

prepared from DL-*p*-nitrophenylalanine (Cyclo Chemical Corp.) via N-chloroacetylation, ammonolysis, and fusion of the resulting glyceryl-*p*-nitrophenylalanine in phenol.⁴ Glyceryl-*p*-nitrophenylalanine, crystallized from water, decomposed above 290°.

Anal. Calcd for C₁₁H₁₃N₃O₅: C, 49.43; H, 4.90; N, 15.73. Found: C, 49.31; H, 4.89; N, 15.75.

3-*p*-Nitrobenzyl-2,5-piperazinedione, also crystallized from water, was obtained as pale yellow needles, mp 300° dec.

Anal. Calcd for C₁₁H₁₁N₃O₄: C, 53.01; H, 4.45; N, 16.86. Found: C, 52.91; H, 4.39; N, 17.03.

Results

The estimated enthalpies by which the folded form of the 3-benzylpiperazine-2,5-diones are stabilized are shown in Table II. In each of the four solvents, the enthalpies for the nitro and unsubstituted compounds are almost identical, and the estimated equilibrium constants, [folded]/[unfolded], do not differ by as much as a factor of 2. If the aromatic ring were acting as a donor of electron density in a donor-acceptor or charge-transfer complex, nitro substitution should destabilize the folded conformation,^{7,8} if the aromatic ring were the acceptor, nitro substitution should increase the stability of the folded form.⁹ Since neither effect is apparent, we think that it is safe to conclude that donor-acceptor interactions are not a major factor in stabilizing the face-to-face arrangement of rings in 3-benzylpiperidine-2,5-diones.

Two other features of the data in Table II should be noted.

In trifluoroacetic acid, stabilization of the folded form of the methoxy and hydroxy compounds is increased by 1 kcal/mol relative to the nitro and unsubstituted cases. There is an almost compensating increase in negative entropy for the folded form. This may indicate specific solvation, involving the oxygen substituents, of the folded form.

If the folded conformation of a given piperazinedione is the same in all solvents, the magnetic effect of the phenyl ring on the 6 proton will also be the same. There is no apparent interference to solvation at the periphery of the piperazinedione ring, and if there are no specific effects of solvation of the substituents on the aromatic ring, changes in $\Delta\delta$ with change in solvent reflect the exclusion of solvent from the face of the piperazinedione ring in the folded form. In this light, it is of interest that the limiting upfield shifts for the *cis* 6 protons of unsubstituted 3-benzylpiperazine-2,5-dione increase significantly with proton acidity of the solvent. An explanation of this trend in terms of the details of solvation will have to be deferred.

Registry No.—2,5-Piperazinedione, 106-57-0; 3-isopropyl-2,5-piperazinedione, 14771-77-8; L-3-*p*-methoxybenzyl-2,5-piperazinedione, 21996-47-4; DL-3-*p*-nitrobenzyl-2,5-piperazinedione, 21996-48-5; glyceryl-*p*-nitrophenylalanine, 21996-49-6; 3-benzyl-2,5-piperazinedione, 10125-07-2; 3-*p*-hydroxybenzyl-2,5-piperazinedione, 5625-49-0.

(7) L. J. Andres and R. M. Keefer [*J. Amer. Chem. Soc.*, **72**, 3113 (1950)] have reported that the formation constant for the complex of nitrobenzene with silver ion is 0.19 l./mol, while that for benzene is 2.4 l./mol.

(8) G. F. Crable and G. L. Kearns [*J. Chem. Phys.*, **66**, 436 (1962)] report ionization potentials of 8.83, 9.56, and 10.18 eV for anisole, benzene, and nitrobenzene, respectively. Ionization potentials should correlate with donor ability in charge-transfer complex formation.

(9) Numerical data for benzene and nitrobenzene as acceptors in complexes are not available, but the π -acid properties of polynitrobenzenes are well known. J. E. Lovelock [*Nature*, **189**, 729 (1961)] reports that the affinity of nitrobenzene for thermal electrons is about 10⁶ that of benzene.

Further Studies on N-Acylamino Acid Esters of 4-(Methylthio)phenol

BRIAN J. JOHNSON¹ AND THERESE A. RUETTINGER

Department of Chemistry, Tufts University,
Medford, Massachusetts 02155

Received July 2, 1969

A new amino acid carboxyl protecting group, the 4-(methylthio)phenyl ester (MTP), has been developed and suggested for use in peptide synthesis by this laboratory.² The attractive feature of this protective ester is its facile conversion without racemization³ to the activated 4-(methylsulfonyl)phenyl ester (MSO₂P).⁴ This method of synthesis has been used successfully for the preparation of an N-carbobenzoxy heptapeptide⁵ and advantageously in the synthesis of an N,N'-dicarbobenzoxy-O-depsipeptide.⁶

The broad range of potential utility for the MTP ester for the preparation of polypeptides prompted an investigation of the actual scope of this method with respect to the stability of amino acids and commonly used protecting groups to the oxidation conditions employed to produce the MSO₂P activated esters. To this end, the N-protected amino acid MTP esters were easily prepared, in good yield, by condensing the N-protected amino acid with 4-(methylthio)phenol, using N,N'-dicyclohexylcarbodiimide (DCC)⁷ (see Table I).

However, oxidation of the N-carbobenzoxy amino acid MTP esters of lysine, alanine, leucine, glycine, and glutamic acid with 30% hydrogen peroxide in glacial acetic acid for 12 hr at room temperature resulted in the corresponding MSO₂P activated esters, even in the presence of the N-trifluoroacetyl and *t*-butyl ester protecting groups. These conditions were found to be too drastic for the *t*-butyloxycarbonyl and *O*-*t*-butyl ether protecting groups as well as the indole nucleus of tryptophan. In order to circumvent these difficulties, new milder oxidation conditions were used: a solution of the N-protected amino acid MTP ester in dioxane was treated with 3 equiv of 85% *m*-chloroperoxybenzoic acid at room temperature for 4 hr. Under these reaction conditions, it was possible to oxidize a large number of N-carbobenzoxy amino acid MTP esters (see Table II) to their corresponding MSO₂P activated esters. Of these amino acids, it is worthy of note that the following sensitive residues were found to be stable to these conditions: the indole nucleus of tryptophan, the nitroguanidine moiety of arginine, and the primary amide of glutamine. Further, these new oxidation conditions allowed the activated MSO₂P ester to be formed in the presence of N-*t*-butoxycarbonyl, N-carbobenzoxy, and *O*-*t*-butyl ether protecting groups.

The utility of the MTP ester also depends to a great extent on the ease with which the N-protecting group

(1) To whom any correspondence should be sent.

(2) B. J. Johnson and P. M. Jacobs, *Chem. Commun.*, 73 (1968).

(3) B. J. Johnson and P. M. Jacobs, *J. Org. Chem.*, **33**, 4524 (1968).

(4) R. Schwyzer and P. Sieber, *Helv. Chim. Acta*, **41**, 2190 (1958). These authors have reported a few 4-(methylsulfonyl)phenyl esters prepared from 4-(methylsulfonyl)phenol through the diaryl sulfite method.

(5) B. J. Johnson and E. G. Trask, *J. Org. Chem.*, **33**, 4521 (1968).

(6) B. J. Johnson, *ibid.*, **34**, 1178 (1969).

(7) J. C. Sheehan and G. P. Hess, *J. Amer. Chem. Soc.*, **77**, 1067 (1955).

TABLE I
 N-ACYL-L-AMINO ACID 4-(METHYLTHIO)PHENYL ESTERS (MTP)

Compd	Registry no.	Reaction conditions	Yield, %	Mp, °C	Molecular formula	Analyses, %								[α] _D
						Calcd				Found				
						C	H	N	S	C	H	N	S	
Z-Ala	17662-73-6	a	73	114	C ₁₈ H ₁₉ NO ₄ S	62.6	5.5		9.3	62.7	5.7		9.6	[α] _D ²⁰ -48.5° (c 1.50, AcOH)
Z-Glu	17662-74-7	a	60	81	C ₂₄ H ₂₉ NO ₆ S	62.7	6.4	3.0		62.55	6.4	3.1		[α] _D ²⁰ -36.8° (c 0.49, MeOH)
OBu- <i>t</i> Z-Glu	22142-09-2	b	10	133.5	C ₂₉ H ₃₂ N ₂ O ₈ S	59.7	5.5		8.0	59.8	5.4		7.8	[α] _D ²⁰ -21.5° (c 3.14, DMF ^c)
γ-NH ₂ BOC-Gly	17646-22-9	a		79	C ₁₄ H ₁₉ NO ₄ S	56.5	6.4		10.8	56.7	6.45		10.6	
Z-Gly	17646-21-8	a	70	110	C ₁₇ H ₁₇ NO ₄ S	61.6	5.2		9.7	61.5	5.2		9.5	
Z-His	22142-12-7	d	37.5	102	C ₂₃ H ₂₇ N ₃ O ₄ S	67.0	5.4	8.4		67.3	5.3	8.2		[α] _D ²⁰ -24.6° (c 5.415, CHCl ₃)
im Bzl Z-Ile	22142-13-8	a	53	77	C ₂₁ H ₂₅ NO ₄ S	65.1	6.5		8.2	64.9	6.2		8.2	[α] _D ²⁷ +20.1° (c 1.82, CHCl ₃)
Z-Leu	22142-14-9	a	41	45	C ₂₁ H ₂₅ NO ₄ S	65.1	6.5		8.2	65.25	6.5		8.3	[α] _D ²⁰ +7.9° (c 1.96, CHCl ₃)
Z-Lys	22142-15-0	a	62	118	C ₂₃ H ₂₅ F ₃ N ₃ O ₅ S	55.4	5.1		6.4	55.1	5.3		6.5	[α] _D ²⁷ +78.4° (c 0.67, CHCl ₃)
ε-TFA Z-Arg	22142-16-1	b	33	105	C ₂₁ H ₂₅ N ₅ O ₆ S	53.0	5.3		6.7	53.4	5.3		6.6	[α] _D ²⁰ -25.8° (c 2.0, CHCl ₃)
NO ₂ Z-Phe	22142-17-2	a	59	115	C ₂₄ H ₂₃ NO ₄ S	68.4	5.5		7.6	68.3	5.4		7.6	[α] _D ²³ +23.0° (c 1.87, CHCl ₃)
Z-Pro	22142-18-3	a	53	86	C ₂₀ H ₂₁ NO ₄ S	64.7	5.4		8.9	64.85	5.7		8.7	[α] _D ²² -87.7° (c 1.75, CHCl ₃)
Z-Sar	22142-19-4	a	55	55	C ₁₅ H ₁₉ NO ₄ S	62.6	5.6		9.3	62.7	5.7		9.1	
BOC-Thr	22142-20-7	a	57		C ₂₃ H ₂₉ NO ₆ S	64.0	6.8		7.4	63.5	7.0		7.3	[α] _D ²⁰ -24.6° (c 5.415, CHCl ₃)
OBzl Z-Try	22142-21-8	a	56	111	C ₂₈ H ₃₁ N ₂ O ₇ S	67.8	5.3		7.0	67.5	5.5		6.8	[α] _D ²⁷ +9.3° (c 2.635, CHCl ₃)
Z-Tyr	22142-22-9	a	38	100	C ₂₃ H ₂₁ NO ₅ S	68.1	6.3		6.5	68.0	6.2		6.5	[α] _D ²⁷ +17.1° (c 3.75, CHCl ₃)
OBu- <i>t</i> Z-Val	17662-75-8	a	70	77	C ₂₀ H ₂₃ NO ₄ S	65.1	6.5	3.6		64.8	6.4	3.7		[α] _D ²⁰ -41.2° (c 1.69, HOAc)

^a Methylene chloride at 0° for ca. 1 hr, then at room temperature overnight. ^b Dimethylformamide-acetonitrile at 0° for 13 hr; then at room temperature overnight. ^c DMF = dimethylformamide. ^d Dimethylformamide at room temperature for 18 hr.

 TABLE II
 N-ACYL-L-AMINO ACID 4-(METHYLSULFONYL)PHENYL ESTERS (MSO₂P)

Compd	Registry no.	Reaction conditions	Yield, %	Mp, °C	Molecular formula	Analyses, %								[α] _D
						Calcd				Found				
						C	H	N	S	C	H	N	S	
Z-Ala	17662-80-5	a	91	106	C ₁₈ H ₁₉ NO ₆ S	57.3	5.1	3.8		57.4	5.2	3.8		[α] _D ²⁰ -41.9° (c 0.42, HOAc)
Z-Glu	17662-82-7	a	86	104	C ₂₄ H ₂₉ NO ₈ S	58.6	5.9	2.8		58.6	5.9	2.9		[α] _D ²⁰ -10.3° (c 0.70, MeOH)
OBu- <i>t</i> Z-Glu	22142-26-3	b	71	166	C ₂₉ H ₃₂ N ₂ O ₇ S	55.3	5.1		7.4	55.4	5.2		7.1	[α] _D ²⁰ -16.6° (c 1.65, DMF ^c)
γ-NH ₂ BOC-Gly	22142-27-4	b	78	143	C ₁₄ H ₁₉ NO ₆ S	51.0	5.8		9.7	50.95	5.9		9.7	
Z-Gly	22142-28-5	a	73	132	C ₁₇ H ₁₇ NO ₆ S	56.2	4.7		8.8	56.1	4.9		8.8	
Z-Ile	22142-29-6	b	70	81	C ₂₁ H ₂₅ NO ₆ S	60.1	6.0		7.6	60.2	6.0		7.6	[α] _D ²⁷ +32.4° (c 1.48, CHCl ₃)
Z-Leu	22142-30-9	b	55	90	C ₂₁ H ₂₅ NO ₆ S	60.1	6.0		7.6	59.85	6.0		7.4	[α] _D ²⁷ -3.7° (c 3.17, CHCl ₃)
Z-Lys	22142-31-0	a	50	117	C ₂₃ H ₂₅ F ₃ N ₃ O ₇ S	52.0	4.9		6.0	52.2	4.9		5.7	[α] _D ²⁷ +13.9° (c 2.38, CHCl ₃)
ε-TFA Z-Arg	22142-32-1	b	40	82.5	C ₂₁ H ₂₅ N ₅ O ₈ S	49.7	5.0		6.3	49.8	4.9		6.05	[α] _D ²⁷ +15.8° (c 1.52, CHCl ₃)
NO ₂ Z-Phe	22142-33-2	b	33	105	C ₂₄ H ₂₃ NO ₈ S	63.6	5.1		7.1	63.6	5.2		7.1	[α] _D ²³ +33.0° (c 1.35, CHCl ₃)
Z-Pro	22142-34-3	a	77	98	C ₂₀ H ₂₁ NO ₆ S	59.6	5.2			59.7	5.4		7.9	[α] _D ²³ -87.7° (c 1.10, CHCl ₃)
Z-Sar	22142-35-4	b	50	98	C ₁₅ H ₁₉ NO ₆ S	57.3	5.1		8.5	57.2	4.9		8.2	
BOC-Thr	22142-36-5	b	38	101	C ₂₃ H ₂₉ NO ₇ S	59.6	6.3		6.9	59.5	6.1		6.9	[α] _D ²⁷ -38.2° (c 1.19, CHCl ₃)
OBzl Z-Try	22142-37-6	b	71	119	C ₂₈ H ₃₁ N ₂ O ₆ S	63.4	4.9		6.5	63.5	4.9		6.5	[α] _D ²⁷ +46.0° (c 1.16, CHCl ₃)
Z-Tyr	22155-46-0	b	50	104.5	C ₂₃ H ₂₁ NO ₇ S	64.0	6.0		6.1	64.0	6.0		6.1	[α] _D ²³ +21.6° (c 2.59, CHCl ₃)
OBu- <i>t</i> Z-Val	22142-38-7	b	60	100	C ₂₀ H ₂₃ NO ₆ S	59.2	5.7		7.9	59.2	5.5		7.75	[α] _D ²⁷ +9.0° (c 2.22, CHCl ₃)

^a Excess 30% hydrogen peroxide in glacial acetic acid at room temperature overnight. ^b 3 mol equiv of 85% *m*-chloroperbenzoic acid at room temperature for 4 hr. ^c DMF = dimethylformamide.

can subsequently be removed. Facile removal of the *N*-*t*-butoxycarbonyl group by treatment of the MTP ester with HCl in glacial acetic acid has already been reported.² Removal of the *N*-carbobenzyloxy protect-

ing group from an amino acid MTP ester is not possible by hydrogenolysis. However, it can be cleaved readily with HBr in glacial acetic acid (see Table III) without interchange between the thio ether and benzyl

TABLE III
 L-AMINO ACID 4-(METHYLTHIO)PHENYL ESTER (MTP) HYDROBROMIDES

Compd	Registry no.	Yield, %	Mp, °C	Molecular formula	Calcd			Analyses, %			[α] _D
					C	H	Br	C	H	Br	
H-Ala	22142-39-8	87	159	C ₁₀ H ₁₄ BrNO ₂ S	41.1	4.8	27.3	41.1	4.7	27.2	[α] _D ²⁰ +4.4° (c 2.98, MeOH)
H-Gly	22142-40-1	100	250	C ₉ H ₁₂ BrNO ₂ S	38.9	4.3	28.7	39.05	4.3	28.7	
H-Ile	22142-41-2	71	191	C ₁₃ H ₂₀ BrNO ₂ S	46.7	6.0	23.9	46.8	5.9	24.15	[α] _D ²⁰ +29.9° (c 1.32, MeOH)
H-Leu	22142-42-3	43	147	C ₁₃ H ₂₀ BrNO ₂ S	46.7	6.0	23.9	46.9	6.2	24.0	[α] _D ²⁰ +17.3° (c 0.375, MeOH)
H-Lys	22142-43-4	44	151	C ₁₅ H ₂₀ BrF ₃ N ₂ O ₆ S	40.5	4.5	17.9	41.2	4.8	16.8	[α] _D ²⁰ +23.3° (c 2.38, MeOH)
ε-TFA											
H-Phe	22155-47-1	82	226	C ₁₆ H ₁₈ BrNO ₂ S	52.2	4.9	21.7	52.1	4.8	21.7	[α] _D ²⁰ +34.7° (c 1.90, MeOH)
H-Pro	22142-44-5	81	135	C ₁₂ H ₁₆ BrNO ₂ S	45.3	5.1	25.1	45.2	4.95	25.3	[α] _D ²⁰ -21.9° (c 1.30, MeOH)
H-Sar	22142-45-6	80	203	C ₁₀ H ₁₄ BrNO ₂ S	41.1	4.8	27.3	41.2	4.9	27.6	
H-Val	17662-76-9	69	216.5	C ₁₂ H ₁₆ BrNO ₂ S	45.0	5.7	25.0	44.95	5.7	25.2	[α] _D ²⁰ +17.3° (c 2.40, MeOH)

bromide, a side reaction which has been observed for N-carbobenzoxymethionine.⁸ This tends to indicate that this side reaction with the MTP ester occurs at a very slow rate or not at all.

From this work a new general activating procedure has been developed for the MTP esters of N-protected amino acids which has been found to extend the utility of the MTP ester for peptide synthesis to most of the sensitive amino acids and protecting groups. However, it is anticipated that this method of activation will be of little use for peptides which include the amino acid residues of methionine, cysteine, and cystine.

Experimental Section⁹

General Procedure for the Preparation of N-Carbobenzoxy-L-amino Acid 4-(Methylthio)phenyl Esters.—The general procedure is illustrated in the preparation of N-carbobenzoxy-L-tryptophan 4-(methylthio)phenyl ester. To an ice-cooled solution of N-carbobenzoxy-L-tryptophan (3.7 g, 12 mmol) in methylene chloride (25 ml) was added N,N'-dicyclohexylcarbodiimide (2.5 g, 12 mmol), followed by the addition of 4-(methylthio)phenol (1.5 g, 12 mmol). The reaction mixture was stirred at 0° for ca. 1 hr, then warmed to room temperature and stirred overnight. The solution was diluted with 25 ml of methylene chloride and the insoluble urea was filtered off and washed with 50-ml portions of methylene chloride. The filtrate and washes were combined, and the solvent was removed under reduced pressure. The oily brown residue was dissolved in ethyl acetate (250 ml) and washed with 10% citric acid solution (100 ml), 10% sodium bicarbonate solution (100 ml), and saturated sodium chloride solution (100 ml) and dried (Na₂SO₄), and the solvent was removed under reduced pressure. The thin, brown oil (6.6 g) was dissolved in chloroform (20 ml) and chromatographed on a SilicAR cc-7 column, using chloroform as the eluent. The crude oils were recrystallized from ethyl acetate-hexane to yield white, solid N-carbobenzoxy-L-tryptophan 4-(methylthio)phenyl ester (3.1 g, 56.4%), mp 108–111°. Further recrystallization from ethyl acetate-hexane gave a white solid: mp 111°; [α]_D²⁷ +9.3° (c 2.635, chloroform).

Anal. Calcd for N-carbobenzoxy-L-tryptophan 4-(methylthio)phenyl ester: C, 67.8; H, 5.3; S, 7.0. Found: C, 67.5; H, 5.5; S, 6.8.

General Procedure for the Preparation of N-Carbobenzoxy-L-amino Acid 4-(Methylsulfonyl)phenyl Esters.—The oxidation of the N-carbobenzoxy-L-amino acid 4-(methylthio)phenyl esters to their sulfone analogs was carried out as illustrated in the preparation of N-carbobenzoxy-L-valine 4-(methylsulfonyl)phenyl ester. To a solution of N-carbobenzoxy-L-valine 4-(methylthio)phenyl ester (1.8 g, 5 mmol) in dioxane (25 ml) was added *m*-chloroperbenzoic acid (2.6 g, 15 mmol). The reaction mixture was stirred at room temperature for ca. 4 hr. The solution was then poured into a solution of sodium bicarbonate (2.1 g, 25 mmol) in water (75 ml). The resulting white suspension was extracted once with ethyl acetate (250 ml); the aqueous phase was saturated with sodium chloride and extracted again with two 150-ml portions of ethyl acetate. The combined ex-

tracts were washed with two 150-ml portions of saturated sodium chloride solution and dried (Na₂SO₄), and the solvent was removed under reduced pressure. The resulting solid (2.6 g) was dissolved in chloroform (15 ml) and chromatographed on a SilicAR cc-7 column, using chloroform as the eluent. The first eight fractions were recrystallized from ethyl acetate-hexane to yield white, solid N-carbobenzoxy-L-valine 4-(methylsulfonyl)phenyl ester (1.2 g, 60%), mp 99–101°. Recrystallization from ethyl acetate-hexane a second time gave a white solid: mp 100–101°; ν_{\max} 1310 and 1145 cm⁻¹ (sulfone); [α]_D²⁷ +9.0° (c 2.2, chloroform).

Anal. Calcd for N-carbobenzoxy-L-valine 4-(methylsulfonyl)phenyl ester: C, 59.2; H, 5.7; S, 7.9. Found: C, 59.2; H, 5.5; S, 7.75.

General Procedure for the Preparation of L-Amino Acid 4-(Methylthio)phenyl Ester Hydrobromides.—The general procedure for the removal of the carbobenzoxy protecting group to yield the hydrobromide salts of L-amino acid 4-(methylthio)phenyl esters is illustrated in the preparation of L-phenylalanine 4-(methylthio)phenyl ester hydrobromide. To a slurry of N-carbobenzoxy-L-phenylalanine 4-(methylthio)phenyl ester (2.1 g, 5 mmol) in glacial acetic acid (10 ml) was added a solution (20 ml) of anhydrous hydrogen bromide (2.7 g, 33 mmol) in a glacial acetic acid. The resulting yellow solution was stirred at room temperature for ca. 35 min. The solvent and excess hydrogen bromide were then removed under reduced pressure. The residual cream-colored solid was slurried with anhydrous ethyl ether, filtered, and recrystallized from anhydrous methanol-anhydrous ethyl ether to yield white, needle-like crystals of L-phenylalanine 4-(methylthio)phenyl ester hydrobromide (1.4 g, 82%), mp 220–225°. Further recrystallization gave a white solid: mp 226°; [α]_D²⁸ +34.7° (c 1.9, methanol).

Anal. Calcd for L-phenylalanine 4-(methylthio)phenyl ester hydrobromide: C, 52.2; H, 4.9; Br, 21.7. Found: C, 52.1; H, 4.8; Br, 21.7.

Acknowledgment.—The authors are indebted to the National Science Foundation, which supported this investigation, and also to the Crown Zellerbach Corp. for samples of 4-(methylthio)phenol.

Acenaphthylene Oxide¹

T. H. KINSTLE AND P. J. IHRIG²

Department of Chemistry, Iowa State University,
Ames, Iowa

Received October 1, 1968

In the course of preparing a series of deuterium-labeled alkylacenaphthylenes for a mass spectral investigation of phenalenium ion formation,³ it became

(1) This work was supported in part by grants from the Research Corporation and Eli Lilly & Co.

(2) National Defense Education Act Fellow, 1967–1968.

(3) T. H. Kinstele and P. J. Ihrig, Abstracts, 153rd National Meeting of the American Chemical Society, Miami, Fla., April 1967, O, 110.

(8) S. Guttman and R. A. Boissonnas, *Helv. Chim. Acta*, **42**, 1257 (1959).

(9) Melting points were taken on a Mel-Temp apparatus and are uncorrected. Analyses were performed by Dr. S. M. Nagy, Belmont, Mass.