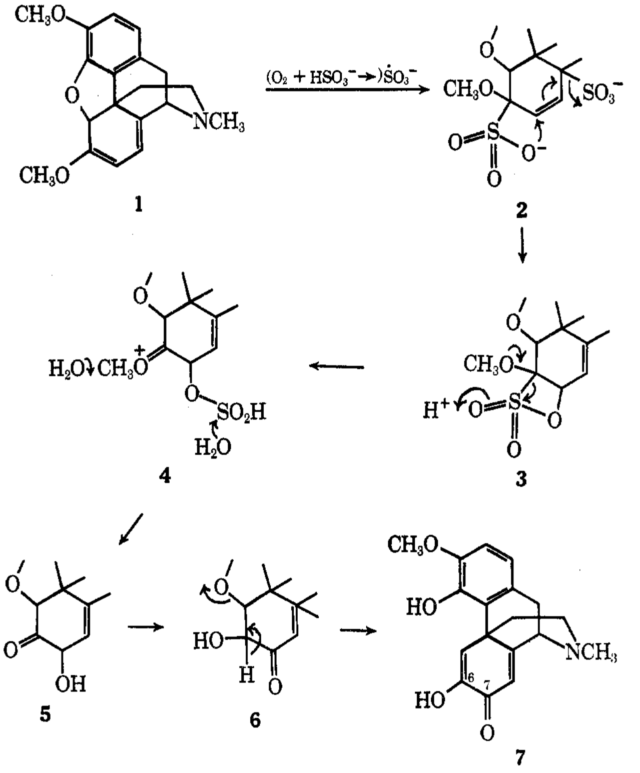
For mechanistic considerations, since only one oxygen atom is incorporated, it is reasonable to assume that it is the oxygen atom at C-7 of **7** which is incorporated from bisulfite. Any mechanism proposed for this transformation must be consistent with the following observations: (a) thebaine is unaffected by a bisulfite solution in the absence of O_2; (b) molecular oxygen must be present during the course of the reaction in order for the conversion to occur; and (c) the source of the oxygen atom which is incorporated into the product is bisulfite.

These conditions have been incorporated in the mechanism proposed in Scheme I. The postulated first step is the 1,4 addition of two bisulfite radical ions to form the disulfonate **2**. The radical ions in turn are proposed as formed by the action of oxygen on aqueous bisulfite, conditions which are well documented to convert olefins to sulfonates and disulfonates[6] *via* radical intermediates. Reaction then proceeds *via* displacement of the sulfonate at position 14 to form the β-sultone **3**. The latter then collapses to **4** which is hydrolyzed to the α-hydroxy ketone **5**. Tautomeric rearrangement to **6** is followed by β elimination to form the morphinandienone, 6-*O*-demethylsalutaridine (**7**). Clearly, alternatives exist for the route from β-sultone **3** to dienone **7** involving essentially the same principles.

SCHEME I



Experimental Section

6-*O*-Demethylsalutaridine (7).—A solution of 9 g of thebaine (**1**) in 250 ml of 1 *N* sodium bisulfite was shaken for 3 hr under an atmosphere of oxygen. The solution was then brought to pH 11 with 30% aqueous sodium hydroxide and extracted with two 75-ml portions of benzene–hexane, 1:1. After drying (Na_2SO_4) and removal of the solvent, the first extract produced 0.67 g of a 2:1 mixture of thebaine and **7** and the second extract produced 0.14 g of a 3:2 mixture of the thebaine and **7**. The aqueous phase was adjusted to pH 8.0 with concentrated HCl and extracted with methylene chloride (four 75-ml portions). The extracts were combined and dried (Na_2SO_4) and the solvent was removed *in vacuo* to yield **7**, 5.10 g (64%) based on thebaine consumed, as a white solid after crystallization from benzene, mp 184–186° turning red-brown, identical with material prepared by the action of alkali on 14-bromocodeinone.[3,4]

Isotopic Experiments. A. ^{18}O Determinations.—Reactions were carried out for 1 hr in the presence of $H_2{}^{18}O$, $^{18}O_2$, or $NaHS^{18}O_3$, and the purified product was examined for ^{18}O by nonoxidative pyrolysis as previously described.[5] The ^{18}O content of the carbon monoxide produced was determined by mass spectrometry. Pyrolysis of an equal amount of unlabeled product provided a natural abundance background determination. The ^{18}O content of the $H_2{}^{18}O$ and O_2 used are 2.0 and 1.6%, respectively. All isotope assays were performed using a Consolidated Electrodynamics Corp. Model 130 mass spectrometer.

B. Apparatus.—The oxidations were conducted in an apparatus[7] which is commonly used for hydrogenation at atmospheric pressure, fitted for the introduction of oxygen instead of hydrogen. All experiments using isotopically enriched materials were conducted with this apparatus.

Registry No.—**7**, 27669-33-6.

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[6] E. E. Gilbert, "Sulfonation and Related Reactions," Interscience, New York, N. Y., 1965, p 150.

[7] K. B. Wiberg, "Laboratory Technique in Organic Chemistry," McGraw-Hill, New York, N. Y., 1960, p 228.

A Novel Intramolecular Rearrangement of a 1,4 Dipole

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While cycloaddition reactions of 1,4 dipoles are well documented,[1,2] intramolecular rearrangements of these dipoles have rarely been observed.[1] We wish to report experimental evidence for a unique 1,4-dipolar intramolecular rearrangement resulting from the reaction of 4-phenyl-1,2,4-triazoline-3,5-dione[3] (**1**) with vinyl esters.

Equimolar quantities of **1** and vinyl acetate (**2**) react in methylene chloride at 60° yielding 1-formyl-2-acetyl-4-phenyl-1,2,4-triazoline-3,5-dione (**3**) exclusively. Isopropenyl acetate (**4**) reacts in a similar manner to give 1-acetylmethyl-2-acetyl-4-phenyl-1,2,4-triazoline-3,5-dione (**5**).

A plausible mechanism for these reactions would involve the unusually stable 1,4 dipole[4] (**6**) as the reactive intermediate, formed *via* initial reaction of the electron-poor nitrogen double bond with the electron-rich double bond of the vinyl ester. The 1,4 dipole, once formed, could undergo an intramolecular nucleophilic attack by nitrogen on the carbonyl carbon displacing the ester oxygen (path a, Scheme I). Intramolecular nucleophilic attack by nitrogen is sterically hindered by large R_2 groups, decreasing the relative yield of the product

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[1] R. Huisgen, *Z. Chem.*, **8**, 290 (1968).

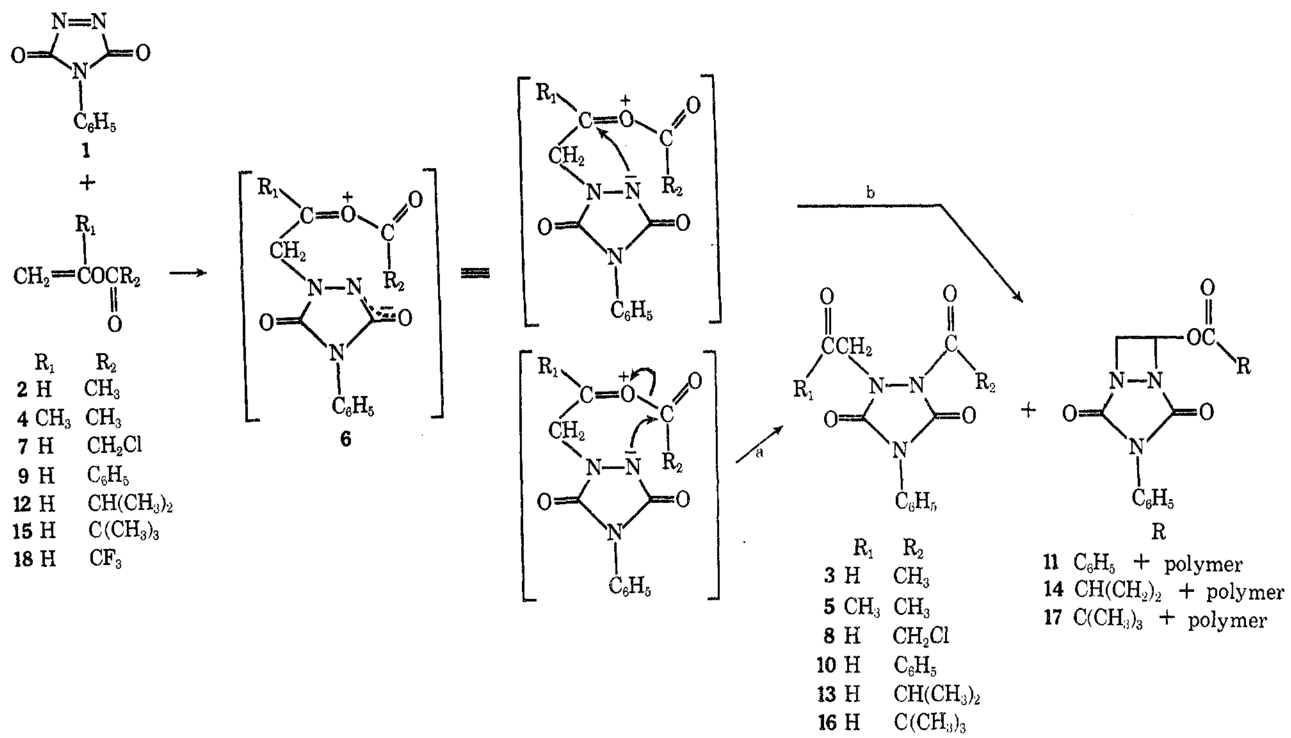
[2] E. K. Von Gustorf, D. V. White, B. Kim, K. Hess, and J. Leitich, *J. Org. Chem.*, **35**, 1155 (1970).

[3] J. C. Stickler and W. H. Pirkle, *ibid.*, **31**, 3444 (1966).

[4] 1,4 dipoles of a similar nature have previously been reported.[5]

[5] (a) Ref 2; (b) S. R. Turner, L. J. Guilbault, and G. B. Butler, *J. Org. Chem.*, **36**, 2838 (1971).

SCHEME I[a]



[a] Structural assignments for **11** are tentative only. See Experimental Section.

resulting from rearrangement (Table I); thus, while the 1,4 dipoles formed in the reactions of **2**, **4**, and vinyl chloroacetate (**7**)[6] rearrange exclusively, the dipoles of vinyl isobutyrate (**12**), vinyl pivalate (**15**), and vinyl benzoate (**9**)[6] form two other products as well, 1,3,5-triazabicyclo[3.2.0]hepta-2,4-diones *via* path b, Scheme I, and polymers by a mechanism previously described.[7]

A third mechanistic possibility—reaction through an acylium ion—can be eliminated on the basis of two reactions listed in Table I. A highly unstable chloroacylium ion would be required as the reactive intermediate in the reaction of **7** with **1**. Also, **9** reacts with **1** to give polymeric material as the major product, contrary to what would be expected (*i.e.*, a high yield of **10**) if a benzacylium ion were the reactive intermediate.

TABLE I

RELATIVE YIELDS OF PRODUCTS

Ester	Yield of trisubstituted triazolinediones, %	Yield of 1,3,5-triazabicyclo[3.2.0]hepta-2,4-diones, %	Yield of polymer, %
2, 4, 7	100	0	0
12	77	8	15
15	42	42	16
9	6	7	87

The apparent differences in reactivities of other vinyl esters offer further evidence for a 1,4-dipolar intermediate. Electron-donating groups located close to the positive center stabilize the dipole, while electron-withdrawing groups have an opposite effect. Thus, in comparison to the vinyl acetate reaction, which required 4 hr for completion,[8] the characteristic red color of **1** disappeared twice as fast in reaction with **4**, ten times slower in reaction with **7**, and vinyl trifluoroacetate (**18**) failed to react after 96 hr.

Experimental Section[9]

General Procedure.—To a solution of 0.500 g (2.86×10^{-3} mol) of **1** in 25 ml of reagent grade methylene chloride (dried over 4-Å molecular sieves) was added 2.86×10^{-3} mol of the vinyl ester. The intense red solution was transferred to a thick-walled glass tube, which was sealed under vacuum following two freeze–thaw cycles in liquid nitrogen. The tube was placed in a 60° constant-temperature bath and removed after color discharge to light yellow was noted. The tube was then opened and the contents were poured through a coarse sintered glass funnel into 250 ml of stirred hexane in order to precipitate any polymer formed. Polymer, if formed, was filtered and the filtrate was evaporated on a rotary evaporator, leaving nonpolymeric products behind. The nonpolymeric products were separated and purified as described below, and dried at 58° (0.03 mm) overnight before microanalysis. All nonpolymeric products were odorless, white, crystalline solids; the polymeric products were odorless, white, amorphous solids. Nmr data may be found in Table II.

1-Formyl-2-acetyl-4-phenyl-1,2,4-triazoline-3,5-dione (**3**) was recrystallized twice from a methylene chloride–hexane solvent pair: yield 0.56 g (75%); mp 130–131°; ir (KBr) 2860 (w), 2750 (w), 1800 (m), 1730 cm^{-1} (s, b).

Anal. Calcd for $C_{12}H_{11}N_3O_4$: C, 55.20; H, 4.20; H, 16.09. Found: C, 55.34; H, 4.28; N, 15.95.

1-Acetylmethyl-2-acetyl-4-phenyl-1,2,4-triazoline-3,5-dione (**5**) was recrystallized twice from a methylene chloride–hexane solvent pair: yield 0.63 g (80%); mp 107–108°; ir (KBr) 1800 (m), 1750 (s), 1730 (s) 1720 cm^{-1} (s).

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(6) Electronic effects may also influence the relative yields of products in the vinyl chloroacetate and vinyl benzoate reactions.

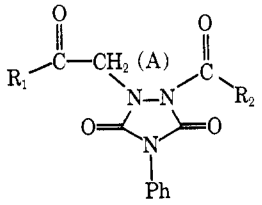
(7) The polymers obtained in these reactions are related to those reported earlier: S. R. Turner, L. J. Guilbault, and G. B. Butler, *Polym. Lett.*, **9** (2), 115 (1971).

(8) The time required for complete disappearance of the characteristic red color of **1**, using 2.86×10^{-3} mol of reactants in all reactions.

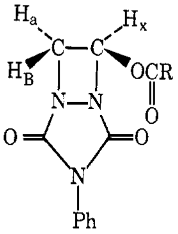
(9) Melting points were taken on a Thomas-Hoover melting point apparatus and are uncorrected. Ir spectra were taken on a Beckman IR-8 spectrophotometer and nmr spectra on a Varian A-60A spectrometer. Mass spectral data were obtained using a Hitachi Perkin-Elmer RMU mass spectrometer and resulted in the molecular ion and reasonable cracking patterns for all products having analytical data. Microanalyses were performed by Atlantic Microlab, Inc., Atlanta, Ga.

Table II

Nmr Data[a]



Compd	R1	R2	A
3	9.56 (s, 1)	2.60 (s, 3)	4.80 (s, 2)
5	2.10 (s, 3)	2.52 (s, 3)	4.78 (s, 2)
8	9.60 (s, 1)	4.97 (s, 2)	4.72 (s, 2)
10	9.66 (s)	b	4.78 (s)
13	9.57 (s, 1)	4.15 (m, 1) 1.25 (d, 6)	4.79 (s, 2)
16	9.53 (s, 1)	1.37 (s, 9)	4.63 (s, 2)



Compd	R	Ha	Hb	Hx	J_{AB}	J_{AX}	J_{BX}
11	b	4.20[c] (m)		6.19 (m)			
14	2.64 (d, 6) 2.23 (d, 6)	4.58 (q, 1)	4.29 (q, 1)	6.56 (q, 1)	10	6	5
17	1.20 (s, 9)	4.60 (q, 1)	4.27 (q, 1)	6.49 (q, 1)	10	6	5

[a] In chloroform-d_1 with 1% TMS as internal standard. Values reported in δ units. *N*-Phenyl protons appeared in the δ 7.41–7.50 region for all compounds. Abbreviations used are s, singlet; d, doublet; q, quartet; m, multiplet. [b] Complex multiplet absorption in the δ 7.2–7.8 region was observed for the two phenyl groups. [c] Complex absorption pattern for both protons.

Anal. Calcd for $C_{13}H_{13}N_3O_4$: C, 56.73; H, 4.76; N, 15.27. Found: C, 56.83; H, 4.80; N, 15.33.

1-Formylmethyl-2-chloroacetyl-4-phenyl-1,2,4-triazoline-3,5-dione (**8**) precipitated upon pouring the reaction mixture into 250 ml of stirred hexane. Nmr spectra of the crude material indicated no polymer formation. Purification was effected by twice recrystallizing the crude product from hexane–methylene chloride: yield 0.80 g (95%); mp 157–158°; ir (KBr) 2880 (w), 2745 (w), 1810 (s), 1760–1710 cm^{-1} (s, b).

Anal. Calcd for $C_{12}H_{10}ClN_3O_4$: C, 48.91; H, 3.42; N, 14.26. Found: C, 49.00; H, 3.58; N, 14.20.

Separation of **1-formylmethyl-2-benzoyloxy-4-phenyl-1,2,4-triazoline-3,5-dione** (**10**) and **3-phenyl-6-benzoyloxy-1,3,5-triazabicyclo[3.2.0]hepta-2,4-dione** (**11**) has not yet been achieved, and their structural assignments have been tentatively made based on the nmr spectrum of the mixture, total yield 0.11 g (13%).

1-Formylmethyl-2-(2-methylpropionyl)-4-phenyl-1,2,4-triazoline-3,5-dione (**13**) and **3-phenyl-6-(2-methylpropionyloxy)-1,3,5-triazabicyclo[3.2.0]hepta-2,4-dione** (**14**) appeared as an oil after evaporation of the solvent. The mixture was dissolved in the minimum amount of methylene chloride necessary to attain solution followed by addition of the minimum amount of hexane necessary to cause slight cloudiness. The solution was allowed to stand at room temperature for 2–3 days, resulting in fractional crystallization (**14** precipitated first) of the solids. The procedure was repeated several times in order to obtain pure samples of each product.

Data for **13** follow: yield 0.50 g (60%); mp 100–101°; ir (KBr) 2870 (w), 2750 (w), 1800 (m), 1735 (s, b), 1720 cm^{-1} (s, shoulder).

Anal. Calcd for $C_{14}H_{15}N_3O_4$: C, 58.13; H, 5.23; N, 14.53. Found: C, 58.29; H, 5.36; N, 14.45.

Data for **14** follow: yield 0.50 g (6.3%); mp 163–164°; ir (KBr) 1780 (m), 1755 (s), 1720 cm^{-1} (s).

Anal. Calcd for $C_{14}H_{15}N_3O_4$: C, 58.13; H, 5.23; N, 14.53. Found: C, 58.00; H, 5.31; N, 14.36.

1-Formylmethyl-2-(2,2′-dimethylpropionyl)-4-phenyl-1,2,4-triazoline-3,5-dione (**16**) and **3-phenyl-6-(2,2′-dimethylpropionyl)-1,3,5-triazabicylo[3.2.0]hepta-2,4 dione** (**17**) were purified using the same procedure employed for **13** and **14**, substituting hexane–ether as the solvent pair.

Data for **16** follow: yield 0.31 g (36%); mp 135–136°; ir (KBr) 2880 (w), 2740 (w), 1780 (m), 1740 (s), 1720 (s), 1700 cm^{-1} (s).

Anal. Calcd for $C_{15}H_{17}N_3O_4$: C, 59.40; H, 5.65; N, 13.85. Found: C, 59.30; H, 5.79; N, 13.69.

Data for **17** follow: yield 0.30 g (36%); mp 171–172°; ir (KBr) 1780 (m), 1750 (s), 1725 cm^{-1} (s).

Anal. Calcd for $C_{15}H_{17}N_3O_4$: C, 59.40; H, 5.65; N, 13.85. Found: C, 59.18; H, 5.70; N, 13.89.

Vinyl trifluoroacetate (**18**) was allowed to stand with **1** for 96 hr at 60°. Approximately 80% of **1** was recovered unreacted along with 10% of a tan solid, which appeared to be an oligomeric decompositon product of **1**.

Registry No.—**3**, 33981-32-7; **5**, 34050-55-0; **8**, 33981-33-8; **10**, 34050-56-1; **11**, 33981-34-9; **13**, 33981-35-0; **14**, 33981-36-1; **16**, 34050-57-2; **17**, 33981-37-2.

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Intramolecular Catalysis in the Aminolysis of Thiol Esters

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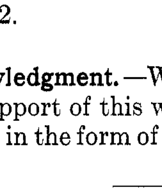
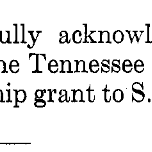
Received October 5, 1971

Although the aminolysis of esters has received considerable study, only one example of intramolecular amine-catalyzed aminolysis in water has been reported.[3] We report here the first example of intramolecular amine-catalyzed aminolysis of a thiol ester in water. 2-Pyridyl thiolacetate (**1a**) was chosen as the thiol ester because the pyridyl nitrogen is in a favorable geometric position to act as a general base and because thiol esters of 2-thiopyridone have an unusually high reactivity in



1a



1b

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[2] To whom inquiries should be addressed.

[3] (a) T. C. Bruice and S. M. Felton, *J. Amer. Chem. Soc.*, **91**, 2799 (1969); (b) S. M. Felton and T. C. Bruice, *ibid.*, **91**, 6721 (1969).