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 μ (C=O), 6.55 and 7.39 μ (NO_2); NMR ($CDCl_3$), δ = 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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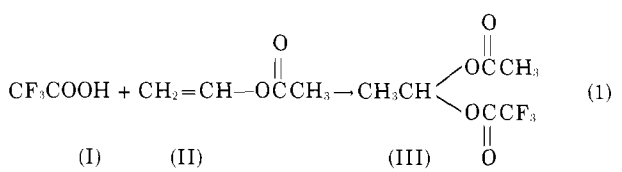
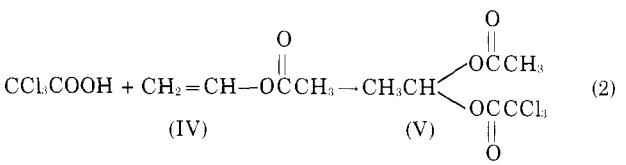
Trichloro- and trifluoroacetic acids fail to give the vinyl ester interchange reaction with vinyl acetate, but add to vinyl acetate to give the unsymmetrical acylals. However, monochloro- and dichloroacetic acids give the vinyl ester interchange reaction in the presence of mercuric acetate–sulfuric acid.

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.



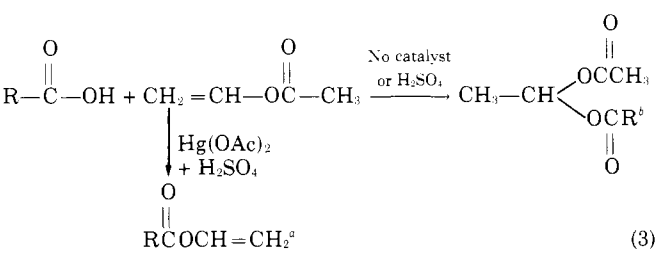
(I) (II) (III) (1)



(IV) (V) (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

Table I. Reaction of Halogenated Acetic Acids with Vinyl Acetate

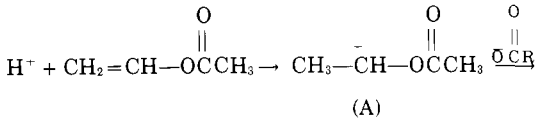
Carboxylic Acid, (6) Moles	Vinyl Acetate, Moles	Catalyst or Additive, Moles	Temp., °C.	Time, Days	Product	Yield, %	B.P., Mm.	n_D, °C.	Calcd., % C	Calcd., % H	Calcd., % Cl	Found, % C	Found, % H	Found, % Cl
Acetic Acid, $K_a = 1.7 \times 10^{-5}$														
2.0	2.0		25	20		0								
		H_2SO_4												
2.0	8.0	0.05	25	2	(VI)	70	56-58 (3.0)	1.4021 (21°)	49.30	6.86	...	48.84	7.02	...
2.0	8.0	0.05	73	1	(VI)	98								
1.0	8.0	...	73	1	(XI)	0								
Chloroacetic Acid, $K_a = 1.5 \times 10^{-3}$														
1.0	4.0	0.025	25	1	(VII)	97	79-80 (3.0)	1.4300 (21°)	39.80	4.98	19.65	39.53	4.96	20.05
1.0	1.0	...	25	21	(VII)	0.8								
1.0	8.0	...	73	1		0								
1.0	8.0	[a]	25	1	(VIII)	39	42-44 (6.0)	1.4433 (23°)	39.20	4.14	29.45	39.21	4.09	29.37
		$HgSO_4$												
1.0	8.0	0.021	25	16	(VIII)	40								
		H_2SO_4												
1.0	8.0	0.005	73	1	(VII)	100								
Dichloroacetic Acid, $K_a = 4.3 \times 10^{-2}$														
1.0	8.0	[a]	25	21	(IX)	80	33-35 (5.0)	1.4563 (25°)	31.00	2.58	45.80	30.77	2.66	45.65
					(X)	14	7w-76 (0.5)	1.4447 (25°)	33.50	3.72	33.00	33.77	3.84	33.13
1.0	8.0		73	1	(X)	85								
1.0	1.0	...	25	17	(X)	60								
		H_2SO_4												
1.0	8.0	0.005	73	1	(X)	54								
Trichloroacetic Acid, $K_a = 0.22$														
1.0	1.0	...	25	5	(V)	35	83-87 (3.0)	1.4496 (23°)	28.65	2.80	42.70	28.29	2.72	42.60
1.0	8.0	[a]	25	3	(V)	45								
1.0	8.0	[a]	73	1	(V)	74								
		$Hg(OAc)_2$												
1.0	8.0	0.021	25	28	(V)	81								
Trifluoroacetic Acid, $K_a = 0.56$														
1.2	1.2	...	25[c]	5	(III)	98	123-124	1.3422 (25°)	36.00	3.50	28.50[d]	35.64	3.80	28.15[d]
		$Hg(OAc)_2$												
0.5	4.0	0.068	25[c]	1	(III)	48								
0.84	6.73	[b]	25[c]	10	(III)	66								

[a] 0.021 mole $Hg(OAc)_2$ + 0.005 mole H_2SO_4. [b] 0.018 mole $Hg(OAc)_2$ + 0.004 mole H_2SO_4. [c] The initial reaction is exothermic, and cooling to this temperature is required. [d] Fluorine.

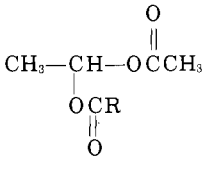
acetate. Dichloroacetic acid slowly reacts and adds to vinyl acetate at room temperature to give the acylal, X. The use of sulfuric acid promotes acylal formation at room temperature with acetic acid and monochloroacetic acid to give VI and VII, respectively. Stronger acids—such as trichloro- and trifluoroacetic acids—react exothermically with vinyl acetate in the absence of catalysts to give acylals III and IV, respectively. Trifluoroacetic acid reacts much more exothermically, and cooling is required in order to control the reaction.

These results suggest that protonation of vinyl acetate to give carbonium ion, A, may be an important first step in the mechanism of this reaction (*5, 8, 10*).

The second step might be the reaction of the carboxylate anion with carbonium ion, A, to give the acylal, as shown below.



(A)



(4)

The suggested mechanism gains support from the observation that the reactivity of the acetic acids increases with an increase in the dissociation constant, K_a, and that the

Table II. Spectral Properties of the Products

Compd.	IR Bands,[a] μ	NMR Data[b]
III	3.40 (w), 5.50 (s), 5.65 (s), 7.00 (w), 7.27 (m), 7.48 (w), 8.25 (s), 8.60 (s), 9.07 (m), 9.41 (m), 9.90 (m), 10.60 (m), 11.40 (w), 11.65 (m)	1.60 d (CH_3—CH), 2.08 s (—OC(=O)—CH_3), 6.98 q (>CH—CH_3).
V	3.40 (w), 3.42 (vw), 5.70 (s), 6.90 (m), 7.00 (w), 7.20 (m), 7.27 (m), 8.02 (s), 8.30 (s), 8.70 (w), 9.25 (s), 9.90 (m), 10.35 (s), 10.65 (s), 11.40 (s), 12.15 (s), 13.10 (w), 13.25 (w), 14.72 (s)	1.65 d (CH_3—CH), 2.10 s (—OC(=O)—CH_3), 6.95 q (>CH—CH_3).
VI	3.35 (w), 3.42 (vs), 5.70 (s), 6.90 (m), 7.30 (s), 8.10 (s), 8.25 (s), 9.55 (s), 9.95 (s), 10.55 (s), 11.17 (m), 12.35 (w), 12.95 (w), 13.65 (w), 14.50 (m),	1.48 d (CH_3—CH), 2.04 s (—OC(=O)—CH_3), 6.82 q (—CH—CH_3).
VII	3.33 (s), 3.38 (vw), 5.68 (s), 6.89 (w), 7.08 (w), 7.17 (w), 7.27 (m), 7.63 (m), 7.80 (m), 8.15 (s), 8.50 (s), 8.65 (s), 9.05 (s), 9.30 (s), 8.87 (m), 10.53 (s), 11.60 (m), 12.67 (w), 14.25 (w),	1.50 d (CH_3—CH), 2.03 s (—OC(=O)—CH_3), 4.10 s (—OC(=O)—CH_2Cl), 6.75 q (>CH—CH_3).
VIII	3.24 (w), 3.35 (w), 3.40 (s), 5.65 (s), 6.06 (s), 7.08 (m), 7.25 (w), 7.65 (s), 7.81 (s), 8.02 (s), 8.65 (s), 10.37 (m), 10.10 (m), 10.80 (w), 11.37 (m), 12.65 (m),	$ClCH_{a2}$—CO—O—C(H_c)=C(H_b)(H_a); 4.12 s (H_d), 4.55 d, 4.65 d (H_a), 4.76 d, 5.00 d (H_b), 7.00 d, 7.25 d (H_c).
IX	3.25 (w), 3.35 (w), 5.68 (s), 6.05 (m), 7.10 (w), 7.25 (w), 7.68 (s), 7.80 (s), 7.93 (s), 8.10 (m), 8.30 (m), 8.60 (s), 8.95 (m), 10.15 (m), 10.65 (m), 11.30 (m), 12.27 (s), 12.90 (w), 13.50 (w), 14.85 (w).	Cl_2—CH_d—CO—O—C(H_c)=C(H_b)(H_a); 4.68 d, 4.78 d (H_a), 4.90 d, 5.12 d (H_d), 6.05 s (H_d), 7.00 d, 7.23 d (H_c).
X	3.33 (w), 3.40 (vw), 5.65 (s), 6.90 (w), 7.20 (w), 7.27 (m) 7.83 (m), 8.20 (s), 8.55 (m), 8.63 (m), 9.10 (s), 9.40 (s), 9.90 (m), 10.45 (s), 10.60 (s), 11.50 (m), 12.30 (m), 12.95 (w), 13.65 (w).	1.50 d (CH_3—CH), 2.08 s (—OC(=O)—CH_3), 6.07 s (OC(=O)—$CHCl_2$), 6.78 q (>CH—CH_3).

[a] Recorded neat between NaCl plates. Abbreviations are (s) strong, (m) medium, (w) weak, (vw) very weak. [b] All chemical shifts are reported in τ values (parts per million) from tetramethylsilane. Abbreviations are s, singlet; d, doublet; t, triplet, q, quartet.

use of sulfuric acid accelerates the rate of reaction. This is also the pathway through which vinyl ethers are cleaved in acid (*7*), and has other analogies, as in the acid-catalyzed isomerization of *cis*-stilbene (*9*) and hydration of styrene (*13*).

The above mechanism is also consistent with the reported acid-catalyzed hydrogen cyanide addition to vinyl acetate to give acetoxyl lactonitrile (*4*).

$$HCN + CH_2{=}CH{-}OCCH_3 \rightarrow CH_3{-}\underset{\displaystyle CN}{\underset{|}{CH}}{-}OCCH_3 \qquad (5)$$

The sole addition of mercuric acetate to mono- or dichloroacetic acid in the presence of vinyl acetate hardly gives the vinyl interchange reaction unless sulfuric acid is also added. The use of hydrochloric acid in equivalent amounts is not as effective. Moreover, the addition of mercuric sulfate also gives the vinyl interchange reaction at a reduced rate in the absence of sulfuric acid.

EXPERIMENTAL

Boiling points are uncorrected. Infrared (IR) spectra were obtained with a Perkin-Elmer Model 21 spectrophotometer. Nuclear magnetic resonance (NMR) were determined neat on a Varian A-60 spectrometer and are referred internally to tetramethylsilane. Vapor phase chromatography (VPC) was performed using a Burrell Kromotog Model K-2 gas chromatograph with a 6-foot × 0.25-inch column packed with silicone DC-200 on Celite at concentration P (Burrell Corp.). Almost all VPC analyses were performed at 138° C., at a helium flow rate of 40 cc. per minute.

Starting Materials. The halogenated acetic acids and the mercury salts were Fisher Scientific highest purity reagents. Glacial acetic was obtained from Merck and Co. Vinyl acetate was obtained from Borden Chemical, Division of Borden, Inc.

General Procedure for the Preparation of Acylals. Reaction of Carboxylic Acids with Vinyl Acetate. The halogenated acetic acid was added to a molar equivalent or excess of vinyl acetate and kept at room temperature for the times specified. At the given times, the vinyl acetate was distilled off and the product distilled, either under reduced pressure or under atmospheric conditions. Further details are given in Table I.

Reaction of Carboxylic Acids with Vinyl Acetate. The halogenated acetic acids containing a given quantity of concentrated sulfuric acid were treated with vinyl acetate as above, exept some were refluxed, as specified in Table I.

General Procedure for the Vinylation of Mono- and Dichloroacetic Acids. The reactions were carried out as in procedure A, using an eightfold excess of vinyl acetate and a specified amount of mercuric acetate–concentrated sulfuric acid.

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Synthesis of Some New Substituted Thioureas

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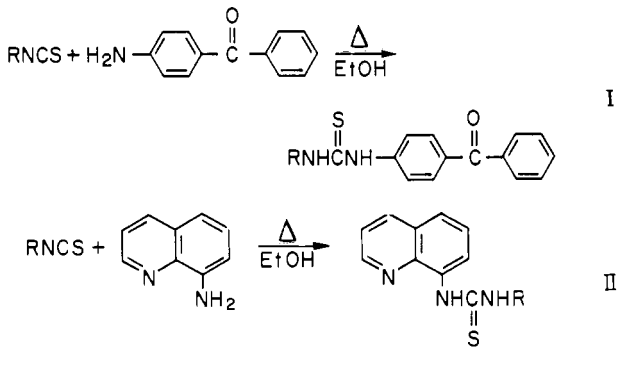
New thiourea derivatives have been synthesized by reacting aryl isothiocyanates with 4-aminobenzophenone and with 8-aminoquinoline.

THE TECHNICAL literature concerned with thiourea and its derivatives is extensive (*4*). These compounds have proven useful in numerous chemical and biological applications (*2*). Of the many preparative methods which have been used for substituted thioureas (*3*), one of the most common involves the direct reaction of isothiocyanates with amines.

During an investigation in this laboratory of the synthesis of new fungicides containing the thiocarbonyl group, two series of previously unreported substituted thioureas have been prepared by reacting aromatic and substituted-aromatic isothiocyanates with 4-aminobenzophenone and with 8-aminoquinoline. Thioureas having structures I and II, respectively, were obtained; this was confirmed by elemental analysis and infrared spectroscopy. The new compounds are listed in Tables I and II.



The electronic absorption spectra, in the near ultraviolet region, of compounds 1 to 10 were measured; the relevant peak wavelengths and molar extinction coefficients are shown in Table III. These data are relevant to the photostabilities of thiourea and its derivatives (*2*), as well as to the possible photoprotectiveness of these compounds (*5*).

The fungistatic effectiveness of the compounds listed in the tables against the microorganisms *A. niger* and *C. globosum* was the following: Compd. 1, 2, 4, and 8: 1000 p.p.m. (*C. g.*); Compd. 7: 10 p.p.m. (*C. g.*), 1000 p.p.m. (*A. n.*). None of the other compounds was fungistatic at concentrations of 1000 p.p.m. or less.

Table I. 1-(4-Benzoylphenyl)-3-(Substituted) Thioureas (I)

Compd. No.	*R*	M.P., °C.	Yield, %	Molecular Formula[a]
1	1-naphthyl	165[b]	89	$C_{24}H_{18}N_2OS$
2	2-naphthyl	169[b]	80	$C_{24}H_{18}N_2OS$
3	*m*-nitrophenyl	181[c]	95	$C_{20}H_{15}N_3O_3S$
4	*p*-nitrophenyl	204[d]	90	$C_{20}H_{15}N_3O_3S$
5	phenyl	168[c]	85	$C_{20}H_{16}N_2OS$

[a] Analysis of all compounds for C, H, N, and S was within 0.24% of the calculated values. These data have been deposited as Appendix A with the ASIS National Auxiliary Publications Service. [b] Recrystallized from benzene–*n*-hexane. [c] Recrystallized from acetone-water. [d] Recrystallized from *p*-dioxane–water.

Table II. 1-(8-Quinolyl)-3-(Substituted) Thioureas (II)

Compd. No.	*R*	M.P., °C.	Yield, %	Molecular Formula[a]
6	1-naphthyl	176[b]	75	$C_{20}H_{15}N_3S$
7	2-naphthyl	175[c]	90	$C_{20}H_{15}N_3S$
8	*m*-nitrophenyl	180[d]	89	$C_{16}H_{12}N_4O_2S$
9	*p*-nitrophenyl	200[d]	79	$C_{16}H_{12}N_4O_2S$
10	phenyl	161[e]	91	$C_{16}H_{13}N_3S$

[a] Analysis of all compounds for C, H, N, and S was within 0.30% of the calculated values. These data have been deposited as Appendix A with the ASIS National Auxiliary Publications Service. [b] Recrystallized from benzene. [c] Recrystallized from acetone-water. [d] Recrystallized from dimethylformamide-water. [e] Recrystallized from ethanol.

EXPERIMENTAL

Melting points were determined using a Fisher-Johns apparatus, and have been corrected. Elemental analyses were performed at the microanalytical laboratory of Weiler and Strauss in Oxford.

The infrared spectra were obtained from KBr pellets with a Model 21 Perkin-Elmer spectrophotometer over the frequency range 3500 to 650 cm.$^{-1}$. The ultraviolet spectra