Stable Sulfonium Ylids

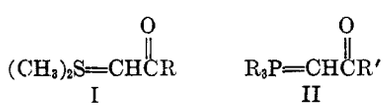
K. W. RATTS AND A. N. YAO

Monsanto Company, Agricultural Division, Research Department, St. Louis, Missouri 63166

Received October 6, 1965

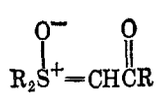
The isolation of several carbonyl-stabilized sulfonium ylids is described. Their synthesis, characterization, and properties are given and compared to the better known phosphonium ylids.

Carbonyl-stabilized sulfonium ylids, I, are unknown as isolable compounds, having been studied only *in situ*.[1,2] The treatment of sulfonium salts with sodium hydride in the presence of Schiff bases to yield β-anilinocinnamamides and esters presumably involves sulfonium ylids.[1] Carbonyl stabilization of phosphorus ylids II produces a decrease in nucleophilicity and basicity such that these compounds are isolable and stable under atmospheric conditions.[3]

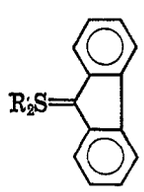


I II

Corey[4] and Metzger[5] have, in separate instances, prepared isolable sulfoxonium ylids (III) which are stabilized by carbonyl groups. Sulfonium ylids, however, have been isolated in only a few instances where the negative charge is delocalized by an aromatic system,[6] such as with dimethyl sulfonium fluorenylid[7] (IV). The isolation of 3-dimethylsulfuranylidene-

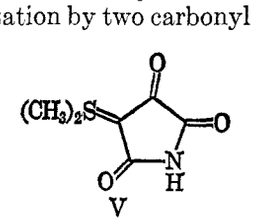


III



IV

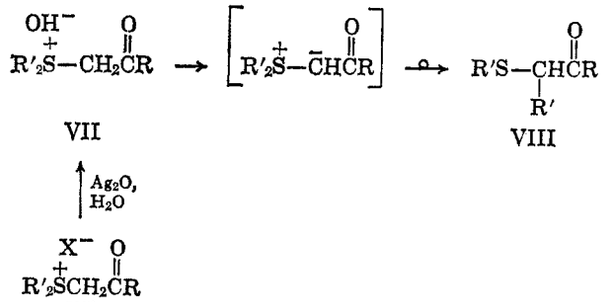
2,4,5-pyrollidinetrione[8] (V), after treatment of carbamoylmethyl dimethyl sulfonium chloride with sodium methoxide and diethyl oxalate, affords one example of stabilization by two carbonyl groups.[9]



V

N,N-Diethyl(dimethylsulfuranylidene)acetamide[10] [I, R = $N(C_2H_5)_2$] and ethyl(dimethylsulfuranylidene) acetate [I, R = OC_2H_5] react normally with Schiff bases and aldehydes[11] to produce intermediate betaines which subsequently lead to products. However, attempts to carry out similar reactions with the corresponding aryl ketones (I, R = substituted phenyl) failed. The surprising lack of reactivity of the phenacyl sulfonium ylids (R = aryl) compared to the ester (R = OC_2H_5) and amide (R = $N(C_2H_5)_2$), and the possibility of a direct study of carbonyl-stabilized sulfonium ylids led us to examine the synthesis, isolation, and properties of these sulfur ylids.

Carbonyl-stabilized sulfonium ylids have been prepared *in situ* by treatment of the appropriate sulfonium salt in tetrahydrofuran with sodium hydride.[1] However, it has been reported[12-14] that the action of silver oxide upon α-sulfonium-substituted carbonyl compounds in aqueous solution yields isolable sulfonium hydroxides (VII) which, *via* sulfonium ylids, produce the rearranged sulfides VIII. Repetition



VII VIII VI

of this synthesis with silver oxide gave a product, mp 56–57°, which, as reported, decomposed on standing and gave a strongly alkaline solution in water. The same compound was obtained using sodium hydroxide at room temperature. Drying the product at room temperature over phosphorus pentoxide provided an analytical sample whose analysis was in agreement with the ylid I, R = C_6H_5, rather than the hydroxide VII, R′ = CH_3; R = C_6H_5. The infrared spectrum, which remained unchanged upon drying except for disappearance of the hydroxyl band (3450 cm^{-1}), also suggested an ylid rather than a sulfonium hydroxide, *i.e.*, the carbonyl frequency is 1520 cm^{-1}. The ylids were also obtained in tetrahydrofuran by treatment of sulfonium salts VI with sodium hydride.

The isolated ylids are listed in Table I and, with the exception of the more reactive ester and amide I,

(1) A. J. Speziale, C. C. Tung, K. W. Ratts, and A. Yao, *J. Am. Chem. Soc.*, **87**, 3460 (1965).

(2) H. Nozaki, K. Kondo, and M. Takaku [*Tetrahedron Letters*, **No. 4**, 251 (1965)] have recently reported isolation of 2-(methylphenylsulfuranylidene)acetophenone.

(3) A. J. Speziale and K. W. Ratts, *J. Am. Chem. Soc.*, **85**, 2790 (1963).

(4) E. J. Corey and M. Chaykovsky, *ibid.*, **86**, 1641 (1964).

(5) H. Metzger and H. Koenig, *Z. Naturforsch*, **18b**, 187 (1963).

(6) (a) E. D. Hughes and K. I. Kuriyan, *J. Chem. Soc.*, 1609 (1935); (b) V. Franzen, *Chem. Ber.*, **94**, 2942 (1961).

(7) C. K. Ingold and J. A. Jessop, *J. Chem. Soc.*, 713 (1930).

(8) E. G. Howard, A. Kotch, R. V. Lindsay, Jr., and R. E. Putnam, *J. Am. Chem. Soc.*, **80**, 3924 (1958).

(9) W. J. Middleton, E. L. Buhle, J. G. McNally, Jr., and M. Zanger [*J. Org. Chem.*, **30**, 2384 (1965)] have synthesized sulfonium dicyanomethylides, $R_2S{=}C(CN)_2$.

(10) It is suggested that these sulfur ylids be named as sulfuranes comparable to the phosphorane nomenclature for phosphorus ylids. $(CH_3)_2S{=}CH_2$ then becomes dimethylmethylenesulfurane; $(CH_3)_2S{=}CHCO_2C_2H_5$, ethyl (dimethylsulfuranylidene)acetate; and $(CH_3)_2S{=}CHCOC_6H_5$, (dimethylsulfuranylidene)acetophenone.

(11) The reaction of aldehydes with sulfonium ylids will be reported in the next paper of this series; see also A. W. Johnson and R. B. LaCount, *J. Am. Chem. Soc.*, **83**, 417 (1961).

(12) S. Smiles, *Proc. Chem. Soc.*, **21**, 93 (1905).

(13) H. Bohme and W. Krause, *Chem. Ber.*, **82**, 426 (1949).

(14) H. Bohme and P. Heller, *ibid.*, **86**, 443 (1953).

TABLE I

SULFONIUM YLIDS $(CH_3)_2S{=}CHCOR$

R	Mp, °C	Yield, %	Calcd, % C	H	Br	N	S	Found, % C	H	Br	N	S
OC_2H_5	Oil	70	...	...	...	...	...	...	...	...	...	...
$N(C_2H_5)_2$	Oil	91	...	...	...	...	...	...	...	...	...	...
C_6H_5	56–57	99	66.62	6.71	...	...	17.79	66.35	6.91	...	...	17.53
$4\text{-}NO_2C_6H_4$	Dec 105, melts 110–111	40	53.32	4.92	...	6.22	14.23	53.41	5.08	...	6.40	14.07
$4\text{-}BrC_6H_4$	121–123	93[a]	46.34	4.28	30.84	...	12.37	46.18	4.39	31.05	...	12.31
$4\text{-}C_6H_4C_6H_4$	143–145	93[b]	74.96	6.29	...	...	12.51	74.84	6.11	...	...	12.68

[a] Before recrystallization, mp 109–114°. [b] Before recrystallization, mp 120–136°.

TABLE II

SPECTRAL DATA FOR $(CH_3)_2S{=}CHCOR$

R	Infrared carbonyl stretching frequency, cm^{-1}[a]	Nmr chemical shifts (area) $(CH_3)_2S$[b]	CH[c]	Ar[d]	CH_2[e]	CH_3	Solvent
OC_2H_5	1620	6.90 (6)	Not seen	...	5.74 (2), J = 7.5	8.52 (3)[f]	$CDCl_3$
$N(C_2H_5)_2$	1540	6.79 (6)	Not seen	...	6.42 (4), J = 7.0	8.59 (6)[e]	$CDCl_3$
$4\text{-}C_6H_5C_6H_4$	1520	7.11 (6)	5.92 (1)	2.53 (9)	...	...	$CDCl_3$
$4\text{-}BrC_6H_4$	1520	7.09 (6)	5.75 (1)	2.40 (4)	...	...	$CDCl_3$
$4\text{-}NO_2C_6H_4$	1520	6.96 (6)	5.63 (1)	1.97 (4)	...	...	$CDCl_3$
$4\text{-}NO_2C_6H_4$		6.86 (6)	5.00	2.04 (4)	...	...	D_2O[g]
C_6H_5	1520	7.22 (6)	5.25 (1)	2.44 (5)	...	...	$CDCl_3$
C_6H_5		6.96 (6)	5.02	2.21	...	...	D_2O[g]
C_6H_5		6.95 (6)	4.83 (2)	2.37 (5)	...	...	CF_3CO_2H
C_6H_5		7.29 (6)	Not seen	2.37–2.83 (5)	...	...	CD_3CN

[a] Chloroform solution. [b] Singlet. [c] Frequently very broad, see ref 15. [d] Multiplet centered at value given. [e] Quartet centered at this value; J values are given in cycles per second. [f] Triplet centered at value given. [g] External TMS standard.

TABLE III

SPECTRAL DATA FOR $(CH_3)_2\overset{+}{S}{-}CH_2COR\ X^-$

R	X	Infrared carbonyl stretching frequency, cm^{-1}[a]	Nmr chemical shifts (area) $(CH_3)_2S$[b]	CH_2[b]	ArH[c]	CH_2[d,e]	CH_3[e]	Solvent
OC_2H_5	Br	1740	6.50 (5)	4.75 (2)	...	5.74 (2), J = 7.5	8.69 (3), J = 7.5[f]	$CDCl_3$
$N(C_2H_5)_2$	Cl	1650	6.56 (6)	4.80 (2)	...	6.15 (4), J = 7.2	8.36 (6), J = 7.2[d]	$CDCl_3$
$4\text{-}C_6H_5C_6H_4$	Br	1660	6.83 (6)	4.56 (2)	2.28 (9)	...	...	$CDCl_3$
$4\text{-}BrC_6H_4$	Br	1675	6.80 (6)	4.47 (2)	2.25 (4)	...	...	$CDCl_3$
$4\text{-}NO_2C_6H_4$	Br	1690	6.80 (6)	4.45 (2)	1.60 (4)	...	...	$CDCl_3$
$4\text{-}NO_2C_6H_4$	Br	...	6.50 (6)	5.00	0.86 (4)	...	...	D_2O[g]
C_6H_5	Br	1670	6.83 (6)	4.61 (2)	2.29 (5)	...	...	$CDCl_3$
C_6H_5	Br	...	6.56 (6)	5.05	2.05 (5)	...	...	D_2O[g]

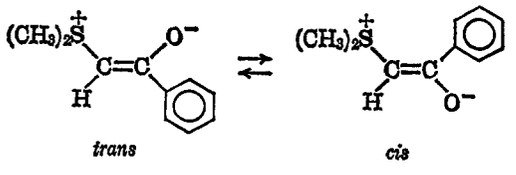
[a] Chloroform solution. [b] Singlet. [c] Multiplet centered at value given. [d] Quartet centered at this value. [e] J values are given in cycles per second. [f] Triplet centered at this time value. [g] External TMS standard.

R = OC_2H_5 and $N(C_2H_5)_2$, respectively, are crystalline solids. Decomposition of these ylids upon standing is relatively slow but decreases with the electron-delocalizing ability of the R groups. In solution the ylid I, R = $4\text{-}C_6H_4NO_2$, is monomeric. The ylids show a shift (110–140 cm^{-1}) in carbonyl frequency characteristic of such structures[3] (see Tables II and III). The protons in the sulfonium salts are deshielded owing to the positive sulfur atom $(CH_3)_2S^+$, τ 6.50–6.83; CH_3SCH_3, τ 7.95). The spectra of the ylids indicate methyl and methine protons shifted upfield in comparison to the salts (I—CH_3, τ 6.78–7.22; CH, τ 5.25–5.92; VI—CH_3, τ 6.50–6.83; CH_2, τ 4.45). The increase in electron density involved in the transformation of salt to ylid causes a concomitant shielding of the protons. The methine proton of the ylids is often quite broad.[15]

The ylids form sulfonium salts upon treatment with acids. Hydrogen bromide yields the corresponding sulfonium bromide and the nmr spectra of the ylids in trifluoroacetic acid are characteristic of sulfonium salts (see Experimental Section).

$$(CH_3)_2S{=}CHCOAr + HX \longrightarrow (CH_3)_2\overset{+}{S}{-}CH_2COAr\ X^-$$

(15) (Triphenylphosphoranylidene)acetophenone exhibits the same type of broadening of the methine proton, $(C_6H_5)_3P{=}CHCOC_6H_5$. The broadening of this peak may be due to a *cis–trans* equilibrium. A rapid interchange of the following type would average the methine proton.



trans *cis*

The new ylids dissolve readily in water to give basic solutions. Although hydration[16] of a phosphorus pentoxide dried sample of the more reactive ylid I, R = C_6H_5, occurred rapidly upon exposure to atmospheric moisture, the less reactive ylid I, R = 4-C_6H_4-NO_2, may be dehydrated by allowing the hydrated sample to stand overnight. The tendency to hydrate is quite dependent upon the aromatic substituent. The infrared spectrum in chloroform and the nmr spectrum in deuteriochloroform of both hydrates exhibit the essential features of the dried ylids (γ_{CO} 1520 cm^{-1}; $(CH_3)_2\overset{+}{S}$, τ 6.96–7.22; CH, τ 5.63–5.25).

It is generally accepted that the d orbitals of sulfur in a sulfonium group stabilize an adjacent carbanion to a greater extent than those of phosphorus in a phosphonium group.[17,18] The Hammett plots[19] for the carbonyl-stabilized ylids (Figure 1) indicate that, although a parallel relationship is obtained, the S-ylids are more basic than the P-ylids. In this comparison, then, the p–d overlap of the phosphonium group appears to be more pronounced than with the sulfonium group. This inversion is quite likely due to the difference in groups (alkyl *vs.* phenyl) attached to the positive atom. The replacement of phenyl groups with alkyl groups causes an increase in the basicity of phosphonium ylids[17] [$(C_6H_5)_3P{=}CBrCOC_6H_5$, 5.0; $(n\text{-}C_4H_9)_3P{=}CBrCOC_6H_5$, 11.3]. The corresponding trimethylphosphonium ylids should be more basic than the S-ylids in Figure 1.[20] The lack of reactivity of these S-ylids is surprising since the P-ylids exhibit reactivity proportional to their basicity.[21]

Hydrolysis of these sulfonium ylids by strong base yields benzoates and presumably trimethylsulfonium hydroxide, whereas phosphonium ylids yield phosphine oxides. After protonation, the S-ylid undergoes attack by base at the carbonyl carbon and cleaves *via* "a reverse aldol reaction." The P-ylids, however, undergo attack at phosphorus with P–C bond cleavage. The difference, as noted previously,[17] is due to the reluctance with which sulfur is attacked by oxy anions. The same behavior was found[22] with nitrogen betaines where nitrogen attack cannot occur owing to the instability of pentacovalent intermediates.

Several new isolable sulfonium ylids have been prepared. The spectra of the compounds are usual for ylid structures. The strong basicity of these sulfonium ylids and the sharp difference in reactivity between I, R = OC_2H_5 or $N(C_2H_5)_2$, and I, R = aryl, is unexpected. Investigation of these anomalies and the reactions of sulfonium ylids is continuing.

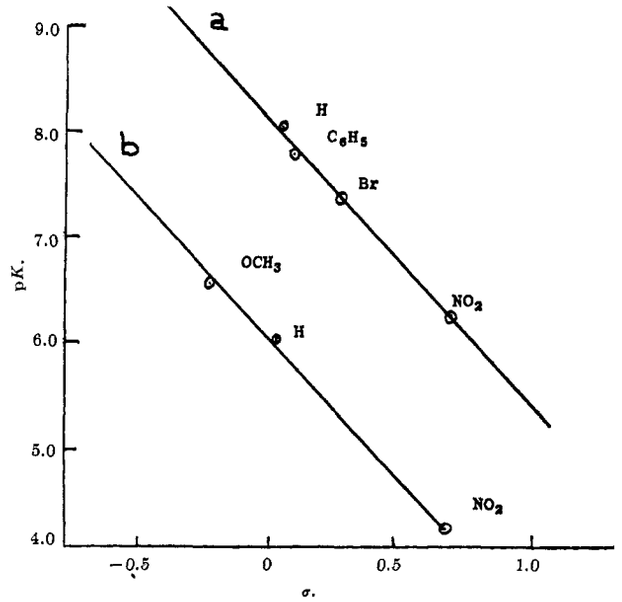


Figure 1.—Hammett plot of the pK_a of ylid conjugate acids *vs.* σ values: (a) curve for the S-ylid, $(CH_3)_2S{=}CHCOC_6H_4$—X-*p*; (b) curve for the P-ylid, $(C_6H_5)_3P{=}CHCOC_6H_4$—X-*p* (p*K* values for the P-ylids were taken from ref 21). σ constants are those for substituted benzoic acids.

Experimental Section[23]

Sulfonium Salts.—The sulfonium salts were prepared by direct reaction of dimethyl sulfide and the α-halocarbonyl compounds. The synthesis of carbethoxymethyl dimethyl sulfonium bromide, N,N-diethylcarbamoylmethyl dimethyl sulfonium chloride, and dimethyl phenacyl sulfonium bromide have been previously described.[1] Other salts prepared are listed.

Dimethyl 4-nitrophenacyl sulfonium bromide, mp 123–125° (83%). *Anal.* Calcd for $C_{10}H_{12}BrNO_3S$: C, 39.22; H, 3.95; Br, 26.10; N, 4.58; S, 10.45. Found: C, 39.27; H, 3.94; Br, 25.89; N, 4.48; S, 10.19.

Dimethyl 4-bromophenacyl sulfonium bromide, mp 128.5–131.0° (85%). *Anal.* Calcd for $C_{10}H_{12}Br_2OS$: C, 35.31; H, 3.56; Br, 47.00; S, 9.43. Found: C, 35.10; H, 3.42; Br, 46.81; S, 9.53.

Dimethyl 4-phenylphenacyl sulfonium bromide, mp 139.5–141.5° (55%). *Anal.* Calcd for $C_{16}H_{17}BrOS$: S, 9.51. Found: S, 10.22.

Synthesis of Sulfonium Ylids.—The procedures used are illustrated with dimethyl phenacyl sulfonium bromide.

A. Sodium Hydride Method.—To a stirred suspension of dimethyl phenacyl sulfonium bromide (13.06 g, 0.05 mole) in tetrahydrofuran (250 ml) was added sodium hydride (2.3 g, 53% dispersion in mineral oil, 0.05 mole) in one portion. The reaction system was connected to a gas meter and stirred for 2 hr or until the evolution of hydrogen stopped (1120 cc, 100%). The mixture was filtered to remove sodium bromide (5.5 g) and the yellow solution was evaporated to a yellow oil which solidified upon addition of petroleum ether (bp 30–75°). The yellow phenacylide (8.95 g, 99%), mp 54–57°, was recrystallized from benzene–petroleum ether: mp 56–57°.

B. Sodium Hydroxide Method.—Dimethyl phenacyl sulfonium bromide (5.0 g, 0.019 mole) was dissolved in water (30 ml). The colored suspension was filtered and the clear filtrate was treated with 10% aqueous sodium hydroxide (50 ml, 0.125 mole). The solution was stirred and then extracted several times with chloroform. The chloroform extract was dried and evaporated to give an orange oil which upon cooling immediately solidified to an orange solid (3.60 g, 100%), mp 72–75°. The infrared spectrum and nmr spectrum were identical with the

(16) Methanol similarly produces an alcoholate.

(17) A. W. Johnson and R. B. LaCount, *Tetrahedron*, **9**, 130 (1960).

(18) W. von E. Doering and A. K. Hoffmann, *J. Am. Chem. Soc.*, **77**, 521 (1955).

(19) An attempt to titrate the conjugate acids of the ylids, $(CH_3)_2S{=}CHCOR$, R = OC_2H_5 and $N(C_2H_5)_2$, under the same conditions was not successful, as the titration is not reversible.

(20) A direct measure of the basicity of the triphenylphosphonium and dimethylsulfonium fluorenylids indicated that the S-ylid is still less basic than the P-ylid; see ref 17. The (dimethylsulfuranylidene)acetophenones are more basic than (triphenylphosphoranylidene)acetophenones, whereas Johnson has reported the reverse is true with the fluorenyl-stabilized ylids. The much greater steric interaction of $(C_6H_5)_3P$ than $(CH_3)_2S$ with the *peri* hydrogens of the fluorenyl system may decrease the coplanarity of the former system so that p–d overlap is reduced. The basicity of the P-ylid may be concomitantly increased by a sufficient amount to reverse the usual order of basicity.

(21) S. Fliszar, R. F. Hudson, and G. Salvadori, *Helv. Chim. Acta*, 1580 (1963).

(22) F. Krohnke, *Chem. Ber.*, **68**, 1177 (1935).

(23) All melting points are uncorrected. Analyses were performed by Galbraith Laboratories, Knoxville, Tenn.

previous phenacylide. Upon recrystallization of the solid as before a 95% yield of product was obtained: mp 56–57°.

C. Silver Oxide Method.—The procedure followed was that of Bohme and Krause.[12] To a suspension of silver oxide (11.58 g, 0.05 mole) in 150 ml of water was added dropwise a solution of dimethyl phenacyl sulfonium bromide (13.06 g, 0.05 mole) in 400 ml of water. Precipitation occurred and, after addition was completed, the solution was filtered and the water was removed by evaporation on a rotary evaporator. The black, syrupy material was dissolved in chloroform and filtered, and the chloroform was evaporated. The residue was kept in a desiccator over sulfuric acid. Crystals were formed and were separated by filtration (7.5 g, 83%), mp 50–55°. The infrared spectrum was identical with that from above methods.

Repeated recrystallization of the sample from benzene–petroleum ether gave a pure sample which was dried over phosphorus pentoxide *in vacuo*. *Anal.* Calcd for $C_{10}H_{12}OS$:[24] C, 66.62; H, 6.76; S, 17.79. Found: C, 66.35; H, 6.91; S, 17.53.

(24) Although molecular weight determinations were always high (Calcd: 180. Found: 244) for this compound, the 4-nitro substituted ylid V, R = CH_3; R′ = 4-$C_5H_4NO_2$, yielded a correct molecular weight by osmometric techniques (Calcd: 224. Found: 227.).

The remaining ylids in Table I were recrystallized from benzene. Repeated efforts to crystallize the ester and amide were unsuccessful.

A solution of the ylid (0.20 g) in ether–chloroform was treated with anhydrous hydrogen bromide. Dimethyl phenacyl sulfonium bromide, 0.26 g (90%), mp 137–138°, was precipitated.

Hydrolysis of (Dimethylsulfuranylidene)acetophenone.—Seven grams (0.039 mole) of the above ylid was dissolved in aqueous potassium hydroxide (70 ml, 1 *N*) and the mixture was refluxed 19 hr. The yellow solution was cooled and extracted with ether (two 10-ml portions), then methylene chloride (two 10-ml portions). The aqueous layer was acidified with 10% hydrochloric acid and extracted with methylene chloride (two 20-ml portions), and the organic layer was dried over magnesium sulfate. Concentration of this solution gave 4.3 g (91%) of benzoic acid.

Measurement of p*K* Values (Figure 1).—The p*K* values were determined by the method given in ref 3.

Sulfur-Containing Polypeptides. II. Selective Removal of S-Protective Groups from Some L-Cysteinyl-L-cysteine Derivatives[1,2]

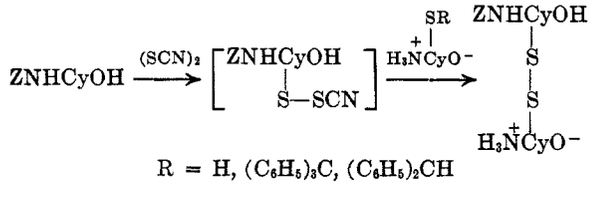
RICHARD G. HISKEY, TOMISHIGE MIZOGUCHI, AND HIROSHI IGETA

Venable Chemical Laboratory, The University of North Carolina, Chapel Hill, North Carolina

Received October 27, 1965

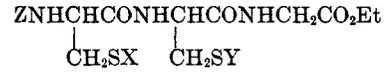
The synthesis of four derivatives of ethyl N-carbobenzoxy-L-cysteinyl-L-cysteinylglycinate is described. The S-protective groups studied were S-triphenylmethyl, S-diphenylmethyl, and S-benzoyl. Mercury(II) acetate was found to cleave selectively the S-triphenylmethyl group while sodium ethoxide selectively removed the S-benzoyl group.

An important aspect of the synthetic problem associated with the preparation of polypeptides "cross-lined" or "looped" at known positions by cysteine residues is the stepwise formation of the disulfide bonds. This, in turn, requires the selective removal of various sulfur-protective groups from the appropriate cysteine residues. One approach to this situation has involved the use of S-protective groups which would exhibit a reactivity gradient toward thiocyanogen, a reagent found[3,4] to convert various cysteine derivatives to the corresponding sulfenylthiocyanates; the latter behave similarly to thiocyanogen and provide unsymmetrical cysteine derivatives when allowed to react with another cysteine compound. In order to obtain maximum



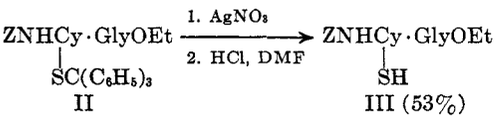
R = H, $(C_6H_5)_3C$, $(C_6H_5)_2CH$

utility from the sulfenylthiocyanate method of disulfide synthesis it appears to be necessary to employ the thiol group of cysteine as well as the S-tri- and -diphenylmethyl thioether derivatives. Therefore, synthetic methods for the conversion of specific S-blocked cysteine residues to the free thiol are required. Although several recent reports[5] have concerned methods for the removal of a single S-protective group in various cysteine peptides, no data are available on the removal of one S-blocking group in the presence of another.[6] The present report concerns the selective cleavage of several S-protective groups (X and Y) in the model tripeptide, ethyl N-carbobenzoxy-L-cysteinyl-L-cysteinylglycinate (I).



Ia, X = $(C_6H_5)_2CH$; Y = $(C_6H_5)_3C$
b, X = $(C_6H_5)_3C$; Y = $(C_6H_5)_2CH$
c, X = C_6H_5CO; Y = $(C_6H_5)_3C$
d, X = $(C_6H_5)_2CH$; Y = C_6H_5CO

The S-triphenylmethyl group was initially reported[7] to be cleaved by the action of hydrogen chloride in chloroform. Subsequently Zervas and Photaki[5a] demonstrated that ethyl N-carbobenzoxy-S-triphenylmethyl-L-cysteinylglycinate (II) was converted to the cysteine derivative (III) by the action of silver nitrate



(1) Part I of this series: R. G. Hiskey and J. B. Adams, Jr., *J. Am. Chem. Soc.*, **87**, 3969 (1965).

(2) Supported by Grant A-3416 from the National Institute of Arthritis and Metabolic Diseases of the National Institutes of Health, U. S. Public Health Service.

(3) R. G. Hiskey and W. P. Tucker, *J. Am. Chem. Soc.*, **84**, 4796 (1962).

(4) R. G. Hiskey and D. N. Harpp, *ibid.*, **87**, 3965 (1965).

(5) (a) L. Zervas and I. Photaki, *ibid*, **84**, 3887 (1962); (b) L. Zervas, I. Photaki, and N. Ghelis, *ibid.*, **85**, 1337 (1963); (c) M. Sokolovsky, M. Wilchek, and A. Patchornik, *ibid.*, **86**, 1202 (1964).

(6) A referee has informed us that a paper on this topic by L. Zervas, *et al.*, has appeared: *ibid.*, **87**, 4922 (1965).

(7) L. Velluz, G. Amiard, J. Bartos, B. Goffinet, and R. Heymes, *Bull. Soc. Chim. France*, 1464 (1956).