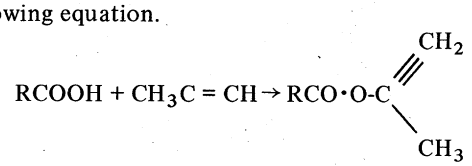
Enol Esters XIII: Synthesis of Isopropenyl Esters by Addition of Carboxylic Acids to Propyne

EDWARD S. ROTHMAN and **SAMUEL SEROTA**, Eastern Utilization Research and Development Division, ARS, USDA, Philadelphia, Pennsylvania 19118

ABSTRACT

The addition of long chain carboxylic acids to propyne under conditions of elevated temperature and pressure takes place in the presence of the zinc salt of the corresponding acid as indicated by the following equation.



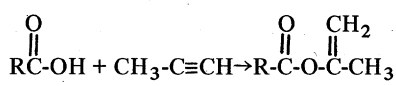
The reactor apparatus is described and the properties of a series of enol esters are listed. This series shows examples with chain length variations of the carboxylic acid moiety of the ester from 8 to 22 carbon atoms.

INTRODUCTION

Isopropenyl stearate (IPS) has been shown to be an unusually versatile synthetic chemical. It is particularly efficient as an acylation agent (1,2), since acetone, the sole reaction product, is expelled in the gaseous form rapidly driving the acylation reaction to completion. The active agent is probably hexadecylketene, since dimers and tetramers (3) of hexadecylketene are isolated when IPS is heated with acid catalyst in the absence of acylatable substrates.

Because our enol ester sample requirements for end use tests [e.g., detergent studies (4)] involved the preparation of large quantities of materials, we found it necessary to modify our previously reported procedures for the synthesis of isopropenyl stearate. Such modification was necessary because of the technical difficulties in handling large quantities of material at the purification and isolation stage. Our previously reported procedures include the carboxylic acid-enol acetate interchange reaction (5) and the addition of carboxylic acids to propyne at atmospheric pressure (3,6,7) using boron trifluoride-mercuric acetate mixed catalyst. The use of mercury salts in the latter procedure would also have precluded the use of the enol ester products for food-oriented uses.

The modified procedure, described in detail below, involves the direct addition of carboxylic acid to propyne under the influence of zinc carboxylate salt catalysis according to Equation 1.



When the required conditions of temperatures and pressures are complied with, the minimum yield of colorless product typically exceeds 90%. Purification involves only the removal of catalyst.

EXPERIMENTAL PROCEDURES

Equipment and Operating Procedures

Figure 1 shows the general apparatus arrangement in diagrammatic form. The reactor consisted of a 2 gal Pressure Products Co. stainless steel autoclave having a working pressure at 25 C of 600 psi and fitted with a 3/4 to 10 Magne Drive stirring unit and Dispersimax stirrer with baffle. The reactor was equipped with a pressure gauge, thermowell, blow out disc rated at 600 psi, and a blow leg. Heat and temperature control were provided by elements in the body of the autoclave. The head gasket was a

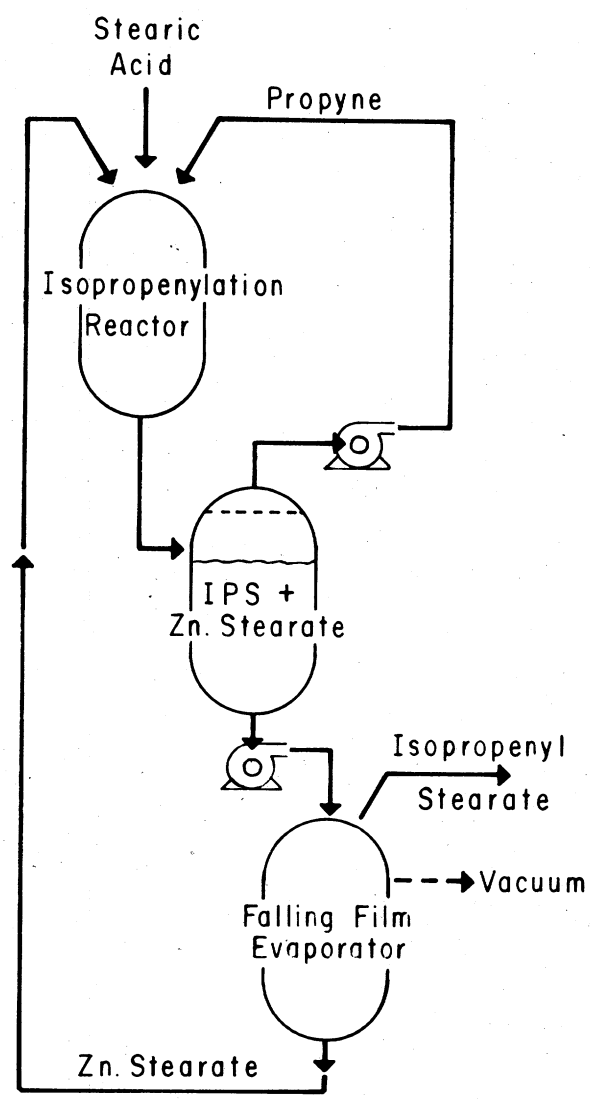


FIG. 1

TABLE I

Enol ester[a]	Mp or bp	Mm	Density (C)	nD (C)
Isopropenyl behenate	49.0-49.2		------	1.4425
Isopropenyl stearate	37-38	(184-9/0.4)	------	1.4416 (40)
Isopropenyl oleate	24		0.8675 (30)	1.4522 (30)
Isopropenyl palmitate	24		0.8585 (30)	1.4435 (30)
Isopropenyl myristate		100/0.7	0.8615 (30)	1.4425 (30)
Isopropenyl laurate (8)	6	114/1	0.8650 (26)	1.4377 (25) 1.4365 (30)
Isopropenyl pelargonate		62/0.15	0.8763 (30)	1.4316 (30)
Isopropenyl octanoate		63/0.4 73/3	0.8810 (30)	1.4256 (30)
Isopropenyl "tallowate"		124/0.075	------	1.4424 (35)
Isopropenyl ξ-phenylstearate		189/0.15	0.9122 (30)	1.4865 (30)

[a]In all cases yields estimated by IR analysis appeared to be quantitative. All isolated yields exceeded 90 moles per cent. New compounds gave elementary analyses in agreement with the expected structures. Impurity analysis has revealed the presence of 1-propenyl esters (from antiMarkownikof addition) in variable amounts as high as 6%; and of vinyl ester arising from ethyne in the propyne, 4%. Allene is inert in the process, and commercial propyne-allene mixtures are usable. The procedure may even be used to purify allene.

Flexatallic gasket, and copper and its alloys were rigorously excluded throughout. The blow leg was connected through a three-way valve directly to a Groen steam kettle containing the melted fatty acid-zinc salt charge. The third side of the valve allowed product recovery. Where production was concerned with repeated, multiple batch synthesis of one enol ester compound, it was not necessary to remove the head. All external lines and valves were steam-traced to prevent freezing of zinc stearate. The operating panel was equipped with a calibrated "through-vision" pressure burette which was filled with liquid propyne by means of a gas cylinder provided with a siphon tube and was further pressurized with nitrogen. Following the burette was a filter, a Lapp Pulsafeeder pump, an outlet tee with pressure gauge, and a bleed valve as well as a ball check valve in the propyne line leading to the bottom of the reactor. Two Barksdale explosion proof switches were connected to the electrical circuit in series to control the pressure developed by the pump. One switch partially closed the circuit when the propyne-nitrogen pressure ensured that the propyne existed in the liquid rather than the gaseous state in order to prevent vapor lock pump problems. The second switch turned off the pump when a preset pressure maximum was indicated by a gauge connected to the autoclave head space, thus preventing runaway pressure buildup and minimizing hazards. These switches ensured, in other words, that the propyne was in the pumpable liquid state, and that a ceiling limit was imposed on the possible pressure buildup.

Isopropenylation Procedure

In what follows only the procedure for converting stearic acid to IPS will be described in detail, and it will be understood that the results are directly applicable to a broad series of aliphatic monocarboxylic acids.

Preparation of Isopropenyl Stearate

The autoclave was preheated to 90-100 C and charged with 4 kg of melted stearic acid and 400 g of melted zinc stearate. After sealing, the autoclave was pressure-tested with dry nitrogen at 500 psi, and vented and purged four times, again with nitrogen at 500 psi. While stirring, the charge was heated to 150 C and the gauge pressure increased to 100 psi with nitrogen and then to 500 psi with admitted propyne. Under these conditions of temperature and catalyst, isopropenylation was complete in about 5 hr. IR analysis of the reactor contents at this point typically showed absence of residual carboxylic acid and of acid anhydride and, after catalyst removal, indicated the presence of isopropenyl stearate as the sole product. The product was isolated by molecular distillation in a falling film apparatus with product collection at 190-200 C/0.5-0.7 mm. The colorless isopropenyl stearate, mp 37-8 C, was identical in all respects with the substance described in earlier publications (5,6), yield 4.2 kg (92%).

DISCUSSION AND RESULTS

The addition of carboxylic acids to propyne under the influence of zinc salt catalyst occurs rapidly at 150 C in a pressure autoclave in the absence of added solvent. The procedure described above for the synthesis of isopropenyl stearate was applied without modification to the synthesis of the homologous derivatives shown in Table I.

Compatibility of Zinc Salt and Carboxylic Acid

Since the ionic zinc salt catalyst and the anion of the carboxylic acid reactant are in dynamic equilibrium zinc stearate is not useful as a general catalyst. It cannot be used, for example, in the isopropenylation of sebacic acid since zinc sebacate forms by metathesis and zinc sebacate is a salt of unusually high melting point and insolubility in molten sebacic acid. By contrast, zinc stearate and stearic acid melt together to form a single, homogeneous liquid phase. If *purissimum* isopropenyl stearate is desired consideration of ionic equilibria will forbid the use of "medicinal grade" or "USP zinc stearate" catalysts which contain considerable proportions of zinc palmitate and other homologs. In such cases where pure homologs are required, the zinc salt may be prepared in situ by combining the stoichiometric amounts of zinc oxide and carboxylic acid.

Alternative Workup Procedures

We have utilized several alternative procedures for the separation of product isopropenyl stearate from zinc stearate catalyst. They are less efficient than falling film distillation but are briefly reported here because they are convenient to carry out in laboratory scale operations. The yields are however generally somewhat lower than by the molecular distillation method.

Alembic Distillation. The reacted autoclave contents, namely the isopropenyl stearate-zinc stearate mixture can be directly distilled in vacuo in ordinary alembic apparatus. The product collects at 217 C/1.5 mm, yield about 80%. "Undistillable" pot residues yield more product when submitted to a second distillation by the falling film technique.

Chromatography. The reacted autoclave contents may

be slurried with five volumes of hexane and passed through five weights of Florisil in a chromatographic column. The column is washed with an additional ten volumes of hexane after which the column eluates are evaporated to leave a residue of pure isopropenyl stearate. Chromatography is not recommended for shorter chain homologs since it is destructive to the enol ester products.

REFERENCES

1. Rothman, E.S., and G.G. Moore, J. Org. Chem. 35:2351-2353 (1970).
2. Rothman, E.S., S. Serota and D. Swern, Ibid. 29:646-650 (1964).
3. Rothman, E.S., JAOCS 45:189-193 (1968).
4. Bistline, R.G., E.S. Rothman, S. Serota, A.J. Stirton and A.N. Wrigley, Ibid. 47 (Suppl.):Abstr. 284 (1970).
5. Rothman, E.S., S. Serota, T. Perlstein and D. Swern, J. Org. Chem. 27:3123-3127 (1962).
6. Serota, S., and E. Rothman, JAOCS 45:525-527 (1968).
7. Rothman, E.S., S. Serota and D. Swern, J. Org. Chem. 31:629-630 (1966).
8. Rothman, E.S., S. Serota and D. Swern, Ibid. 29:646-650 (1964); A. Sabel, J. Smidt, R. Jira and H. Prigge, Chem. Ber. 102:2939-2950 (1969).

[Received December 21, 1970]