Purification of A.—A crude sample of 4.55 g of A was dissolved in 10 ml of warm CCl_4 and applied to the Florisil column. Elution with five 25-ml portions of low-boiling petroleum ether (bp 30–60°) gave 3.0 g of oil, ν_{CO} 1850 cm^{-1}, still containing a small amount of B (by ir): $n^{26}D$ 1.6124; d^{26} 0.833. It solidified to a glass at −70° and the nmr spectra showed sharp singlets at δ 5.95 and 7.10 ppm in the proper 10:1 ratio.

Anal. Calcd for $C_{15}H_{11}O_2Br$: C, 59.42; H, 3.66; Br, 26.35. Found: C, 59.60; H, 3.34; Br, 26.30.

The molecular weight by vapor osmometer was 350 g/mol, compared with the calculated value of 303.

Conversion of A into B.—When a boiling solution of 2 g of A in 25 ml of methanol was chilled in a Dry Ice–acetone bath, a 1.8 g yield of B (mp 125–132°, ν_{CO} 1760 cm^{-1}) was obtained. The nmr spectra showed broadened singlets at δ 5.8 and 7.0 ppm in the proper ratio.

Anal. Calcd for $(C_{15}H_{11}O_2Br)_4$: C, 59.42; H, 3.66; Br, 26.35; mol wt, 1212. Found: C, 59.33; H, 3.80; Br, 26.49; mol wt, 1380.

The polymer was amorphous by X-ray diffraction.

Alkaline Titration of B.—While there was no evidence for acid end groups in B (from ir), samples in DMSO could be titrated with 0.21 *N* NaOH. Assuming conversion of B into C 2 mol of NaOH would be required. The observed molecular weight from titration was 1186, comparing favorably to the 1380 determined by vapor osmometry and the theoretical value for $n = 2$ of 1212. Acidification after titration precipitated 98% of the initial sample as C.

Anal. Calcd for $C_{60}H_{45}O_8Br_3$: C, 63.56; H, 4.00; Br, 21.15. Found: C, 63.57; H, 4.32; Br, 20.26.

Saponification of B and C.—Weighed samples of B (or C) were refluxed in 100 ml of 1 *N* ethanolic KOH for 40 hr. From back-titration with 1 *N* HCl, two samples of B were found to consume 2.02 and 2.00 equiv of NaOH per monomer unit. For C, 2.24 equiv of NaOH per monomer unit was consumed. After titration, addition of concentrated HCl precipitated I, mp 173–174°, in high yield.

The saponification mixture after refluxing contained a white crystalline precipitate. In one case, this material was collected by filtration, dissolved in water, and treated with KI and starch. Acidification produced a dark blue color. For two polymer samples, the precipitate was dissolved in water, acidified, treated with KI, and titrated with 0.1 *N* thiosulfate, showing 11.5 and 11% of the calculated titer. The ethanol filtrate when treated similarly showed only an additional 2.5%. Presumably the majority of the hypobromite was consumed by oxidizing the ethanol solvent, a reaction which can be used to prepare bromoform.

Bromination of I_{Na} was accomplished by dissolving 10 g of I and 1.6 g of NaOH in 200 ml of water followed by dropwise addition of 6.4 g of bromine with stirring at 50°. After cooling, the reaction mixture was extracted with three 100-ml portions of ether. The ether was washed with 1% sodium bisulfite then 2% alkali, 5% hydrochloric acid, and water. Drying and evaporation left 7.03 g of yellow oil, ν_{CO} 1850 and 1690 cm^{-1}. The ratio of A to E could be approximated from the ir spectrum and the elementary analysis of the mixture could then be rationalized on the basis of the composition indicated.

Anal. Calcd for 63.5% A, 14.1% D, 22.2% E: C, 66.08; H, 4.12; Br, 21.18. Found: C, 66.21; H, 4.42; Br, 21.16.

No separation was effected on Florisil, but on Woelm alumina (1.5 × 5 in) elution with petroleum ether (bp 30-60°) gave 0.32 g (3%) of D, identified by uv and ir spectra. Elution with CCl_4 gave 0.45 g (10%) of E (ν_{CO} 1690 cm^{-1}, mp 53–55°) after recrystallization from methanol. The lactone unfortunately could not be eluted from the alumina column.

Bromination of II_{Na} (10 g) similarly gave 1.12 g (25%) of E (from 4.6 g of crude neutral oil showing ν_{CO} 1850 and 1690 cm^{-1}). Acidification of the alkaline extract gave 2.0 g of I. Under conditions which completely converted the lactone A from silver salt into macrocyclic polymer B, the β-lactone (A′) obtained from sodium salt bromination was stable in boiling methanol, yielding no precipitate on cooling, and leaving an oil on evaporation with the same ratio of ir absorption at 1850 and 1690 cm^{-1} as before heating in methanol.

Registry No.—I_{Ag}, 19926-54-6; I_{Na}, 15352-96-2; II_{Ag}, 19926-56-8; II_{Na}, 15352-97-3; A, 19926-34-2; C, 19926-35-3.

Enol Esters. IX.[1] The Use of Isopropenyl Esters as Acylation Agents. A Convenient Synthesis of Acyl Fluoride

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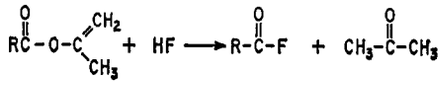
Received August 30, 1968

Isopropenyl stearate, I, the stearoylated enol of acetone, is a versatile stearoylating agent. Its high degree of acylation activity is very probably associated with the ease of its thermal cleavage[1] to hexadecylketene. In preceding papers,[1,3] we have described the synthesis of this reactive reagent and have detailed its use in the acylation of amides, imides, and several other compounds. We have now found further examples of the general utility of isopropenyl stearate taken as an example of an enol ester and would like here to present our findings. As will be seen below the reactions are general enol ester reactions and not limited solely to isopropenyl stearate.

When a stream of hydrogen fluoride is passed into an isopropenyl ester (whether neat or in solution in dry



ether) acetone is liberated leaving behind a residue, or a solution of, acyl fluoride. This acid fluoride synthesis was carried out in four aliphatic examples chosen for variation in chain length using isopropenyl acetate, octanoate, octadecanoate, and azelate esters. The acylated products are formed cleanly in high yield. The method offers advantages over the procedure of Olah and Kuhn,[4a] who found that, when they used anhydrides as starting materials, only those derived from C_2 or C_3 acids reacted with hydrogen fluoride fast enough at hydrogen fluoride reflux temperature for preparative utility. These authors prefer to use acid chlorides at −10 to +5°. The present procedure for acyl fluoride preparation does not require the intermediary preparation of acid chloride,[4b] but it should be noted that, if desired for other purposes, acyl chlorides may be similarly prepared uncontaminated by reagents used in their preparation by using hydrogen chloride gas in place of hydrogen fluoride. This acyl chloride synthesis compares well[5] with existing literature procedures using phosphorus trichloride, thionyl chloride,[6] or oxalyl chloride[7] in simplicity of operation, in yield, and particularly in purity of product.

(1) For the previous paper in this series, see E. S. Rothman, *J. Amer. Oil Chem. Soc.*, **45**, 189 (1968).

(2) Agricultural Research Service, U. S. Department of Agriculture.

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

(4) (a) G. A. Olah and S. J. Kuhn, *J. Amer. Chem. Soc.*, **82**, 2380 (1960); *J. Org. Chem.*, **26**, 237 (1961). (b) F. Seel and J. Langer, *Chem. Ber.*, **91**, 2553 (1958).

(5) Because of the importance to the food industry we anticipate that isopropenyl stearate will become a commercially available bulk chemical.

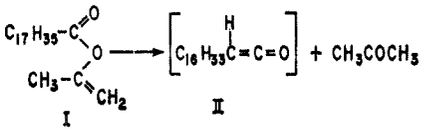
(6) H. H. Bosshard, R. Mory, M. Schmid, and H. Zollinger, *Helv. Chim. Acta*, **42**, 1658 (1959).

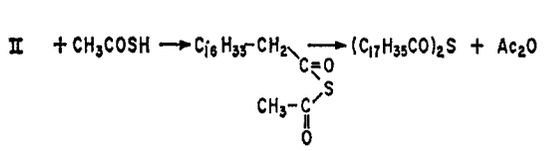
(7) H. E. Kenney, G. Maerker, and E. T. Donahue, *J. Amer. Oil Chem. Soc.*, in press.

Stearoyl fluoride is a crystalline solid melting at 34° and may be distilled without decomposition at 130° at 0.05 Torr. It will be noted that the fluoride melts higher than the 22° melting stearoyl chloride and does not decompose with loss of hydrogen halide during redistillations as does, to a degree, stearoyl chloride.

Acetyl fluoride may be prepared by the enol ester procedure, but added technical problems result from the near-coincidence of the boiling points of acetyl fluoride, bp 20°, and hydrogen fluoride, bp 19°. This problem may be avoided by using exactly equivalent amounts of isopropenyl acetate and hydrogen fluoride (or a slight excess of the former, bp 97°). The reaction itself is quantitative since the enol ester ir bands completely disappear, and only a separation from acetone, bp 56°, is required. We have found further utility for isopropenyl stearate in SH acylations. Both mercaptans and thiophenols may be stearoylated by this reagent, and often the reactions go at temperatures well below those required for OH or NH acylation. We have prepared phenyl thiostearate from thiophenol, benzyl thiostearate from benzyl mercaptan, isobutyl thiostearate from isobutyl mercaptan, and dodecyl thiostearate from dodecyl mercaptan. The easy preparation of the last-named compound contrasts sharply with the results of Sasin, Schaffer, and Sasin,[8] who reported that dodecyl thiostearate does not form even after 24 hr at 250° by the attempted base-catalyzed interchange reaction between methyl stearate and dodecyl mercaptan.

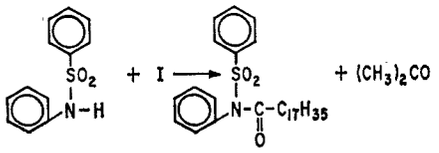
Thiolacetic acid was also successfully stearoylated, but the proximate product acetic stearic thioanhydride was not isolable because of rapid dismutation to stearic thioanhydride and acetic thioanhydride. This change recalls the analogous conversion[9] of acetic–stearic mixed anhydride into acetic and stearic anhydrides. The thioanhydride formulation is based upon the absence of C–O (single bond) infrared absorption bands, and from the reaction of the compound with



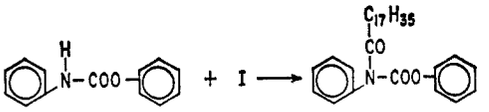


n-butylamine to form N-butylstearamide as the sole crystallizable product. Isopropenyl thiostearate was *not* obtained on reaction with isopropenyl acetate.

Another class of difficult-to-stearoylate compounds yielding easily to the enol ester reagent is the sulfonamide group. Although benzenesulfonamide has two potentially reactive hydrogen atoms attached to nitrogen, only one of these is replaced by the stearoyl group. N-Benzylbenzenesulfonamide and N-phenylbenzenesulfonamide monostearoylate without presenting any difficulties due to hindrance or inductive effects, but sulfanilamide gave only a distearoylated product.



We have also been able to stearoylate several urethan derivatives. As examples, phenyl N-phenylcarbamate, ethyl N-phenylcarbamate, and benzyl N-phenylcarbamate all formed N-stearoyl derivatives.



Products of stearoylation reactions with isopropenyl stearate are given in Table I.

Experimental Section

Stearoyl Fluoride. Procedure A.—Into isopropenyl stearate, 20 g, melted in a Teflon reaction vessel at 110–120° was bubbled a stream of dry hydrogen fluoride for 0.75 hr, after which the vessel was cooled and flushed with dry nitrogen. The infrared spectrum showed complete reaction: ir (CS_2) 1843.4 (C=O) and 1081.7 ± 0.3 cm^{-1} (CF). The product was distilled, bp 130° (0.05 mm) [lit.[4b] bp 169–169.5° (11 mm)], or alternatively directly crystallized from hexane to give flattened needles, mp 34°. In large-scale operations it was possible to do the recrystallization without a special drybox apparatus as long as the material was covered with hexane.

Procedure B.—Into a solution of 20 g of isopropenyl stearate in 350 ml of dry ether was passed a stream of hydrogen fluoride for 2 hr. Infrared analysis showed after solvent evaporation that the residue consisted of pure stearoyl fluoride. Ethyl stearate ir bands were completely absent. The product was completely colorless and the yield quantitative.

Anal. Calcd for $C_{18}H_{35}FO$: C, 75.47; H, 12.32; F, 6.63. Found: C, 75.88; H, 12.53; F, 6.39.

Stearoyl Chloride.—By methods analogus to procedure A (time, 1 hr; temp, 140°) and procedure B but using dry hydrogen chloride gas, pure stearoyl chloride, mp 21.9°, was obtained identical in all respects with an authentic specimen.

Octanoyl Fluoride *via* Isopropenyl Octanoate.—Methylacetylene was condensed to the liquid phase and 60 ml was diluted with 100 ml of methylene chloride at −10°. Mercuric acetate, 16 g, and octanoic acid, 67 g, were added and the mixture was stirred for a minimum of 0.5 hr. Boron trifluoride etherate (0.4 ml) was added and the temperature was maintained at +30°, avoiding higher temperatures leading to anhydride formation and lower temperatures which arrest the reaction completely. After 4 hr stirring the catalyst was neutralized with 4 g of NaOAc and solids were filtered off. The mixture was distilled to give 64 g (70%) of crude ester, bp 63° (0.4 mm). The product was freed of color by a pass through a short Florisil column. The analytical sample of isopropenyl octanoate obtained by redistillation had bp 73° (3 mm).

Anal. Calcd for $C_{11}H_{20}O_2$: C, 71.69; H, 10.94. Found: C, 71.75; H, 11.01.

A sample of isopropenyl octanoate, bp 68° (0.1 mm), in a Teflon apparatus was heated to 35° for 1 hr during which time anhydrous hydrogen fluoride was bubbled through. The reaction product was orange in color and contained contaminant octanoic acid as evidenced by ir bands at 1700 cm^{-1}. The mixture was extracted with pentane and the lower, colored layer was discarded. Distillation gave octanoyl fluoride (yield 50%): bp 33° (0.3 mm), 43° (1.7 mm), 162–165° (760 mm) [lit.[4a,10] bp 80° (14 mm)]; ir 1844 (C=O) and 1082 cm^{-1} (CF).

Acetyl Fluoride.—Into a Teflon bottle containing 25 g of commercial isopropenyl acetate was distilled slightly less than an exact equivalent (5 g) of hydrogen fluoride. After a reaction

(8) G. S. Sasin, P. R. Schaeffer, and R. Sasin, *J. Org. Chem.*, **22**, 1183 (1957).

(9) E. S. Rothman, S. Serota, T. Perlstein, and D. Swern, *ibid.*, **27**, 3123 (1962).

(10) G. Olah, S. Kuhn, and S. Beke, *Chem. Ber.*, **89**, 862 (1956).

TABLE I

Substance to be stearoylated	Product obtained	Reaction conditions: Time, min	Reaction conditions: Temp, °C	Mp, °C	Lit. mp	Yield, %
Dodecyl mercaptan	Dodecyl thiostearate	5	125	56–57	54–55[f]	85
Isobutyl mercaptan	Isobutyl thiostearate	5	88	22–23	23[g]	67
Benzyl mercaptan	Benzyl thiostearate	5	120	60.5–61.5	59.5–60[h,i]	80
Thiophenol	Phenyl thiostearate	30	120	38–39.5	39–40[i]	76
Thiolacetic acid	Stearic thioanhydride	60	135	81–81.5	79.5–80.5[i]	95
p-Toluenesulfonamide	N-Stearoyl-*p*-toluenesulfonamide	5	150	97.0–97.2	98–99[k]	80
N-Phenyl-*p*-toluenesulfonamide	N-Phenyl-N-stearoyl-*p*-toluenesulfonamide[a]	7	150	107.5–108.5		85
N-Benzyl-*p*-toluenesulfonamide	N-Benzyl-N-stearoyl-*p*-toluenesulfonamide[b]	7	150	65.0–65.8		64
Sulfanilamide (0.33 equiv)	N,N′-Distearoylsulfanilamide[c]	10	200	135–138		80
Benzyl N-phenylcarbamate	Benzyl N-phenyl-N-stearoylcarbamate[d]	10	160	67–68		87
Phenyl N-phenylcarbamate	Phenyl N-phenyl-N-stearoylcarbamate[e]	15	180	59.5–60.0		45

[a] *Anal.* Calcd for $C_{31}H_{47}NO_3S$: C, 72.47; H, 9.22; S, 6.30. Found: C, 72.76, H, 9.45; S, 6.30. [b] *Anal.* Calcd for $C_{32}H_{49}NO_3S$, C, 72.82; H, 9.36; N, 2.65; S, 6.08. Found: C, 72.81; H, 9.44; N, 2.56; S, 6.28. [c] *Anal.* Calcd for $C_{42}H_{76}N_2O_4S$: C, 71.55; H: 11.26; S, 4.55. Found: C, 71.85; H, 11.26; S, 4.16. [d] *Anal.* Calcd for $C_{32}H_{47}NO_3$: C, 77.85; H, 9.59; N, 2.84. Found: C, 78.05; H, 9.62; N, 2.85. [e] *Anal.* Calcd for $C_{31}H_{45}NO_3$: C, 77.62; H, 9.46; N, 2.92. Found: C, 77.99; H, 9.76; N, 2.76. [f] R. Sasin, *et al.*, *J. Amer. Oil Chem. Soc.*, **35**, 192 (1958). [g] G. S. Sasin, R. Sasin, and N. Capron, *J. Org. Chem.*, **21**, 852 (1956). [h] See ref 8. [i] J. M. Purcell and H. Susi, *Appl. Spectrosc.*, **19**, No. 4, 105 (1965). [j] Y. Hirabayashi, M. Mizuta, and T. Mazume. *Bull. Chem. Soc. Jap.*, **38**, 1099 (1965). [k] G. M. Ford, *Iowa State Coll. J. Sci.*, **12**, 121 (1937); *Chem. Abstr.*, **32**, 4943 (1938).

time of 2 hr the reaction flask was placed in a 50° bath and the acetyl fluoride was distilled away from acetone using a tall, unpacked Teflon fractionating column to yield 11 g of high-purity, water-white acetyl fluoride identical in every respect with an authentic sample, and free of acetone as evidenced by in frared spectrum. Hydrofluoric acid was absent. The distillate gave no turbidity on mixing with carbon disulfide and could be stored in glass vessels.

Azelaoyl Fluoride.—A stream of hydrogen fluoride was bubbled through 45 g of diisopropenyl azelate[11] at 85° for 1.25 hr in Teflon apparatus. Only a slight darkening of color was noticeable. The ir spectrum showed no residual enol ester absorption bands but acetone absorption bands were evident. The analytical sample (yield 63%) was obtained by distillation: bp 80° (0.01 Torr); ir (CS_2) 1820 (C=O), 1075 cm^{-1} (CF).

Anal. Calcd for $C_9H_{14}O_2F_2$: C, 53.32; H, 7.83; F, 21.09. Found: C, 53.11; H, 7.80; F, 20.93.

(11) E. S. Rothman, S. Serota, and D. Swern, *J. Org. Chem.*, **31**, 629 (1966).

General Procedure for Stearoylation with Isopropenyl Stearate.—To 1 equiv of isopropenyl stearate at the indicated reaction temperature 1 equiv of the substance to be acylated was added followed by a catalytic amount of sulfuric acid (2 drops/10 g of isopropenyl ester). After the mixture was heated the indicated length of time, the product was isolated either by directly crystallizing, or by chromatography on Florisil (see Table I above).

Registry No.—Stearoyl fluoride, 1511-79-1; isopropenyl octanoate, 19886-81-8; azelaoyl fluoride, 13022-57-6; N-phenyl-N-stearoyl-*p*-toluenesulfonamide 19886-83-0; N-benzyl-N-stearoyl-*p*-toluenesulfonamide, 19886-84-1; N,N′-distearoylsulfanilamide, 19922-50-0; benzyl N-phenyl-N-stearoylcarbamate, 19886-85-2; phenyl N-phenyl-N-stearoylcarbamate, 19886-86-3.