carried out at 300 °C for 2 h. The reaction products were identified by spectral and VPC comparison with authentic samples as diphenyl sulfide (0.361 g, 1.94 mmol), *p*-toluenesulfonamide (0.117 g, 0.684 mmol), and toluene (3.2 mg, 0.035 mmol).[11] A nonvolatile black residue (0.218 g) was also recovered from the pyrolysis tube.

An attempt to pyrolyze **11** at 250 °C resulted in only a trace amount of decomposition and the recovery of 98% starting sulfilimine.

Pyrolysis of *p*-Toluenesulfonamide (7). Under conditions identical to those described above, **7** (0.605 g, 3.54 mmol) was pyrolyzed at 300 °C for 1 h. VPC analysis showed toluene (22.8 mg, 0.248 mmol, 7%) as the only product present. Considerable black char was noted in the pyrolysis boat.

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Registry No.—**3,** 13150-75-9; **11,** 13150-76-0; chloramine-T, 127-65-1; diphenyl sulfide, 139-66-2.

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Migration of Acyl Groups in Acetyl–Alkoxycarbonyl Mixed Diacyl Derivatives of *o*-Aminophenol

Edgar D. Smith* and Lee Elrod, Jr.

Department of Chemistry, Graduate Institute of Technology, University of Arkansas, Little Rock, Arkansas 72203

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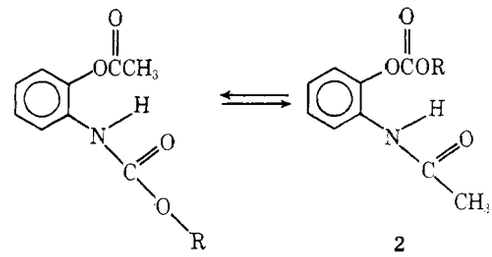
In an earlier article it was shown that the migration results obtained with several typical acyl groups were generally consistent with the hypothesis that the more stable isomer was that one with the poorer electron releasing group attached to nitrogen.[1] As discussed in some detail by Amundsen and Ambrosio, all reported work with acylalkoxycarbonyl mixed diacyls has resulted in isolation of only the isomer in which the alkoxycarbonyl group is attached to nitrogen.[2] Since these results are not consistent with the usually assumed order of the relative electron releasing powers of alkyl and alkoxy groups, it is felt desirable to investigate the synthesis and isomerization behavior of representative acetyl–alkoxycarbonyl systems. The present work presents results obtained with the acetyl–benzyloxycarbonyl and the acetyl–*n*-butoxycarbonyl systems **1–2.** System **1a** and **2a** was studied earlier



1 2

a, R = $PhCH_2$
b, R = *n*-Bu

by Amundsen and Ambrosio who were unable to prepare **2a** and found only the urethane on saponification of **1a.** System **1b** and **2b** had not been studied prior to this work and it was chosen since it represents a more clear-cut comparison of the relative electron-donating powers of an alkyl and an alkoxy functional group.

The diacyl derivatives were prepared by *O*-acylation of the *N*-alkoxycarbonyl and *N*-acyl compounds. Isomerization of purified samples of **1a** and **2a** in absolute alcohol was complete in 2 h at 26 °C and resulted in the formation of an equilibrium mixture containing 96.5% of 1a. Isomerization of **1b** and **2b** was very much slower than for **1a** and **2a** but after 380 h an equilibrium mixture was obtained containing 94.5% **1b.**

In pyridine solution, isomerization was much slower for both pairs of isomers. However, the same equilibrium composition was reached for **1a** and **2a** in about 24 h standing in pyridine at 25 °C. With **1b** and **2b, 1b** contained only 2% isomerized product after 382 h of standing time, while **2b** contained 54% of the isomerized product.

Saponification of either **1a** or **2a** gave a mixture containing 32, 50, and 18% of benzyl *o*-hydroxycarbanilate, benzoxazolone, and *o*-hydroxyacetanilide, respectively. Converting the benzoxazolone weight to benzyl *o*-hydroxycarbanilate from which it was derived[3] showed that saponification must have initially produced 83% benzyl *o*-hydroxycarbanilate. Since both isomers gave the same composition of saponification products, it seems clear that isomerization in the alkaline solution was rapid relative to saponification. It also seems clear that **2a** saponified faster than **1a** since it may be calculated that equal rates of saponification of the equilibrium mixture would yield a mixture of monoacyls containing 97.8% of benzyl *o*-hydroxycarbanilate.

Saponification of **1b** and **2b** produced only 4% of benzoxazolone in contrast to the 50% obtained with **1a** and **2a.** Correcting for this by-product as before, isomer **1b** yielded 93% *n*-butyl o-hydroxycarbanilate while isomer **2b** gave only 84% of this monoacyl. Thus, while isomerization in this system is much faster than saponification, there appears to be less difference in these rates than was the case for the **1a–2a** system. Had the saponification rates of **1b** and **2b** been equal and equilibrium attained instantly, it may be calculated that the saponification mixture would have contained 96.9% *n*-butyl *o*-hydroxycarbanilate. The most likely explanation of these results is that **2b** saponifies more rapidly than **1b** and that some saponification of **2b** occurs before it has had time to completely isomerize to the equilibrium mixture.

Experimental Section

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.

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Table I. Diacyl Derivatives of *o*-Aminophenol [a]

No.		Registry No.	Mp, °C	UV_{max} [b] λ, nm	UV_{max} [b] ($\epsilon \times 10^{-3}$)	IR, μm Ester	IR, μm Amide
1a	Benzyl *o*-acetoxycarbanilate	5211-52-9	93–5	233	20.0	5.78	5.78
2a	*o*-Acetamidophenylbenzyl carbonate	64682-86-6	88–90	239	11.9	5.73	5.90
1b	*n*-Butyl *o*-acetoxycarbanilate	64682-87-7	Oil	238	18.4	5.75[c]	5.75[c]
2b	*o*-Acetamidophenyl-*n*-butyl carbonate	64682-88-8	55–7	233	16.0	5.66	5.98

[a] Satisfactory analytical data (average ±0.2% for C, H) were reported for all new compounds listed in this table. [b] *n*-Hexane solutions. [c] Small but definite absorption at 5.62 μm.

Table II. Approximate Retention Time and Response Data for Acyl Derivatives of *o*-Aminophenol with Chloroform Developing Solvent [a]

Compd name	Registry no.	R_t, min	Peak ht, mm/μg
Benzyl *o*-acetoxycarbanilate (**1a**)		1.25	31
n-Butyl *o*-acetoxycarbanilate (**1b**)		1.28	24
Benzyl *o*-hydroxycarbanilate	64682-89-9	1.70	29
n-Butyl *o*-hydroxycarbanilate	64682-90-2	1.72	28
o-Acetamidophenylbenzyl carbonate (**2a**)		2.25	86
o-Acetamidophenyl-*n*-butyl carbonate (**2b**		2.28	105
Benzoxazolone	59-49-4	3.80	14
o-Hydroxyacetanilide	614-80-2	7.80	25

[a] Burdick and Jackson "distilled in glass" solvent containing about 1% ethanol stabilizer was modified by the addition of 0.2% by volume acetic acid. The solvent flow rate was 3 mL/min with a back pressure of about 2500 psig.

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. The developing solvent was chloroform (ethanol stabilized) to which 0.2% (v/v) acetic acid was added. Standard solutions were prepared in chloroform and no evidence of isomerization of the mixed diacyls in this solvent was observed after several weeks standing.

A. Preparation of Monoacyl Derivatives. Benzyl and *n*-butyl *o*-hydroxycarbanilate were prepared by the method of Groenvik.[4] The melting points of these compounds were in agreement with literature values and each gave only a single peak when analyzed by HPLC. The *o*-hydroxyacetanilide was obtained from Aldrich Chemical Co.

B. Preparation of Mixed Diacyl Derivatives. Benzyl *o*-Acetoxycarbanilate (1a). This mixed diacyl was prepared by the reaction of acetyl chloride with benzyl *o*-hydroxycarbanilate in acetic acid solution. In a typical preparation, 0.5 g of benzyl *o*-hydroxycarbanilate was dissolved in 25 mL of acetic acid and 0.5 mL (theory = 0.15 mL) of acetyl chloride was added over a period of 3 h with continuous stirring. HPLC analysis of an aliquot showed that 30% conversion had been obtained. An additional 0.5 mL of acetyl chloride was added and the mixture was stirred overnight. Analysis showed that 99% conversion had occurred. The solution was poured over 250 mL of cracked ice with stirring. The white precipitate formed weighed 0.63 g (54% theory) and melted at 93–4 °C. Recrystallization from 30% benzene in cyclohexane yielded 0.30 g of hard granular crystals melting at 93.5–94.5 °C. HPLC analysis showed the presence of 1% unreacted benzyl *o*-hydroxycarbanilate and 1.5% **2a**.

***o*-Acetamidophenylbenzyl Carbonate (2a).** The desired product was synthesized by treating 1 g of *o*-hydroxyacetanilide dissolved in 56 mL of 10% pyridine in acetone with 3 mL of benzyl chloroformate (theory = 0.94 mL) dissolved in 10 mL of acetone. The benzylchloroformate was added dropwise to the stirred *o*-hydroxacetanilide solution over a period of 30 min, and the resulting mixture was poured into 25 mL of 10% aqueous HCl. Most of the acetone was removed by evaporation in a hood overnight and the aqueous suspension was extracted with chloroform. The chloroform extract was filtered and evaporated to obtain 2.20 g of a gummy solid. This was triturated with 15 mL of cyclohexane to remove some oily material. The extracted crystals weighed 1.55 g and HPLC analysis showed them to contain 9% benzoxazolone and 9% unreacted *o*-hydroxyacetanilide. Three recrystallizations from 10% chloroform in cyclohexane yielded 0.5 g of light feathery crystals melting at 88–90 °C. Very remarkably, a 50/50 mixture of **1a** and **2a** showed practically no depression in mp, the mixture melting from 88–92 °C! HPLC analysis showed the presence of 1.5% **1a**, 1.5% *o*-hydroxyacetanilide, and 1.0% benzyl *o*-hydroxycarbanilate in the purified **2a** crystals.

***n*-Butyl *o*-Acetoxycarbanilate (1b).** This product was prepared by treating 2 g of *n*-butyl *o*-hydroxycarbanilate dissolved in 60 mL of 4% pyridine in ethyl ether solution with 1.7 mL of acetyl chloride (theory = 0.68 mL). The acetyl chloride was added dropwise over about 1 h and the reaction mixture was stirred overnight. The ether solution was extracted three times with 30-mL portions of 1.6 N HCl to remove pyridine and pyridine hydrochloride and then with two 30-mL portions of water to remove the residual acid. Evaporation of the ether left 1.5 g of a slightly yellowish oil which resisted all attempts to cause it to crystallize from various solvent mixtures. HPLC analysis showed the oil to contain about 8% of *n*-butyl *o*-hydroxycarbanilate as the only detectable impurity. This impurity was reduced to 3% by dissolving the oil in hot hexane and cooling slowly so that the more insoluble *n*-butyl *o*-hydroxycarbanilate precipitated selectively. Evaporation of the hexane solution left 0.5 g of clear oil melting at about −30 °C.

***o*-Acetamidophenyl-*n*-butyl Carbonate (2b).** This compound was prepared by slurrying 1.5 g of *o*-hydroxyacetanilide with 50 mL of ethyl ether and 3.4 mL of *n*-butyl chloroformate (theory = 0.94 mL). A solution of 4 mL of pyridine in 30 mL of ether was added with constant stirring over a period of 1 h. The reaction mixture was stirred for 3 h and extracted with three 50-mL portions of 3 N HCl to remove pyridine and pyridine hydrochloride and with two 50-mL portions of water to remove the acid. Evaporation of the ether yielded about 5 mL of a viscous yellow oil. The oil was dissolved in 70 mL of boiling hexane, carbon treated, and allowed to cool slowly to −10 °C. After several days of standing long white needles were obtained which melted at 55–7 °C. HPLC analysis showed only trace amounts of **1b** to be present. However, on standing at room temperature this material slowly reverted to an oil which was principally isomer **1b**. For example, two batches of this isomer stored at room temperature for 44 and 47 days after recrystallization were found to contain 83 and 87%, respectively, of **1b**.

C. Isomerization of Mixed Diacyls. For isomerization rate studies of **1a** and **2a** relatively concentrated solutions (1–2%) were prepared in absolute ethanol and aliquots diluted tenfold with $CHCl_3$ at appropriate time intervals. In this way, the isomerization was quenched so that replicate analyses could be made if required, and the solution concentrations were adjusted to the proper range for HPLC analysis. The rate of isomerization of **1b** and **2b** was very slow so that it was found more convenient to evaporate aliquots of approximately 0.4% solutions and reconstitute these with $CHCl_3$ just prior to analysis. In all cases, solutions were made up accurately so that material balance calculations could be made on the basis of the analytical results. The standard deviation of these balances was estimated to be ±5% of the amount present.

D. Saponification of Mixed Diacycls. Isomers **1a** and **2a** were saponified by stirring 0.10 g at room temperature in 10 mL of 1.0% NaOH. The dense granular crystals of **1a** dissolved very slowly even with continuous stirring and powdering of the larger granules. Complete solution required about 1 h. In marked contrast, **2a** dissolved completely in about 5 min. Both mixtures were stirred an additional 20 min after a clear solution of **1a** was obtained, the solutions were acidified, and the white powdery precipitate which formed was filtered. The material recovered in this way was found to be nearly pure benzyl *o*-hydroxycarbanilate as was previously reported for the saponification of **1a** by Amundsen and Ambrosio. Since, however, only 14% of the theoretical quantity expected (assuming 100% conversion to this monoacyl) was recovered, the aqueous filtrates were extracted with $CHCl_3$ and the extract was analyzed by HPLC. Benzoxazolone

and o-hydroxyacetanilide in about a 3:1 ratio were found in this extract, along with a small amount of additional benzyl o-hydroxycarbanilate. Conversion of the benzoxazolone weight to benzyl o-hydroxycarbanilate from which it was formed gave average material balances of 75%.

Isomers **1b** and **2b** were saponified by stirring 0.20-g samples with 10 mL of 2% NaOH. Solution was complete in about 15 min and the reaction mixtures were stirred for an additional 2 h before being acidified. The acid mixtures were evaporated to dryness, the residues were extracted with 15 mL of $CHCl_3$, and these extracts were filtered and diluted to 25 mL for HPLC analysis. The material balances in these saponifications averaged 65%.

Registry No.—Acetyl chloride, 75-36-5; benzyl chloroformate, 501-53-1; butyl chloroformate, 592-34-7.

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Styrene Bromination: Evidence for a Bridged Rate-Determining Transition State

George H. Schmid

Department of Chemistry, University of Toronto, Toronto, Ontario, Canada M5S 1A1

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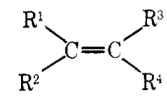
The mechanism of the bromination of styrene and its derivatives has been the subject of debate.[1] An open carbonium-ion-like rate-determining transition state has been proposed on the basis of stereochemical evidence[2] and the magnitude of the negative ρ values[3] for bromination of ring substituted styrenes. A bridged rate-determining transition state has been proposed, based upon the observation that the initial enthalpy difference between pairs of cis,trans isomeric alkenes was increased at the bromination transition state.[4]

One way of resolving this problem is to compare the structure-reactivity profiles of bromination with two model reactions: one involving a bridged, the other an open-ion-like rate-determining transition state. The following reactions have been chosen as models. Protonation of alkenes in acid-catalyzed hydrations has been established to proceed by an open ion through the entire range of reactivity.[1,5] The addition of arenesulfenyl halides to alkenes is a reaction which proceeds through a bridged rate-determining transition state for the entire range of reactivity.[1] The purpose of this note is to make such a comparison of the bromination, hydration, and addition of 4-chlorobenzenesulfenyl chloride to the following compounds. The rate data are collected in Table I.

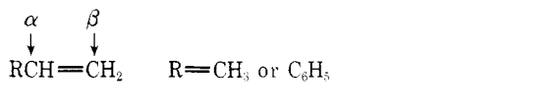
Table II. Ratios $k(\alpha\text{-}CH_3)/k(H)$ and $k(\beta\text{-}CH_3)/k(H)$

Compd	Br_2 in HOAc	Br_2 in CH_3OH	ArSCl in TCE	Hydration
2-Phenylpropene (**2**)/styrene (**1**)	60.7		4.27	1070
cis-1-Phenylpropene (**3**)/styrene (**1**)	0.80		0.69	
trans-1-Phenylpropene (**4**)/styrene (**1**)	1.10		1.91	0.34
Methylpropene (**6**)/propene (**5**)		89	2.7	7500
cis-2-Butene (**7**)/propene (**5**)		43	6.5	1.68
trans-2-Butene (**8**)/propene		28	2.1	0.71



	R^1	R^2	R^3	R^4		R^1	R^2	R^3	R^4
1	C_6H_5	H	H	H	**5**	CH_3	H	H	H
2	C_6H_5	CH_3	H	H	**6**	CH_3	CH_3	H	H
3	C_6H_5	H	CH_3	H	**7**	CH_3	H	CH_3	H
4	C_6H_5	H	H	CH_3	**8**	CH_3	H	H	CH_3

The effect of substituting a methyl group for a hydrogen on the rate of addition is used as the mechanistic probe. For purpose of comparison, the positions of the methyl groups which replace the olefinic hydrogens in styrene and propene can be designated α and β as follows:



The effect of substituting the olefinic hydrogens on styrene and propene by methyl groups on the rates of addition is different for the two limiting mechanisms. By expressing the rates as the ratios $k(\alpha\text{-}CH_3)/k(H)$ and $k(\beta\text{-}CH_3)/k(H)$, this fact is clearly demonstrated as shown in Table II.

Several points are evident from the data in Table II. As expected, substituting a methyl group in the α position has the greatest effect on hydration where an open ion is formed. The $k(\alpha\text{-}CH_3)/k(H)$ ratio for the bromination of styrene is not unusually large. It is about the same as propene and much smaller than that for hydration.

The small variation in the ratio $k(\alpha\text{-}CH_3)/k(H)$ and $k(\beta\text{-}CH_3)/k(H)$ for additions of bromine and 4-chlorobenzenesulfenyl chloride in the propene series indicate a bridged rate-determining transition state in accordance with the accepted mechanisms of these additions.[1] The methyl substitutents affect the rates of bromination more than those of

Table I. Rates of Hydration, Bromination, and Addition of 4-Chlorobenzenesulfenyl Chloride at 25 °C

Compd	Registry no.	$k_2(Br_2)$,[a] $M^{-1}\,s^{-1}$	$k_g(Br_2)$,[b] $M^{-1}\,s^{-1}$	k_2(ArSCl), $M^{-1}\,s^{-1}$	$k_2(H^+)$,[e] $M^{-1}\,s^{-1}$
Styrene (**1**)	100-42-5	11.2		62.0[c]	0.326×10^{-6}
2-Phenylpropene (**2**)	98-83-9	680		265[c]	0.967×10^{-4}
cis-1-Phenylpropene (**3**)	766-90-5	8.89		43.0[c]	
trans-1-Phenylpropene (**4**)	873-66-5	12.3		118[c]	1.12×10^{-7}
Propene (**5**)	115-07-1		30.7	205[d]	0.495×10^{-7}
Methylpropene (**6**)	115-11-7		2730	550[d]	0.371×10^{-3}
cis-2-Butene (**7**)	590-18-1		1310	1340[d]	8.32×10^{-8}
trans-2-Butene (**8**)	624-646		847	434[d]	3.51×10^{-8}

[a] In acetic acid solvent, ref 6. [b] In methanol containing 0.2 M NaBr, ref 7. [c] In 1,1,2,2-tetrachloroethane, ref 8. [d] In 1,1,2,2-tetrachloroethane, ref 9. [e] The second-order rates of hydration were obtained by dividing the observed rates extrapolated to $H_0 = 0$ by the acidity function h_0 for that acidity, ref 10.

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