REACTIONS OF (2-ACYLVINYL)TRIALKYLAMMONIUM SALTS WITH NUCLEOPHILIC REAGENTS

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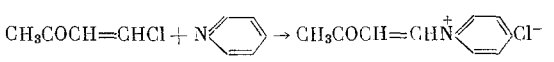
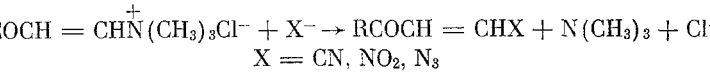
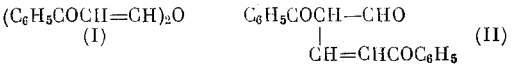
We [1], Kochetkov [2, 3], and co-workers have shown previously for a number of cases that 2-chlorovinyl ketones can be used as acylvinylating* agents, which afford wide possibilities for the synthesis of compounds of various classes. It was found subsequently that (2-acylvinyl)trialkylammonium salts are more powerful acylvinylating agents. A quaternary ammonium salt of this type was first prepared by Yakubovich and Merkulova [4] by the reaction of 4-chloro-3-buten-2-one with pyridine:



The paper [5] gives a description of the synthesis of (2-acylvinyl)trialkylammonium slats (AS) by the reaction of alkyl and aryl 2-acylvinyl ketones with aliphatic tertiary amines. The presence of a powerful electron-acceptor ammonium group in the β-position, whose –I effect is incomparably greater than the –I effect of chlorine in 2-chlorovinyl ketones, greatly raises the electrophilic power of the β-carbon in the AS. This circumstance, and also the ability of the AS to dissolve in water, enable us to use them for the synthesis of previously inaccessible 2-cyano- [6], 2-nitro- [7], and 2-azido- [8] -vinyl ketones.



It should be mentioned that in some cases it is advantageous to use AS instead of 2-chlorovinyl ketones because contamination of products [8] with unchanged original ketones, which are difficult to separate, can then be avoided. The main disadvantage of work with AS lies in their fairly rapid decomposition in an aqueous medium, which is accelerated in presence of bases. Kochetkov and co-workers [5] have found that under the action of sodium bicarbonate (2-benzoylvinyl)trimethylammonium chloride is "hydrolyzed" in aqueous solution with formation of a compound which on the basis of the elemental analysis and of molecular weight measurements can be either 3,3'-oxydiacrylophenone (I) or 2,4-dibenzoyl-3-butenal (II).



Thus, it was shown that this compound reacts with phenylhydrazine with formation of 1,3-diphenylpyrazole. Under the action of sodium methoxide in absolute methanol it gives benzoylacetaldehyde and its dimethyl acetal, and with 2-naphthol in presence of a solution of anhydrous ferric chloride in concentrated hydrochloric acid it forms 2-phenylnaphtho[2,1-b]pyrylium chloroferrate (III). However, these chemical properties also do not allow us to make a choice between formulas (I) and (II), for the possibility cannot be excluded that the substance (II) will give these reaction products. This possibility will readily be allowed (Scheme 1) if we assume that as a result of attack by the nucleophilic reagent (e.g., OCH_3^-) the carbanion (III) is formed and is stabilized by the elimination of the stable anion of benzoylacetaldehyde from the β-position. The latter readily reacts further with the nucleophilic reagent in the case of 2-naphthol or phenylhydrazine.

*By "acylvinylation" [the Russian term is literally "ketovinylation"] (a term proposed by N. K. Kochetkov) is understood the introduction of a 2-acylvinyl group into the molecule.

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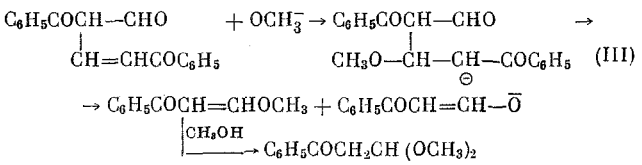
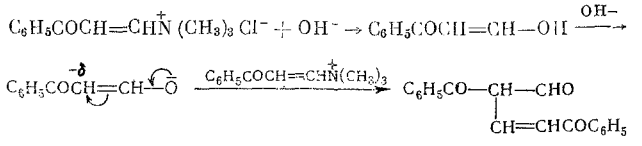
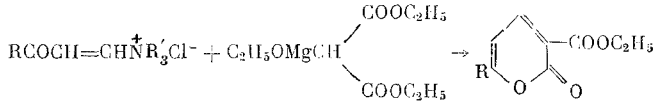
Scheme 1



The IR spectrum of this substance does not contain a strong absorption band in the region of 1670 cm^{-1}, which usually corresponds to a conjugated carbonyl group. The formula (I) must therefore be rejected. Moreover, it is contraindicated also by the value of its melting point (153-156°), which is too high for a bis(substituted vinyl) ether, and its poor solubility in the usual organic solvents. The presence of a strong absorption band in the IR spectrum of a crystalline sample (mineral oil mull) at 1570 cm^{-1} and of a strong band at 1620 cm^{-1} for a saturated solution of the substance in acetonitrile, which can be assigned to a chelated carbonyl [9], suggests that the structure (II) is the more probable, because it allows the formation of a chelated carbonyl as a result of the possibility of keto-enol and ring-chain tautomerism and the formation of stable intramolecular hydrogen bonds. Also, the IR spectrum of the crystalline sample contains absorption bands at 1170 cm^{-1} (vibrations of an ether C–O group) and 1006 cm^{-1} (vibrations of C–OH) and also weak bands at 1642 and 1658 cm^{-1}, which may be assigned to the stretching vibrations of a double bond. Hence, in the decomposition of the AS with water we consider that successive O- and C-Acylvinylation occurs: first at the hydroxy group of the water molecule and then at the carbon atom of the benzoylacetaldehyde formed:



The C-acylvinylation of β-dicarbonyl compounds by AS has been observed previously by Kudryashov and Kochetkov [10] for the case of reactions with (ethoxymagnesio)malonic ester:



In the course of work with aromatic AS we have observed several times that the above-discussed "hydrolysis" is facilitated by the presence of electron-acceptor groups in the phenyl group. Thus, (2-aroylvinyl)trimethylammonium chlorides containing an ortho or para bromine atom are "hydrolyzed" even by atmospheric moisture during keeping (Table 1); it is all the more impossible to keep these compounds in the form of aqueous solutions. It is interesting that the replacement of one methyl group by benzyl in the AS changes the course of the "hydrolysis." The (2-benzoylvinyl)benzyldimethylammonium chloride which we prepared gave 3-(dimethylamino)acrylophenone and benzyl alcohol under the action of water, which probably arose from the ease with which a stable benzyl cation is eliminated.

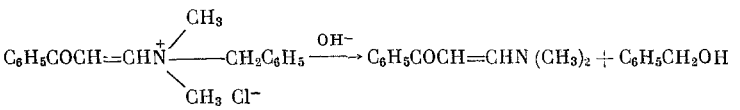
TABLE 1.* $ArCOCH(CHO)CH = CHCOAr$

Ar	M.p., °C	Found, %			Calculated, %		
		C	H	Hal	C	H	Hal
C_6H_5†	153-156 (butanone)	77.65	5.13	-	77.69	5.03	-
o-BrC_6H_4‡	134-136 (alcohol)	48.87	3.18	35.99	48.56	2.94	35.98
p-BrC_6H_4	210 (acetonitrile)	49.78	2.91	36.92	49.57	2.77	36.65

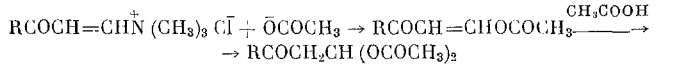
*We did not prepare these compounds specially, but isolated them from AS preparations which had been kept for a long time.

†[5] gives m.p. 152-153°.

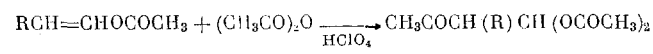
‡Hemihydrate.



Apart from information on the "hydrolysis," we report another case of O-acylvinylation, namely, the reaction of AS with the acetate ion in glacial acetic acid, as a result of which we developed a method for the synthesis of diacetyl acylals of acylacetaldehydes (Table 2). We must mention that various attempts to use 2-chlorovinyl ketones for this purpose were not successful. Experiment showed that the acetate ion cannot be acylvinylated in an aqueous medium, because in this case the above-mentioned 2,4-diaroyl-3-butenals for aromatic AS and triacylbenzenes for aliphatic are formed. We therefore used glacial acetic acid as medium; this readily adds at the double bond of the intermediately formed 2-acetoxyvinyl ketones.



To avoid addition we also used dimethylformamide as solvent for the reaction of (2-acetylvinyl)trimethylammonium chloride with potassium acetate and obtained 4-acetoxy-3-buten-2-one (see Table 2) by which we showed the possibility in principle of synthesizing 2-acetoxylvinyl ketones. The formation of β-keto aldehyde acylals, also in low yields as in our case, was described in a brief communication by Wagner and Rall [11], who obtained them by the addition of acetic anhydride at the double bond of vinyl acetate and its substitution products in presence of catalysts:



However, these authors give no details of the synthesis. 2-Acetoxyvinyl ketones [12] and 3-acetoxyacrolein [13] have been prepared by the acetylation of salts of the corresponding β-dicarbonyl compounds in an inert solvent, and the former have been proposed for use as polymerizable monomers and as fungicides [12].

The structures of the compounds which we synthesized were proved by the conversion of 4-acetoxy-3-buten-2-one and acetoacetaldehyde diacetyl acylal [4,4-diacetoxy-2-butanone] into the known 4-anilino-3-buten-2-one and 2-methylnaphtho[2,1-b]pyrylium chloroferrate(III). We have reported on the N-acylvinylation of aromatic amines [14], and in the case of diamines [15] such as p-phenylenediamine and benzidine only AS are suitable for the preparation of N,N'-bis-2-acylvinyl diamines, because acylvinylation with 2-chlorovinyl ketones leads mainly to mono-N-substituted products.

In this work we also showed the possibility in principle of effecting the N-acylvinylation of α-amino acids: we used AS in reactions with glycine and its ethyl ester in an aqueous medium, and as a result we developed a method for the synthesis of the previously unknown N-(2-acylvinyl)glycines (Table 3). We

TABLE 2.

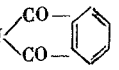
Substance	Yield %	B.p. (p. mm) or m.p., °C	n_D^{20}	d_4^{20}	MR		Found %		Calculated %	
					found	calculated	C	H	C	H
$CH_3COCH{=}CHOCOCH_3$*	35	93-94 (16)	1.4648	1.077	32.87	30.98	56.00	6.47	56.24	6.29
$CH_3COCH_2CH(OCOCH_3)_2$†	23	114-116 (5)	1.4272	1.136	42.39	42.23	51.30	6.44	51.06	6.42
$C_3H_7COCH_2CH(OCOCH_3)_2$	27	134-136 (7)	1.4312	1.082	51.54	51.46	55.29	7.47	55.54	7.45
$C_6H_5COCH_2CH(OCOCH_3)_2$	57	82-84 (pet. ether)	-	-	-	-	62.70	5.82	62.59	5.64

*[12] gives: b.p. 60-61° (0.4 mm); n_D^{20} 1.4553.

†[11] gives: b.p. 86-87° (0.08 mm); yield 28%.

TABLE 3. RCOCH=CHNHCH$_2$COOR'

R	R'	Yield %	B.p. (p, mm) or m.p., °C	n_D^{20}	d_4^{20}	Found, %			Calculated, %		
						C	H	N	C	H	N
CH_3	C_2H_5	52	138-139 (4)	1.5231	1.091	56.41	7.63	-	56.14	7.60	-
C_6H_5	H	58	135 (decomp., from CH_3NO_2)	-	-	64.08	5.25	6.71	64.37	5.43	6.82
C_6H_5	C_2H_5	55	95-97 (alcohol)	-	-	66.90	6.50	6.13	66.93	6.48	6.06

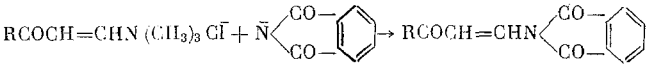
TABLE 4. RCOCH=CHN 

R	Yield, %	M.p., °C	Found, %				Calculated, %			
			C	H	N	Br	C	H	N	Br
CH_3	80	157-159 (from benzene)	66.79	4.28	6.66		66.97	4.21	6.50	
C_3H_7	89	106-108 (from alcohol)	69.15	5.32	6.09		69.12	5.39	5.76	
C_6H_5	61	135-136 (from alcohol)	73.67	4.19	5.18		73.47	4.29	5.05	
p-BrC_6H_4	49	177-178	57.34	2.84	3.95	22.20	57.32	2.83	3.93	22.43
o-BrC_6H_4	60	148-149 (from alcohol)	57.48	2.83	22.36	22.36	57.32	2.83	22.43	22.43

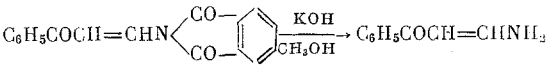
found that N-(2-benzoylvinyl)glycine ethyl ester is hydrolyzed by fusion with alkali to the corresponding acid, but in hydrolysis in aqueous potassium hydroxide solution hydrolytic cleavage of the double bond occurs.

$$RCOCH{=}CH\overset{+}{N}(CH_3)_3Cl^- + NH_2CH_2COOR' \rightarrow RCOCH = CHNHCH_2COOR'$$

We also made attempts to N-acylvinylate amides, but only in the case of phthalimide were we successful. It was found that (2-aroylvinyl)trimethylammonium salts readily react with potassiophthalimide in an aqueous medium. Aliphatic AS acylvinylate potassiophthalimide only in the indifferent solvent dimethylformamide (Table 4).



The structures of the 2-phthalimidovinyl ketones obtained were proved by the hydrolysis of the phenyl ketone to the known 3-aminoacrylophenone:



EXPERIMENTAL

Reaction of 2,4-Dibenzoyl-3-butenal with Phenylhydrazine. A solution of 2.78 g of 2,4-dibenzoyl-3-butenal and 2.7 g of phenylhydrazine in 30 ml of glacial acetic acid was refluxed for two hours and then left overnight. On the next day the reaction mixture was poured into 150-200 ml of water, and the dark-colored oil which separated was rubbed out in a dish with a few drops of methanol, and it then crystallized. The yield of 1,3-diphenylpyrazole was 3.12 g (70%); m.p. 82-83°. [16] gives m.p. 84-85°.

Preparation of 2-Phenylnaphtho[2,1-b]pyrylium Chloroferrate(III) from 2,4-Dibenzoyl-3-butenal. A solution of 5 g of anhydrous ferric chloride in 10 ml of concentrated HCl was added to 2.78 g of 2,4-dibenzoyl-3-butenal and 2.88 g of 2-naphthol in 30 ml of glacial acetic acid.

There was an orange precipitate of 2-phenylnaphtho[2,1-b]pyrylium chloroferrate (III), m.p. 186-187°; yield 7.0 g (76%). [17] gives m.p. 187.5-188°. A mixture with a known sample melted without depression.

Reaction of 2,4-Dibenzoyl-3-butenal with Sodium Methoxide. 5.56 g of 2,4-dibenzoyl-3-butenal was added with stirring to a solution of sodium methoxide prepared by dissolving 0.5 g of sodium in 70 ml of methanol. Stirring was continued further for two hours, and the mixture was left overnight. On the next day the reaction mixture was poured into 300 ml of cold water, the whole was extracted with ether, the extract was dried over Na_2SO_4, and ether was driven off. Distillation gave 3.5 g (45%) of benzoylacetaldehyde dimethyl acetal, b.p. 110-112° (2 mm). [18] gives b.p. 111-113° (2 mm). With 2- naphthol in glacial acetic acid under the action of a solution of anhydrous ferric chloride in concentrated HCl it gives 2-phenylnaphtho[2,1-b]pyrylium chloroferrate(III). A mixture with a known sample melts without depression. On acidification of the aqueous alkaline layer we isolated benzoylacetaldehyde.

Preparation of N,N-Dimethylbenzylamine.* With continuous passage of nitrogen a 1500-ml three-necked flask fitted with stirrer, dropping funnel, and reflux condenser was charged with 800 ml of dry ether and 5.7 g of lithium aluminum hydride. A solution of 44.7 g of N,N-dimethylbenzamide in 80 ml of dry ether was added dropwise to the suspension with stirring at room temperature. After the addition of N,N-dimethylbenzamide the reaction mixture was stirred for 2.5 h and decomposed by the slow addition of 30 ml of alcohol and then 10% NaOH solution until the precipitate was dissolved completely. The ether layer was removed, and the aqueous layer was extracted twice with ether. The ethereal solution was dried over solid KOH, ether was driven off, and N,N-dimethylbenzylamine was distilled in a stream of nitrogen. By redistillation over sodium in a stream of nitrogen we obtained 19.2 g (47%) of N,N-dimethylbenzylamine, b.p. 177-180°. [21] gives b.p. 180-181°.

Preparation of (2-Benzoylvinyl)benzyldimethylammonium Chloride. 19.2 g of N,N-dimethylbenzylamine was added dropwise with cooling and stirring to a solution of 23.7 g of 3-chloroacrylophenone in 150 ml of dry ether. At first an oil was precipitated, and with standing this crystallized. The ether layer was decanted, and the precipitated was washed with a fresh portion of ether. The (2-benzoylyinyl)benzyldimethylammonium chloride obtained (yield 41 g; 95%) was very hygroscopic, and we did not succeed in preparing it in an analytically pure state, because even traces of moisture promoted its decomposition.

Decomposition of (2-Benzoylvinyl)benzyldimethylammonium Chloride with Water. 100 ml of water was added to 10 g of (2-benzoylvinyl)benzyldimethylammonium chloride, and after two hours the reaction mixture was extracted with ether, and ether was evaporated from the extract. The residue was a mixture of 3-(dimethylamino)acrylophenone and benzyl alcohol. Crystals of 3-(dimethylamino)acrylophenone were pressed out on a porous filter and recrystallized from hexane; m.p. 90-91°. [22] gives m.p. 92°. Benzyl alcohol was driven from the oil pressed off [b.p. 101-105° (25 mm)], and with phenyl isocyanate this gave an addition product of m.p. 76-78° (petroleum ether). [23] gives m.p. 78°. A mixture with a known sample melted without depression.

Synthesis of 4-Acetoxy-3-buten-2-one. With vigorous stirring and cooling with ice 16.35 g of finely ground (2-acetylvinyl)trimethylammonium chloride was added in portions to 14.7 g of potassium acetate in 100 ml of dry dimethylformamide. After one hour stirring was stopped, the precipitate formed was filtered off, dimethylformamide was driven from the solution, and vacuum distillation gave 4.5 g (35%) of 4-acetoxy-3-buten-2-one, a mobile liquid of pleasant odor which decolorizes potassium permanganate solution. The constants and analysis are given in Table 2.

Preparation of 2-Methylnaphtho[2,1-b]pyrylium Chloroferrate(III) from 4-Acetoxy-3-buten-2-one. 1 ml of a solution prepared from 1 g of anhydrous $FeCl_3$ and 1.5 ml of concentrated HCl was added to a mixture of 0.53 g of 4-acetoxy-3-buten-2-one, 0.59 g of 2-naphthol, and 5 ml of glacial acetic acid. The precipitate formed was filtered off and washed with a little glacial acetic acid and dry ether. After recrystallization from glacial acetic acid we obtained 1.4 g (87%) of 2-methylnaphtho]2,1-b]pyrylium chloroferrate(III), m.p. 150-152°. [19] gives m.p. 150-151°. A mixture with a known sample melted without depression.

Reaction of 4-Acetoxy-3-buten-2-one with Aniline. 0.21 g of aniline was added to a solution of 0.3 g of 4-acetoxy-3-buten-2-one in 2 ml of ether. After five hours ether was evaporated,

*According to [20], N,N-diethylbenzamide is reduced to benzyl alcohol by lithium aluminum hydride.

and the residue was washed with water and recrystallized. The yield of 4-anilino-3-buten-2-one (α-form) was 0.3 g (81%); m.p. 103-105°. [24] gives m.p. 103-104.5°. A mixture with a known sample melted without depression.

Method of Synthesis of Acylacetaldehyde Diacetyl Acylals. A mixture of 0.2 mole of a (2-acylvinyl)trimethylammonium chloride, 0.2 mole of anhydrous sodium acetate, and 30-40 ml of glacial acetic acid was heated with stirring for 20 min at 90-95° (in the case of acyl = C_6H_5CO—at the boil); the mixture was cooled and poured into cold water. The oil which separated was extracted with ether (often a small amount was obtained of sparingly ether-soluble triacetylbenzene for acyl = CH_3CO or 2,4-dibenzoyl-3-butenal for acyl = C_6H_5CO; these were readily separated by filtration of the ethereal solution). The ether extract was washed with water, sodium bicarbonate solution, and again water, and it was dried over sodium sulfate. Ether was driven off, and in the case of acyl = CH_3CO and C_3H_7CO the residue was vacuum-distilled, while for acyl = C_6H_5CO the crystals were pressed off from the oil and recrystallized from petroleum ether. Yields, constants, and analyses are given in Table 2.

Preparation of 2-Methylnaphtho[2,1-b]pyrylium Chloroferrate(III) from 4,4-Diacetoxy-2-butanone. 1 ml of a solution prepared from 1 g of $FeCl_3$ and 1.5 ml of concentrated HCl was added to a mixture of 0.6 g of 4,4-diacetoxy-2-butanone, 0.45 g of 2-naphthol, and 5 ml of glacial acetic acid. The precipitate formed was filtered off and washed with a little glacial acetic acid + ether. The yield of 2-methylnaphtho[2,1-b]pyrylium chloroferrate(III) was 1 g (83%); m.p. 150-151° [19]. A mixture with a known sample melted without depression.

Acylvinylation of Glycine Ethyl Ester. A solution of 0.1 mole of a (2-acylvinyl)trimethylammonium chloride in the least possible amount of water was added dropwise with cooling and vigorous stirring to 0.1 mole of glycine ethyl ester in 90 ml of water. When the whole of the quaternary ammonium salt had been added, cooling was stopped and stirring was continued further for two hours. N-(2-Benzoylvinyl)glycine ethyl ester came down as a precipitate, which was filtered off, washed on the filter with cold water, and dried. N-(2-Acetylvinyl)glycine ethyl ester was isolated from solution by precipitation with potassium carbonate and subsequent repeated extraction with ether. Yields, constants, and analyses are given in Table 3.

Preparation of N-(2-Benzoylvinyl)glycine. a) A solution of 6.45 g of (2-benzoylvinyl) trimethylammonium chloride in 25 ml of water was added with cooling to a solution of 2.43 g of glycine and 1.16 g of NaOH in 15 ml of water. After 20 min the reaction mixture was acidifed to Congo Red by the slow addition of 6% H_2SO_4, and a little ether was added to improve the crystallization of the precipitate of N-(2-benzoylvinyl)glycine. The precipitate was filtered off and washed on the filter with cold water and ether.

b) N-(2-Benzoylvinyl)glycine ethyl ester was fused with potassium hydroxide or potassium carbonate in a test tube. The melt formed was treated with water, and the aqueous solution was acidified. The N-(2-benzoylvinyl)glycine which separated (m.p. 133-134°) melted without depression in admixture with the sample prepared by method (a). When heated with aqueous potassium hydroxide solution, N-(2-benzoylvinyl)glycine ethyl ester underwent hydrolytic cleavage at the double bond with formation of acetophenone, identified in the form of its 2,4-dinitrophenylhydrazone.

Preparation of Alkyl 2-Phthalimidovinyl Ketones. 0.1 mole of a (2-acylvinyl)trimethylammonium chloride was added with stirring to a suspension of 0.1 mole of potassiophthalimide in 200 ml of dimethylformamide. After two hours precipitated potassium chloride was filtered off, and dimethylformamide was vacuum-distilled from the filtrate. The residue of the alkyl 2-phthalimidovinyl ketone was recrystallized. Yields, constants, and analyses are given in Table 4.

Preparation of Aryl 2-Phthalimidovinyl Ketones. A filtered solution of 0.1 mole of a (2-aroylvinyl)trimethylammonium chloride and 0.1 mole of trimethylamine hydrochloride in water was added rapidly to 0.1 mole of potassiophthalimide in 90 ml of water. The mixture was left for 20-30 min. The precipitate formed was filtered off, washed with 1% NaOH solution and water, and dried. Yields, constants, and analyses are given in Table 4.

Hydrolysis of 3-Phthalimidoacrylophenone. 2.77 g of 3-phthalimidoacrylophenone was added to a solution of 1 g of KOH in 50 ml of methanol. The reaction mixture was heated to the boil, left for two days at room temperature, treated with 200 ml of water, and extracted with ether. The extract was washed with water and dried over sodium sulfate; ether was evaporated. The residue was the α-form of 3-aminoacrylophenone, yield 0.9 g (61%); m.p. 69-70° (twice from heptane); picrate, m.p. 173-175°. [25] gives m.p. 70°; picrate, m.p. 174-175°. Mixtures with known samples melted without depression.

We are greatly indebted to L. B. Senyavina for determining IR spectra.

CONCLUSIONS

1. (2-Acylvinyl)trialkylammonium salts are more convenient acylvinylating agents than 2-chlorovinyl ketones.

2. Methods were developed for O- and N-acylvinylation on the basis of reactions of these salts with sodium or potassium acetate, glycine, and potassiophthalimide.

LITERATURE CITED

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