromethane at room temperature, three products were obtained. One of these, isolated in 8% yield, was identified as phenyl 2-iododimedonyl ether (7), a known rearrangement product.[10] A second compound, isolated in 36% yield, was 2-(2-benzthiazolyl)dimedone (8), the structure of which was confirmed by its comparison with authentic material prepared by the action of bromine on dimedone-2-thiocarboxanilide (10).[11]



7 8 9 10