1.3 (m, 2, CH_2), 2.30 (s, 6, NCH_3), 2.53 (m, 1, CH), 3.1 (s, 2, NH and OH), and 3.83 (m, 1, CH). A picrate derivative of the isomeric mixture had mp 87–89 °C (lit.[7] threo mp 103.5–105 °C, erythro mp 86–87 °C).

Anal. Calcd for picrate $C_{12}H_{18}N_4O_8$: C, 41.62; H, 5.24; N, 16.18. Found: C, 41.76; H, 5.52; N, 16.20.

4-Methylamino-4-methyl-2-pentanol (7): bp 70 °C (10 mm) [lit. bp 115 °C (16 mm),[7] 184.5–185.5 °C (750 mm)[9]]; NMR (D_2O) δ 1.27 (s, 6, CH_3), 1.28 (d, 3, CH_3), 1.63 (m, 2, CH_2), 2.32 (s, 3, NCH_3), 4.07 (m, 1, CH). A picrate derivative had mp 154 °C (lit.[7,9] mp 156–158 °C).

1-Dimethylamino-3-aminobutane (8). The procedure was similar to procedure 1 above. Thus, 10.6 g (0.20 mol) of NH_4Cl was dissolved in 200 ml of methanol and cooled with ice, and 11.2 g (0.20 mol) of KOH was added all at once. After all of the KOH had reacted, 16.2 ml (0.20 mol) of crotonaldehyde dissolved in 40 ml of methanol was added dropwise. That addition was immediately followed by the addition of 16.2 g (0.20 mol) of Me_2NH·HCl and then the dropwise addition of a solution of 5.23 g (25% excess of 0.067 mol) of $NaBH_3CN$ in 40 ml of MeOH. The product was worked up in the manner described under 1 above except that no attempt was made to dry it. A yield of 40% was estimated by NMR after distillation through a 10-mm Vigreux column. Traces of water and MeOH remained in the product: bp of mixture 93 °C (740 mm) [lit.[10] bp 55 °C (16 mm)]; NMR ($CDCl_3$) δ 1.21 (d, 3, CH_3), 1.68 (m, 2, CH_2), 2.32 (s, 6, NCH_3), 2.4 (m, 3, CH_2 and CH), and 3.37 (s, 2, NH_2). A picrate had mp 180 °C (lit.[10] mp 181 °C).

1-Amino-3-dimethylaminobutane (9). The preparation of 9 was the same as for 8 above except that the introductions of the NH_4Cl and Me_2NH·HCl were reversed. After the product had been crudely distilled, it was dried employing a benzene azeotrope as in procedure 1 above. A yield of 15% was obtained: bp 46 °C (10 mm) [lit.[11] bp 154–156 °C (pressure not given)]; NMR ($CDCl_3$) δ 1.03 (d, 3, CH_3), 1.63 (m, 2, CH_2), 1.08 (s, 2, NH_2), 2.30 (s, 6, NCH_3), 2.6 (m, 3, CH_2 and CH). A picrate derivative had mp 204 °C (lit.[11] mp 204 °C).

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Registry No.—**1**, 57757-16-1; *meso*-**2**, 60978-26-9; *dl*-**2**, 60978-27-0; *meso*-**2** dipicrate, 60978-28-1; *dl*-**2** dipicrate, 60978-29-2; **3**, 60978-30-5; **4**, 2704-55-4; **5**, 42142-55-2; *erythro*-**6**, 53019-16-2; *threo*-**6**, 53089-02-4; *erythro*-**6** picrate, 60978-31-6; *threo*-**6** picrate, 60978-32-7; **7**, 42142-50-7; **8**, 13022-87-2; **9**, 60978-33-8; crotonaldehyde, 4170-30-3; methyl vinyl ketone, 78-94-4; mesityl oxide, 141-79-7; dimethylamine HCl, 506-59-2; dimethylamine, 124-40-3; 3-penten-2-one, 625-33-2.

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Migration of Acyl Groups in *o*-Aminophenol. 1. The Acetyl–Benzoyl, Acetyl–*p*-Nitrobenzoyl, and Acetyl–Propionyl Systems

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The synthesis and characterization of six mixed diacyl derivatives of *o*-aminophenol is described. It is shown that the rearrangements which have created so much uncertainty in this area in the past are actually solvent-catalyzed isomerizations which were minimized in this work by the proper choice of reaction and recrystallization solvents. In pyridine and in ethanol, isomerization resulted in the formation of dynamic equilibrium mixtures in accord with the theoretical predictions of Le Rosen and Smith in 1949. The compositions of the equilibrium mixtures and of the mixtures of monoacyls obtained on saponification were also in general agreement with the theoretical predictions of these authors. However, the failure to obtain isomerization in acetone, ether, water, or acetic acid solvents appears to cast doubt on their assumption of a general acid–base catalyzed isomerization mechanism. Further work to test this mechanism was deferred because of inconsistencies in the isomerization rates which appear to be due to the presence of unknown trace impurities.

The rearrangements occurring in *N,O*-diacyl derivatives of *o*-aminophenol wherein the two acyl groups are different (mixed diacyls) have been studied extensively in the older literature.[1-4] A 1968 Russian review article lists 228 references dealing with these migrations and related phenomena.[5] As noted in this review, these reactions are of theoretical interest as well as being of considerable practical importance in organic synthesis. In general, the mechanism of these reactions has remained obscure because of the inability of these earlier workers to separate and analyze the labile product mixtures which they obtained.

Le Rosen and Smith were the first workers to provide quantitative results for one of these systems (acetyl–benzoyl) and their work strongly indicated that the rearrangements were actually isomerizations of the mixed diacyls caused by the catalytic influence of the solvents used in preparing and purifying these products.[6] They further showed that isomerization was rapid in alkaline medium so that saponification in dilute base gave a mixture of the two possible monoacyl products. A theoretical explanation of their findings was presented which seemed to clarify the reasons for the many conflicting results reported to that time. They suggested that the isomerizations were general acid or base catalyzed so that an equilibrium mixture of the mixed diacyls was formed in

Table I. Approximate Times for Equilibrium to Be Reached and Composition of Equilibrium Solutions

	Alcohol		Pyridine	
	Time, h	% NA[a]	Time, h	% NA[a]
o-Acetamidophenyl benzoate	20	83	240	83
o-Benzamidophenyl acetate	24	83	580	81
o-Acetamidophenyl p-nitrobenzoate	32	66		
o-(p-Nitrobenzamido)phenyl acetate	24	65		
o-Acetamidophenyl propionate	50	63	30	61
o-Propionamidophenyl acetate	50	63	30	62

[a] Calculated weight percent of the more stable N-acetyl mixed diacyl isomer.

acidic or basic solvents. The principle of "minimum charge concentration" was developed to predict the more stable isomer and thereby the approximate composition of the expected equilibrium mixtures.

The reinvestigation of past work in this field called for by Le Rosen and Smith was halted by the untimely death of Dr. Le Rosen. Apparently, other workers failed to pursue the leads provided by Le Rosen and Smith because of the formidable analytical problems involved. A great deal of expertise in columnar chromatography was required at that time, and it was thought that the required pure mixed diacyls could be obtained only by means of preparative chromatography. Accordingly, despite the theoretical and practical importance of this work, the field remained dormant since 1949 except for a recent article by Amundsen and Ambrosio on rearrangements with N,O-acyl–alkoxycarbonyl derivatives of o-aminophenol.[7]

With the recent advent of modern high-performance liquid chromatography (HPLC) the way was at last cleared to performing the separations and analyses of the labile mixed diacyl products. It is the purpose of this article to present preliminary findings with three acyl systems chosen to test the hypotheses proposed by Le Rosen and Smith.

Results and Discussion

A. Preparation and Isomerization of Mixed Diacyls. The work of Le Rosen and Smith showed that isomerization of the mixed diacyls was catalyzed by pyridine and by ethanol. The first solvent was generally used by earlier workers in the synthesis of the mixed diacyls and the second was frequently used in recrystallization of the crude products. Thus, mixtures of the two possible mixed diacyls were usually obtained and, when ethanol was used for recrystallization, the same equilibrium mixture resulted so that it appeared that only one mixed diacyl could be prepared. In this work, initial attempts to prepare the mixed diacyls in the absence of pyridine were unsuccessful in that very low conversions were obtained. However, it was found that the second acylation could be carried out at room temperature in ether or acetone containing minor amounts of pyridine (2–10%). Under these conditions, little isomerization occurred and the pure mixed diacyls were isolated by recrystallization of the crude products from benzene or hexane.

Since Le Rosen and Smith had proposed that the isomerizations were instances of general acid–base catalysis, it was surprising to find that these isomerizations were not catalyzed by ether or acetone (Lewis bases). It was even more surprising to find that isomerization did not occur in glacial acetic acid and that this solvent could be used without incorporation of a basic catalyst in the synthesis of o-benzamidophenyl acetate from o-benzamidophenol. Finally, it was found that the water-soluble acetyl–propionyl mixed diacyls isomerized very slowly in water or in dilute hydrochloric acid solution. While these observations cannot be said to completely invalidate the assumption of a general acid–base catalysis mechanism, they do strongly suggest that this assumption must be tested further. However, it was decided that such work should be deferred because of the anomalous isomerization behavior of the "crude" mixed diacyls discussed below.

The approximate time required for equilibrium to be established and the concentration of the more stable o-acetamidophenyl esters obtained at these times in absolute ethanol and in pyridine solutions are summarized in Table I for the six recrystallized mixed diacyls studied in this work. The values given in this table represent the averaged results obtained from several isomerizations carried out at room temperature (about 25 °C) with 0.5–2.0% solutions of the indicated mixed diacyl. As a first approximation, the isomerizations appeared to be first-order reactions, but no attempt has yet been made to obtain rigorous kinetic data for these isomerizations. This is primarily because it was discovered that the isomerization rates were greatly influenced by the presence of unknown trace impurities. For example, a "crude" sample of o-acetamidophenyl benzoate precipitated from aqueous pyridine still contained 98% of the unrearranged isomer after 71 h in absolute alcohol. The liquid chromatographic analysis of this "crude" sample showed it to be nearly pure with only traces of the opposite isomer and unreacted o-acetamidophenol present. This anomalous behavior was noted with other crude mixed diacyl isomers studied herein and tests showed that this behavior was not attributable to residual pyridine since similar results were obtained with "crude" mixed diacyl samples precipitated from acetic acid. It was also shown that addition of 0.5% pyridine or hydroquinone caused recrystallized p-nitrobenzamidophenyl acetate to isomerize appreciably faster in alcohol than in the absence of these free-radical inhibitors. These observations are very puzzling and may provide a valuable clue to the overall reaction mechanism. Meanwhile, however, the main value of the results listed in Table I was to show that acyl migrations were indeed isomerizations caused by the influence of certain solvents such as alcohol and pyridine.

With the acetyl–p-nitrobenzoyl mixed diacyls, the results of isomerization in 90% aqueous ethanol were essentially the same as in absolute alcohol. However, isomerization of the acetyl–benzoyl mixed diacyls was very much slower in 95% aqueous alcohol and complete equilibrium was not obtained even after 900 h. In addition, extensive solvolysis to form the monoacyls occurred in this solvent and this solvolysis reaction was much greater for the o-benzamidophenyl acetate than for its isomeride. In anhydrous methanol, the mixed diacyls of the acetyl–benzoyl system isomerized very rapidly so that equilibrium was reached in only 5 h. Again, extensive solvolysis occurred so that after 5 h the mixtures contained about 13% of the monoacyls and after 144 h about 87% of the monoacyls was present. The ratio of the percent o-acetamidophenyl benzoate to o-benzamidophenyl acetate remained constant from 5 to 144 h, however, and was the same (within experimental error limits) as that observed in the absolute alcohol or pyridine solutions. Thus, it was concluded that the isomerization solvent did not affect the final equilibrium composition attained.

Table II. Melting Points of Mixed Diacyl Derivatives of *o*-Aminophenol

No.	Compd	Mp, °C Found	Mp, °C Lit.
I	*o*-Acetamidophenyl benzoate	138–140	139–141[a]
II	*o*-Benzamidophenyl acetate	141–145	138–140[a]
III	*o*-Acetamidophenyl *p*-nitrobenzoate	165–167	
IV	*o*-(*p*-Nitrobenzamido)phenyl acetate	143–144	
V	*o*-Acetamidophenyl propionate	72–73	57–75[b]
VI	*o*-Propionamidophenyl acetate	102–103	85–103[b]

[a] Reference 6a. [b] Reference 3.

The acetyl–propionyl mixed diacyls were unusual in that they were appreciably soluble in water. Surprisingly, no trace of the monoacyls were detected when isomerizations were carried out in this solvent and isomerization proceeded very slowly being only about 90% complete for either isomer after 245 h.

B. Saponification of Mixed Diacyls. Le Rosen and Smith predicted that saponification of either pure mixed diacyl (or mixtures thereof) should result in a mixture of the two possible monoacyls. They reasoned that this should occur since isomerizations in alkaline solution were very rapid, and that the more unstable isomer should saponify faster than its isomeride. In this work, saponifications were carried out with a 20% excess of aqueous NaOH. The mixed diacyls were stirred with the aqueous alkali until complete solution was obtained and for at least 30 min thereafter to ensure complete saponification. The resulting clear solutions were acidified and extracted with chloroform to ensure complete recovery of the monoacyls. The chloroform extracts were then diluted to an appropriate volume and aliquots analyzed by HPLC. No interferences from the acids resulting from saponification were observed although peaks were seen for benzoic and *p*-nitrobenzoic acid. The results of these saponifications confirmed the predictions of Le Rosen and Smith in that a mixture of the two possible monoacyls was obtained in each case. The relative percentages of *o*-acetylaminophenol found were 26, 66, and 44% for the acetyl–benzoyl, acetyl–*p*-nitrobenzoyl, and acetyl–propionyl systems, respectively. No significant difference in these percentages was noted for the two mixed diacyls in each system so these values represent the averaged result. It should be noted that the value of 26% *o*-acetylaminophenol is appreciably different from the value of 37% reported by Le Rosen and Smith for the acetyl–benzoyl system, and this discrepancy is probably due to the more refined methods of extraction and analysis used here. While no significance is attached to the relative quantities of monoacyls produced by saponification at present, these ratios, taken together with the mixed diacyl ratios in the equilibrium mixture, should prove useful in assessing the relative rates of saponification of the mixed diacyls. For example, in the acetyl–*p*-nitrobenzoyl system the saponification rates of the two mixed diacyls must be nearly identical since the monoacyl mixture obtained on saponification corresponds exactly to that which would be predicted on this basis from the mixed diacyl equilibrium composition. In the other two systems, the monoacyl derived from the less stable mixed diacyl isomer predominated showing that this isomer saponified appreciably faster than its isomeride.

Finally, since the mixed diacyls of the acetyl–propionyl system were water soluble, it was felt worthwhile to carry out an acid hydrolysis of these compounds. A 1% solution of each isomer was stirred at room temperature for 3 days with 1.6 N HCl and the resulting mixture extracted with chloroform. In each case, the extracts were free of the mixed diacyls and the monoacyl resulting from rearrangement and hydrolysis constituted only 7% of the monoacyl mixtures. Thus, it was evident that isomerization in acid media was slow relative to hydrolysis in marked contrast to the results obtained with hydrolysis in base.

Experimental Section

The synthesis and characterization of compounds used in this work are described below. Melting points are uncorrected and were taken on a Fisher digital melting point analyzer. Infrared spectra were recorded from potassium bromide disks on a Perkin-Elmer Model 21 spectrophotometer. Ultraviolet spectra were recorded using a Bausch and Lomb Model 600 UV–visible spectrophotometer.

The chromatographic analyses were performed using a Waters ALC/GPC 202 liquid chromatograph equipped with a differential ultraviolet detector (254 nm) and a 30 cm × 4 mm (i.d.) μ-Porasil column. Normal hexane was used as the principal developing solvent in all cases and was modified by the addition of small amounts of chloroform and ethanol. In isomerization experiments, the chromatographic conditions were chosen such that the two possible monoacyls were clearly separated. Standard solutions were prepared in chloroform and although this solvent contained about 1% ethanol as a stabilizer, no evidence of isomerization of the mixed diacyls was observed even after several months standing.

Isomerization experiments were carried out by periodically analyzing solutions containing 0.5–2.0% (w/v) of the mixed diacyl. Generally, 1-μl aliquots of the alcohol solutions were injected directly into the chromatograph, since it was found that the results so obtained gave reliable concentration results. However, for pyridine solutions it was necessary to evaporate aliquots to dryness and reconstitute these with chloroform before chromatographing.

A. Preparation of Monoacyl Derivatives of *o*-Aminophenol. The preparation of these stable derivatives has been adequately described in the earlier literature and need not be repeated in detail here. However, it was discovered early in this work that they were best prepared in high purity by saponification of the homogeneous diacylated derivatives. For example, when equimolar quantities of benzoyl chloride and *o*-aminophenol (sublimed product, mp 170–171 °C) were reacted in pyridine solution, the resulting product contained 19% of the homogeneous diacyl. It was found that recrystallization of this mixture from various solvents was not an efficient way of purifying the desired monoacyl. On the other hand, saponification of the *o*-dibenzoylaminophenol gave good yields of the *o*-benzamidophenol, which was then easily purified by recrystallization.

B. Preparation of Mixed Diacyl Derivatives of *o*-Aminophenol. Generally, the *N*-acetyl isomers were prepared satisfactorily by acylating *o*-acetamidophenol with the appropriate acid chloride or anhydride in pyridine followed by recrystallization from nonpolar solvents. The more unstable *O*-acetyl isomers were prepared in glacial acetic acid or in acetone containing 2–10% of pyridine. Use of these reaction solvents gave minimal isomerization and a reasonable rate of reaction. The crude products were obtained by pouring the reaction mixture over ice or by evaporating to dryness as described in detail below.

1. *o*-Acetoamidophenyl Benzoate. Reaction of *o*-acetamidophenol in pyridine solution with a 15% excess of benzoyl chloride followed by pouring the solution over cracked ice gave a light tan product melting at 141–143 °C. Analysis by LC showed that the recovered product contained about 2.5% of the rearranged isomer. Recrystallization from benzene with carbon treatment gave white needles melting at 137.5–139 °C in 62% yield. A single liquid chromatographic peak was observed for the recrystallized compound.

2. *o*-Benzamidophenyl Acetate. Acetylation of *o*-benzamidophenol with a 10% excess of acetyl chloride in glacial acetic acid gave a 75% yield of crude product melting at 141–145 °C. Recrystallization of this fine white powder yielded white needles, mp 141–145 °C. LC

Table III. Infrared Carbonyl Absorption Bands in Mixed Diacyl Derivatives

Compd[a]	Equil %	Ester, μm	Amide, μm	Δμm[b]
I	83	5.77	5.90	0.13
II	17	5.65	6.00	0.35
III	66	5.69	5.96	0.27
IV	34	5.63	5.98	0.35
V	63	5.65	6.00	0.35
VI	37	5.65	5.98	0.33

[a] See Table II for compound identification. [b] Amide absorption minus ester absorption.

Table IV. Ultraviolet Absorption Maxima of Mixed Diacyls

Compd	Solvent	Absorption maxima λ, nm	Absorption maxima $\epsilon \times 10^{-3}$
I	Cyclohexane[a]	234	32.5
II	Hexane[a]	266	12.5
III	Hexane	244	28.8
IV	Hexane	241	19.3
		295	10.8
V	Hexane	240	11.2
VI	Hexane[a]	240	15.5

[a] Because of their low solubility, these solutions were prepared by dilution of chloroform solutions and their absorbance measured against appropriate blank samples diluted similarly.

6. o-Propionylamidophenyl Acetate. The acetylation of o-propionylamidophenol was carried out using a 1200% excess of acetyl chloride in acetone. Pyridine was eliminated from this preparation since its presence seemed to promote the formation of tars. The solvent and excess acetyl chloride were removed under vacuum, leaving a tarry residue which was dissolved in hot benzene and carbon treated. On cooling, tan crystals separated (40% yield) which melted at 100.5–102 °C. A final recrystallization from benzene yielded white needles melting at 101.5–103 °C. LC analysis showed less than 0.5% of unreacted o-propionylamidophenol to be present, and the opposite isomer was not detected.

C. Characterization of Compounds. 1. Melting Point Data. The melting point data for the mixed diacyl compounds prepared in this work are summarized in Table II. The data for the better known stable monoacyls and homogenous diacyls are not recorded here but were in good agreement with the literature values. Good agreement with the literature data for the acetyl–benzoyl mixed diacyls was also obtained, but it is obvious from the wide melting point range recorded that impure products were obtained by earlier workers with the mixed diacyls of the acetyl–propionyl system. The mixed diacyls of the acetyl–p-nitrobenzoyl system with o-aminophenol were prepared for the first time.

2. Infrared Absorbtion Data for Ester and Amide Carbonyl Bands of Mixed Diacyl Derivatives (Table III). It was initially thought that the separation of the infrared ester and amide carbonyl bands would prove to be useful in assigning structures to the mixed diacyl derivatives. Theoretically, one might expect to find a wider separation of these bands in the more unstable of the mixed diacyl isomers owing to the greater differences in charge on the ester and amide carbonyl carbons. It was further thought that the magnitude of these differences might be a measure of the relative stabilities of these isomers. These ideas appear to work for the first two systems but clearly fail in the third and are probably too unsophisticated to have much merit.

Table V. Carbon and Hydrogen Analyses of Mixed Diacyl Derivatives of o-Aminophenol[a]

Registry no.	No.	Compd	Theory % C	Theory % H	Found % C	Found % H
60949-47-5	I	o-Acetamidophenyl benzoate	70.6	5.13	70.5	5.14
60978-39-4	II	o-Benzamidophenyl acetate	70.6	5.13	70.5	5.18
60949-48-6	III	o-Acetamidophenyl p-nitrobenzoate	60.0	4.03	59.9	4.05
60949-49-7	IV	o-(p-Nitrobenzamido)phenyl acetate	60.0	4.03	60.0	4.06
60949-50-0	V	o-Acetamidophenyl propionate	63.8	6.32	63.8	6.36
60978-38-3	VI	o-Propionamidophenyl acetate	63.8	6.32	63.9	6.37

[a] Results of single analyses performed by Atlantic Microlab, Inc., Atlanta, Ga.

analysis showed the recrystallization compound to contain 0.3% of the opposite isomer.

3. o-Acetamidophenyl p-Nitrobenzoate. Reaction of o-acetamidophenol with a 10% excess of p-nitrobenzoyl chloride in pyridine solution followed by precipitation over ice gave a 53% yield of crude product, mp 162–167 °C. Two recrystallizations from benzene gave white needles melting at 165–167 °C. LC analysis showed that 0.7% o-(p-nitrobenzamido)phenyl acetate was present in the recrystallized product.

4. o-(p-Nitrobenzamido)phenyl Acetate. o-(p-Nitrobenzamido)phenol was reacted with acetyl chloride in acetone solution containing 4% pyridine. A large excess (300%) of acetyl chloride was found to be required for good conversion. On pouring this reaction mixture over cracked ice, an 88% yield of crude product was obtained melting at 140–143 °C. Recrystallization from benzene with carbon treatment yielded yellow crystals melting at 143–144 °C. LC analysis of the recrystallized product showed it to contain 0.5% of the rearranged isomer.

5. o-Acetamidophenyl Propionate. o-Acetamidophenol was reacted in acetone solution containing 1% pyridine with propionic anhydride (470% excess). Evaporation of the solvent produced a brown oil which was dissolved in 50% hexane in benzene and carbon treated. An 18% yield of white needles were recovered which melted at 72–73 °C. Analysis by LC showed the product to contain 2.6% of the rearranged isomer. Additional recrystallizations from various hexane–benzene mixtures failed to remove the undesired isomer. Mixture melting points with both o-propionylamidophenol and o-propionylamidophenyl propionate gave large melting point depressions.

3. Ultraviolet Absorbtion Data for Mixed Diacyls. The ultraviolet absorbtion maxima for the mixed diacyls prepared in this work are recorded in Table IV. The only literature data available were for the acetyl–benzoyl compounds and these agreed well with the data obtained in this work. These data may be useful both for characterization and for increasing analysis sensitivity in liquid chromatography where a variable wavelength detector is available. However, sensitivity with a 254-nm fixed wavelength detector was very good and full scale deflection was obtained with about 2–3 μg samples of these compounds.

Registry No.—o-Acetamidophenol, 614-80-2; benzoyl chloride, 98-88-4; o-benzamidophenol, 3743-70-2; acetyl chloride, 75-36-5; p-nitrobenzoyl chloride, 122-04-3; o-(p-nitrobenzamido)phenol, 3743-17-7; propionic anhydride, 123-62-6; o-propionylamidophenol, 6963-37-7.

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