precipitate was noted. The mixture was heated and filtered to give 4.4 g of material which was washed with chloroform leaving 4.0 g of solid melting at 108–115°. The solid was taken up in 200 ml of ethyl ether in which 1.8 g was dissolved with difficulty. From this there was obtained 1.5 g of product melting at 115.5–117°. In addition, the original thionyl chloride chloroform filtrate yielded 0.6 g of product which upon recrystallization from ethyl ether melted at 115–117.5° to make the total yield 2.4 g (48%).

Anal. Calcd for C, 26.65; H, 3.70; O, 35.60; S, 23.70. Found: C, 26.50; H, 3.69; O, 35.83; S, 23.68.

Registry No.—II, 15441-06-2; III, 15441-07-3; IV, 15441-08-4; V, 15441-10-8; VI, 15441-09-5.

Preparation and Decomposition of 1-Benziloylimidazole

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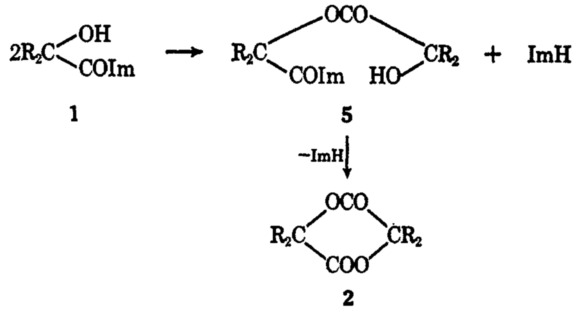
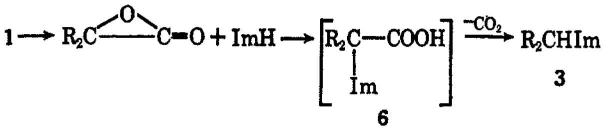
Staab,[1] in his detailed investigations on the synthesis and chemistry of the 1-acylimidazoles, stated that inter- and intramolecular esterification would complicate the isolation of the acylimidazole when a hydroxy acid and 1,1′-carbonyldiimidazole react. Although experimental verification appears to be lacking, such difficulties are given as the reason for the poor yields obtained in reactions involving mandelic and salicylic acids.[2] It has now been found that 1-benziloylimidazole (**1**) can be prepared in satisfactory yield from benzilic acid and 1,1′-carbonyldiimidazole and that **1** displays many of the normal reactions of 1-acylimidazoles. 1-Benziloylimidazole is a crystalline solid which is stable at ambient temperature for an extended period of time and which, in contrast to some of the other acylimidazoles, is moderately resistant to hydrolysis by the moisture in laboratory air.

When **1** is either heated by itself at 145–150° or refluxed in acetonitrile, a rapid and complex decomposition occurs. Carbon dioxide is evolved and imidazole, benzilide (**2**), 1-benzhydrylimidazole (**3**), 1,3-dibenzhydrylimidazolium benzilate (**4**), and a low-molecular weight polyester of benzilic acid are formed. Although no studies have been made to elucidate the mechanism, the routes (eq 1, 2, and 3) to these products are proposed, where R is phenyl and Im is 1-imidazolyl.



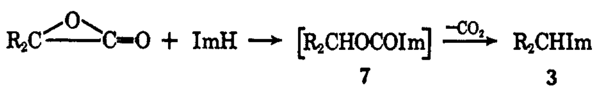
(1)

To obtain **3**, a rearrangement of **1** followed by a decarboxylation is necessary. Perhaps imidazole is eliminated in a concerted reaction and diphenylacetolactone is formed; the α-lactone ring is then opened by a nucleophilic attack of imidazole on the carbon atom bearing the phenyl groups to give **6**, which loses carbon dioxide (eq 2). The same hypothetical intermediate is implicated in the formation of α-methoxydiphenylacetic acid during the decomposition of di-*t*-butylperoxy-diphenylmalonate in methanol.[3]



(2)

A much less favored possibility would involve the formation of 1-carbodiphenylmethoxyimidazole (**7**) by imidazole reattacking the α-lactone at the carbonyl group with ring opening at the carbon–carbon bond rather than through a carbon–oxygen bond (eq 3).



(3)

Staab and Mannschreck[4] have reported that the related compound, 1-carbobenzyloxyimidazole, RCH_2OCOIm, loses carbon dioxide at 100–110° to furnish 1-benzylimidazole in about 70% yield.

Once some of the 1-benzhydrylimidazole, **3**, is formed, it compares with the imidazole in the nucleophilic attack on carbon in the α lactone. Such a reaction would lead to the 1,3-dibenzhydrylimidazolium salt, **4**. Alternatively, benzhydryl benzilate, which might arise through a hydrolysis of the acylimidazole bond in **5**, followed by a decarboxylation, could alkylate **3**. Benzhydryl benzilate, however, was not isolated.

The polyester of benzilic acid could arise by a polymerization of the hypothetical α lactone with imidazole as the initiating nucleophile. Other reactions which suggest the intermediacy of this lactone also gave a polymer.[3]

The 1-benzhydrylimidazole **3** does not arise from a reaction of benzilide (**2**) with imidazole since a 1-hr fusion of these compounds in a 1:3 molar ratio at 145–150° did not yield **3**.

Experimental Section

1-Benziloylimidazole.—Benzilic acid (5.15 g, 0.0226 mole) and 3.7 g (0.0229 mole) of 1,1′-carbonyldiimidazole were mixed in 50 ml of dry acetonitrile; gas was rapidly evolved, and complete solution was obtained. The product, which began to crystallize in about 10 min, was filtered after the solution had stood 2 hr at 25° and then overnight at 5°, and washed twice with 5-ml portions of cold, dry acetonitrile to give 4.0 g (63.5%), mp 143–144°, with vigorous gassing. The decomposition point remained unchanged when the compound was recrystallized rapidly from acetonitrile.

Anal. Calcd for $C_{17}H_{14}N_2O_2$: C, 73.36; H, 5.07; N, 10.07. Found: C, 72.94; H, 4.83; N, 10.17.

The infrared spectrum shows a carbonyl absorption at 5.78 μ. Since there is no absorption in the 2.8–3.1 μ region, it is concluded that the hydroxyl group is strongly hydrogen bonded, most likely to the unsubstituted nitrogen of the imidazole ring.

The nmr spectrum in $(CD_3)_2SO$ shows a peak at τ 2.81 corresponding to ten protons and four other single protons at 1.8, 2.3, 2.5, and 3.2, respectively.

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(1) H. A. Staab, *Angew. Chem., Intern. Ed. Engl.*, **1**, 351 (1962).

(2) H. A. Staab and H. Bräunling, *Ann.*, **54**, 119 (1962).

(3) P. D. Bartlett and L. B. Gortler, *J. Am. Chem. Soc.*, **85**, 1864 (1963).

(4) H. A. Staab and A. Mannschreck, *Chem. Ber.*, **95**, 1284 (1962).

About 30 min was required for 2.0 g of the compound to dissolve at ambient temperature in a solution of 1 g of sodium hydroxide, 20 ml of water, and 10 ml of ethanol. When the solution was acidified after 16 hr, 1.6 g (97.5%) of benzilic acid was recovered.[5]

Thermolysis of 1-Benziloylimidazole.—The title compound (1.9 g) in a small flask was placed in an oil bath preheated to 150°. Within 5 min the sample melted and began to evolve carbon dioxide (qualitative test); the total heating time was 20 min and the final bath temperature, 145°. Water-soluble, white needles (mp 89–90°) sublimed to the cooler portion of the flask; their infrared spectrum was the same as that for imidazole. The cooled, gummy residue was triturated with ether plus water, then with ether. The small amount of poorly soluble residue was boiled with 3 ml of acetonitrile and cooled; there was recovered 0.12 g (9%) of white solid (mp 193–195°) whose infrared spectrum was the same as that for **benzilide**.

The combined ether–water extracts were separated and the ether layer washed once more with water. Cooling the ethereal solution at 5° for several days gave 0.15 g of a white solid, mp 180–190°. Two recrystallizations from absolute ethanol raised the melting point to 190.5–191.5° dec. The analyses are consistent with those required for **1,3-dibenzhydrylimidazolium benzilate**. The melting point and infrared spectrum were identical with those for the product obtained from 1,3-dibenzhydrylimidazolium chloride (mp 199–200°) and sodium benzilate in ethanol.

Anal. Calcd for $C_{43}H_{36}N_2O_3$: C, 82.14; H, 5.77; N, 4.46. Found: C, 82.39; H, 5.72; N, 4.57.

Evaporating the ether solution left 1.04 g of semisolid residue which was fractionally crystallized from cyclohexane. The less soluble material was more benzilide (0.32 g, 22%); the more soluble fraction (0.3 g, 19%) melted at 87.5–88.5° after several recrystallizations from cyclohexane. Admixture with a sample of **1-benzhydrylimidazole** made from imidazole and diphenylchloromethane did not depress the melting point; the infrared spectra of the two samples were also identical.

Anal. Calcd for $C_{16}H_{14}N_2$: C, 82.02; H, 6.02; N, 11.96; mol wt, 234.3. Found: C, 81.88; H, 6.05; N, 11.91; mol wt, 235.

In a related experiment, 5.15 g of benzilic acid and 3.7 g of 1,1′-carbonyldiimidazole in 50 ml of dry acetonitrile were refluxed for 2 hr; the solvent was removed and residue worked up as above. There was recovered 1.7 g (32%) of 1-benzhydrylimidazole (mp 83–86°), 0.9 g (19%) of impure 1,3-dibenzhydrylimidazolium benzilate (mp 170–180°), and 0.5 g of **polyester of benzilic acid** (carbonyl absorption 5.8 μ).

Anal. Calcd for $(C_{14}H_{10}O_2)_x$: C, 79.98; H, 4.79. Found in one experiment: C, 81.29; H, 5.86; N, 3.64. Found in a second experiment: C, 80.43; H, 5.45; N, 2.16; mol wt, 1150.

Registry No.—**1**, 15441-11-9; **3**, 7189-67-5; **4**, 15448-88-1.

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[5] The formation of benzilic acid upon hydrolysis eliminates the isomeric, 1-carbodiphenylmethoxyimidazole, $R_2CHOCOIm$, as the structure of the product from the benzilic acid and 1,1′-carbonyldiimidazole reaction. The slow rate of solution of **1** in basic solution argues against **6** as a possible structure for the reaction product.

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ortho Metalation of N-Substituted Benzenesulfonamides by Excess *n*-Butyllithium. Condensation with Carbonyl Compounds. Cyclizations[1]

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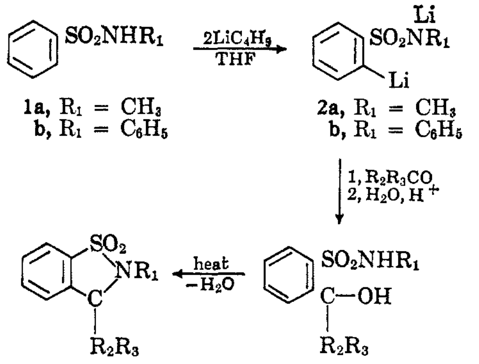
As an extension of previous work on N-methylbenzamide,[2] we have found that N-methyl- and N-phenylbenzenesulfonamides (**1**) undergo *ortho* metalation, as well as N-metalation, with excess *n*-butyllithium to form dilithiosulfonamides **2**, as evidenced by condensations with carbonyl compounds to give *ortho* derivatives (Scheme I, Table I). *ortho* Metalation was also observed with N-phenyl-*p*-tolylsulfonamide. The carbinols underwent thermal cyclodehydration at 200–230° to form the sultams (cyclic sulfonamides); this reaction was facilitated by acids (Table II). Attempts to cyclize the carbinol sulfonamide derived from cyclohexanol were unsatisfactory. In the case of the **4b**, cyclodeamination to the sultone **5** also occurred in low yield, as previously observed.[3]

Scheme I



1a, $R_1 = CH_3$
b, $R_1 = C_6H_5$

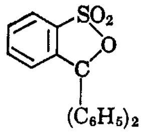
2a, $R_1 = CH_3$
b, $R_1 = C_6H_5$

3a, $R_1 = CH_3$, $R_2 = R_3 = C_6H_5$
b, $R_1 = R_2 = R_3 = C_6H_5$
c, $R_1 = R_2 = CH_3$, $R_3 = C_6H_5$
d, $R_1 = R_2 = C_6H_5$, $R_3 = CH_3$
e, $R_1 = CH_3$, $R_2 = H$, $R_3 = C_6H_5$

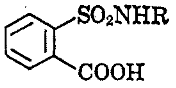
4a, $R_1 = CH_3$, $R_2 = R_3 = C_6H$
b, $R_1 = R_2 = R_3 = C_6H_5$
c, $R_1 = R_2 = CH_3$, $R_3 = C_6H_5$
d, $R_1 = R_2 = C_6H_5$, $R_3 = CH_3$

As indicated in the Tables, the yields of the carbinol sulfonamides and sultams were generally good to excellent. Table II further shows that all three of the methods of cyclodehydration to form sultams were suitable with the N-methyl carbinol sulfonamides, but that only the hydrobromic acid and thermal methods were satisfactory with the N-phenyl carbinol sulfonamides. The sulfuric acid method failed with the latter compounds apparently because of sulfonation of the anilino ring, since water-soluble material was produced.

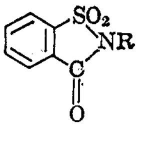
The structures of the products were supported by analyses (see Tables I and II) and infrared spectra. The spectra of the carbinol sulfonamides exhibited strong peaks in the regions of 1330–1300 and 1155–1145 cm^{-1} for the SO_2 group and sharp peaks of medium strength in the regions 3520–3450 and 3400–3250 cm^{-1} for the OH group and NH group of the secondary sulfonamide, respectively. The spectra also showed peaks in the regions 780–710 and 710–670 cm^{-1} for four and five adjacent aromatic hydrogens. The



5



6a, $R = CH_3$
b, $R = C_6H_5$



7a, $R = CH_3$
b, $R = C_6H_5$

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[1] Supported by the Army Research Office (Durham) and by Public Health Service Research Grant No. CA 04455-09 from the National Cancer Institute.

[2] W. H. Puterbaugh and C. R. Hauser, *J. Org. Chem.*, **29**, 853 (1964).

[3] A. Mustafa and M. K. Hilmy, *J. Chem. Soc.*, 1339 (1952).