peratures, 3 can also extrude 1, leaving the coordinatively unsaturated dinuclear complex B which rapidly dimerizes to 5. At no time do we observe any 2 in these reactions[3] and therefore suggest that it is formed by reaction of 1 or a derived photoproduct with trace amounts of atmospheric oxygen.

Acknowledgments. We are grateful to the National Science Foundation and the Chevron Research Corporation for partial support of this work.

(13) Camille and Henry Dreyfus Foundation Teacher–Scholar, 1970–1975.

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Convenient Synthesis of Silver Hyponitrite

Sir:

Silver hyponitrite is the starting material for the synthesis of alkyl hyponitrites, which are useful low-temperature sources of alkoxy radicals.[1-5] Numerous syntheses of sodium and silver hyponitrites have appeared in the literature.[5-9] Most are tedious, hazardous, poorly described, or require large quantities of mercury. In our hands, one procedure gave no product and the reaction mixture from another ignited during work-up.

The method described below is a modification of that of Weitz and Vollmer[10] which takes advantage of the known solubility of sodium in benzophenone solutions.[11] The yield is low (it might be improved by inverse addition), but the synthesis is shorter and more convenient than earlier procedures. The reaction of sodium in hexamethylphosphoramide[12] with nitric oxide proceeded exothermically, but the product was more difficult to isolate.

A 500-ml three-necked flask was equipped with a gas inlet, a magnetic stirrer, and an outlet connected to a bubbler. The inlet tube was connected by a T-joint so either N_2 or NO could be added. The flask was charged with 100 ml of 1,2-dimethoxyethane and 150 ml of toluene (each distilled from blue Na and benzophenone solutions). Benzophenone (26 g) was added and the solution was flushed with N_2. Sodium (6.9 g) was then extruded as wire into the solution, and the flask was surrounded by an ice bath. After flushing with N_2, stirring was begun, and nitric oxide was admitted at a rate such as to maintain a slight positive pressure. Shaking the flask greatly increased the rate of gas uptake. The re-

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(10) E. Weitz and W. Vollmer, *Ber.*, **57**, 1015 (1924).
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action was nearly complete within 20 min. After stirring 1 hr under NO, the solution was flushed with N_2. Water (10 ml) was added dropwise with stirring (foaming), and the solution was extracted with additional water (70 ml) in three portions. Absolute ethanol (200 ml) was added to the combined extracts, and the solution was swirled with cooling if necessary to induce crystallization. The Na salt was filtered off and washed with absolute ethanol and ether. After drying in air, the cream solid weighed 3.5 g but contained bound ethanol and water.

A solution of silver nitrate (6.0 g) in water (600 ml) was added slowly with vigorous stirring to a 1 % solution of the Na salt until the precipitate began to discolor.[13] About 420 ml was required. The product was filtered off, washed with water, and dried over P_2O_5 at 25° and 0.5 Torr. The yellow solid contained 77.5 % Ag (Volhard method[14]) and weighed 3.5 g (8 % based on Na). With excess methyl bromide the product afforded methyl hyponitrite, a spontaneously explosive liquid that will be described elsewhere in detail.

Acknowledgment. This work was supported, in part, by Grant R 802288 from the Environmental Protection Agency.

(13) The product is black if silver is in excess.[7]
(14) H. H. Willard, N. H. Furman, and C. E. Bricker, "Elements of Quantitative Analysis," 4th ed, D. Van Nostrand Co., Princeton, N. J., 1956, p 129.

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Chemistry of the Sulfur–Nitrogen Bond. VIII. N-Alkylidenesulfinamides[1]

Sir:

We wish to report the synthesis of a new class of reactive sulfur–nitrogen compounds,[2] N-alkylidenesulfinamides (N-(arylsulfinyl)imines), 1. Compounds 1a–e were prepared in good yield by dropwise addition of 1 equiv of m-chloroperbenzoic acid to a two-phase system containing the corresponding N-alkylidenesulfenamides[3] in chloroform and water–sodium bicarbonate. Although the C–N double bond in imines is known to be oxidized to oxaziridines[4] under these conditions, we were unable to detect any of these products.
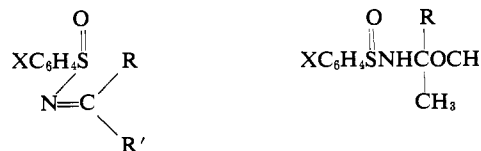
1a, X = H; R = R' = CH₃
b, X = H; R = H; R' = C₆H₅
c, X = 4-Cl; R = H; R' = C₆H₅
d, X = 3-NO₂; R = H; R' = CH₃
e, X = 3-NO₂; R = H; R' = C₆H₅

2a, X = H; R = CH₃
b, X = 3-NO₂; R = H

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(3) F. A. Davis, W. A. R. Slegeir, S. Evans, A. Schwartz, D. L. Goff, and R. Palmer, *J. Org. Chem.*, **38**, 2809 (1973).
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Table I. Thermal Decomposition of N-Alkylidenesulfinamides

Sulfinimine	% yield	Mp, °C	Solvent[a]	Temp, °C	Time, hr	Products[b] (% yield)
1b	92	78–79	Benzene	80	36	**6b** (44), **7b** (44),[c] **4** (82)
			Ethyl acrylate	90	15	**8a** (60),[11] **7b** (10), **4** (71)
1c	93	95–96	Benzene	80	36	**6c** (35), **7c** (24),[d] **4** (75)
			Ethyl acrylate	90	15	**8b** (77),[11] **4** (77)
1d	95	84–15	Benzene	80	15	**6d** (51), **7d** (20)[e]
			Methyl propynoate	100	15	**9** (71)
1e	85	96–98	Benzene	80	24	**6e** (31), **7e** (29),[e] **4** (85)
			Ethyl acrylate	90	14	**8c** (56), **7e** (10)
			Methyl propynoate	90	14	**9** (72)

[a] Molar ratio of ethyl acrylate and methyl propynoate to sulfinimines, 25:1 and 15:1, respectively. [b] Determined by a combination of gas chromatography and column chromatography. [c] S. Oae, R. Nomara, Y. Yoshikawa, and W. Tabaki, *Bull. Chem. Soc. Jap.*, **42**, 2903 (1969). [d] G. Bulmer and F. Mann, *J. Chem. Soc.*, 684 (1945). [e] G. Leandri and A. Tundo, *Ann. Chim. (Paris)*, **44**, 255 (1954); *Chem. Abstr.*, **49**, 15782h (1955).

N-Alkylidenesulfinamides **1b–e** were crystalline solids whereas **1a** was an oil for which a satisfactory analysis could not be obtained. The infrared spectra of **1a–e** showed strong S–O stretching at 1080 cm^{-1}. The diastereotopic methyl groups in **1a** consist of a broad doublet at ambient temperature which reversibly coalesced to a singlet at 55°. The calculated[5] free energy ($\Delta G^{\ddagger}$) for stereomutation was 17.0 kcal/mol and is 3 kcal/mol lower than that observed for the corresponding N-alkylidenesulfenamide.[6]

Whereas **1b** was obtained as a single diastereomer its precursor was a 56/44 mixture of *E* and *Z* diastereomers.[3] The preference for a single diastereomer for **1b**, presumably *E*, may reflect an enhanced stability as a result of an attractive interaction between the sulfinyl oxygen and the proton on the imino carbon (*vide infra*).

N-Alkylidenesulfenamides have proven to be relatively stable compounds with most of their reactions occurring at the S–N rather than the C–N bond.[1] By contrast the sulfinyl group in **1a–e** greatly activates the C–N double bond. Compound **1a** was the most reactive and was rapidly hydrolyzed in moist air to benzenesulfinamide.

Both **1a** and **1d** rapidly react with methanol to give adducts **2a–b** in 90 and 50% yields, respectively. Adduct **2b** was formed as a 70/30 mixture (by nmr) of two diastereoisomers.[7] N-Benzylidenesulfinamides, **1b**, **c**, and **e**, were more stable and failed to react with water or alcohols under comparable conditions.

N-Alkylidenesulfinamides prepared from aldehydes undergo a Cope-type elimination to yield arylsulfenic acids (**3**). Sulfenic acids have been implicated in a wide variety of organsulfur reactions[8] but have been little studied owing to their inherent instability. When heated in benzene for 15–36 hr, **1b–c** decompose to give disulfide (**6**), thiolsulfonate (**7**), and nitrile (**4**) as major products[9] (Scheme I). These results are summarized in Table I.

(5) The free energy for stereomutation was calculated from the equation $K_c = \Delta v_0 \, \pi/2^{1/2}$ and the Eyring equation ($\Delta v_0 = 13.5$ Hz).
(6) F. A. Davis, W. A. R. Slegeir, and J. M. Kaminski, *J. Chem. Soc., Chem. Commun.*, 634 (1972).
(7) The major isomer crystallized as yellow plates mp 96–97° and minor isomer as white needles, mp 101–102°.
(8) (a) N. Kharasch in "Organic Sulfur Compounds," Vol. 1, N. Kharasch Ed., Pergamon Press New York, N. Y., 1961, Chapter 32; (b) E. Block, *J. Amer. Chem. Soc.*, **94**, 642 (1972); (c) J. R. Shelton and K. E. Davis, *ibid.*, **89**, 718 (1967); *Int. J. Sulfur Chem.*, **3**, 197, 205 (1973); (d) J. E. Baldwin, G. Hofle, and S. C. Choi, *J. Amer. Chem. Soc.*, **93**, 2810 (1971); (e) B. C. Pal, M. Uziel, D. G. Doherty, and W. E. Cohn, *ibid.*, **91**, 3634 (1969); (f) R. D. G. Copper, *ibid.*, **92**, 5010 (1970); (g) T. S. Chou, J. R. Burgtorf, A. L. Ellis, S. R. Lammert, and S. P. Kukolja, *ibid.*, **96**, 1609 (1974).
(9) A number of minor products were detected whose structures are under investigation.
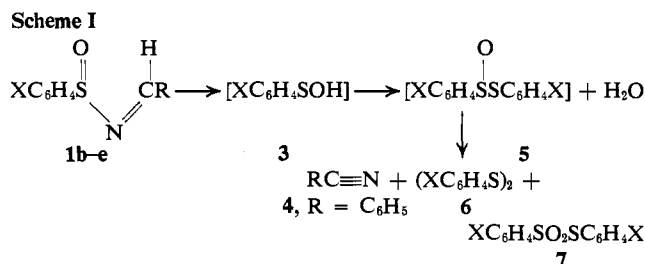
Scheme I

The isolation of **4**, **6**, and **7** in the thermal decomposition of **1b–e** is consistent with the formation of an arylsulfenic acid, **3**, which gives the thiolsulfinate, **5**, and water[10] (Scheme I). Arylthiosulfinates are unstable and disproportionate to give disulfide and thiolsulfonate.[11] Alkylsulfenic acids prepared by the decomposition of thiolsulfinate esters[8b] and *tert*-butyl sulfoxide[8c] gave alkyl thiolsulfinate esters.

The formation of the sulfenic acid was confirmed by trapping experiments with ethyl acrylate or methyl propynoate to give **8** and **9**[12] (Table I).

8a, X = H
b, X = 4-Cl
c, X = 3-NO₂
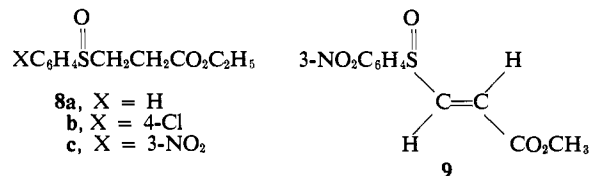
N-Alkylidenesulfinamides are a potentially useful intermediate for organic synthesis and are a mild, high yield[13] source of arylsulfenic acids.

(10) Water as detected in the decomposition of **1b–e**.
(11) P. Koch, E. Ciuffarin, and A. Fava, *J. Amer. Chem. Soc.*, **92**, 5971 (1971); D. Barnard, *J. Chem. Soc.*, 4675 (1957).
(12) Adducts **8a** and **c** were oils that decomposed on heating; **8b** was a solid, mp 78–79°. Compounds **8a** and **b** were prepared independently by condensing the corresponding thiol with ethyl acrylate followed by oxidation with *m*-chloroperbenzoic acid. Adduct **9** crystallized from ether as white needles, mp 91–92; *J* = 15 Hz.
(13) As indicated by the yield of benzonitrile isolated (Table I).

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Crotyllithium by Direct Metalation.
Relative Stabilities of *Z*- and *E*-Crotyl Anions[1]

Sir:

In 1965 Bank, Schriesheim, and Rowe rationalized the rapid base-catalyzed isomerization of 1-butene to *Z*-2-

(1) Presented in part at the First Fall Organic Conference, American Chemical Society, N. Falmouth, Mass., Sept 30, 1973.