

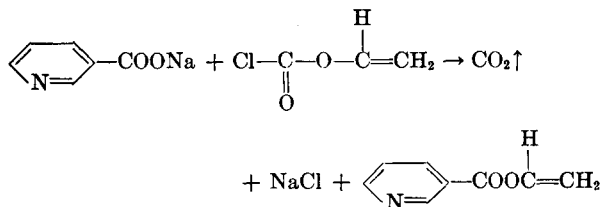
NOTES

Polyvinyl Nicotinate

Vinyl esters of aromatic acids containing heterocyclic nitrogen atoms are difficult to prepare. The difficulties involved in their preparation are associated with the low solubilities of the corresponding acids in most solvents and the basic nitrogen which interferes in normal reaction catalysis. Vinyl nicotinate, for example, has been synthesized but only by using high pressure acetylene and only in very low yield.¹ No mention of polyvinyl nicotinate is found in the literature. Over a period of time, we have made various attempts at synthesizing vinyl nicotinate without resorting to high pressure conditions. For those who are interested in this monomer type, we are reporting our observations below.

Reaction of acetylene with nicotinic acid in pyridine solution in the presence of a mercuric sulfate catalyst failed to yield any product. Several attempts to dehydrate β -hydroxyethyl nicotinate were unsuccessful. Exchange reactions between vinyl acetate and nicotinic acid in pyridine solution, or vinyl acetate and methyl nicotinate in the presence of sulfuric acid (which precipitated as the nicotinate salt) also failed to yield the desired ester. The pyrolysis of ethylene glycol bisnicotinate likewise proved futile. In an attempt to prepare β -chloroethyl nicotinate as an intermediate for dehydrohalogenation, a water-soluble, polymerlike material was obtained which was probably the polymeric quaternary salt.

Reaction of sodium nicotinate with vinyl chloroformate² yielded a trace of vinyl nicotinate:



The bulk of the reaction product, however, was a brown, unidentified solid which appeared polymeric.

Enough vinyl nicotinate to work with was finally prepared from the reaction of nicotinic acid and divinyl mercury³ in benzene solution:

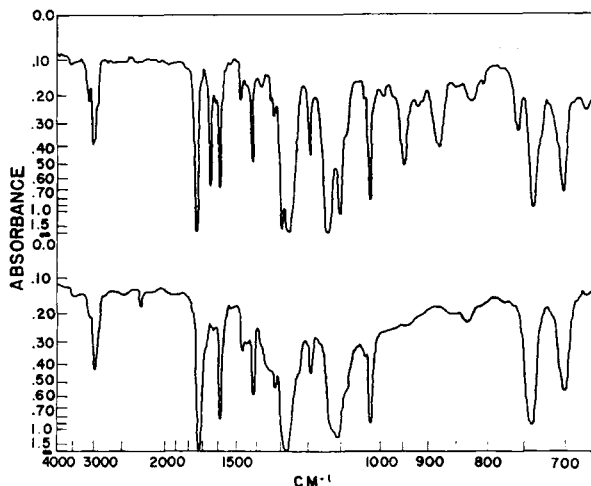
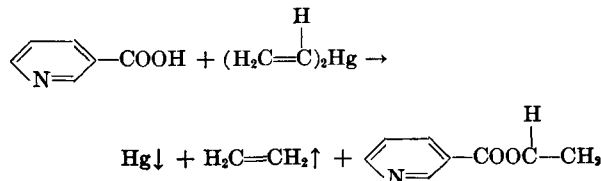


Fig. 1. Infrared spectra of vinyl nicotinate monomer (upper curve) and polyvinyl nicotinate (lower curve).

The monomer is a liquid, b.p. 105°C./12 mm., which is readily polymerized with radical catalysts to yield a solid polymer. Polyvinyl nicotinate is a film-former and is soluble in acetone, benzene, alcohol, and aqueous mineral acids.

The infrared spectra of vinyl nicotinate monomer and its homopolymer are in accord with the chemical structures (cf. Fig. 1). The monomer shows characteristic vinyl ester absorption at 1650, 945, and 878 cm.⁻¹. These bands are not present in the polymer. The carbonyl absorption of the monomer at 1750 cm.⁻¹ is shifted to 1730 cm.⁻¹ in the polymer.

References

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