Solvent Effect in a Sterically Controlled Synthesis of Optically Active α-Amino Acids from α-Keto Acids by Hydrogenolytic Asymmetric Transamination[1]

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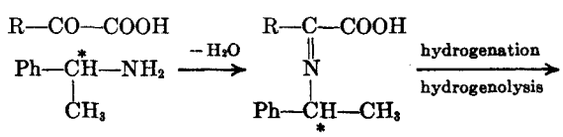
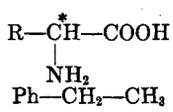
Received May 31, 1968

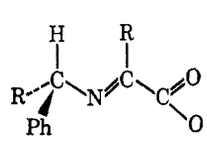
The solvent effect of the hydrogenolytic asymmetric transamination of α-keto acid with optically active α-alkylbenzylamine was studied by the use of various solvent systems. The possible steric course of the asymmetric synthesis was discussed.

Several nonenzymatic asymmetric syntheses of α-amino acids from their corresponding α-keto acids have been reported.[3-9] Hiskey and Northrop[5] reported the syntheses of optically active α-amino acids from the Schiff bases of α-keto acids with (*S*)(−)- and (*R*)(+)-α-methylbenzylamine by catalytic hydrogenation and subsequent hydrogenolysis. Harada[7] reported

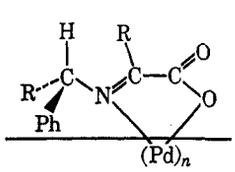




the syntheses of several optically active amino acids from α-keto acids by the use of (*S*)(+)- and (*R*)(−)-α-phenylglycine in alkaline aqueous solution. Recently, Kanai and Mitsui[8] reported the synthesis of optically active phenylglycine by the Hiskey method[4] and proposed a steric course for the asymmetric synthesis. In a recent study in this laboratory,[10] many Hiskey-type reactions were carried out in order to study the steric course using several α-keto acids and using optically active α-methyl- and α-ethylbenzylamine. From these results, it was proposed[10] that the possible conformation of the reactants could be structure I and that structure I would be a five-membered cyclic complex with the catalyst, as shown in structure II. Thus the sterically



I



II

controlled syntheses of α-amino acids from the Schiff bases of corresponding α-keto acids with optically active α-alkylbenzylamine would be explained by the formation of intermediate chelate structure II under the reaction conditions.

In the present study, in order to clarify further the steric course of the catalytic hydrogenation reaction of the Schiff bases of α-keto acids with optically active α-alkylbenzylamines, the solvent effect of the reaction was studied. The keto acids used were pyruvic acid, benzyl pyruvate, phenylglyoxylic acid, oxaloacetic acid, and α-ketoglutaric acid. Optically active amines used were (*S*)(−)- and (*R*)(+)-α-methylbenzylamine, (*S*)(−)- and (*R*)(+)-α-ethylbenzylamine, and (*R*)(+)-α-(1-naphthyl)ethylamine. Summarized results are shown in Table I.

Optically active alanine was synthesized from pyruvic acid (R′ = H) or benzyl pyruvate (R′ = $C_6H_5CH_2$) by the use of various optically active alkylamines (reactions 1–23 in Table I). Summarized results show that the optical activity of the synthesized alanine depends on the solvent used. When a less polar solvent was used, the optical activity of the resulting alanine was found to be higher (60–80%) and, when a polar solvent was used, lower optical activity (30–50%) of alanine resulted. In reactions 10–15 in Table I, higher optical activity was obtained by the use of hexane and ethyl acetate and lower optical activity resulted from the use of an aqueous dioxane solution (reaction 15). In the synthesis of glutamic acid by the use of (*S*)(−)-methylbenzylamine, when less polar solvents were used (reactions 27–29), (*S*)(+)-glutamic acid was formed as predicted by the intermediate substrate–catalyst complex. However, when polar solvents were used (reactions 30–33), (*R*)(−)-glutamic acid resulted under the same conditions. Optical activity of the resulting glutamic acid decreased dependent on the increase of polarity of the solvent used and finally the configuration of the resulting glutamic acid was reversed to the opposite structure. In other words, the configuration of glutamic acid prepared by the use of (*R*)(+)-ethylbenzylamine and (*S*)(−)-ethylbenzylamine using ethanol and a methanol–water–NaOH mixture (reactions 33 and 34, respectively) was found to be the same, *i.e.*, (*R*)(−)-glutamic acid.

Figure 1 shows the relationship between the optical activities of the amino acids and the dielectric constants of the solvents used. Because of the difficulty in estimating the dielectric constants of the mixed solvents, only a few reactions using rather simple systems are plotted in Figure 1. Generally, optical activities of the resulting amino acids decreased dependent on the increase of the dielectric constant.

The observed fact that the optical activity of the resulting amino acid decreased (alanine) or the sign of the activity inversed (glutamic acid) suggests that the

(1) Sterically controlled synthesis of optically active organic compounds VI. Part V: K. Harada and K. Matsumoto, *J. Org. Chem.*, **32**, 1794 (1967). Contribution No. 105 of the Institute of Molecular Evolution, University of Miami.

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(10) K. Harada and K. Matsumoto, *J. Org. Chem.*, **32**, 1794 (1967).

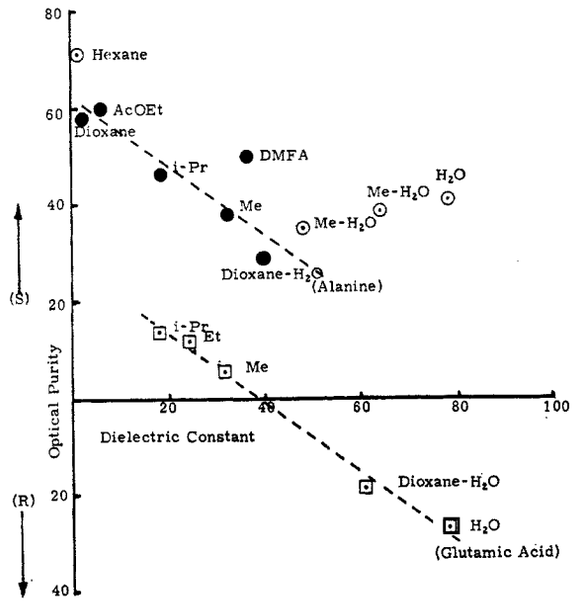

Figure 1.—Relationship between optical activities of synthesized amino acids and dielectric constants of the solvents used. Alanine was prepared from benzyl pyruvate and (*S*)(−)-α-methylabenzylamine. Glutamic acid was synthesized from α-ketoglutaric acid and (*S*)(−)-α-methylbenzylamine; ⊙ means that the reaction mixture was not homogeneous in the alanine syntheses.

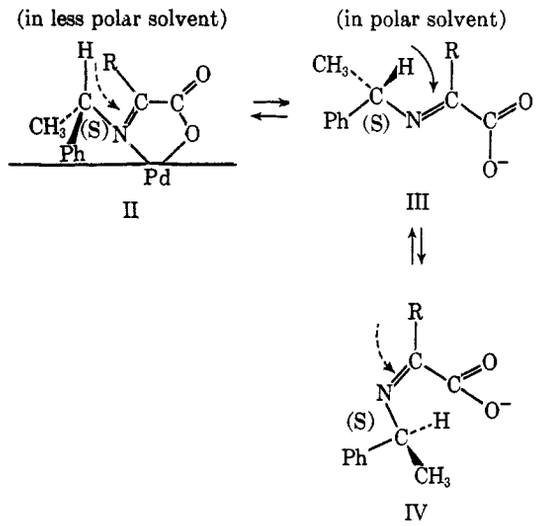

Figure 2.—Conformation of the substrate in polar and in less polar solvent.

conformation of the substrate molecule changes depending on the solvent used. As was discussed in the earlier study,[10] structure II could be the preferred conformation under conditions using a less polar solvent (hexane, ethyl acetate, alcohol). The reasons for choosing structure II are (1) electrostatic attraction between substrate and catalyst in such less polar solvents is stronger than that in polar solvents and (2) the solvation of the substrate in these less polar solvents is weak, so that the substrate could react easily with the catalyst to form the intermediate complex. On the other hand, when polar solvents were used, (1) electrostatic attraction between substrate and catalyst is weaker and (2) the strong solvation of the substrate interferes with the attraction between substrate and catalyst to form the intermediate complex. Therefore, it could be assumed that the more polar the solvent used, the greater the chance the substrate might exist in free forms in the solution. The inversion of sign of the optically active glutamic acid suggests that structure II would not be the major conformation in the polar solvent.

Figure 2 shows the postulated conformations of the substrate in polar and in less polar solvents. In the polar solvents, the proportion of nonchelate conformations III and IV could increase. When the substrate, the Schiff base of α-keto acid with optically active α-alkylamine, is hydrogenated in the polar solvent, structures III and IV could be adsorbed on the palladium catalyst at the less bulky side of the molecule without forming the intermediate complex. Therefore, when (*S*)-alkylbenzylamine was used, structures II, III, and IV resulted in the (*S*)-, (*R*)-, and (*S*)-amino acid, respectively, after catalytic hydrogenation and hydrogenolysis.

In the synthesis of alanine, structure II could be the major conformation throughout the synthesis. However, the increase of polarity of the solvent resulted in the increase of structure III so that the resulting optical activity of alanine decreased with the increasing polarity of the solvent. In the synthesis of glutamic acid, structure II could also be the major conformation in the less polar solvent. However, in the polar solvent structure III might be the major conformation. In the synthesis of aspartic acid, structures II and III might be the major conformations in the less polar and polar solvents, respectively, as in the glutamic acid synthesis. Therefore, in the polar solvent, (*R*)(−)-aspartic acid could be obtained by the use of (*S*)(−)-α-methylbenzylamine (reaction 26). However, oxaloacetic acid also resulted in (*S*)(+)-alanine. The alanine could be assumed to be synthesized from pyruvic acid which is a β-decarboxylation product of oxaloacetic acid. Accordingly, structure II could be the major conformation in the optically active alanine formation from the resulted pyruvic acid.

Free amino acids shown in Table I were isolated by ion-exchange resin. The optical activities were measured without further purification because such procedures resulted in fractionation of the optical isomers. The isolated free amino acids were converted into DNP-amino acids in the usual manner[11] and the DNP derivatives were purified by Celite column chromatography[12] without fractionation of optical isomers.[6,7,10] Therefore, the optical purity of the DNP-amino acids is more reliable than that of isolated crude free amino acids. In some experiments (in Table I), optical purity of the free amino acid is much lower than that of the corresponding DNP-amino acid, probably because of impurities.

Optical purities of amino acids prepared by the use of (+)-(1-naphthyl)ethylamine were found to be very high (78–86%). The assignment of the configurations of (−)-α-(1-naphthyl)ethylamine and (−)-α-ethylbenzylamine have been made already by the use of the optical rotary dispersion method.[13,14] Chemical evi-

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TABLE I

OPTICALLY ACTIVE AMINO ACIDS PREPARED BY THE USE OF VARIOUS SOLVENTS

	R—CO—COOR′	Confign of amine[a]	Reaction	Solvent[b]	Yield, %	Confign of amino acid	[α]D of isolated amino acid[d] (c, 5 N HCl)	Optical purity, %, of amino acid[e]	[α]D of DNP-amino acid[f] (c, 1 N NaOH)	Optical purity,[h] %
Ala	R = Me	(S)(−)-Me	1	THF	33	(S)(+)-Ala	+9.0 (3.09)	62	+94.4 (0.22)	66
	R′ = H		2	EtOH	78	(S)(+)	+9.2 (3.55)	63	+96.9 (0.33)	67
			3	H_2O, pyridine	78	(S)(+)	+4.1 (3.17)	28	+56.9 (0.36)	40
			4	H_2O, NaOH	69	(S)(+)	+3.8 (3.14)	26	+47.3 (0.53)	33
		(S)(−)-Et	5	EtOH	76	(S)(+)	+7.5 (3.46)	52	+72.8 (0.57)	52
			6	EtOH, H_2O, NaOH	65	(S)(+)	+4.1 (3.51)	28	+53.5 (0.40)	37
			7	MeOH:H_2O (1:4), NaOH	75	(S)(+)	+2.2 (3.47)	9	+28.4 (0.49)	31
		(R)(+)-Naph	8	EtOH	76	(R)(−)	−11.6 (3.75)	80	−120 (0.40)	83
			9	EtOH, H_2O, NaOH	65	(R)(−)	−10.7 (3.13)	74	−105 (0.47)	73
	R = Me	(S)(−)-Me	10	Hexane[c]	75	(S)(+)	+7.9 (3.48)	55	+10.3 (0.45)	72
	R′ = Benzyl		11	AcOEt	49	(S)(+)	+6.4 (2.92)	44	+87.0 (0.55)	60
			12	*i*-PrOH	56	(S)(+)	+5.0 (4.63)	34	+65.7 (0.47)	46
			13	DMFA	47	(S)(+)			+72.1 (0.52)	50
			14	MeOH	61	(S)(+)	+1.4 (5.58)	10	+55.0 (0.52)	38
			15	Dioxane:H_2O (45:55)	71	(S)(+)			+41.2 (0.49)	29
			16	MeOH:H_2O (2:1)[c]	75	(S)(+)			+50.1 (0.46)	35
			17	MeOH:H_2O (1:2)[c]	63	(S)(+)			+55.8 (0.48)	39
			18	MeOH:H_2O (1:4)	76	(S)(+)	+3.4 (3.16)	14	+27.0 (0.51)	29
			19	H_2O[c]	45	(S)(+)	+3.0 (3.40)	21	+59.6 (0.45)	41
		(R)(+)-Me	20	Dioxane	72	(R)(−)	+4.2 (1.95)	29	−83.3 (0.56)	58
		(R)(+)-Et	21	Hexane[c]	66	(R)(−)	−5.7 (2.83)	39	−107 (0.49)	74
		(R)(+)-Naph	22	Hexane[c]	31	(R)(−)	−8.9 (2.22)	61	−124 (0.47)	86
			23	AcOEt	31	(R)(−)	−6.8 (1.73)	47	−112 (0.52)	78
Ph-gly	R = Ph	(S)(−)-Me	24	EtOH	73	(S)(+)-Ph-gly	+47.6 (2.51)	28	−36.0 (0.89)[g]	30
	R′ = H		25	H_2O, NaOH	60	(S)(+)	+38.6 (2.10)	23	−28.3 (0.90)[g]	24
Asp	R = CH_2COOH	(S)(−)-Me	26	EtOH, H_2O, NaOH	38	(S)(+)-Ala	+7.56 (2.99)	50	+84.0 (0.38)	58
	R′ = H				11	(R)(−)-Asp	−11.1 (2.84)	44	−41.0 (0.39)	45
Glu	R = $(CH_2)_2$-COOH	(S)(−)-Me	27	*i*-PrOH, $(C_2H_5)_3N$	82	(S)(+)-Glu	+3.7 (3.57)	12	−11.5 (0.85)[g]	14
	R′ = H		28	EtOH	74	(S)(+)	+4.2 (3.55)	13	−9.6 (0.68)[g]	12
			29	MeOH, tri Et amine	78	(S)(+)	+1.9 (2.68)	6	−4.1 (1.27)[g]	5
			30	Dioxane:H_2O (2:8), tri Et amine	60	(R)(−)	−5.9 (3.46)	19	+14.8 (0.75)[g]	19
			31	MeOH:H_2O (1:2), NaOH	68	(R)(−)	−8.3 (2.75)	26	+21.9 (0.67)[g]	27
			32	H_2O, pyridine	55	(R)(−)	−8.6 (2.27)	27	+21.9 (0.57)[g]	27
		(R)(+)-Et	33	EtOH	75	(R)(−)	−0.47 (2.82)	2	+5.17 (0.72)[g]	6
		(S)(−)-Et	34	H_2O:MeOH (2:1), NaOH	56	(R)(−)	−7.7 (3.04)	25	+24.1 (0.65)[g]	30

[a] (S)(−)-Me, (S)(−)-α-methylbenzylamine ([α]^{25}D −42.3°, benzene); (R)(+)-Me, (R)(+)-α-methylbenzylamine ([α]^{25}D +41.5°, benzene); (S)(−)-Et, (S)(−)-α-ethylbenzylamine ([α]^{25}D −21.0°, benzene); (R)(+)-Et, (R)(+)-α-ethylbenzylamine, ([α]^{25}D +21.7° benzene); (R)(+)-Naph, (R)(+)-α-(1-naphthyl)ethylamine ([α]^{25}D +88.0°, benzene). [b] THF, tetrahydrofuran; DMFA, dimethylformamide. When free α-keto acids (1 mol) were used, 2 mol of optically active amine were added. Pyridine, sodium hydroxide, and triethylamine were also used to neutralize the keto acids. [c] The reaction mixtures were not homogeneous solutions. [d] Optical rotations of amino acids which were isolated by the use of ion exchange resins were listed. [e] Defined as ([α]D obsd/[α]D lit. × 100. (S)-Ala, [α]^{25}D +14.6° (5 N HCl); (S)-Ph-gly, [α]^{25}D +168° (5 N HCl); (S)-Asp, [α]^{25}D +25.4° (5 N HCl); (S)-Glu, [α]^{25}D +31.8° (5 N HCl): J. P. Greenstein and M. Winitz, "Chemistry of Amino Acids," Vol. 3, John Wiley & Sons, Inc., New York, N. Y., 1961 (alanine, p 1819; phenylglycine, p 2694; aspartic acid, p 1856; glutamic acid, p 1929). [f] Dinitrophenylamino acids were isolated by column chromatography. [g] Optical rotations were measured in glacial acetic acid. [h] Defined as [α]D obsd/[α]D lit. × 100. DNP-(S)-Ala, [α]^{25}D +143.9° (1 N NaOH); DNP-(S)-Asp, [α]^{25}D +91.9° (1 N NaOH); DNP-(S)-Glu, [α]^{25}D +80.8° (AcOH): K. R. Rao and H. A. Sober, *J. Amer. Chem. Soc.*, **76**, 1328 (1954); DNP-(R)-Phe-gly, [α]^{25}D +119.2° (AcOH).

dence obtained in this study also supports the fact that the configuration of (+)-(1-naphthyl)-ethylamine and (−)-α-ethylbenzylamine could be *R* and *S*, respectively. It was found in this study that the α-(1-naphthyl)ethylamine is also hydrogenolyzed to α-ethylnaphthalene and ammonia as α-alkylbenzylamine[5,10] and phenylglycine[7] by the use of palladium hydroxide on charcoal.

Experimental Section[15]

Optically active amines are as follows: (S)(−)-α-methylbenzylamine,[16,17] [α]^{25}D −42.3° (benzene); (R)(+)-α-methylbenzylamine,[16,17] [α]^{25}D +41.5° (benzene); (S)(−)-α-ethylbenzylamine,[14,18] [α]^{25}D −21.0° (benzene); (R)(+)-α-ethylbenzylamine,[14,18] [α]^{25}D +21.7° (benzene); (R)(+)-α-(1-naphthyl)-ethylamine, [α]^{25}D +88.0° (benzene).

(15) All optical rotation measurements were carried out by the use of the Rudolph Model 80 polarimeter with PEC-101 photometer. All hydrogenations and hydrogenolyses were carried out by the use of Parr 3910 shaker-type hydrogenation apparatus.

(16) W. Theilacker and H. Hinkler, *Chem. Ber.*, **87**, 690 (1954).

(17) W. Leithe, *Ber.*, **64**, 2831 (1931).

(R)(−)-Alanine.—A solution of pyruvic acid, 0.88 g (0.01 mol) in 30 ml of ethanol, was mixed with a solution of (R)(−)-α-(naphthyl)ethylamine, 3.42 g (0.02 mol) in 40 ml of ethanol, and the solution was kept standing for 30 min at room temperature. To this was added 1.0 g of 10% palladium on charcoal, and the solution was hydrogenated for 10 hr at room temperature (initial pressure, 40 psi). The catalyst was removed by filtration and washed with 3 *N* hydrochloric acid to remove N-substituted alanine. The combined solution was evaporated to dryness under reduced pressure. Water was added and the solution evaporated to dryness to minimize free hydrochloric acid. The residue was dissolved in 60 ml of water and the pH was adjusted to about 4.5 by the use of sodium hydrogen carbonate. Palladium hydroxide on charcoal,[5] 3.0 g, was added to the solution and hydrogenolysis was carried out for 24 hr. After hydrogenolysis was completed, the catalyst was removed by filtration. The solution was then acidified by hydrochloric acid and evaporated to dryness and the residue was extracted with absolute alcohol. The alcoholic solution was evaporated to dryness under reduced pressure and the residue was dissolved in 10 ml of water. The solution was applied to a Dowex 50-X2 column (hydrogen form) and alanine was eluted with 1 *N* ammonia. Fractions which contained alanine were combined and evaporated to dryness *in vacuo*.

(18) A. J. Little, J. McLean, and F. J. Wilson, *J. Chem. Soc.*, 337 (1940).

Alanine (680 mg, 76%) was obtained, $[\alpha]^{25}D$ −11.6° (*c* 3.75, 5 *N* HCl), 80% optically pure. The alanine was converted into DNP-alanine in the conventional manner,[11] and the resulting DNP derivative was purified by the use of a Celite column treated with pH 7.0 citrate buffer.[12] The DNP-alanine was extracted and crystallized: mp 170–173°; $[\alpha]^{25}D$ −120° (*c* 0.40, 1 *N* NaOH), 83% optically pure.

Optically active aspartic acids were prepared in the same way as above from oxaloacetic acid (reaction 26). The resulting aspartic acid and alanine were separated by the use of a Dowex 2-X8 column (formate form) by eluting with water. The aspartic acid combined with the resin was eluted with 1 *N* formic acid.

Other experimental procedures used in this study were similar to those which were reported already.[10]

Registry No.—(*S*)(+)-ala, 56-41-7; (*R*)(−)-ala, 338-69-2; (*S*)(+)-ala benzyl ester, 17831-01-5; (*R*)(−)-ala benzyl ester, 17831-02-6; (*S*)(+)-ph-gly, (*S*)(+)-asp, 56-84-8; (*R*)(−)-asp, 1783-96-6; (*S*)(+)-glu, 56-86-0; (*R*)(−)-glu, 6893-26-1.

Acknowledgment.—This work was supported by Grant No. NsG-689 of the National Aeronautics and Space Administration. The authors wish to express their thanks to Dr. Howard B. Powell and Dr. Cecil M. Criss for valuable discussion and to Mr. Charles R. Windsor for amino acid analysis.

Novel 1-Thiovinyl Phosphates and Related Materials

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Received August 23, 1966

Phosphites react with aryl and aralkyl chlorothiolacetates to give principally 1-thiovinyl phosphates; simple alkyl chlorothiolacetates give mixtures containing appreciable amounts of the isomeric phosphonates. Di- and trichlorothiolacetates give almost exclusively phosphates. Several of the phosphates were oxidized to the corresponding 1-sulfinyl and 1-sulfonylvinyl analogs. Proof of structure and mechanisms are given.

The literature on the reaction of halothiolacetates and trialkyl phosphites has been confusing. As early as 1951, S-ethyl,[1,2] S-carbethoxymethyl, S-phenyl, and other S-aryl trichlorothiolacetates[2] with triethyl phosphite were claimed to give phosphonates. Mel'nikov, *et al.*,[3,4] claimed the phosphonate structure for the products from ethyl, *p*-chlorophenyl, and 2,4,5-trichlorophenyl chlorothiolacetates similar to the products obtained from alkyl and aryl chloroacetates.[5] Patent literature[6−8] available after most of the work reported herein had been completed has disclosed 1-thiovinyl phosphates and the corresponding 1-sulfinylvinyl phosphates having only —C=CHCl and —C=C-Cl_2 groups. The —C=CCl_2 compounds might be expected since the structure of the reaction products obtained from trialkyl phosphites and trichloroacetates has been shown[9−11] to be that of the vinyl phosphate; however, the corresponding phosphonate structure from the trichloroacetates has also been indicated in some earlier literature.[12,13] More recently, Gololobov[14] reported a series of 1-thiovinyl phosphates obtained from S-ethyl mono-, di-, and trichlorothiolacetates and phosphites. Gololobov reported obtaining mixtures with the monochloro ester and only vinyl phosphates with the di- and trichloro esters.

(1) Ciba A.-G., Switzerland Patent 310,409 (1955).
(2) Farbenfabriken Bayer A.-G., German Patent Application F10,391 (120 23/03) (1955).
(3) N. N. Mel'nikov, *et al.*, USSR Patent 116,879 (1958).
(4) N. N. Mel'nikov, Ya. A. Mandel'baum, and V. I. Lomakina, *J. Gen. Chem. USSR* (Engl. Transl.), **29**, 3252 (1959).
(5) Ciba A.-G., Switzerland Patent 310,410 (1955).
(6) Sumitomo Chemical Industries Co., Ltd., Japan Patent Publication No. 4998 (1960).
(7) Sumitomo Chemical Industries Co., Ltd., Japan Patent Publication No. 13148 (1960); see also 17015 (1960).
(8) Sumitomo Chemical Industries Co., Ltd., Japan Patent Publication No. 16438 (1960).
(9) P. Mueller (to J. R. Giegy A.-G.), Switzerland Patent 326,948 (1958).
(10) Sumitomo Chemical Industries Co., Ltd., Japan Patent Publication No. 13147 (1960).
(11) F. W. Lichtenthaler, *Chem. Rev.*, **61**, 607 (1961).
(12) R. Sallmann (to Ciba Ltd.), U. S. Patent 2,830,927 (1958).
(13) R. Sallmann (to Ciba Ltd.), U. S. Patent 2,861,914 (1958).
(14) Yu. G. Gololobov, *J. Gen. Chem. USSR* (Engl. Transl.), **35**, 1246 (1965).

1-Thiovinyl Phosphates.—Our work independently showed that alkyl esters of monochlorothiolacetates gave mixtures while the corresponding aryl esters gave predominantly the 1-thiovinyl phosphates. All of the di- and trichloro esters used in this work gave the vinyl phosphates as the only detectable product.

The S-substituted 1-thiovinyl phosphates,[15] yields, analyses, and properties are shown in Tables IA and IB. Yields in general were high. The phosphates generally are high-boiling liquids, not well purified by distillation. In one case where the thiovinyl phosphate (**1**) and the isomeric phosphonate were separated by distillation, the phosphonate was the higher boiling. Elemental analysis does not distinguish the 1-thiovinyl phosphates from the isomeric phosphonate; however, infrared spectra clearly established the 1-thiovinyl phosphate structure and were also used to detect the presence of phosphonate. Calibrated infrared spectra were not obtained, and a minimum of 5–10% of the phosphonate could probably be detected.

Proof of Structure.—It was noted early in this work that the infrared spectra did not confirm the phosphonate structure, primarily owing to the absence of a carbonyl band in the 5.5–6.0-μ region. The phosphate structure was assigned on the basis of the presence of a C=C band in the 6–6.2-μ region and a split P→O band characteristic of phosphates.[16]

The spectrum of **1**, like those of all of the 1-thiovinyl phosphates, had no C=O absorption at 5.89 μ which was present in the spectra of the phosphonates of this type. A moderately strong C=C absorption at 6.21 μ was present in **1** but absent in the phosphonates. Also, **1** had a split P→O absorption at 7.7 and 7.8 μ which is characteristic of a phosphate group, while the phosphonates had a single P→O absorption at 7.95 μ characteristic of a phosphonate grouping.[17]

(15) L. F. Ward, Jr., and D. D. Phillips (to Shell Chemical Co.), U. S. Patent 3,069,313 (1962).
(16) J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1956.
(17) F. S. Mortimer, *Spectrochim. Acta*, **9**, 270 (1957).