

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

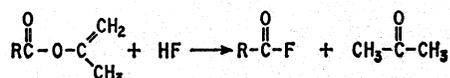
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Isopropenyl stearate, I, the stearylated enol of acetone, is a versatile stearylating agent. Its high degree of acylation activity is very probably associated with the ease of its thermal cleavage¹ to hexadecylketene. In preceding papers,^{1,3} we 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 C₂ or C₃ 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 with existing literature procedures using phosphorus trichloride, thionyl chloride,⁶ or oxalyl chloride⁷ 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.

| Substance to be stearoylated | Product obtained | Reaction conditions | | Mp, °C | Lit. mp | Yield, % |
|---|---|---------------------|----------|-------------|------------------------|----------|
| | | Time, min | Temp, °C | | | |
| 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 ^j | 95 |
| <i>p</i> -Toluene-sulfonamide | N-Stearoyl- <i>p</i> -toluenesulfonamide | 5 | 150 | 97.0-97.2 | 98-99 ^k | 80 |
| N-Phenyl- <i>p</i> -toluene-sulfonamide | N-Phenyl-N-stearoyl- <i>p</i> -toluene-sulfonamide ^a | 7 | 150 | 107.5-108.5 | | 85 |
| N-Benzyl- <i>p</i> -toluene-sulfonamide | N-Benzyl-N-stearoyl- <i>p</i> -toluene-sulfonamide ^b | 7 | 150 | 65.0-65.8 | | 64 |
| Sulfanilamide (0.33 equiv) | N,N'-Distearoyl-sulfanilamide ^c | 10 | 200 | 135-138 | | 80 |
| Benzyl N-phenyl-carbamate | Benzyl N-phenyl-N-stearoylcarbamate ^d | 10 | 160 | 67-68 | | 87 |
| Phenyl N-phenyl-carbamate | Phenyl N-phenyl-N-stearoylcarbamate ^e | 15 | 180 | 59.5-60.0 | | 45 |

^a *Anal.* Calcd for C₃₁H₄₇NO₃S: C, 72.47; H, 9.22; S, 6.30. Found: C, 72.76; H, 9.45; S, 6.30. ^b *Anal.* Calcd for C₃₂H₄₉NO₃S, 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 C₄₂H₇₆N₂O₄S: C, 71.55; H, 11.26; S, 4.55. Found: C, 71.85; H, 11.26; S, 4.16. ^d *Anal.* Calcd for C₃₂H₄₇NO₃: C, 77.85; H, 9.59; N, 2.84. Found: C, 78.05; H, 9.62; N, 2.85. ^e *Anal.* Calcd for C₃₁H₄₅NO₃: 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 infrared 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 azelate¹¹ at 85° for 1.25 hr in Teflon apparatus. Only a slight darkening of color was noticeable. The infrared 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); ν (CS₂) 1820 (C=O), 1075 cm⁻¹ (CF).

Anal. Calcd for C₉H₁₄O₂F₂: C, 53.32; H, 7.83; F, 21.09. Found: C, 53.11; H, 7.80; F, 20.93.

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.