[Contribution from the Chemical Laboratory of Purdue University]

ACYL DERIVATIVES OF ORTHO-AMINOPHENOL. II

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When diacyl derivatives of *o*-aminophenol are prepared by introducing the acyl groups in a certain order and then the order of introduction is reversed, identical products are usually obtained due to a rearrangement. This does not hold true in the case of the groups, which are structural isomers, studied in this paper, and in the case of the acetyl and propionyl groups, studied by Nelson and Davis,[1] and also in the case of certain groups studied by Raiford and co-workers.[2] The object of this investigation has been: (1) to study the behavior of very closely related groups when substituted in *o*-aminophenol; (2) to investigate the behavior of *o*-aminophenols acylated with structurally isomeric groups.

The following pairs of groups were used:

$—CO_2C_2H_5$ and $—CO_2C_4H_9$; $—CO_2C_3H_7$ and $—CO_2C_4H_9$;
$—CO_2C_3H_7(n)$ and $—CO_2C_3H_7(iso)$; $—CO_2C_4H_9(n)$ and $—CO_2C_4H_9(iso)$

Butyl *o*-hydroxycarbanilate was acylated with ethyl chlorocarbonate and a stable diacyl obtained which yielded butyl *o*-hydroxycarbanilate on saponification. When ethyl *o*-hydroxycarbanilate was acylated with *n*-butyl chlorocarbonate, the same diacyl was obtained as above and the saponification product was butyl *o*-hydroxycarbanilate. The carbethoxy group in the second diacyl had migrated from the nitrogen to the oxygen during the preparation of the compound.

When butyl *o*-hydroxycarbanilate was acylated with *n*-propyl chlorocarbonate a stable diacyl formed, which yielded butyl *o*-hydroxycarbanilate on saponification. Treatment of propyl *o*-hydroxycarbanilate with *n*-butyl chlorocarbonate resulted in the same diacyl as that from butyl *o*-hydroxycarbanilate, and the saponification product was butyl *o*-hydroxycarbanilate.

*iso*Propyl *o*-hydroxycarbanilate was acylated with *n*-propylchlorocarbonate and gave a mixture of the two diacyls. The conclusion was drawn from the fact that the saponification product, when mixed either with propyl *o*-hydroxycarbanilate or *iso*propyl *o*-hydroxycarbanilate, caused a depression of the melting point. When propyl *o*-hydroxycarbanilate was acylated with *iso*propyl chlorocarbonate a partial rearrangement again occurred as indicated by the fact that the saponification product caused a depression of the melting point of either of the mono-acyl derivatives.

The acylation of *iso*butyl *o*-hydroxycarbanilate with *n*-butyl chlorocarbonate also gave a mixture of two diacyls as shown by the saponification product causing a depression of the melting point of each of the mono-

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[1] Nelson and Davis, This Journal, **48,** 1677 (1926).

[2] Raiford and others, *ibid.*, (a) **46,** 2305 (1924); (b) **47,** 1115 (1925).

acyls. When butyl *o*-hydroxycarbanilate was acylated by means of *iso*butyl chlorocarbonate no rearrangement took place. This conclusion was reached from the behavior of the melting point of the saponification product.

Experimental Part

The mono-acyl derivatives of *o*-aminophenol were prepared by Groenvik's method from *o*-aminophenol and *n*-butyl, *iso*butyl, *n*-propyl, and *iso*propyl chlorocarbonates as follows: 10 g. of *o*-aminophenol was suspended in 200 cc. of ether and 3 cc. of the chlorocarbonate was added. The ether solution was filtered and evaporated. The crystals thus obtained were recrystallized twice from dil. alcohol and once from hot water.

TABLE I

MONO-ACYL DERIVATIVES

		Analysis			
				N, %	
o-Hydroxycarbanilate	Formula	M. p., °C.	Yield, %	Calcd.	Found
Butyl	$HOC_6H_4NHCO_2C_4H_9$	87.5	53	6.72	6.66
*iso*Butyl	$HOC_6H_4NHCO_2C_4H_9$	86.0	64	6.72	6.50
Propyl	$HOC_6H_4NHCO_2C_3H_7$	78.0	65	7.18	7.05
*iso*Propyl	$HOC_6H_4NHCO_2C_3H_7$	85.0	64	7.18	7.05

The diacyl derivatives of *o*-aminophenol were prepared by the Schotten-Baumann method from the mono-acyl derivatives and the chlorocarbonates as follows. Three g. of the mono-acyl derivative was dissolved in 75 cc. of water containing 1 g. of potassium hydroxide (slightly more than the calculated amount). After solution was complete, an excess (about 2 cc.) of the chlorocarbonate was added. The oil which formed was extracted with ether and the ether evaporated. A brown oil remained. Attempts were made to crystallize this substance from various organic solvents but it persisted in separating as a viscous liquid. When the substance was dissolved in alcohol and water was added, an emulsion formed. The substance was purified by several extractions of such emulsions with ether. Analysis was made by the Kjeldahl method.

Attempts to purify these disubstitution products of *o*-aminophenol by distillation in a vacuum resulted in the formation of flaky crystals with a silky luster and a greasy, graphite-like texture. After several weeks they became purplish. Analysis showed they were not the disubstitution products, but compounds containing a higher percentage of nitrogen.

The diacyls were saponified by dissolving in 10% potassium hydroxide solution and then acidifying with hydrochloric acid. The precipitate was purified by recrystallization from dil. alcohol.

Ethylcarbonate of Butyl *o*-Hydroxycarbanilate ($C_2H_5CO_2OC_6H_4NHCO_2C_4H_9$).—This compound was prepared from ethyl *o*-hydroxycarbanilate and *n*-butyl chlorocarbonate. It was a viscous brown liquid.

Anal. Calcd. for $C_{14}H_{19}NO_5$: N, 5.00. Found: 5.19.

On saponification a material was obtained which by purification from alcohol melted at 85°. By a mixed-melting-point determination this proved to be butyl *o*-hydroxycarbanilate.

On distillation in a vacuum the ethyl carbonate of butyl *o*-hydroxycarbanilate gave a crystalline decomposition product as shown by the analysis; m. p., 64.5°.

Anal. Calcd. for $C_{14}H_{19}NO_5$: N, 5.00. Found: 6.45.

On saponification of this crystalline substance, butyl *o*-hydroxycarbanilate was formed.

This diacyl was also prepared by introducing the acyl groups in the reverse order and was shown to be identical with that first formed by the fact that it gave the same saponification product and also the same decomposition product on distillation in a vacuum.

Propylcarbonate of Butyl *o*-Hydroxycarbanilate ($C_3H_7CO_2OC_6H_4NHCO_2C_4H_9$).—This was prepared from propyl *o*-hydroxycarbanilate and *n*-butylchlorocarbonate. It was a viscous, brown oil.

Anal. Calcd. for $C_{15}H_{21}NO_5$: N, 4.75. Found: 4.95.

On saponification a crystalline material was formed which, on purification from alcohol, melted at 84°. By a mixed-melting-point determination this was proved to be butyl *o*-hydroxycarbanilate. Distillation of the diacyl in a vacuum gave a crystalline decomposition product; m. p., 72–73°.

Anal. Calcd. for $C_{15}H_{21}NO_5$: N, 4.75. Found: 5.70.

On saponification this decomposition product gave butyl *o*-hydroxycarbanilate.

This diacyl was also prepared by introducing the acyl groups in the reverse order and was shown to be identical with that first formed, by the fact that it gave the same saponification product and the same decomposition product on distillation in a vacuum.

Propylcarbonate of *iso*Propyl *o*-Hydroxycarbanilate ($C_3H_7CO_2OC_6H_4NHCO_2$-C_3H_7).—This was prepared from *iso*propyl *o*-hydroxycarbanilate and *n*-propyl chlorocarbonate. It was a viscous, brown oil. On saponification a crystalline product was formed which after recrystallization melted at 74.5–76°. The mixed melting points with both propyl *o*-hydroxycarbanilate and *iso*propyl *o*-hydroxycarbanilate were depressed, indicating that a partial rearrangement had occurred. Analysis of the monoacyl produced by the saponification of the oil showed the calculated amount of nitrogen.

Anal. Calcd. for $C_{10}H_{13}NO_3$: N, 7.18. Found: 6.9.

Distillation of the diacyl in a vacuum gave a crystalline decomposition product as shown by the analysis; m. p., 54–56°.

Anal. Calcd. for $C_{14}H_{19}NO_5$: N, 5.0. Found: 6.15.

Saponification of this decomposition product gave a compound melting at 74.5–75.5°.

***iso*Propylcarbonate of Propyl *o*-Hydroxycarbanilate** ($C_3H_7CO_2OC_6H_4NHCO_2$-C_3H_7).—This was prepared from propyl *o*-hydroxycarbanilate and *iso*propyl chlorocarbonate. It was a viscous oil. Saponification yielded a product melting at 77.5–78°. When this was mixed with the saponification product of propylcarbonate of *iso*propyl *o*-hydroxycarbanilate the melting point was lowered. The melting points of both propyl *o*-hydroxycarbanilate and *iso*propyl *o*-hydroxycarbanilate were depressed when these substances were mixed with this product. A partial rearrangement had evidently taken place. Distillation of this diacyl product in a vacuum produced a crystalline decomposition product; m. p., 53.5–55.5°. A mixed melting point of this product with the decomposition product of the propylcarbonate of *iso*propyl *o*-hydroxycarbanilate was indefinite and lower.

Butylcarbonate of *iso*Butyl *o*-Hydroxycarbanilate ($C_4H_9CO_2OC_6H_4NHCO_2C_4H_9$).—This was prepared from *iso*butyl *o*-hydroxycarbanilate and *n*-butyl chlorocarbonate. A viscous oil separated which, on saponification, gave a product melting at 74°. Mixed-melting-point determinations with both butyl *o*-hydroxycarbanilate and *iso*butyl *o*-hydroxycarbanilate proved that it was identical with neither of these substances. The melting points indicated, however, that although some rearrangement had taken place most of the diacyl had not rearranged. On distillation of the diacyl in a vacuum a crystalline decomposition product was formed melting at 54–56°.

Anal. Calcd. for $C_{16}H_{23}NO_5$: N, 4.55. Found: 5.75.

***iso*Butylcarbonate of Butyl *o*-Hydroxycarbanilate** ($C_4H_9CO_2OC_6H_4NHCO_2C_4H_9$).—This was prepared from butyl *o*-hydroxycarbanilate and *iso*butyl chlorocarbonate. A viscous oil was obtained which on saponification gave a product melting at 84.5°. When this was mixed with *iso*butyl *o*-hydroxycarbanilate the melting point was depressed; this was not the case when it was mixed with butyl *o*-hydroxycarbanilate, showing that no rearrangement had taken place. On distillation in a vacuum the characteristic decomposition product was formed, melting at 63.5–64.5°. When this was mixed with some of the decomposition product from the butylcarbonate of *iso*butyl *o*-hydroxycarbanilate melting at 54° the melting point was 52–55°, showing the products to be dissimilar.

Anal. (decomposition product). Calcd. for $C_{16}H_{23}NO_5$: N, 4.55. Found: 5.7.

Summary

1. The heavier *n*-carbobutoxy group will replace the carbethoxy or the *n*-carbopropoxy groups from the nitrogen in *o*-aminophenol diacyls.

2. When *o*-aminophenol is acylated with the structural isomers, *n*-carbopropoxy and *iso*carbopropoxy groups, irrespective of their original positions, a partial rearrangement occurs. Evidently the differences which control the rearrangement are not sufficiently strong to carry it to completion, and a mixture of the two possible isomers results. It is possible that a state of equilibrium exists.

When the corresponding compounds with the *n*- and *iso*butoxy groups are made, their behavior is somewhat different. While the butyl carbonate of *iso*butyl *o*-hydroxycarbanilate rearranges partially, giving a mixture of the two isomers, *iso*butylcarbonate of butyl *o*-hydroxycarbanilate was not found to change.

3. Several new acyl derivatives of *o*-aminophenol have been prepared and studied.

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