

A cyclical permutation of the subscripts of Equation 23 furnishes  $\log \gamma_3/\gamma_2$  and  $\log \gamma_1/\gamma_3$ . It was assumed that the solutions were type 3 of Redlich and Kister's classification for which the constant  $D_{12}$  of Equation 22 is zero. Further it was assumed that the ternary constants in Equation 23 were zero. The results of the curve fitting were as follows:

Methyl ethyl ketone (1)-toluene (3) system:	
$B_{13}$	= 0.157
$C_{13}$	= 0.0372
Methyl ethyl ketone (1)-heptane system (2)	
$B_{12}$	= -0.48
$C_{12}$	= -0.0094
Heptane (2)-toluene (3) system	
$B_{23}$	= -0.119
$C_{23}$	= -0.024
Methyl ethyl ketone (1)-benzene (4) system	
$B_{14}$	= 0.074
$C_{14}$	= -0.031

Using these constants for the ternary system methyl ethyl ketone (1)-heptane (2)-toluene (3), substituted in Equations 23, the vapor compositions corresponding to the experimental liquid compositions were computed and are compared with the experimental vapor compositions in Table IX. In virtually all cases, the agreement is excellent and attests to the value of Redlich and Kister's relations for the correlation and extrapolation of equilibrium data.

#### CONCLUSION

In view of the high probability of error in vapor-liquid equilibrium measurements it seems desirable to check the thermodynamic consistency of such experimental data by the Gibbs-Duhem equation. Methods for accomplishing this have been presented and illustrated by data for the system methyl ethyl ketone-*n*-heptane-toluene. These data have been represented by curves shown to be thermodynamically consistent to within  $\pm 0.002$  mole fraction unit based on methyl ethyl ketone in the vapor phase and to within  $\pm 0.2^\circ$  C. The experimental data

appear to be accurate to within  $\pm 0.004$  mole fraction unit and  $\pm 0.2^\circ$  C. The data have also been represented by Redlich and Kister's empirical equations.

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# Reactions of Isopropenyl Acetate

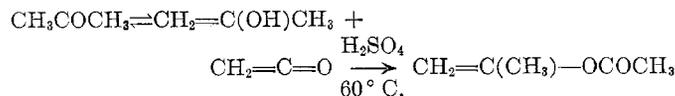
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Isopropenyl acetate is a unique acetylating agent, which is decomposed into the original components, ketene and acetone, by heating in the presence of acid catalysts. Isopropenyl acetate is superior to ketene and acetic anhydride for enol acetylation and it reacts with all enolizable carbonyl compounds—that is, any carbonyl compound containing at least one available hydrogen atom on a carbon atom adjacent to the carbonyl group—to form enol acetates in good yields. The enol acetylation is an equilibrium reaction and it is driven to completion by distilling off acetone continuously as it is formed. Isopropenyl acetate is particularly useful for acetylating organic compounds where mild acetylation conditions are required. Copolymers and terpolymers of isopropenyl acetate with other polymerizable compounds containing olefinic unsaturation are suitable for fibers and resins.

ISOPROPENYL acetate was suggested by Plauson as a reaction product of methyl acetylene and acetic acid (15). Hennion and Nieuwland first prepared isopropenyl acetate or 2-acetoxy-1-propene by condensing methyl acetylene with acetic acid in the presence of boron trifluoride etherate catalyst (9). In 1942 Gwynn and Degering reported the enol acetyla-

tion of acetone with ketene in the presence of sulfuric acid catalyst to form isopropenyl acetate in good yield (5).



Isopropenyl acetate is prepared continuously by feeding acetone containing 1 to 1.4% sulfuric acid and ketene in a 2 to 1 mole ratio to a reactor heated to  $60^\circ$  to  $68^\circ$  C. Unreacted ketene is recovered as acetic anhydride by scrubbing the off-gas with glacial acetic acid. The conversion of ketene to isopropenyl acetate averages between 38.4 and 41.2%. With acetylsulfoacetic acid catalyst the conversion of ketene to isopropenyl acetate averages between 75 and 85% and a lower mole ratio of acetone to ketene is used. Isopropenyl acetate yields of 90% based on ketene and 92 to 94% based on acetone are obtained. Isopropenyl acetate is separated by distillation and usually contains traces of dissolved ketene. Dissolved ketene can be removed by washing with sodium bicarbonate and redistilling.

In Table I the physical properties for pure isopropenyl acetate are compared with those reported by previous investigators.

Isopropenyl acetate is decomposed into the original components, ketene and acetone, by heating in the presence of acid

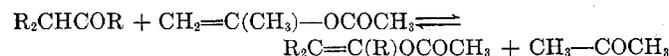
catalysts, and is a unique acetylating agent. It is of special interest in the formation of enol acetates of enolizable carbonyl compounds—i.e., any carbonyl compound containing at least one available hydrogen on an adjacent carbon atom.

#### ENOL ACETYLATION

The preparation of enol acetates using acetic anhydride and sodium acetate is not generally applicable to all enolizable compounds. Although ketene is generally applicable (5, 6, 11, 16), it is an unstable compound and has a tendency to polymerize to diketene and dehydroacetic acid under the influence of heat and acid or alkaline catalysts. If the compound to be acetylated is difficultly enolizable, the enol acetylation takes place slowly and low yields are obtained where ketene is used as the acetylating agent. With aldehydes ketene has the further disadvantage that where diketene is formed in appreciable amounts, the acetylation is complicated by a secondary reaction, the condensation of diketene with the aldehyde to form an alpha, beta unsaturated ketone (1).



Isopropenyl acetate does not polymerize under acetylation conditions. Its reaction with enolizable carbonyl compounds can be represented by the equation:



wherein R represents hydrogen or hydrocarbon residues. As shown, the enol acetylation is an equilibrium reaction, which is driven to completion by distilling off acetone continuously as it is formed. The isopropenyl acetate can be considered as a ketene carrier which liberates the ketene in situ as the acetylation takes place.

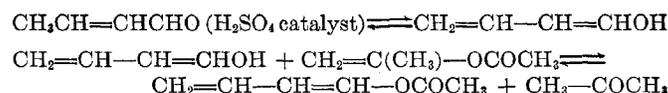
Although isopropenyl acetate is the preferred enol acetylating agent because of its stability and ease of manufacture, the reaction between enol esters and enolizable carbonyl compounds is general and vinyl acetate, isobutenyl acetate, and the like may be employed. Where the carbonyl compound to be acetylated has a higher vapor pressure than the carbonyl compound liberated by the enol ester during the acetylation, an equilibrium mixture can be prepared. The acid catalyst is neutralized and the components of the equilibrium mixture are separated by fractional distillation—e.g., vinyl acetate is prepared by autoclaving a mixture of acetaldehyde and excess isopropenyl acetate in the presence of 0.4% sulfuric acid.

TABLE I. PHYSICAL CONSTANTS OF ISOPROPENYL ACETATE

Constant	Tennessee Eastman	Gwynn and Degering (5)	Hennion and Nieuwland (9)
Boiling point, ° C.	96.6 (748)	96 (750)	92.94 (736)
$d_4^{20}$	0.9173	( $d_{25}^{25}$ ) 0.9308	0.9090
$d_4^{20}$	0.9202	...	...
$n_D^{20}$	1.4001	1.4001	1.4033
Mol. refraction (calcd.)	26.477	...	26.477
Mol. refraction (found)	26.41	...	26.73
Parachlor (calcd.)	242 <sup>a</sup>	...	...
Parachlor (found)	239.2	...	...

<sup>a</sup> Using Sugden's values.

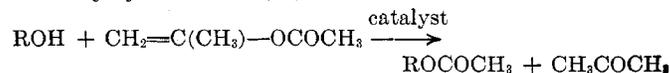
Enol acetylation of enolizable carbonyl compounds is a source of many valuable polymerizable monomers. For example, crotonaldehyde is enol acetylated with isopropenyl acetate to give a 95% yield of 1-acetoxy-1,3-butadiene.



Ethyl pyruvate is enol acetylated with isopropenyl acetate to form ethyl  $\alpha$ -acetoxyacrylate. Diacetyl and isopropenyl acetate react to form both the mono-enol acetate, methyl  $\alpha$ -acetoxyvinyl ketone, and the dienol acetate, 2,3-diacetoxy-1,3-butadiene (?). Acetophenone and isopropenyl acetate react to form  $\alpha$ -acetoxy styrene and acetone. Methyl vinyl ketone and methyl isopropenyl ketone are enol acetylated with isopropenyl acetate to form 2-acetoxy-1,3-butadiene and 2-acetoxyisoprene, respectively. A summary of enolizable carbonyl compounds acetylated with isopropenyl acetate is reported in Table II.

#### REACTIONS WITH ALCOHOLS AND AMINES

Isopropenyl acetate reacts with primary, secondary, and tertiary alcohols, phenols, polyhydroxy compounds, hydroxy esters, and ammonia and amines to form esters and amides. The degree of acetylation is measured by the quantity of acetone formed and it is usually desirable to remove the acetone continuously by distillation (10).



As an acetylating agent isopropenyl acetate has the distinct advantages of general applicability, high yields, and ease of

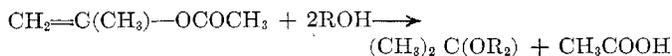
TABLE II. BOILING POINTS AND REFRACTIVE INDEXES OF ENOL ACETATES

Carbonyl Compound	Enol Acetate	Yield, %	B.P., ° C.	Pressure, Min.	$n_D^{20}$
Acetaldehyde	Vinyl acetate	75	72	740	1.3942
Paraldehyde	Vinyl acetate	83	72	740	...
Butyraldehyde	1-Buten-1-ol acetate	64	128	732	1.4049
Isobutyraldehyde	Isobutenyl acetate	71	124-126	740	1.4197
Methyl ethyl ketone	1-Buten-2-ol acetate	...	...	...	...
	2-Buten-2-ol acetate	96	118-119	740	1.4120
Methyl isobutyl ketone	4-Methyl-1-penten-2-ol acetate	92	143-145	740	1.4164
	4-Methyl-2-penten-2-ol acetate	...	...	...	...
Cyclohexanone	Cyclohexenyl acetate	99	180	732	1.4573
			96	50	...
Acetophenone	$\alpha$ -Acetoxy styrene	88	85	2	1.5330
Diacetyl	Methyl $\alpha$ -acetoxyvinyl ketone	43	32	5	1.3911
	2,3-Diacetoxy-1,3-butadiene	19	53	5	1.4372
Acetylacetone	1-Methyl-2-acetylvinyl acetate	61	84	10	1.4521
	2,4-Diacetoxypiperylene	24	114	10	1.4694
Methyl pyruvate	Methyl $\alpha$ -acetoxyacrylate	23 <sup>a</sup>	62	...	...
Ethyl pyruvate	Ethyl $\alpha$ -acetoxyacrylate	37 <sup>a</sup>	99-100	135	...
Ethyl acetoacetate	Ethyl $\beta$ -acetoxycrotonate and isomer	92	94	10	1.4420
Ethyl levulinate	Ethyl 4-acetoxy-4-pentenoate and isomer	95	89	5	1.4361
Crotonaldehyde	1-Acetoxy-1,3-butadiene	90	58.5	40	1.4460
$\gamma$ -Ethyl acrolein	1-Acetoxyisoprene	86	87	40	...
Methyl vinyl ketone	2-Acetoxy-1,3-butadiene	69	54	40	1.4420
Methyl propenyl ketone	2-Acetoxypiperylene	82	87	40	...
Methyl isopropenyl ketone	3-Acetoxyisoprene	74	62	40	1.4450
2-Chlorocrotonaldehyde	1-Acetoxy-2-chloro-1,3-butadiene	70	58	20	...

<sup>a</sup> Low yields shown are due to polymerization of enol acetate during enol acetylation.

acetylation. It is particularly useful in the acetylation of compounds such as *tert*-butyl and amyl alcohols, and  $\alpha$ - and  $\beta$ -hydroxy esters and nitriles which have a tendency to dehydrate in the presence of acetic anhydride. The acetylation is carried out in the presence of 0.1 to 0.5% of a suitable esterification catalyst such as sulfuric acid or *p*-toluenesulfonic acid.

Isopropenyl acetate and alcohols react in the presence of catalysts comprising a mixture of mercuric oxide and the complexes formed from boron trifluoride with alcohols, ethers, or carboxylic acids to form ketals (3).



Primary and secondary aliphatic amines react vigorously with isopropenyl acetate in the absence of catalysts to form the *N*-alkyl acetamides. With aromatic amines such as aniline and 1-naphthylamine the reaction is less vigorous and a strong acid catalyst is advantageously employed.



where R is hydrogen, alkyl, or aryl.

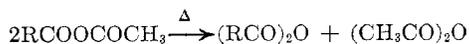
Esters and amides formed by the reaction of isopropenyl acetate with alcohols and amines are reported below.

#### REACTION WITH ACIDS

Organic carboxylic acids and isopropenyl acetate react in the presence of sulfuric acid catalyst to form mixed anhydrides and acetone.



This is a convenient method of preparing mixed anhydrides and the acetone can be removed at low temperatures so that a negligible amount of disproportionation occurs. Where the mixed anhydride is not the desired product, the reaction is completed simply by distillation of the mixed anhydride.



Isopropenyl acetate is particularly valuable for the preparation of the anhydrides of unsaturated acids such as acrylic, methacrylic, and crotonic acids, and aromatic acids such as benzoic acid, naphthoic acid, and others.

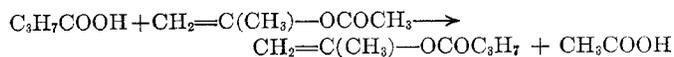
Halogen acids and isopropenyl acetate react to form acetyl halides and acetone.



The reaction is carried out by adding anhydrous hydrochloric or hydrobromic acid to a mixture of isopropenyl acetate and a suitable inert organic diluent such as diethyl ether at 0° to 10° C.

#### ACIDOLYSIS

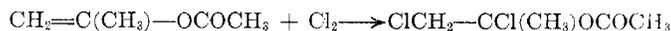
Isopropenyl acetate and organic carboxylic acids react in the presence of ester interchange catalysts to form acetic acid and isopropenyl esters. Butyric acid and isopropenyl acetate react in the presence of a catalyst consisting of mercuric acetate and boron trifluoride etherate to form isopropenyl butyrate and acetic acid.



Mixtures of mercuric oxide or mercuric acetate and complexes formed from boron trifluoride with ethers, alcohols, or carboxylic acids were found to be the most active catalysts. A catalyst mixture of mercuric acetate and sulfuric acid is slightly less active.

#### HALOGENATION

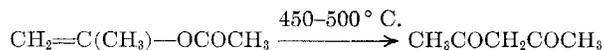
Halogens and isopropenyl acetate react to form  $\alpha,\beta$ -dihalogenoisopropyl acetate (17).



The halogenation is accomplished by adding the halogen to isopropenyl acetate cooled to 0° C. A rapid addition to the double bond takes place and the product is fractionated at reduced pressure.  $\alpha,\beta$ -Dichloroisopropyl acetate condenses with thiourea to form 2-amino-4-methyl thiazole (17).

#### PYROLYSIS

Under the influence of heat and in the presence or absence of catalysts isopropenyl acetate is isomerized to a  $\beta$ -diketone (2). The isomerization is accomplished by passing isopropenyl acetate through a tube packed with Pyrex rings and heated at 450° to 500° C. A contact time of 1 to 2 seconds is used.



Vapor phase isomerization is superior to the liquid phase isomerization in the presence of mineral acid catalysts both in respect to the yield of  $\beta$ -diketone and the quality of the product.

At temperatures above 500° C. and at longer contact times pyrolysis to form ketene takes place. This can be assumed to be a secondary reaction, as ketene is a known pyrolysis product of acetylacetone.

#### POLYMERIZATION

Isopropenyl acetate homopolymerizes in the presence of peroxide catalysts to form viscous liquids of low molecular weight. Vinyl chloride and isopropenyl acetate were emulsion copolymerized in sealed tubes at 45° C. (8). The polymerization was complete in approximately 40 hours and fine, white powders containing 18 to 32% isopropenyl acetate were obtained. The copolymer was dissolved in acetone and stabilized with lead naphthenate. Films were formed from the acetone dopes and the film strips were softened by immersion in hot water and drawn into fibers.

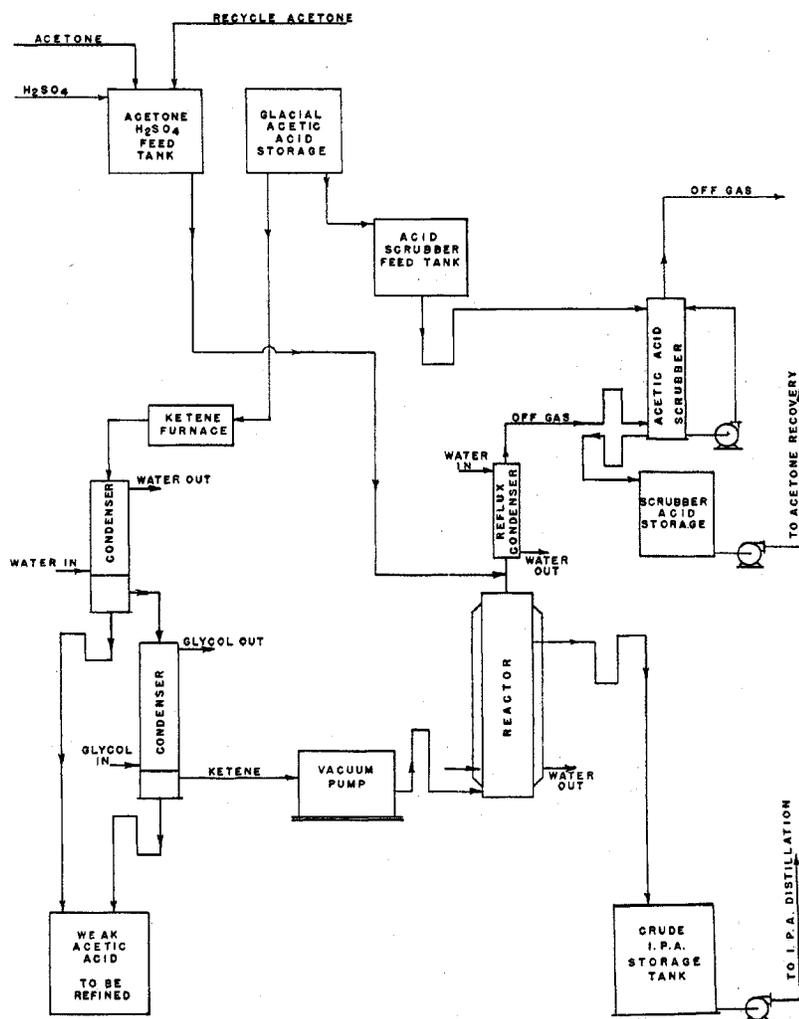
Isopropenyl acetate was copolymerized with esters of maleic and fumaric acids to form clear, colorless resins (12). Maleic anhydride and isopropenyl acetate were also copolymerized to form clear resins (13). Binary and ternary copolymers of isopropenyl acetate with esters of fumaric and maleic acid and combinations thereof were prepared in the mole ratios of one isopropenyl acetate with 1 to 4.5 of the fumarate or maleate esters or combinations thereof. Cast sheeting from these copolymers has a specific gravity of 1.12  $\pm$  0.01, refractive index of 1.47  $\pm$  0.01, and water absorption of 0.3%. The cast sheets are clear and colorless and the light transmittance is good. Emulsion and bead copolymers were also prepared and were suitable for molding.

#### ENOL ACETYLATION

**1-BUTEN-1-OL ACETATE.** Seventy-two grams of *n*-butyraldehyde, 150 grams of isopropenyl acetate, and 2 grams of *p*-toluenesulfonic acid were heated to reflux on a Vigreux column, 45 cm. long. Acetone was distilled off gradually as it was formed. The reaction mixture was cooled and then neutralized with saturated sodium bicarbonate solution. After drying the organic layer by azeotroping out the water with unchanged butyraldehyde and excess isopropenyl acetate, 34 grams of 1-buten-1-ol acetate were obtained; boiling point at 732 mm., 128° C.,  $n_D^{20}$  1.4049.

**VINYL ACETATE.** One hundred thirty-two grams of paraldehyde, 400 grams of isopropenyl acetate, and 4 grams of acetylsulfoacetic acid were autoclaved at 120° C. for 3 hours. The catalyst was neutralized with solid sodium bicarbonate and the mixture distilled. Ninety-six grams of acetone and 71 grams of vinyl acetate were recovered in addition to acetaldehyde, unchanged paraldehyde, and isopropenyl acetate.

**1-ACETOXY-1,3-BUTADIENE.** To 2000 grams of isopropenyl acetate containing 20 grams of *p*-toluenesulfonic acid and 5 grams



Isopropenyl Acetate Manufacture

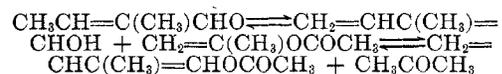
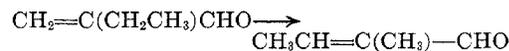
of copper acetate were added 1050 grams of crotonaldehyde (15 moles) over a period of 2 to 3 hours. The reaction was carried out in a packed column 1 inch in inside diameter and 6 feet high and the acetone formed was removed continuously. When the theoretical quantity of acetone had been distilled off, the crude product was flash distilled at 2 to 5 mm. 1-Acetoxy-1,3-butadiene was purified by redistilling the flashed product; boiling point at 40 mm., 58° C.,  $n_D^{20}$  1.4460. The yield based on crotonaldehyde was 90%.

**1-ACETOXY-2-CHLORO-1,3-BUTADIENE.** Two hundred grams of isopropenyl acetate containing 1 gram of acetylsulfoacetic acid were mixed with 104 grams (1 mole) of  $\alpha$ -chlorocrotonaldehyde (14) and heated on a steam bath for 2 hours. Distillation gave 53 grams of acetone and 103 grams of 1-acetoxy-2-chloro-1,3-butadiene; boiling point at 20 mm., 58° C.

**1-BUTEN-2-OL ACETATE AND 2-BUTEN-2-OL ACETATE.** Two hundred sixteen grams of methyl ethyl ketone, 300 grams of isopropenyl acetate, and 2 grams of sulfuric acid were mixed and heated to reflux. The theoretical quantity of acetone was distilled off and the catalyst was neutralized with anhydrous sodium acetate. Three hundred twenty-eight grams of the isomeric enol acetates of methyl ethyl ketone were obtained; boiling point at 740 mm., 118–119° C.,  $n_D^{20}$  1.4120.

**2-ACETOXY-1,3-BUTADIENE.** Seventy grams of methyl vinyl ketone, 200 grams of isopropenyl acetate, and 2 grams of sulfuric acid were refluxed and the acetone formed was distilled out continuously. One gram of copper acetate was added and the crude product was flash distilled at 2 mm. from a water bath at 70° C. Redistillation at 40 mm. gave 78 grams of 2-acetoxy-1,3-butadiene; boiling point 54° C.,  $n_D^{20}$  1.4430. Similar procedures were used in the preparation of the enol acetates of isobutyraldehyde, methyl isobutyl ketone, cyclohexanone, acetophenone, diacetyl, acetylacetone, pyruvate esters, ethyl aceto-

acetate, ethyl levulinate, ethacrolein, methyl propenyl ketone, and methyl isopropenyl ketone. Ethacrolein forms an enol acetate by a double bond shift (4):



#### ACETYLATION OF HYDROXY COMPOUNDS

**BUTYL ACETATE.** One hundred grams of isopropenyl acetate, 74 grams of butyl alcohol, and 2 drops of sulfuric acid were mixed and subjected to distillation. Fifty-six grams of acetone were obtained at 55–56° C. A 98% conversion of butyl alcohol to butyl acetate was obtained; boiling point at 735 mm., 125° C.

**GLYCEROL TRIACETATE.** One hundred grams of isopropenyl acetate were mixed with 30 grams of glycerol and 3 drops of sulfuric acid. Acetone was distilled off at atmospheric pressure and 57.5 grams were recovered. The sulfuric acid catalyst was neutralized with magnesium carbonate and glycerol triacetate was distilled at 113–115° C. at 2 mm. The yield was quantitative.

The ethyl, *n*-propyl, isobutyl, *sec*-butyl, *tert*-amyl, and phenyl acetates were prepared in the same manner. Methyl  $\alpha$ -acetoxypropionate and methyl  $\alpha$ -acetoxyisobutyrate from methyl lactate and methyl  $\alpha$ -hydroxyisobutyrate, respectively, ethylene glycol monoacetate and diacetate, and  $\beta$ -acetoxypropionitrile and  $\alpha$ -acetoxyisobutyronitrile from ethylene cyanohydrin and acetone cyanohydrin were prepared in better than 95% yields using this procedure.

#### ACETYLATION OF AMINES

***N*-ISOBUTYLACETAMIDE.** Seventy-three grams of isobutylamine were added gradually to 100 grams of isopropenyl acetate in a small still. A vigorous reaction took place and the acetone was distilled off continuously. Distillation of the residue gave a 94% yield of *N*-isobutylacetamide; boiling point at 1 mm., 81–82° C.,  $n_D^{20}$  1.4380,  $d_4^{20}$  0.8975. Per cent nitrogen: calculated 12.2, found 12.6.

***N*-ACETYLMORPHOLINE.** Eighty-seven grams of morpholine reacted with 100 grams of isopropenyl acetate in the same manner as above. A 90% yield of *N*-acetylmorpholine was obtained; boiling point at 1 mm., 89° C.,  $n_D^{20}$  1.4337,  $d_4^{20}$  1.1162, melting point –23.5° C. Per cent nitrogen: calculated 10.85, found 10.73.

***N*-( $\beta$ -HYDROXYETHYL)-ACETAMIDE.** Sixty-three grams of monoethanolamine and 105 grams of isopropenyl acetate reacted as above to form 85.5 grams (81% yield) of *N*-( $\beta$ -hydroxyethyl)-acetamide; boiling point at 1 mm., 135–140° C.,  $n_D^{20}$  1.4721,  $d_4^{20}$  1.1165.

**ACETANILIDE.** Fifty-five grams of isopropenyl acetate, 46.5 grams of aniline, and 10 drops of sulfuric acid were mixed at 25° C. The mixture was fractionated on a short Vigreux column and acetone distilled off in theoretical amount. The dark residue solidified on cooling and was triturated with aqueous ethyl alcohol (50 volume %) to extract colored impurities. The recrystallized acetanilide melted at 112–114° C.

Alpha-naphthylamine, ethylenediamine, ethylamine, *n*-butylamine, and *p*-aminophenol also reacted with isopropyl acetate in the same manner to form the corresponding *N*-substituted acetamides.

#### REACTION WITH ACIDS AND ANHYDRIDE FORMATION

**ACETIC ANHYDRIDE.** Sixty grams of acetic acid, 100 grams of isopropenyl acetate, and 3 drops of sulfuric acid were distilled on a small fractionating column. Fifty-six grams of acetone were recovered boiling at 55° to 60° C. Distillation of the residue gave a 97.4% yield of acetic anhydride.

**BUTYRIC ANHYDRIDE.** Eighty-eight grams of butyric acid and 2 drops of concentrated sulfuric acid were added to 100 grams of isopropenyl acetate. The mixture was distilled at atmospheric

TABLE III. COPOLYMERIZATION OF ISOPROPENYL ACETATE AND VINYL CHLORIDE

Run No.	IPA-VCl Monomers		Catalyst	% Yield	% Cl <sub>2</sub> in Product	% VCl Equiv.	IPA-VCl in Product	
	Weight %	Mole ratio					Weight %	Mole ratio
8	26/74	1/4.5	Bz <sub>2</sub> O <sub>2</sub>	63	40.2	70.6	29.4/70.6	1/3.85
49-1	20/80	1/6.5	(NH <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	91	46.6	82	18/82	1/7.3
49-2	26/74	1/4.5	(NH <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	28	46.2	81.5	18.5/81.5	1/7
52-2	20/80	1/6.5	(NH <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	31	38.3	67.4	32.6/67.4	1/3.3

pressure through a fractionating column and 55.6 grams of acetone were removed at 55° to 60° C. The undistilled residue after reaching 125° C. was fractionated at reduced pressure. In addition to acetic anhydride, 75 grams of butyric anhydride were obtained. Propionic, valeric, caproic, crotonic, acrylic, methacrylic, and benzoic anhydrides were prepared by the same procedure. With acrylic, methacrylic, and crotonic acids, 0.1 to 0.5% copper acetate was added as a polymerization inhibitor.

**ACETYL HALIDES.** Thirty-five grams of anhydrous hydrogen chloride were passed into a mixture of 100 grams of isopropenyl acetate and 100 grams of diethyl ether at 0° C. The mixture was refluxed for 2 hours. Distillation at atmospheric pressure through a small column packed with glass helices gave 41 grams of acetyl chloride.

Acetyl bromide and acetyl iodide were prepared in the same manner.

#### ACIDOLYSIS

**ISOPROPENYL BUTYRATE.** Two hundred grams of isopropenyl acetate, 88 grams of butyric acid, 2 grams of mercuric acetate, and 1 ml. of boron trifluoride etherate were allowed to stand at 20° to 25° C. for 24 hours. Two grams of anhydrous sodium acetate were added and the reaction mixture was filtered and distilled. Forty-two grams of isopropenyl butyrate were obtained; boiling point at 740 mm., 133° C.,  $n_D^{20}$  1.4144.

#### HALOGENATION

**$\alpha,\beta$ -DICHLOROISOPROPYL ACETATE.** Three hundred grams of isopropenyl acetate were stirred and cooled to 0° C. Chlorine gas was passed into the cold isopropenyl acetate, while the temperature was maintained at 0° C. by cooling, until 220 grams of chlorine were added. Nitrogen gas was bubbled through the chlorination mixture to sweep out any residual free chlorine. Distillation at reduced pressure gave a 74% yield of  $\alpha,\beta$ -dichloroisopropyl acetate; boiling point at 40 mm., 45-46° C.,  $n_D^{20}$  1.4344,  $d_4^{20}$  1.2158. Chlorine: calculated 41.5%, found 40.8%.

$\alpha,\beta$ -Dibromoisopropyl acetate prepared in the same manner had the constants, boiling point at 40 mm., 62-63.5° C.,  $n_D^{20}$  1.4714,  $d_4^{20}$  1.6249. Bromine: calculated 61.5%, found 61.8%.

#### PYROLYSIS

**ACETYLACETONE.** Five hundred grams of isopropenyl acetate were passed through a Pyrex tube, 1 inch in inside diameter and 20 inches long packed with Pyrex rings and heated to 450° C. A contact time of 1.5 to 2 seconds was used. A 74% conversion to acetylacetone was obtained with an over-all yield based on the isopropenyl acetate converted of 91%.

At 550° C. the yield of acetylacetone dropped to 56% and 39 grams of ketene were condensed out in a dry ice trap and polymerized to diketene.

#### POLYMERIZATION

**VINYL CHLORIDE-ISOPROPENYL ACETATE COPOLYMER.** Seven grams of isopropenyl acetate and 28 grams of vinyl chloride were weighed out in a Pyrex pressure tube cooled to -60° C. A solution of 0.1 gram of ammonium persulfate and 0.5 gram of gum arabic in 100 ml. of demineralized water and cooled to 3° to 4° was added and the tube was sealed. The emulsion was tumbled at 45° C. in a heated cabinet for 40 hours. The polymer was coagulated in 1% sodium chloride solution and formed 32 grams of a fine, white powder containing 46.6% chlorine.

The polymer was dissolved in acetone containing 0.1% lead naphthenate and skins were coated. The clear, transparent skins were cut into strips and immersed in hot water at 90° C., where they were drawn into fibers. Dry and wet spinning techniques followed by a steam draft were also used in the preparation of fibers.

The results of several typical emulsion polymerizations are reported in Table III.

**ISOPROPENYL ACETATE-FUMARATE ESTER CAST POLYMERS.** Cast polymers were prepared by refluxing the desired monomer mixture at reduced pressures so that the isopropenyl acetate would barely reflux at 50° C. An acid peroxide, 0.5% benzoyl peroxide, was usually used. When the viscosity was approximately 200 centipoises, the polymer mixture was cast. The casting cell was then immersed in a water bath at 60° to 70° C. and the polymerization was completed in 48 hours.

**ISOPROPENYL ACETATE-FUMARATE ESTER, BEAD POLYMERIZATION.** Two hundred ninety-seven grams of isopropenyl acetate (2.97 moles), 183 grams of dimethyl fumarate (1.27 moles), 120 grams of diethyl fumarate (0.72 mole) (isopropenyl acetate-fumarate mole ratio = 1.5/1), 6 grams of acetic acid, 0.18 gram of benzoyl peroxide (0.03%), and 2.4 grams of gum arabic were added to a 5-pint bottle. Demineralized water was boiled to remove dissolved air, cooled to 60° C., and added to the monomer mixture to fill the 5-pint container approximately 95% full. Beads were formed by tumbling the mixture at 37 to 40 r.p.m. in a cabinet heated to 60° C. for 40 to 48 hours. The yield of fine, clear, colorless beads washed with water and dried at 60° C. is 85 to 95%.

The beads are suitable for transfer molding. Increased hardness and higher impact and flexural and tensile strengths are obtained by extracting the beads with aqueous ethanol (70%) to remove unreacted monomers.

#### SUMMARY

Isopropenyl acetate is an excellent enol acetylating agent and reacts with all enolizable compounds—that is, any compound containing at least one hydrogen atom on a carbon atom adjacent to the carbonyl group—to form enol acetates in good yields.

Isopropenyl acetate is superior to ketene and acetic anhydride for acetylating organic compounds and is particularly useful where mild acetylation conditions are required. The degree of acetylation can be determined by separating off the acetone as it is formed.

Copolymers of isopropenyl acetate with vinyl chloride are suitable for fibers. Copolymers of isopropenyl acetate with esters of maleic and fumaric acids are hard, clear, colorless resins.

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