tions reported by Berse and coworkers,[2] afforded in our hands *S*-*p*-aminobenzyl-L-cysteine. The reduction involved the absorption of 3 equiv of hydrogen and the hydrogenated mixture gave a negative nitroprusside test for sulfhydryl. Berse and coworkers[2] who claimed that hydrogenation of *p*-nitrobenzyl-L-cysteine afforded cysteine have used the Hopkins reagent (10% $HgSO_4$ in 5% aqueous H_2SO_4)[8] for its isolation as a mercury mercaptide. The mercaptide was finally converted to L-cystine by treatment with hydrogen sulfide followed by aerial oxidation. Pursuing exactly the same procedure we have obtained L-cystine from *S*-*p*-aminobenzyl-L-cysteine.

It is therefore concluded that the benzylic C–S bond in *S*-*p*-nitrobenzyl-L-cysteine did not undergo hydrogenolysis during the catalytic hydrogenation, while the benzylic C–S bond in the resulting *S*-*p*-aminobenzyl-L-cysteine was readily cleaved by mercury salts. Comparative experiments showed that *S*-benzyl- and *S*-*p*-nitrobenzyl-L-cysteine are unaffected by the Hopkins reagent under similar conditions.

Experimental Section

Melting points were determined with a Büchi apparatus under controlled conditions: heating the oil rapidly to a temperature ~20° lower than the melting point and then raising the temperature 5°/min until decomposition occurred. Nmr spectra were recorded with a Varian A-60 spectrometer.

***S*-*p*-Nitrobenzyl-L-cysteine.**—L-Cysteine hydrochloride monohydrate (17.5 g, 0.10 mol) was added, under a nitrogen atmosphere, at 0–3°, to 1 *N* NaOH (300 ml). To this was added with vigorous stirring, during 30 min, a solution of *p*-nitrobenzyl chloride (17.2 g, 0.10 mol) in freshly distilled peroxide-free dioxane (150 ml). After being stirred for additional 30 min at 0–3°, and 30 min at room temperature, the mixture was washed with ether and then acidified (pH 4–5) with concentrated hydrochloric acid (~10 ml). Concentration to 300 ml *in vacuo* (10 mm), followed by cooling (to 5°), afforded a precipitate which was filtered and washed successively with water (100 ml), ethanol (100 ml), and ether (100 ml). The crude product (23.3 g), mp 192–195°, was recrystallized from water to give 17.5 g (68%) of light yellow crystals, mp 202° dec (lit. mp 172.5–174°,[7] mp 233–234° for hydrate[2]). Two more recrystallizations from water followed by drying during 20 hr at 50° (1 mm) over P_2O_5 afforded an analytical sample: mp 197° dec; $[\alpha]^{20}D$ −4.0° (*c* 1.0, 1 *N* HCl); nmr (D_2O + CF_3CO_2D)[9] δ 2.84 (d, 2, *J* = 6 Hz, $CHCH_2S$), 3.63 (s, 2, SCH_2Ar), 4.11 (t, 1, *J* = 6 Hz, CH), 7.23 (d, 2, *J* = 9 Hz, Ar), 7.77 (d, 2, *J* = 9 Hz, Ar).

Anal. Calcd for $C_{10}H_{12}N_2O_4S$: C, 46.9; H, 4.7; N, 10.9; S, 12.5. Found: C, 47.0; H, 4.8; N, 10.7; S, 12.6.

The ethyl ester hydrochloride had mp 172–173° (lit. mp 172–173°,[2] mp 161–163°[7]).

***S*-*p*-Aminobenzyl-L-cysteine Monohydrochloride.**—A solution of *S*-*p*-nitrobenzyl-L-cysteine (1.37 g, 5.3 mmol) in ethanol (100 ml) and 1 *N* hydrochloric acid (50 ml) was hydrogenated at room temperature and at atmospheric pressure over 10% palladium/charcoal (345 mg). After the absorption of 3 equiv of hydrogen (7–8 hr) the catalyst was removed by filtration. The filtrate, which gave a negative nitroprusside test for sulfhydryl, was evaporated *in vacuo*. The oily residue was dissolved in ethanol–water (19:1 v/v 25 ml) and the solution was brought to pH 4–5 by addition of pyridine (~0.8 ml). Crystallization of the product started immediately. After this was kept for 24 hr at 5°, the yellow crystalline precipitate was filtered and washed with ethanol (10 ml) and then with ether (10 ml). The crude product (1.17 g), mp 207–208° dec, was recrystallized from ethanol–water (50 ml, 9:1 v/v) to give 0.95 g (68%) of the title compound: mp 215–216° dec; $[\alpha]^{20}D$ −5.5° (*c* 1.0, 1 *N* HCl); nmr (D_2O) δ 2.94 (d, 2, *J* = 6 Hz, $CHCH_2S$), 3.80 (s, 2, SCH_2Ar), 3.90 (t, 1, *J* = 6 Hz, CH), 7.25–7.65 (m, 4, Ar).

Anal. Calcd for $C_{10}H_{15}ClN_2O_2S$: C, 45.7; H, 5.7; N, 10.7; S, 12.2. Found: C, 45.6; H, 5.9; N, 10.4; S, 12.1.

Action of Mercury Salts on *S*-*p*-Aminobenzyl-L-cysteine.—To a stirred solution of *S*-*p*-aminobenzyl-L-cysteine (1.13 g, 4.3 mmol) in ethanol (100 ml) and 1 N hydrochloric acid (50 ml) Hopkins reagent (10% $HgSO_4$ in 5% aqueous H_2SO_4,[8] 75 ml) was added. Precipitation of a mercury mercaptide started within a few minutes. The mixture was stirred for additional 20 hr, filtered, and washed successively with water (20 ml), ethanol (20 ml), and ether (20 ml). The solid (1.86 g), mp >250°, was suspended in water (50 ml) and then saturated with H_2S. After 15 min the precipitated mercury sulfide was filtered off and excess of H_2S was removed *in vacuo*. The mixture was made alkaline by addition of 3 *N* NaOH (~4 ml), and air was bubbled through during 2.5 hr. Crystallization began on adjusting the pH to ~4 by addition of 3 *N* hydrochloric acid. The mixture was kept overnight at 5° and then filtered and washed successively with water (10 ml) and acetone (10 ml) to give crude cystine (0.41 g) mp 245–248° dec. This was dissolved in 1 *N* NaOH (3.4 ml) and then precipitated by addition of 1 *N* hydrochloric acid (3.4 ml). The solid was filtered and washed successively with water (10 ml), ethanol (10 ml), and ether (10 ml) to give 0.39 g (76%) of cystine, mp 248–250° dec (lit.[2] mp 255–260°), $[\alpha]^{25}D$ −212° (*c* 1.04, 1 *N* HCl) {lit.[2] $[\alpha]^{25}D$ −225° (*c* 1.04, 1 *N* HCl)}.

Registry No.—*S*-*p*-Nitrobenzyl-L-cysteine, 6341-94-2; *S*-*p*-aminobenzyl-L-cysteine monohydrochloride, 35340-27-3.

Acknowledgment.—The authors thank Professor W. Taub for discussions and encouragement.

(8) F. G. Hopkins, and S. W. Cole, *J. Physiol. (London)*, **27**, 418 (1901–1902).

(9) A few drops of CF_3CO_2D were added to assist the solution of the sample in D_2O.

Enol Esters. XV.[1] Synthesis of Highly Hindered Esters *via* Isopropenyl Ester Intermediates

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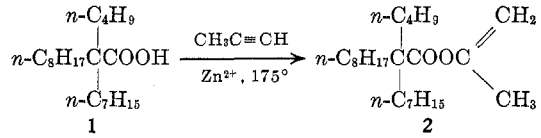
In recent years we have demonstrated the powerful acylation properties of isopropenyl esters, compounds capable of acylating even weakly nucleophilic secondary amides and imides.[3] We presently report the application of isopropenyl esters to the facile acylation of highly hindered alcohols. Our test compound, 2-butyl-2-heptyldecanoic acid[4] (**1**), was totally inert to esterification with ethanolic hydrogen chloride under reflux for periods up to 70 hr[5] but the isopropenyl ester of compound **1** rapidly acylated hindered as well as normal alcohols in a few minutes under our usual operating conditions.[3] Conversion of compound **1** to its isopropenyl ester **2** was obtained by our standard method[6] in accordance with the reaction shown by eq 1. Isopropenyl ester **2** efficiently acylated the fol-



(1)

(1) Previous paper in this series: E. S. Rothman and G. G. Moore, *Tetrahedron Lett.*, 1065 (1971).

(2) Eastern Marketing and Nutrition Research Division, ARS, USDA.

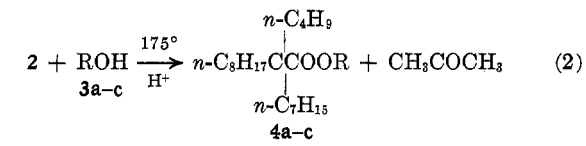
(3) E. S. Rothman, S. Serota, and D. Swern, *J. Org. Chem.*, **29**, 646 (1964).

(4) P. E. Pfeffer, L. S. Silbert, and J. M. Chirinko, Jr., *ibid.*, **37**, 451 (1972).

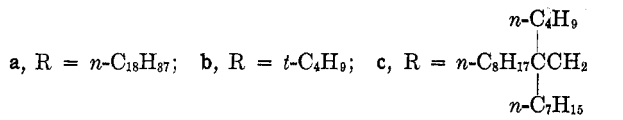
(5) See A. I. Vogel, "Practical Organic Chemistry," 3rd ed, Wiley, New York, N. Y., 1966, for a discussion of esterification techniques.

(6) E. S. Rothman and S. Serota, *J. Amer. Oil Chem. Soc.*, **48**, 373 (1971).

lowing representative alcohols—*n*-octadecanol (**3a**), 2-methyl-2-propanol (**3b**), and 2-butyl-2-heptyldecanol (**3c**) (obtained by sodium in alcohol reduction of **2**)—to the corresponding esters **4a**, **4b**, and **4c** in good



(2)



yields. The acylations when carried out neat at 175° with a trace of acid catalyst were complete in 5–10 min.

The mechanism of the acylation is uncertain, but it is evident that a ketene intermediate cannot be involved with trialkylacetic acid derivatives. Our previous work with isopropenyl stearate indicated the formation of hexadecylketene as the probable intermediate in the acylation reaction.[7] Apparently, there is more than one pathway available in isopropenyl ester acylations.

Experimental Section

The carboxylic acid starting material was of higher purity than 99% as estimated by glc. Products described below were of a similar order of purity as assayed by the same method.

Isopropenyl 2-Butyl-2-heptyldecanoate (**2**).—The carboxylic acid **1** (9.5 g, 0.029 mol) and ZnO (61 mg) were heated in an autoclave[5] with propyne under N_2 (auxiliary pressure 400 psi) for 70 hr. Zinc salts were removed by chromatography on Florisil and the liquid ester **2** (9.5 g, 90%) was eluted with pentane: ir (CS_2) 1740 (C=O), 1670 (C=C), 838 (C=CH_2) cm^{-1}; nmr (CCl_4) δ 4.58 (s, 1, C=CH), 4.53 (s, 1, C=CH), 1.90 (s, 3, C=CCH_3), 1.75–0.70 (m, 41); mass spectrum, *m/e* (rel intensity) 309 (1.24), 281 (92.8), 85 (58), 57 (100).

Anal. Calcd for $C_{24}H_{46}O_2$: C, 78.62; H, 12.65. Found: C, 78.81; H, 12.75.

Octadecyl 2-Butyl-2-heptyldecanoate (**4a**).—A mixture of enol ester **2** (406 mg, 1.11 mmol) and *n*-octadecanol (300 mg, 1.11 mmol) was melted, treated with *p*-toluenesulfonic acid (5 mg), and heated for 6 min at 180° (Woods metal bath). The ir of the crude product was similar to the ir of the analytical sample. Purification for removal of catalyst was effected by dissolving in pentane and filtering through a small plug of Florisil in a microcolumn to give the ester **4a** (591 mg, 92%): ir (CS_2) 1727 cm^{-1} (C=O); nmr δ 4.00 (t, 2, OCH_2) 1.70–0.70 (m, 76); mass spectrum, *m/e* (rel intensity) 57 (100, butyl), 99 (17.5, heptyl), 113 (12, octyl), 253 (0.9, octadecyl), 269 (1.33, octadecyloxy), 281 (48, trialkylmethyl), 309 (1.19, trialky acetyl). The gaseous product of the reaction was acetone al confirmed by conversion to the 2,4-dinitrophenylhydrazone derivative, mp 125° (lit.[8] mp 126°). Prolonged hydrolysis of **4a** with aqueous alcoholic potassium hydroxide under vigorous conditions gave a single acid identical with the starting acid **1** in glc retention time (single peak) and ir. The ester **4a** is a liquid.

Anal. Calcd for $C_{59}H_{78}O_2$: C, 80.89; H, 13.58. Found: C, 80.93; H, 13.74.

tert-**Butyl 2-Butyl-2-heptyldecanoate** (**4b**).—The enol ester **2** (200 mg, 0.55 mmol) and *p*-toluenesulfonic acid (2 mg) were heated to 200° (Woods metal bath) and an excess of dry 2-methyl-2-propanol was added as rapidly as possible through a reflux condenser (caution); this was followed by a 3-min reaction time. (The procedural modification was necessary owing to the low boiling point of the alcohol.) The product was contaminated with a little anhydride[9] removable by a pass in pentane solution through a microcolumn of mildly alkaline alumina (Florisil was unsuitable since the anhydride impurity eluted easily and with the same R_f value as the ester). The *tert*-butyl ester **4b** (156 mg, 75%) gave ir (CS_2) 1721 cm^{-1} (C=O); nmr (CCl_4) δ 1.42 [s, 9, $C(CH_3)_3$], 1.40–0.70 (m, 41); mass spectrum (*m/e*, rel intensity), 281 (31), 57 (100).

Anal. Calcd for $C_{25}H_{50}O_2$: C, 78.47; H, 13.17. Found: C, 78.52; H, 13.15.

2-Butyl-2-heptyldecanol (**3c**).—A sample of the enol ester **2** (700 mg, 1.9 mmol) was dissolved in dry ethanol and treated with an excess of sodium metal until the rate of metal dissolution became very sluggish. Dilution with water, extraction of the organic material with ether, drying ($MgSO_4$), and solvent removal gave the carbinol **3c**. To prepare the analytically pure material, small amounts of impurities[10] were removed by chromatography on Florisil. The product (475 mg, 85%) was eluted with CH_2Cl_2: ir (CS_2) 3620 (OH), 1193 cm^{-1} (CO); nmr (CCl_4) δ 3.25 (s, 2, CH_2OH) 1.62 (s, 1, OH) 1.50–0.70 (m, 41); mass spectrum (*m/e*, rel intensity) 281 (100).

Anal. Calcd for $C_{21}H_{44}O$: C, 80.69; H, 14.19. Found: C, 81.02; H, 14.02.

2′-Butyl-2′-heptyldecyl 2-Butyl-2-heptyldecanoate (**4c**).—The alcohol **3c** (105 mg, 0.34 mmol) and the enol ester **2** (123 mg, 0.34 mmol) were heated to 195° for 6 min in the presence of *p*-toluenesulfonic acid (2 mg). Gas evolution (acetone vapor) was immediate. The product was freed of catalyst by passing its pentane solution through a Florisil column to yield ester **4c** (199 mg, 95%): ir (CS_2) 1720 (C=O), 1190 cm^{-1} (CO); nmr ($CDCl_3$) δ 3.76 (s, 2, OCH_2) 1.70–0.70 (m, 82); mass spectrum (*m/e*, rel intensity) 57 (100, butyl), 99 (39, heptyl), 113 (0.4, octyl), 281 (100, trialkylmethyl), 295 (9.7, RCH_2).

Anal. Calcd for $C_{42}H_{84}O_2$: C, 81.22; H, 13.63. Found: C, 81.28; H, 13.66.

Registry No.—**2**, 35341-91-4; **3c**, 35341-92-5; **4a**, 35341-93-6; **4b**, 35341-94-7; **4c**, 35341-95-8.

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(7) Such indications in the case of isopropenyl stearate include (a) isolation of tetrameric hexadecylketene as the sole product when no acylatable substrate was provided [see E. Rothman, *J. Amer. Oil Chem. Soc.*, **45**, 189 (1968)], (b) loss of half the deuterium label when the isopropenyl ester of α-deuteriostearic acid was used as the acylation agent (unpublished data), and (c) formation of stearic *anhydride* or *tert*-butyl stearate *from addition of water* or 2-methyl-2-propanol, respectively, to an isopropenyl stearate–acid catalyst mixture which had been heated to 200° and cooled to room temperature prior to addition of reagent (unpublished data).

(8) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, Ed., "Systematic Identification of Organic Compounds," 4th ed, Wiley, New York, N. Y., 1962, p 221.

(9) The anhydride of acid **1** [ir (CS_2) 1803, 1737 cm^{-1}] may arise *via* the following sequence: dehydration of 2-methyl-2-propanol liberating water, hydrolysis of **2** to acid **1**, and reaction of **1** with **2**.

(10) The impurities were essentially traces of acid **1**, its ethyl ester, and a nonpolar fraction, apparently the ether corresponding to alcohol **3c**.

A Facile Reduction of Unsaturated Compounds Containing Nitrogen[1]

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Catalytic hydrogenation reactions involving compounds containing nitrogen have been reported to give a variety of products depending on reaction condi-

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