tial amount (60 grams) of polymeric material was left after distillation. Attempts to characterize this material were unsuccessful—the infrared spectrum showed ether, hydroxyl, ketone, and ester linkages.

*p*-CRESOL. *p*-Cresol was prepared as follows. The reaction mixture from the oxidation of II in *t*-butyl alcohol was distilled to remove most of the solvent and lower-boiling components. The residue was refluxed 5 minutes with 2*N* aqueous hydrochloric acid, cooled, and extracted with benzene. The *p*-cresol was separated, and the yield determined by thin-layer chromatography.

ACKNOWLEDGMENT

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# Reactions of *p*-Nitrotoluene Carbanion

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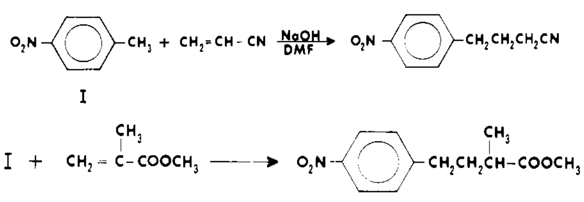
**p-Nitrotoluene carbanion adds to acrylonitrile and methyl methacrylate to give 4-(4-nitrophenyl)butyronitrile and methyl 2-methyl-4-(4-nitrophenyl)butyrate, respectively.**

ADDITION reactions of *p*-nitrotoluene carbanion have been impaired for the most part by the facile oxidation (*8, 9, 10*) and dimerization (*2, 3, 8, 9*) of the anion. Reactions with aldehydes have resulted in low yields of product, at best, and in most cases the only significant product has been the dehydrodimer, 4,4′-dinitrobibenzyl, or 4,4′-dinitrostilbene (*2–5*). The addition to aryl aldehydes can be directed to give good yields of product if conducted in polar aprotic solvents, such as dimethylformamide and dimethylacetamide (*6*).

This reaction has been extended to the addition of *p*-nitrotoluene carbanion to the activated double bonds of such substrates as acrylonitrile and methyl methacrylate. The addition proceeds readily, though in low yield, at room temperature to afford the 1 to 1 adducts, as well as higher molecular weight products.



The reactions occur to a reasonable extent at room temperature with sodium hydroxide catalysis and are sufficiently fast to compete with the known dimerization of the anion (*2, 3, 8, 9*) and the homopolymerization of acrylonitrile and methyl methacrylate (*7*). Whether or not the reactions are reversible under these conditions, as was established for the aldehyde adducts, has not been determined as yet.

## EXPERIMENTAL

**4-(4-Nitrophenyl)butyronitrile.** A 250-ml. 3-necked flask fitted with magnetic stirrer, thermometer, and reflux condenser was charged with 27.4 grams (0.2 mole) of *p*-nitrotoluene and 40 ml. of dimethylformamide (DMF). To the resulting greenish yellow solution was added, under nitrogen and with stirring, 0.6 gram (0.015 mole) of freshly ground sodium hydroxide. To the red solution was added 10.4 grams (0.2 mole) of acrylonitrile in 35 ml. of DMF over a 1-hour period. After 2 hours, 1.5 ml. of concentrated (36%) hydrochloric acid was added and the solution filtered. Evaporation of solvent under reduced pressure gave a dark red semisolid residue. Treatment with hot chloroform gave 15.5 grams of insoluble light orange solid, m.p. 105° to 125° C.—higher molecular weight products from *p*-nitrotoluene and acrylonitrile. The red chloroform extract was evaporated under vacuum to a red oil, which was extracted with hot petroleum ether to remove the unreacted *p*-nitrotoluene. The 6.5 grams of red oily residue was distilled at 169–73° C. and 1.0 to 0.6 mm. (*1*) of Hg to yield 1.3 grams of substantially pure 4-(4-nitrophenyl)butyronitrile; IR (neat), 4.4$\mu$ (CN), 6.55 and 7.39$\mu$ ($NO_2$); NMR ($CDCl_3$), $\delta$ = 8.13 and 7.35 (2d, 4, ArH), 3.05–1.90 (m, 6, $CH_2$).

Hydrolysis of 0.7 gram of this liquid with 3.5 ml. of concentrated sulfuric acid and 3.0 ml. of water at reflux for 0.5 hour gave 0.66 gram of a white solid, 4-(4-nitrophenyl)butyric acid, which had m.p. 92–3° C. (*11*) on recrystallization from toluene.

**Methyl-2-methyl-4-(nitrophenyl)butyrate.** Thirteen and seven-tenths grams (0.1 mole) of *p*-nitrotoluene, 10.01 grams (0.1 mole) of methyl methacrylate, and 50 ml. of DMF were charged into a 250-ml. 3-necked flask fitted with a nitrogen inlet tube, magnetic stirrer, thermometer, and reflux condenser at room temperature. To the light yellowish green solution was added under nitrogen 1.0 gram (0.025 mole) of freshly ground sodium hydroxide. The reaction turned a vivid green initially, and after 1 hour a dark blue color formed. The reaction solution was acidified with 125 ml. of a 5% hydrochloric acid solution, whereupon a red oil separated from the mixture. The reaction mixture was extracted with three 50-ml. portions of benzene. The extracts were combined and dried over magnesium sulfate, and the solvent was vacuum-evaporated with water and oil pumps to 12.01 grams of a red oil, which started to crystallize at room temperature. After removal of most of the unreacted *p*-nitrotoluene by distillation at 90–5° C. and 0.25

mm. of Hg, there was obtained 2.2 grams of a light orange-red oil. The oil was dissolved in a chloroform–petroleum ether mixture, charcoal-treated, filtered, and vacuum-evaporated to yield 1.9 grams of the desired methyl 2-methyl-4-[(4-nitrophenyl)butyrate] as a light yellow liquid; IR (neat), 5.72 $\mu$ (C=O), 6.55 and 7.39 $\mu$ ($NO_2$); NMR ($CDCl_3$), $\delta$ = 8.1 and 7.3 (2d, 4, ArH), 3.68 (s, 3, $OCH_3$), 3.0-1.75 (m. 5, CH, $CH_2$), 1.16 (d, 3, $CH_3$).

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# Vinyl Ester Interchange Reaction

## Reaction of Halogenated Acetic Acids with Vinyl Acetate

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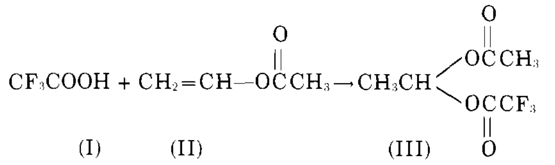
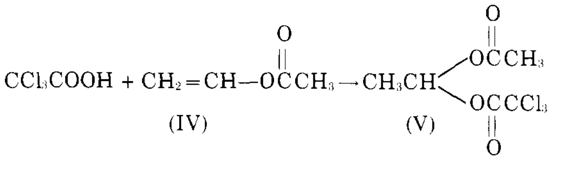
**Trichloro- and trifluoroacetic acids fail to give the vinyl ester interchange reaction with vinyl acetate, but add to vinyl acetate to give the unsymmetrical acylals. However, monochloro- and dichloroacetic acids give the vinyl ester interchange reaction in the presence of mercuric acetate–sulfuric acid.**

THE VINYL ester interchange or transvinylation method employing vinyl acetate is a synthetically useful reaction whereby many aliphatic and aromatic carboxylic acids are converted to their vinyl esters in the presence of a catalytic amount of mercuric acetate or other mercury salts (*1, 12, 15, 16*). The vinylation of several long-chain aliphatic acids in 30 to 70% yields has been reported by Swern (*15*), using a procedure first described by Toussaint and MacDowell (*16*). The vinylation of benzoic acid by this procedure yields vinyl benzoate (*16*) in 73% yield, vinyl propionate (*16*) in 50% yield, and vinyl stearate (*1*) in 88% yield.

The reaction of trifluoro- and trichloroacetic acids with vinyl acetate by the above procedure failed to give vinyl trifluoroacetate and vinyl trichloroacetate. The isolated products could be accounted for by the addition of the carboxylic acid across the double bond of vinyl acetate to give the acylals shown in Equations 1 and 3.



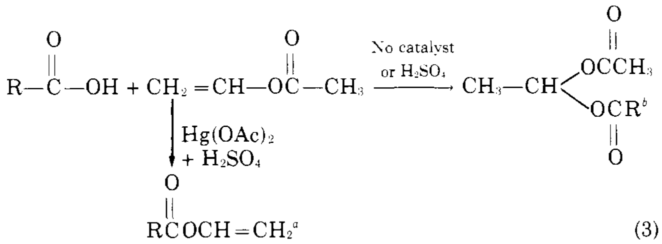
$$\underset{(I)}{CF_3COOH} + \underset{(II)}{CH_2{=}CH{-}O\overset{O}{\overset{\|}{C}}CH_3} \rightarrow \underset{(III)}{CH_3CH\begin{cases} O\overset{O}{\overset{\|}{C}}CH_3 \\ O\underset{\underset{O}{\|}}{C}CF_3 \end{cases}} \qquad (1)$$



$$CCl_3COOH + \underset{(IV)}{CH_2{=}CH{-}O\overset{O}{\overset{\|}{C}}CH_3} \rightarrow \underset{(V)}{CH_3CH\begin{cases} O\overset{O}{\overset{\|}{C}}CH_3 \\ O\underset{\underset{O}{\|}}{C}CCl_3 \end{cases}} \qquad (2)$$

Carrying out this reaction in the absence of mercury salts or other additives also gave the products shown in Equations 1 and 2.

Scheme I. Reaction of Carboxylic Acids with Vinyl Acetate



(3)

$^a$R = $-CH_2Cl$ (VIII), $-CHCl_2$ (IX); $-CCl_3$ and $-CF_3$ yield acylals.
$^b$R = $-CH_3$ (VI), $-CH_2Cl$ (VII), $-CHCl_2$ (X), $-CCl_3$ (V), $-CF_3$ (III).

Carboxylic acids other than acetic (*2*), benzoic (*2*), methacrylic (*3*), and stearic acid (*11*) have not been reported to add readily across the double bond of vinyl acetate. Even these acids are ordinarily unreactive, unless catalyzed by sulfuric acid (*2*), sulfur oxides (*14*), or mercuric oxide (*3*).

Scheme I describes the products and Table I describes the conditions of the reaction of vinyl acetate with acetic and halogenated acetic acids, with or without catalysts. Table II lists the identifying infrared and NMR spectral properties of the products.

The results in Table I indicate that as the dissociation constants of the hologenated acetic acids increase, the tendency to add to vinyl acetate also increases. Acetic acid and monochloroacetic acid alone fail to react with vinyl