We encountered the need to prepare large quantities of high optical purity (−)-α-pinene in order to convert it to optically active pinonic acid, to be used during the course of another investigation.

The isomerization of β-pinene to α-pinene has previously been carried out with rosin acids,[2] palladium black saturated with hydrogen,[3,4] and more recently with iron pentacarbonyl.[1]

Each of the above procedures has certain drawbacks that are overcome by our present method. For example, although the palladium experiment gave almost quantitative conversion of β- to α-pinene, the conversion to the optically active product was only 82%. In addition, large amounts of palladium are required for large scale conversion.

With iron pentacarbonyl, although an optical yield of 96.9% is obtained, one gets only a 45% conversion of β- to α-pinene.

We wish to report a very convenient method for preparing large quantities of optically pure -α-pinene, in excellent yield utilizing inexpensive benzoic acid.

Although this acid is strong enough to promote isomerization of β- to α-pinene, it apparently does not lead to side products caused by opening of the cyclobutane ring, nor to any δ-pinene which could be expected as a result from further isomerization of α-pinene.

Isomerization of β-pinene {$[\alpha]^{25}D$ −20.13° (neat) (optical purity 88.7%}, with 15 mol % benzoic acid for 48 hr at reflux temperatures produces α-pinene {$[\alpha]^{25}D$ −45.01° (neat) (optical purity 87.9%)}, in essentially quantitative yields. This procedure which gives an optical yield of 99.0%, as well as the quantitative conversion of β- to α-pinene, makes this an excellent method for this isomerization reaction.

During this investigation, the isomerization was followed utilizing gas–liquid partition chromatography. The disappearance of β-pinene and the formation of α-pinene could be followed utilizing a Carbowax 20M column. Both starting material and product were identified by comparison of their known infrared and nmr spectra.

Chemicals.—β-Pinene was donated by the Crosby Chemical Company, Picayunne, Miss., and benzoic acid was purchased from Aldrich Chemical Company. The β-pinene was redistilled on a Nester–Faust lab still spinning-band column before use (purity 99.5+% by glc analysis.)

Analysis.—Gas chromatographic analysis was conducted on an Aerograph 90-P-3 equipped with a thermal conductivity detector, a 15-ft column of Carbowax 20M (20%) on Chromosorb W, 60–80 mesh, using helium as a carrier gas. Nuclear magnetic resonance spectra were run on a Joelco 60-MHz spectrometer and infrared spectra on a Perkin-Elmer Model 337 Infracord.

Isomerization Procedure.—Benzoic acid (200 g, 1.67 mol), 1100 ml (7.0 mol) of freshly distilled β-pinene, $[\alpha]^{25}D$ −20.13°, and 0.39 g of hydroquinone were placed into a 3 l. three-neck flask equipped with a magnetic stirrer, condenser, and gas inlet tube. The system was maintained under an inert atmosphere by passing N_2 through a bubbler at such a rate as to maintain a steady reflux. Heat was applied and this mixture was refluxed for 48 hr. During this reflux period, samples of the mixture were analyzed at 12-hr intervals to determine reaction progress by gas–liquid chromatography. At the end of the reflux period, the crude α-pinene mixture was carefully added to a stirring solution of saturated $NaHCO_3$ in a 4-l. beaker. After neutralization of the benzoic acid, the organic layer was separated, washed with three 500-cc portions of water, and then dried over anhydrous Na_2SO_4.

Distillation of the crude α-pinene through a Nester–Faust lab still spinning-band column yielded 895 g [95.5% yield of (−)-α-pinene]: bp 155–156°; $n^{25}D$ 1.4645; $[\alpha]^{25}D$ −45.01°.

Registry No.—(−)-β-Pinene, 18172-67-3; (−)-α-pinene, 7785-26-4.

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Additions of Tributyltin Hydride to Terpenes

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Received September 15, 1969

The additions of tributyltin hydride[1] to optically active terpenes such as α- and β-pinenes, limonene, and camphene can be expected to proceed asymmetrically, to give an optically active product.

The analogous additions of organosilicon hydrides to these terpenes under irradiation with uv light or in the presence of chloroplatinic acid as catalyst have been thoroughly investigated by E. Frainnet[2,3] and R. Tanaka.[4] The addition of organotin hydrides to common α olefins has also been investigated; free-radical processes occur to give the tin terminated adducts.[5]

In the present experiments, azobisisobutyronitrile was mainly used as the radical generator and the reaction was carried out in a sealed tube at reaction temperatures from 75 to 200° for 24 hr. The yield of the adducts increased with the temperature rise.

β-Pinene and limonene gave 1:1 adducts in good yields, and formation of hexabutylditin, the inevitable side product, was small. α-Pinene, however, gave no real adduct even at the highest temperature (200°), no doubt because the internal double bond is relatively unreactive;[6] hexabutylditin and the products from contaminating terpenes predominated. With camphene, no substantial yield of adduct was obtained under any conditions despite of its terminal double bond. Analogous reactions were also studied with the five *p*-menthenes-1, -2 (*trans*), -3, -1(7), and

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(1) K. Hayashi, J. Iyoda, and I. Shiihara, *J. Organometal. Chem.*, **10**, 81 (1967).
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(3) R. Calas and E. Frainnet, *ibid.*, **243**, 595 (1956).
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(5) W. P. Neumann, H. Niermann, and R. Sommer, *Justus Liebigs Ann. Chem.*, **659**, 27 (1962).
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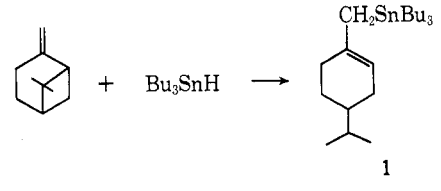
TABLE I
SPECTRA OF THE ADDUCTS AND IODINE DERIVATIVES

Compd no.	Ir, cm^{-1} [a]	Nmr, τ
1	1640, 900, 810 (inner double bond), 1380, 1350 (*gem*-Me), 1150 (s) (*i*-Pr)	9.2 (s, 8, $-CH_2Sn$) 9.15 (d, t, 15, J = 6 Hz, Me in *i*-Pr and Me in Bu_3Sn) 8 ~ 9 (m, 18, $-CH_2-$ in *p*-menthene and in the middle methylene in Bu_3Sn) 8.35 (s, 2, $>C=C-CH_2Sn$) 4.6 (m, 1, $>C=CH-$)
2	1650, 900, 810 (inner double bond), 1350	9.2, 9.15 are almost same as **1** 8 ~ 9 (m, 18, $-CH_2-$) 8.4 (s, 3, $>C=C-CH_3$) 4.9 (m, 1, $>C=CH-$)
3	1380, 1350 (*gem*-Me), others are the same as *trans-p*-menthane besides Bu_3Sn absorption	9.2, 9.15 are almost same as **1** 8.4 (m, 20, $-CH_2-$ in *p*-menthane and Bu_3Sn)
4	1660, 910, 800 (inner double bond), 1160 (s) (*i*-Pr)	9.15 (d, 6, Me in *i*-Pr) 6.15 (s, 2, $>C=C-CH_2I$) 4.1 (m, 1, $>C=C-H$)
5	Almost same as **2**	9.2, 9.15, 8 ~ 9 are all same as **2** except one Bu decrease. 4.8 (m, 1, $>C=C-H$)
6	1370, 1350 (*gem*-Me), 1230, 1130 (s) (*i*-Pr), and others	9.1 (d, 6, J = 6 Hz in *i*-Pr) 8.4 (m, 8, $-CH_2-$ in *trans-p*-menthane) 7.9 [s, 3, $>C(I)CH_3$]

[a] Here are the mostly mentioned peaks of terpene portion, but **1**, **2**, **3**, and **5** have other absorptions assigned to the tributyltin groups: H. Geissler and H. Kriegsmann, *J. Organometal. Chem.*, **85**, 11 (1968).

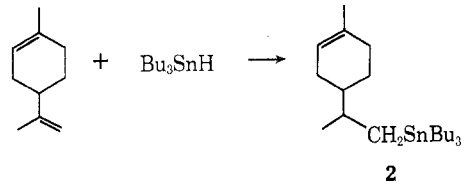
-8(9) (*trans*), but only menthene-1(7) gave an appreciable amount of an adduct. Without radical generators, β-pinene merely could give the adduct with the yield of over 90% at 200° for 24 hr, but other terpenes needed them as the catalyst.

The following equations are typical of the type of reactions involved.



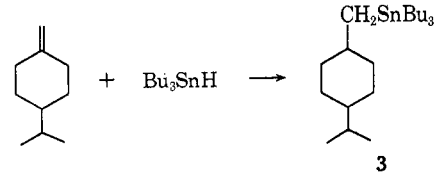
(1)

1



(2)

2

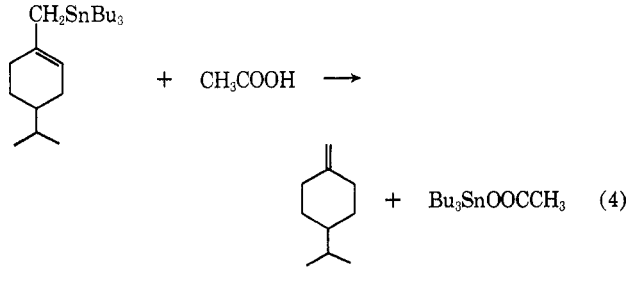


(3)

3

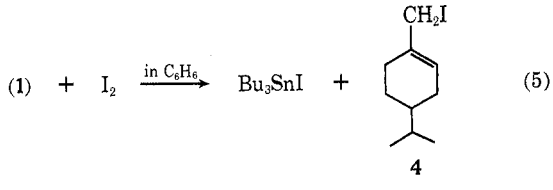
In all cases the addition is in competition with coupling of tributyltin radicals to give hexabutylditin.

The structures of the adducts were deduced from the ir and nmr spectra (Table I). Noted differences between the adducts in ir were the presence of *gem*-methyls absorption peaks in 1380 and 1350 cm^{-1} for the β-pinene and 1(7)-menthene adducts, but not for the limonene adduct. With the β-pinene adduct, the formation of *p*-menthene-1(7) by cleavage with acetic acid afforded strong support for the ring-opened structure; the reaction involves the easy cleavage of tin effected by the β-positioned double bond as shown in eq 4.



(4)

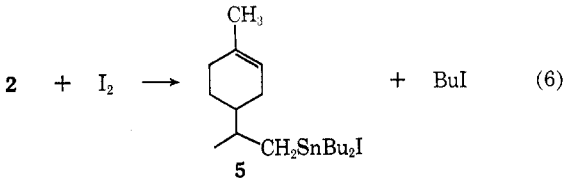
Another interesting reaction of the β-pinene adduct was the easy cleavage by 0.1 *N* iodine benzene solution at room temperature. The products are tributyltin iodide and the corresponding *p*-menthyl iodide as shown in eq 5. The limonene adduct is indifferent to



(5)

4

this dilute iodine solution, but crystal iodine brought the cleavage of butyltin bond according to eq 6.



(6)

5

TABLE II
ADDITION OF TRIBUTYLTIN HYDRIDE TO TERPENES AND THEIR IODINE DERIVATIVES

Product	Compd no.	Yield, %	Bp, °C (mm)	$n^{25}D$	d^{25}_4	$[\alpha]^{25}D$, deg	Formula	Calcd, % C	Calcd, % H	Found, % C	Found, % H
(−)-7-Tributylstannyl-*p*-menthene-1	1	74[a]	171–175 (1.5)	1.4969	1.060	−35.9	$C_{22}H_{44}Sn$[b]	61.84	10.38	61.44	10.31
(+)-9-Tributylstannyl-*p*-menthene-1	2	62[a]	182–186 (3)	1.4946	1.071	+27.2	$C_{22}H_{44}Sn$[b]	61.84	10.38	61.88	10.82
7-Tributylstannyl-*trans*-*p*-menthane	3	29[a]	183–185 (4)	1.4864	1.067		$C_{22}H_{46}Sn$	61.54	10.80	61.34	10.93
(−)-7-Iodo-*p*-menthene-1	4	51	94–97 (4)	1.5459	1.383	−46.2	$C_{10}H_{17}I$	45.46	6.48	45.23	7.04
9-[Dibutyliodostannyl]-*p*-menthene-1	5	49	208–210 (6)	1.5481	1.415	+0.31[c]	$C_{18}H_{35}SnI$	43.49	7.09	43.17	7.33
trans-1-Iodomenthane	6	25	80–82 (4)	1.5118	1.287		$C_{10}H_{19}I$	45.12	7.19	45.19	7.38

[a] Reaction temperature 200° for 24 hr. [b] Molecular weight determined by cryoscopic method in benzene were 423 for 1 and 408 for 2 against calcd, 427. [c] Racemization was taken out by iodine.

Further addition at the remaining double bond in the hexene ring of the 1:1 adduct was found to be impossible. It was found that these adducts show optical activity. Unreacted terpenes which were recovered also retained their original optical purity. These facts are taken as the features of the radical character of the addition reaction. The adduct and their iodine derivatives obtained are summarized in Table II with their physical constants and analyses.

Experimental Section

Boiling points are uncorrected. Carbon–hydrogen analysis were performed by Yanagimoto C. H. N. Corder. Optical rotation of the terpenes, both starting and recovering, and the addition products were mostly measured as $[\alpha]^{25}D$ (C = 10 in ethanol) by the Yanagimoto optical rotational dispersion spectrometer ORD-3. The nmr spectra were recorded on a Nippon Denshi C-60 instrument in CCl_4 solutions. The glpc analysis of these organotin compounds is possible by using Beckman gas chromatograph GC-M column of silicone grease DC-HV on Celite 545, 60–80 mesh, 6 mm × 3.1 m, 240°, He 1.92 atm, and the retention time of hexabutylditin appeared at 52 min, whereas the adduct fractions of β-pinene, limonene, and menthene-1(7) were all the same at 38 min, and tetrabutyltin was 7.5 min. This analytical result showed the good agreement with the one obtained by the combination of iodimetry and alkalimetry mentioned below.

Materials.—(+)-α-Pinene was used after one distillation: bp 55–60° (24 mm); $n^{25}D$ 1.4657; $[\alpha]^{25}D$ +17.0°; and glpc (PEG-6000, 4 mm × 2.5 m, 130°, He 50 cc/min, same in below), α-pinene 91.4, camphene 3.7, and β-pinene 5.0%. (−)-β-Pinene was obtained from Nippon Terpene Chemical Co. Ltd.: bp 64–65° (23 mm); $n^{25}D$ 1.4736; $[\alpha]^{25}D$ −17.2°; glpc, β-pinene 98.0% and α-pinene 2.0%. (+)-Limenene gave bp 69–71° (20 mm): $n^{25}D$ 1.4696; $[\alpha]^{25}D$ +113.9°; glpc, limonene 96.4%, β-pinene 2.5%, α-pinene 0.4%, and others 0.7%. Camphene was supplied as crystals: $[\alpha]^{25}D$ +6.5°; glpc, camphene 82.4% and tricyclene 17.6%.

p-Menthene-1 and -3 were obtained from the precise fractional distillation of *p*-menthene mixture given by Nippon Terpene Chemical Co. *p*-Menthene-1 gave bp 172.2–173.0°, $n^{25}D$ 1.4563, and menthene-3 gave bp 165–167.5°, $n^{25}D$ 1.4466, and the purity of these menthenes was 75.5+% when accompanied with *p*-menthane. *p*-Methene-2 (*trans*) was prepared by the reported method[7] from *p*-toluenesulfonic acid ester of *l*-menthol, bp 65° (24 mm), $n^{20}D$ 1.4493. *p*-Menthene-1(7) was prepared from the β-pinene adduct by acetic acid cleavage as written below and *p*-menthene-8(9) (*trans*) from isopulegyl chloride[8] reduction with tributyltin hydride, $n^{25}D$ 1.4473, d^{25}_4 0.7989, and the ir was close to that already reported.[9] Tributyltin hydride was prepared by the reported method[1] (97.6% pure) and azobisisobutyronitrile (AIBN) and benzoyl peroxide (BPO) were used as the commercial materials.

General Procedure.—Terpene (13.6 g, 0.1 mol), tributyltin hydride (14.6 g, 0.05 mol), and AIBN (0.3 g, 0.002 mol) were sealed into a Pyrex tube (2.0 cm × 50 cm) under a nitrogen blanket and heated for 24 hr at the setting temperature. The product was filtered to remove the small amount of crystals which originated from AIBN and the tin metal deposited during the reaction, and then the product was distilled under vacuum to recover the unreacted terpene, tributyltin hydride, and the adduct in the order mentioned. The adduct fraction was purified by extracting with ethanol of about ten times volume. The contaminating hexabutylditin, which was hardly dissolved in ethanol, was separated as the lower layer and the upper layer was subjected to the repeated distillations after the solvent was distilled off.

(−)-β-Pinene Addition. (−)-7-Tributylstannyl-*p*-menthene-1 (1).—Tributyltin hydride was added to (−)-β-pinene even at 75°; the adduct (30.4%) had the same physical constants and composition as the one obtained at 200°. One example of the adduct analysis with the combination of the iodimetry and alkalimetry was carried out as follows: the sample (0.4774 g) was obtained without catalyst, was dissolved in 20 ml of benzene, and was titrated with 0.1 *N* iodine benzene solution. The end point was very clear owing to the sudden color remaining from a trace of excess iodine and the titers were 20.7 ml (f = 1.01). Ethanol (20 ml) was poured into this end point solution in order to obtain the solubility of the benzene and water titers of 0.1 *N* (f = 1.045) alkali solution. Phenolphthalein was used as the indicator, and 10.9 ml was required for neutralization. The titers of iodine were seen to be about twice that of the alkali. The purity of the adduct was calculated as 96.5%.

(+)-α-Pinene Addition.—The yield of the higher fraction[10] was only 4.7% at a reaction temperature of 75°; so the reaction was mainly carried out at 200°, even though it was 20–25% far less than in the above case. It was found that the higher fraction always contained a considerable amount of β-pinene adduct owing to the greater reactivity of this pinene contamination, but no real α-pinene adduct was present.

Cleavage Reaction with Acetic Acid.—β-Pinene adduct (15 g) and glacial acetic acid (15 ml) were admixed and held at room temperature. After several hours, this mixture had solidified into a white crystalline mass which showed the formation of tributyltin acetate. By vacuum distillation, the fraction of bp 80–123° (22 mm) was obtained to which was added a small amount of water. The oily layer appeared. Redistillation of this layer gave the fraction, bp 68° (23 mm), 2.9 g (60%), $n^{25}D$ 1.4556, d^{25}_4 0.8078 (lit.[2] $n^{25}D$ 1.4580, d^{25}_4 0.819). The composition was found by glpc to be *p*-menthene-1(7), 94.0%; *cis*-*p*-menthane, 4.0%; and others, 2.0%. The limonene adduct was uneffected by glacial acetic acid at 100° for several hours.

Cleavage Reaction with Iodine of the β-Pinene Adduct, 7-Iodo-*p*-menthene-1 (4).—Initially, it was found that the analytical value of the iodine absorption in this adduct by Hanus reagent was 4.04 equiv/mol. In order to separate the iodination products, the following experiment was carried out. To the β-pinene adduct 16 g (0.0374 mol) of iodine crystals was added gradually at room temperature; the adduct reacted rapidly as

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(8) F. W. Semmler, and Ch. Rimpel, *Ber.*, **39**, 2582 (1906).
(9) B. M. Mitzner, E. T. Theimer, and S. K. Freeman, *Appl. Spectrosc.*, **19**, No. 6, 169 (1965).

(10) This fraction, bp 150–175° (**3**), $n^{25}D$ 1.4917, was found to be tributyl isopropyltin, by analysis and molecular weight determination: ir, 1380 cm^{-1} (*gem*-Me); nmr τ 9.15 (d, 15, *J* = 6 Hz, *i*-Pr and Me in Bu_3Sn).

Anal. Calcd $C_{15}H_{34}Sn$: C, 54.08; H, 10.28, mol wt, 333. Found: C, 53.87; H, 10.27; mol wt, 350.

This compound together with tributyltin cyanide was always produced in the reactions using AIBN, and these were understood to be formed when cyanoisopropyl radical in the intermediate was hydrogenated by another tin hydride.

noted by the disappearance of the iodine color and generation of a considerable amount of heat which necessitated occasional water cooling. Just at the equivalent, the amount of iodine was 8 g (0.062 mol). Vacuum distillation gave these fractions: bp 98–129° (4 mm), 12 g; 131–135° (4 mm), 10.6 g; and 150–165 (4 mm), 2 g. The first fraction was again treated with a dilute alkaline solution, extracted by ether and worked up by the usual procedure to give 7-iodo-*p*-menthene-1 (**4**). This substance was fairly unstable and changed to a brown color by liberation of free iodine and polymerized material after a few days. The second fraction was found to be tributyltin iodide from ir; its purity was determined as 98.6% by alkali titration. In the case of Hanus reagent, a further iodination of this tributyltin iodide to dibutyltin iodide and butyl iodide was recognized.

Cleavage Reaction with Iodine of the Limonene Adduct. 9-(Dibutyliodostannyl)-*p*-menthene-1 (5).—Iodine absorption by Hanus reagent was 4.16 equiv/mol. This was indifferent to the dilute iodine solution, but with iodine crystals it reacted at room temperature. To the limonene adduct, 20 g (0.05 mol), was added iodine crystals, 12.3 g (0.10 mol), in portions. Vacuum distillation gave three fractions: bp 129–136° (4 mm), 1.9 g, tributyltin iodide; 149–158° (4 mm), 7.6 g, the mixture of dibutyltin diiodide and tributyltin iodide (ratio, 44:56 wt %); 185–196° (4 mm), 12.3 g. In the trap 5.1 g of liquid was obtained. The third was redistilled, and alkali titration showed 98% purity as in **5**. The trap condensate was redistilled (bp 128–129°, n^{25}D 1.4954, d^{25}_4 1.543) and found to be *n*-butyl iodide. This iodide (**5**) was again subjected to further iodination and obtained was *trans*-1-iodo-*p*-menthane (**6**) which was derived from the hydroiodination of *p*-menthene-1 or -1(7).

Attempted Preparation of 1:2 Adduct from the 1:1 Adducts.—β-Pinene adduct (5 g), tributyltin hydride (3.4 g), and AIBN (0.05g) were charged in the Pyrex tube and heated for 24 hr at 200°. After opening the tube, the contents were separated by vacuum distillation. Unreacted tributyltin hydride, bp 81–105° (33 mm), 2.8 g, and the adduct, bp 185–197° (3 mm), 5.5 g, were obtained, but no residue was found as in the 1:2 adduct.

Registry No.—**1**, 25828-13-1; **2**, 25828-14-2; **3**, 25828-15-3; **4**, 25828-16-4; **5**, 25828-17-5; **6**, 25828-18-6; tributyltin hydride, 688-73-3.

The Synthesis of *O*-Acylamino Acids

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Received December 1, 1969

Presently available methods for the synthesis of *O*-acylamino acids are based on the reaction of an anhydride with the parent amino acid.[2,3] These methods obviously restrict the *O*-acylating agent to one which can be obtained in the form of an anhydride and, consequently, cannot be applied to the synthesis of, for example, pure *O*-oxalyl and *O*-malonyl derivatives. This paper describes a more general method for the synthesis of *O*-acylamino acids from the readily available acyl chlorides.

The following *O*-acylamino acids were synthesized with yields (as per cent of parent amino acid) shown in parentheses: *O*-oxalyl-L-homoserine (9%), *O*-malonyl-L-homoserine (32%), *O*-malonyl-L-serine (39%), and *O*-succinyl-L-serine (19%). The properties of these preparations and the criteria used to assess their purity are listed below. The parent amino acid was the sole detectable organic impurity.

A. Acid Hydrolysis to the Parent Amino Acid and Organic Acid.—The preparations were hydrolyzed in 1 *M* HCl and then subjected to paper chromatography as described in the Experimental Section. The sole detectable products from these hydrolyses were the parent amino acid and organic acid.[4]

B. Loss of Ninhydrin Reaction under Alkaline Conditions.—Under alkaline conditions *O*-acylamino acids undergo a loss in ninhydrin reactivity, which has been ascribed to an "O → N acyl transfer."[3,5] Each *O*-acylamino acid was incubated in 2 *N* ammonium hydroxide at room temperature for 10 min and then lyophilized to dryness. The residue was dissolved in water and electrophoresed on paper. Comparison with untreated controls showed that the ninhydrin reaction observed with each *O*-acylamino acid was completely eliminated by preincubation with ammonium hydroxide.

C. Quantitative Determination with the Hydroxylamine Assay.—Within the limits of accuracy of the assay (*ca.* ±10%), each preparation was judged to be pure.

D. Paper Chromatography.—Varying amounts of each preparation were chromatographed in solvents A, B, and C, and the organic acids and amino acids were visualized as described in the Experimental Section. The sole impurity detected was the parent amino acid. *O*-Oxalylhomoserine was estimated to contain *ca.* 10% homoserine; the other preparations contained a barely detectable proportion (less than 5%) of the parent amino acid.

E. Elemental Analysis.—The values determined differed from the calculated values by less than 0.3%, with the exception of *O*-malonyl-L-homoserine. With *O*-malonyl-L-homoserine the values for C and H differed by 1.50 and 0.37%, respectively. The observed analysis is consistent with that of a preparation containing *ca.* 4% water[6] in addition to the known trace of homoserine (see D above).

F. Nmr Spectra.—The nmr spectra were consistent with the proposed structures and exhibited no significant peaks other than those attributable to the *O*-acylamino acid. It was estimated that the parent amino acid would have to represent at least 20% of the total preparation to permit its detection.

In addition to the above *O*-acylamino acids, a small quantity of *O*-oxalyl-L-serine was synthesized. Several

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(2) S. Nagai and M. Flavin, *J. Biol. Chem.*, **242**, 3884 (1967).

(3) M. Flavin and C. Slaughter, *Biochem.*, **4**, 1370 (1965).

(4) An acid which was chromatographically distinct from the parent organic acid was commonly observed in the products of hydrolysis. This acid was obviously an artifact formed from the products of hydrolysis, since its formation could be reproduced when parent amino acid and organic acid were together (but not separately) subjected to the same procedure of acid hydrolysis and lyophilization described for the *O*-acylamino acids.

(5) To the best of our knowledge, the evidence that *O*-acylamino acids undergo an "O → N acyl transfer" is equally consistent with their conversion to a cyclic hemiacetal-like structure as proposed by the following: C. A. Grob and C. Wagner, *Helv. Chim. Acta*, **38**, 1699 (1955); G. Fodor and J. Kiss, *J. Amer. Chem. Soc.*, **72**, 3495 (1950); E. E. van Tamelen, *ibid.*, **73**, 5773 (1951); A. Nickon and L. F. Fieser, *ibid.*, **74**, 5566 (1952). In this note, the term "O → N acyl transfer" will be used to include both of the above possible reactions.

(6) Elemental analyses were performed on samples that were dried overnight *in vacuo* at 50°.