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Reaction of Benzoin with Aminobenzoic Acids and with *p*-Ethylaniline

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Brief studies of the reaction of benzoin with the three aminobenzoic acids and with *p*-aminophenylacetic acid are reported.

DURING STUDIES on the reactions of amino acids with sugars, several simplified model systems (*3, 4*) were examined.

Weckowicz had already studied the ortho isomer, anthranilic acid, in this reaction (*5*), and Cameron and co-workers had reported the use of ethyl *p*-aminobenzoate and of *p*-aminophenylacetic acid (*1*). These workers had thoroughly proved the structures of their products. In general, the equation was

$$C_6H_5\text{-CO-CHOH-}C_6H_5 + ArNH_2 \rightarrow C_6H_5CH(NHAr)\text{-CO-}C_6H_5 + H_2O$$

As exaplained (*3*), the amine group initially attacks the carbonyl position to yield an unstable α-hydroxy imine [$PhC(=NAr)CHOHPh$] which tautomerizes to the α-amino ketone.

Several points about the previous work need clarification. Cameron's group ran most of their reactions at 100° C., and under these conditions found that *o*-substituted anilines would not react with benzoin. Weckowicz, however, had previously shown that anthranilic acid reacted smoothly with aniline in the melt at higher temperatures. We confirm this. This study was extended to the *m*- and *p*-aminobenzoic acids. The expected *m*- and *p*-(desylamino)benzoic acids

$$C_6H_5CH(COC_6H_5)\text{—}NHC_6H_4COOH$$

were formed in about the same yields as that found for the ortho isomer.

Weckowicz treated his *N*-desylanthranilic acid with an excess of phenylhydrazine in acetic acid and obtained a compound, m.p. 229–230°, for which the empirical formula $C_{33}H_{27}N_5$ was suggested based on analytical data. Since this is the melting point of benzoin phenylosazone and since his analytical data correspond better with the osazone formulation ($C_{26}H_{22}N_4$) than with the C_{33} formula, we have repeated this reaction. We find that the substance of m.p. 229–230° is indeed the phenylosazone and we find that the other two (desylamino)benzoic acids as well as *p*-(desylamino)phenylacetic acid also give rise to this osazone:

$$PhCOCHPh\text{-}NHAr + 3PhNHNH_2 \rightarrow PhNHN{=}CPh\text{-}CPh{=}NNHPh + ArNH_2 + PhNH_2 + NH_3 + H_2O.$$

The Schiff base reported (*2*) by Emerson and co-workers from the reaction of benzoin and *p*-ethylaniline is surely

Table I. (Desylamino)benzoic Acids

Isomer	M.P., ° C.	Anal., % N, Found, (Calc'd., 4.23)
Ortho	226.5–228.5 (dec., gas)[a]	4.25
Meta	182–184	4.38
Para	246–256 (dec., gas)[b]	4.28

[a] Weckowicz reported m.p. 231–232° (*5*).
[b] This compound turns bright yellow at 235°.

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the desylamine, namely, α-phenyl-α-(*p*-ethylanilino)acetophenone, $C_2H_5C_6H_4NHCHPh\text{-}CO\text{-}Ph$, rather than the reported hydroxy imine, $C_2H_5C_6H_4N = CPh\text{-}CHOH\text{-}Ph$.

EXPERIMENTAL

Mixtures of 8.5 grams (0.04M) of benzoin with 5.5 grams (0.04M) of each of the three aminobenzoic acids were heated without solvent in an oil bath to 180°. All three mixtures lost water at as low a temperature as 130°, rapidly at 160–170°. The crude *o*- and *p*-(desylamino)benzoic acids solidified in the bath, the meta isomer on cooling. After two crystallizations from glacial acetic acid the *o*-, *m*- and *p*-(desylamino)benzoic acids were obtained in yields of 5.9, 5.6, and 5.9 grams, respectively (48, 46, 48%). For analysis, the para compound was recrystallized once more from acetic acid, the ortho compound from methanol, and the meta compound from a mixture of benzene and methanol. *p*-(Desylamino)phenylacetic acid, m.p. 189°, was obtained in a similar reaction. Our m.p. and analyses agreed with the melting point reported (*1*) and with the theoretical composition.

Small samples of the three (desylamino)benzoic acids and of *p*-(desylamino)phenylacetic acid were heated with an excess of phenylhydrazine in acetic acid. On cooling, all of the solutions gave abundant precipitates of yellow, crystalline benzoin phenylosazone, m.p. 229–230°. Mixed melting points with pure, authentic benzoic phenylosazone were not depressed.

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Viscosity of Sulfur Dioxide at 200° C. for Pressures Up to 3500 P.S.I.

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Experimental viscosities for sulfur dioxide have been determined at 200° C. and pressures ranging from 250 to 3500 p.s.i.g. using a transpiration type viscometer. The temperature of 200° C. was arbitrarily selected since it is somewhat above the critical temperature of sulfur dioxide (T_c = 430.7° K.). The pressure was varied beyond the critical pressure of the substance, P_c = 1143 p.s.i.a., so that the viscosity behavior of sulfur dioxide in the critical region would be well defined.

INCREASING interest in the area of transport properties makes it necessary that viscosities, thermal conductivities, and self-diffusivities be established both at normal pressures and at the high pressures required to define the dense phase region. Investigations of this type have been conducted by Lohrenz (*8*), who measured viscosities of light hydrocarbons in their liquid state with a falling cylinder viscometer, and by Comings, Mayland, and Egly (*4*), who determined viscosity values for a number of gases at elevated pressures by the use of a transpiration-type viscometer.

Individual viscosity correlations have been presented in the literature for several pure substances at high pressures in the dense gaseous and liquid phases (*2*, *11*). This information is largely restricted to substances of a nonpolar nature. Theiss (*13*) has developed a reduced state viscosity correlation for water in the gaseous and liquid states from the experimental data available in the literature for this substance. Shimotake (*10*) used a transpiration-type viscometer to establish the viscosity of ammonia for temperatures of 100°, 150°, and 200° C. and pressures up to 5000 p.s.i. and used these data to develop a reduced state viscosity correlation for this substance.

To expand the information on the viscosity behavior of polar substances, experimental viscosities for sulfur dioxide have been determined in this study. Such measurements are desirable, since the only viscosity values reported for sulfur dioxide at high densities are those of Awbery and Griffiths (*1*) and Stakelbeck (*12*) for the liquid region and meager and scattered data presented by the latter investigator for the gaseous region. The present study was particularly concerned with the establishment of the viscosity behavior of sulfur dioxide in the vicinity of the critical point, since no experimental viscosities have been reported for this region.

EXPERIMENTAL PROCEDURE AND RESULTS

A transpiration-type viscometer was used with an approach similar to that described previously (*10*) to determine experimental viscosities of sulfur dioxide at 200° C.