The fluorosulfonate **2a**[12] was selected for initial study because fluorosulfuric acid is one of the strongest known pure acids[14] and as a result the fluorosulfonate ion would be expected to be a very effective leaving group. That this is actually the case was apparent when it was found that triphenylvinyl fluorosulfonate undergoes acetolysis to triphenylvinyl acetate[15] at room temperature (25°, half-life 33 hr).

Rate studies led to specific rate constants and activation parameters which are recorded in Table I. In all reactions the rates were cleanly first order. Changes in sodium acetate concentration showed only small effects on the rate, thus excluding either an SN2 substitution reaction by acetate or an acetate addition–elimination reaction. A change from proteated to deuterated solvent also showed essentially no effect on the rate. The absence of a solvent isotope effect can be taken as strong evidence[16] against the addition mechanism that was demonstrated by Peterson and Indelicato[7] for the solvolysis of 1-cyclohexenyl and *cis*-2-buten-2-yl tosylates. Support for this conclusion is found in the facts that the acetolysis of triphenylvinyl tosylate is about 10^4 slower than that of the fluorosulfonate.

Table I. Rate Constants and Activation Parameters for Acetolysis of Vinyl Sulfonates at 150.8°

Compd	k, sec^{-1}	k_{rel}	$\Delta H^{\pm}$, kcal/mol	$\Delta S^{\pm}$, eu
2a	0.699[a-d]	13,500	23.3	−6.5
2b	2.16[a-c]	41,700	24.3	−2.0
2c	5.18×10^{-5} [e,f]	1	25.7	−20.3

[a] Extrapolated from rate data obtained at lower temperatures. [b] Acetolysis kinetics followed by uv. [c] About 10^{-4} *M* in ester. Buffered with approximately 25 *M* excess of sodium acetate. [d] The acetolysis of this compound was also followed titrimetrically. The rate constant was identical with that obtained by the uv method. [e] Acetolysis kinetics followed titrimetrically. [f] About 0.005 *M* in ester. Buffered with slight molar excess of sodium acetate.

While this work was under way Streitwieser, Wilkens, and Kiehlmann[17] reported a study of the acetolysis of ethyl trifluoromethanesulfonate (triflate). It was found that the triflate undergoes solvolysis some 30,000 times faster than the tosylate. Inasmuch as fluorosulfuric acid and trifluoromethanesulfuric acid have both been submitted as candidates for the strongest known pure acid,[14,18] we felt that it would be interesting to compare the rates of solvolysis of the vinyl fluorosulfonate with the corresponding vinyl triflate.[19] Acetolysis occurred 3.1 times (150.8°) faster than the fluorosulfonate, thus indicating that the trifluoromethanesulfonate ion is a slightly better leaving group (in this system) than the fluorosulfonate ion.[20]

Acetolysis of triphenylvinyl tosylate was also examined. Although the rate of the reaction was over 10^4 slower than the corresponding fluorosulfonate or triflate a change from proteated to deuterated solvent once again showed essentially no effect on the rate and as a result we must conclude that this reaction also proceeds by a simple heterolysis mechanism.

Finally, it is interesting to attempt to compare the rate of ionization of the unsaturated system with a suitable aliphatic sulfonate. For a model, we have selected the tosylate of 1,2,2,2-tetraphenylethanol. Although solvolysis of this material has not been reported, a solvolysis rate constant of at least 10^{-3} at 25° can be extrapolated from known systems[21] with fair confidence.[22] Extrapolation of the rate of acetolysis of triphenylvinyl fluorosulfonate to 25° gives a rate constant of about 10^{-5}. Assuming an acceleration of the fluorosulfonate relative to the tosylate of at least 10^4 gives a difference of 10^6 between the vinyl and the saturated sulfonates.[23] Although numerous assumptions are included in this game with numbers, it certainly points up the fact that bonding a sulfonic acid ester to a carbon–carbon double bond dramatically reduces its tendency to ionize. The probable reasons for this have been amply discussed elsewhere.[5,7]

Acknowledgment. The authors gratefully acknowledge support for this work received from the Petroleum Research Fund administered by the American Chemical Society.

(12) To the best of our knowledge, the synthesis of only one other vinyl fluorosulfonate has been reported.[13]

(13) M. A. Belaventsev, G. A. Sokol'skiy, and I. L. Knunyants, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2461 (1967); *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 2344 (1967).

(14) R. J. Gillespie, *Accounts Chem. Res.*, 1, 202 (1968).

(15) The triphenylvinyl fluorosulfonate and the triphenylvinyl triflate gave essentially quantitative yields of triphenylvinyl acetate from their acetolysis. The triphenylvinyl tosylate gave a 39% yield of the corresponding acetate.

(16) For lead references on solvent isotope effects on similar systems see D. S. Noyce and R. M. Pollack, *J. Am. Chem. Soc.*, 91, 119 (1969).

(17) A. Streitwieser, Jr., C. L. Wilkins, and E. Kiehlmann, *ibid.*, 90, 1598 (1968).

(18) T. Gramstad, *Tideskr. Kjemi, Bergvesen Met.*, 19, 62 (1959). R. N. Haszeldine and J. M. Kidd, *J. Chem. Soc.*, 4228 (1954); E. S. Lane, *Talanta*, 8, 849 (1961); R. E. Banks and R. N. Haszeldine in "The Chemistry of Organic Sulfur Compounds," Vol. II, N. Kharasch and C. Y. Meyers, Ed., Pergamon Press, New York, N. Y., 1966, Chapter 6.

(19) The authors express their appreciation to Minnesota Mining for furnishing us with a sample of trifluoromethanesulfuric acid which was used for this synthesis.

(20) An ionization mechanism (in contrast to an addition–elimination mechanism) is further supported by the observation that solvolysis of the vinyl triflate goes 1.6 times faster in 98% aqueous ethanol than in acetic acid. Grunwald and Winstein *Y* values (E. Grunwald and S. Winstein, *J. Am. Chem. Soc.*, 70, 846 (1948)) predict similar "ionizing power" for these two solvents. Similar rates would not be expected for the addition–elimination mechanism.[7] By varying the water content, an "*m*" value of 0.56 was obtained. The predominant product in all cases was triphenylvinyl ethyl ether.

(21) H. C. Brown, R. Bernheimer, and K. J. Morgan, *J. Am. Chem. Soc.*, 87, 1280 (1965); S. Winstein and H. Marshall, *ibid.*, 74, 1120 (1952); S. Winstein and B. K. Morse, *ibid.*, 74, 1133 (1952).

(22) This includes an approximate steric acceleration from the three β-phenyls of 400. Miller and Kaufman[5] report no steric acceleration (in fact, small retardation) from the two β-phenyl groups in the ionization of α-phenylvinyl halides. This surprising difference between the saturated and unsaturated systems is presently under investigation for the sulfonic acid ester systems. If no steric acceleration is found, then our model is obviously a poor one.

(23) Peterson and Indelicato[7] estimate a minimum rate difference of 5.7×10^4.

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Received May 9, 1969

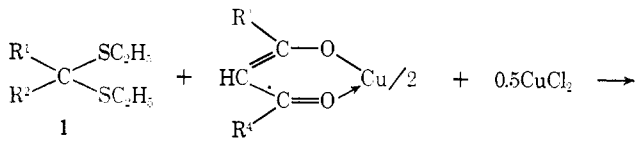
The Reactions of Bivalent Sulfur Compounds–Copper(II) Complexes

Sir:

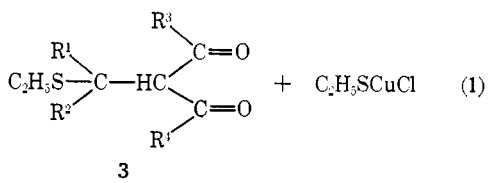
In this communication, the reactions of the bivalent sulfur compounds, such as benzaldehydediethylmercaptal (**1a**), benzophenone diethyl mercaptole (**1b**), and

ethyl orthotrithioformate (**1c**) with copper(II) salts of 1,3-dicarbonyl compounds, active methylene compounds, or aromatic compounds such as anisole, in the presence of $CuCl_2$, are reported.

Relatively little work has been reported on a synthetic study by the use of copper(II) salts of 1,3-dicarbonyl compounds probably due to their great stability.[1] In fact, even when bis(acetylacetonato)copper(II) (**2a**) and **1a** are refluxed in dioxane, reaction does not occur and the starting materials are recovered quantitatively. On the other hand, when **1a** and **2a** are stirred in the presence of a 0.5 *M* amount of $CuCl_2$ in THF at room temperature, a blue precipitate of **2a** disappears and a green precipitate appears immediately. This precipitate disappears soon and the solution turns clear. After being stirred for 9 hr, 3-(α-ethylmercaptobenzyl)-pentane-2,4-dione is obtained in 92% yield. In all cases, C-substituted products are produced exclusively and no detectable amount of O-substituted product is obtained.



1 **2**

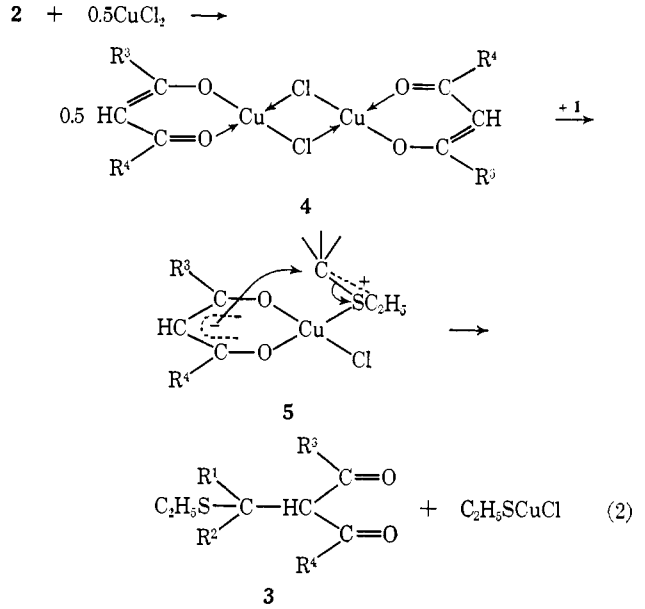


3 (1)

R^1	R^2	R^3	R^4	Yield, %
CH_3	CH_3	C_6H_5	C_6H_5	55
C_6H_5	C_6H_5	H	SC_2H_5	73
C_6H_5	C_6H_5	H	C_6H_5	82
CH_3	OC_2H_5	H	C_6H_5	58

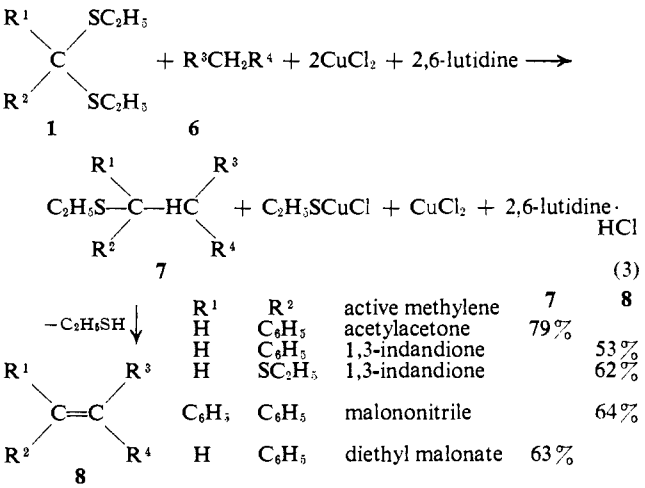
The reaction may be explained by assuming an initial formation of a double nuclear complex (**4**) from **2** and $CuCl_2$.[2] **4** reacts with the sulfur compounds (**1**) to afford a chelate (**5**) by the coordination of the bivalent sulfur atom of **1** to the copper atom of **4**. The chelate (**5**) changes into the condensation products **3** and C_2H_5SCuCl by way of an internal nucleophilic displacement as sketched in eq 2.

Based on this result, the reactions of **1** with the other nucleophilic reagents, such as active methylene compounds **6** and anisole, in the presence of $CuCl_2$, were tried with the expectation that the coordinated intermediate of **1** and $CuCl_2$ would act as an electrophile. It was established that, in the presence of two equimolar amounts of $CuCl_2$ and an equimolar amount of 2,6-lutidine, malononitrile reacts with **1a** in THF at room temperature to afford the condensation product, benzylidenemalononitrile, in 65% yield. Similarly the condensation products **7** are obtained from **1a**, **b**, and **c** and active methylene compounds **6** as shown in



4 **5** **3** (2)

eq 3. In some cases, olefinic compounds (**8**) result by the loss of ethylmercaptan from **7**.



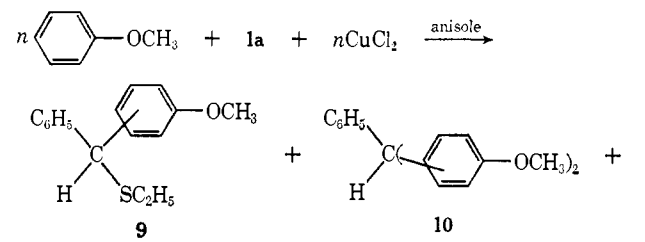
1 **6** **7** (3)

	R^1	R^2	active methylene	**7**	**8**
$-C_2H_5SH$	H	C_6H_5	acetylacetone	79%	
	H	C_6H_5	1,3-indandione		53%
	H	SC_2H_5	1,3-indandione		62%
	C_6H_5	C_6H_5	malononitrile		64%
	H	C_6H_5	diethyl malonate	63%	

8

It was further found that a weakly acidic methylene compound as cyclohexanone reacts with 2 equiv of **1a**, in the presence of 4 equiv of $CuCl_2$ and a catalytic amount of $Et_2O \cdot BF_3$, in ether to give 2,6-dibenzylidenecyclohexanone in 65% yield.

Anisole also reacts with **1a** in the presence of $CuCl_2$ at room temperature with the vigorous evolution of hydrogen chloride to yield substituted products, anisylphenylmethyl ethyl sulfide (**9**) and dianisylphenylmethane (**10**), in high yields according to eq 4.



9 **10** (4)

	9	**10**
$n=1$	62%	19%
$n=2$		83%
$n=3$		100%

(1) M. Conrad and M. Guthzert, *Ber.*, **19**, 19 (1886); H. D. Murdock and D. C. Nonhebel, *J. Am. Chem. Soc.*, **84**, 2153 (1962).

(2) The double nuclear complex of **2a** and $CuCl_2$ is isolated as a green precipitate by treating equimolar amounts of **2a** and $CuCl_2$ in THF under the dry nitrogen atmosphere. Its elemental analysis is $C_5H_7O_2$-CuCl and it was also found that this complex is readily hydrolyzed to give $CuCl_2$ and **2a**.

The ratio of **10** to **9** increases as the molar amount of $CuCl_2$ increases.

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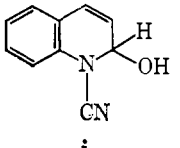
Alkaloid Studies. V.[1] Reaction of Tertiary Amines with Cyanogen Bromide under Solvolytic Conditions

Sir:

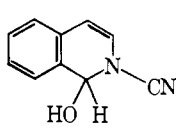
We wish to report the use of water and alcohols as participating solvents in the von Braun reaction. Classically,[2] reactions of tertiary amines with cyanogen bromide are normally carried out in inert solvents such as ether, chloroform, or benzene, and only meager information is available on the course of the reaction in hydroxylic solvents.[3] In addition, configurational changes occurring around the carbon which picks up bromide in the von Braun cyanogen bromide reaction have not been thoroughly studied. We have found that yohimbanes and alloyohimbanes react with cyanogen bromide in ethanol–chloroform or in aqueous tetrahydrofuran to give high yields of 3-substituted 3-secocyanamides. These result from ring opening between $N_{(b)}$ and C-3 with concomitant introduction of hydroxyl or ethoxyl groups at C-3.[4] The reaction is noteworthy in that: (i) it occurs cleanly at benzylic positions, (ii) it allows the introduction of hydroxyl or alkoxyl groups, and (iii) it occurs without formation of troublesome reactive bromides.

Reaction of 2 moles of yohimbine (**1**) with 1 mole of cyanogen bromide in ethanol–chloroform (1:3) for 20 hr at room temperature yields, after removal of precipitated **1**·HBr, 94% of (3*R*)-ethoxy-3-secocyanamide **5**:[5,6] mp 115–125°: $[\alpha]^{25}D$ −27° (*c* 1, pyridine); ν_{max}^{KBr} 2198 (CN), 1718 cm^{-1} (CO); $\delta_{TMS}^{CDCl_3}$ 1.07 (3H, t) (CH_3-CH_2O–), 3.80 (3 H, s) ($COOCH_3$), 4.33 (1 H, m) (C_3–H). Under the same conditions pseudoyohimbine (**2**) gives 59% of (3*S*)-ethoxy-3-secocyanamide **6** [mp 174–176°; $[\alpha]^{25}D$ −97° (*c* 1, pyridine); ν_{max}^{KBr} 2208 (CN), 1704 cm^{-1} (CO); $\delta_{TMS}^{CDCl_3}$ 1.18 (3 H, t) (CH_3CH_2O–), 3.78 (3 H, s) ($COOCH_3$), 4.78 (1 H, m) (C_3–H)] and 9% of (3*R*)-ethoxy compound **5**. In tetrahydrofuran–water (2.5:1) yohimbine (**1**) and cyanogen bromide give 81% of (3*R*)-hydroxy-3-secocyanamide **7** [$\delta_{TMS}^{DMSO-d_6}$ 3.70 (3 H, s) ($COOCH_3$), 4.80 (1 H, d) (C_3–OH), 4.97 (1 H, m) (C_3–H)] whereas pseudoyohimbine (**2**) gives 35% of (3*S*)-hydroxy-3-secocyanamide **8** [$\delta_{TMS}^{DMSO-d_6}$ 3.53 (3 H, s) ($COOCH_3$), 5.07 (1 H, m) (C_3–H), 5.15 (1 H, d) (C_3–OH)] and 10% of (3*R*)-hydroxy compound **7**.

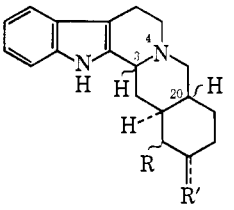
Methyl reserpate (**13**), with cyanogen bromide in ethanol–chloroform, affords 70% of (3*S*)-ethoxy derivative **15** [mp 258–260°; $\delta_{TMS}^{CDCl_3}$ 4.68 (1 H, m) (C_3–H)] whereas methyl 3-isoreserpate (**14**) affords 59% of (3*R*)-ethoxy derivative **16** [mp 270–272°; $\delta_{TMS}^{CDCl_3}$ 4.27 (C_3–H)]. In aqueous tetrahydrofuran, methyl reserpate gives 70% of (3*S*)-hydroxy-3-secocyanamide **17** which, when refluxed with ethanol, is converted exclusively to (3*S*)-ethoxy-3-secocyanamide **15**[7] (stereospecific replacement with retention of configuration).[8,9]



i



ii

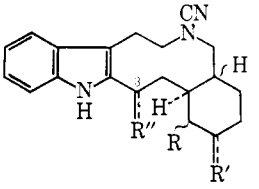


1, 3α-H, 20β-H, R = ---CO_2CH_3; R′ =

2, 3β-H, 20β-H, R = ---CO_2CH_3; R′ =

3, 3α-H, 20β-H, R = H; R′ = O

4, 3α-H, 20α-H, R = —CO_2CH_3; R′ =



5, 20β-H, R = ---CO_2CH_3; R′ =  ; R″ =

6, 20β-H, R = ---CO_2CH_3; R′ =  ; R″ =

7, 20β-H, R = ---CO_2CH_3; R′ =  ; R″ =

8, 20β-H, R = ---CO_2CH_3; R′ =  ; R″ =

9, 20β-H, R = H; R′ = O; R″ =

10, 20α-H, R = —CO_2CH_3; R′ =  ; R″ =

11, 20β-H, R = H; R′ = O; R″ =

12, 20β-H, R = H; R′ = R″ = O

(1) Alkaloid Studies. IV: J. D. Albright, J. C. Van Meter, and L. Goldman, *Lloydia*, **28**, 212 (1965).

(2) H. A. Hageman, *Org. Reactions*, **7**, 198 (1953).

(3) Quinolines and isoquinolines are reported to give hydroxy-substituted derivatives such as i and ii in the presence of moisture;[2] however, it has not been established that these derivatives are formed through bromo intermediates.

(4) A. F. Casy and M. M. A. Hassan [*Tetrahedron*, **23**, 2075 (1967)] have reported the cyclization of 6-dimethylamino-4,4-diphenyl-3-heptanol with cyanogen bromide to give 2-ethyl-3,3-diphenyl-5-methyltetrahydrofuran—an example of an internal alcohol function reacting with the initially formed quaternary cyanodimethylammonium bromide.

(5) All products reported here are new compounds; elemental analyses and infrared, ultraviolet, pmr, and mass spectra support the assigned structures.

(6) *R,S* configurational nomenclature is used to denote configuration at the asymmetric C-3 center.

(7) A closely related reaction is conversion of 18-hydroxyibogaine to 18-methoxyibogaine with acidic methanol: G. Büchi and R. E. Manning, *J. Am. Chem. Soc.*, **88**, 2532 (1966).

(8) Replacement of a C-3 hydroxyl group in 3-secocyanamides must depend on the stereochemistry of the ring fusion between the ten- and six-membered rings because the C-3 hydroxyl in **8** and **11** is not replaced by refluxing in ethanol. Ease of replacement and retention of configuration may result from participation of the C-16 ethoxycarbonyl function in **17**.

(9) See P. B. D. de la Mare in "Molecular Rearrangements," Vol. I, P. de Mayo, Ed., Interscience Publishers, New York, N. Y., 1963, pp 30–51, for a discussion on retention of configuration in allylic cationic intermediates.