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[Contribution No. 98 from the Department of Chemistry, University of Tennessee]

The Catalytic Hydrogenation of the Benzene Nucleus. VII. The Hydrogenation of Benzilic Acid

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The half-hydrogenated products of benzilic acid have been analyzed by means of the color developed by benzilic acid in sulfuric acid. It has been demonstrated that this color is influenced by the partially hydrogenated product, and an explanation given. It has been shown that benzilic acid is almost five times more readily adsorbed on platinum catalyst than phenylcyclohexylglycolic acid.

In an earlier publication[1] it was demonstrated that the rate of hydrogenation of a compound containing two benzene rings was essentially the same as that of the corresponding half-hydrogenated compound which contained one benzene and one cyclohexane ring. However, the original material was largely converted to the half-hydrogenated intermediate before complete saturation. Apparently the composition of a partially hydrogenated sample was determined by the adsorption characteristics of the unhydrogenated and half-hydrogenated materials rather than by their individual hydrogenation rate constants. For diphenylacetic acid, analyses by esterification rates indicated that the half-hydrogenated material was essentially pure phenylcyclohexylacetic acid; for diphenylglycolic (benzilic) acid, a similar situation was not found. The following gives the details of analysis of mixtures of these two acids together with the calculation of their relative adsorption on platinum catalyst.

Experimental

The preparations of benzilic and phenylcyclohexylglycolic acids have been previously described.[1]

Dicyclohexylglycolic acid was prepared by the complete hydrogenation of benzilic acid. All hydrogenations were carried out in a standard low-pressure Parr catalytic reduction apparatus using Adams platinum catalyst and acetic acid solvent.

A Beckman model DU ultraviolet spectrophotometer and a Coleman model 14 universal spectrophotometer were used for obtaining absorption spectra.

Analyses.—An investigation of the ultraviolet absorption of benzilic and phenylcyclohexylglycolic acids in ethanol solution showed that use of this property could not be made for following the course of the hydrogenations. The primary difference between the absorption curves is that of intensity only, see Fig. 1. However, benzilic acid develops a deep red color when dissolved in concentrated sulfuric acid.[2] The absorption spectrum of this solution is shown in Fig. 2. At 500 mμ similar solutions of phenylcyclohexylglycolic or dicyclohexylglycolic acids do not absorb. In addition, the benzilic acid "solution" was found to obey Beer's law over the concentration range of 1 to 8 micrograms per ml. Since it appeared that partially hydrogenated mixtures could be analyzed by this method, identical samples of benzilic acid were partially hydrogenated and the catalyst and solvent removed. Solutions of the resulting solids in sulfuric acid were compared with standard benzilic acid solutions, and the curve (dotted line) shown in Fig. 3 obtained.

A material balance calculation shows that this curve is impossible, for the minimum amount of benzilic acid present at any stage of the hydrogenation is represented by curve A in the figure. Further investigation showed that the spectral transmission of the solutions made from the partially hydrogenated benzilic acid were considerably different from those of pure benzilic acid. A new set of standards was made up from various amounts of phenylcyclohexylglycolic acid plus equimolecular mixtures of dicyclohexylglycolic and benzilic acids. The solids were completely dissolved in ether, the solvent evaporated, and sulfuric acid then added. By comparing half-hydrogenated benzilic acid with these standards it was found that 17.5% of benzilic acid was present. Since there must be an equal number of moles of completely hydrogenated product, 65% of the intermediate phenylcyclohexylglycolic acid was present.

Discussion

Colorimetric Standards.—It is known that certain carboxylic acids are ionized in sulfuric acid as[3]

$$\mathrm{RCOOH} + 2\mathrm{H_2SO_4} \longrightarrow \mathrm{H_3O^+} + 2\mathrm{HSO_4^-} + \mathrm{RCO^+}$$

It is also known that in sulfuric acid, diphenylcarbinol and triphenylcarbinol ionize thus[4]

$$(\mathrm{C_6H_5})_3\mathrm{COH} + 2\mathrm{H_2SO_4} \longrightarrow (\mathrm{C_6H_5})_3\mathrm{C^+} + \mathrm{H_3O^+} + 2\mathrm{HSO_4^-}$$

$$(\mathrm{C_6H_5})_2\mathrm{CHOH} + 2\mathrm{H_2SO_4} \longrightarrow (\mathrm{C_6H_5})_2\mathrm{CH^+} + \mathrm{H_3O^+} + 2\mathrm{HSO_4^-}$$

and that triphenylacetic acid liberates carbon monoxide.[5]

Since benzilic acid slowly liberates a gas (CO) when dissolved in sulfuric acid, one might expect a reaction such as

$$(\mathrm{C_6H_5})_2\mathrm{COHCOOH} + 4\mathrm{H_2SO_4} \longrightarrow (\mathrm{C_6H_5})_2\mathrm{C^{++}} + 2\mathrm{H_3O^+} + 4\mathrm{HSO_4^-} + \mathrm{CO}$$

If such a reaction were correct, the use of colorimetric standards made from pure benzilic acid for analyzing partially hydrogenated benzilic acid should have been successful. If macroscopic crystals of benzilic and phenylcyclohexylglycolic acid are dissolved in sulfuric acid, the color charac-

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(1) H. A. Smith, D. M. Alderman, Jr., C. D. Shacklett and C. M. Welch, This Journal, **71**, 3772 (1949).

(2) *Cf.* "Beilstein's Handbuch der organischen Chemie," 4th ed., Vol. X, Verlag Julius Springer, Berlin, Germany, 1927, p. 342.

(3) H. P. Treffers and L. P. Hammett, This Journal, **59**, 1708 (1937).

(4) A. Hantzsch, *Ber.*, **54**, 2573 (1921); H. A. Smith and R. J. Smith, This Journal, **70**, 2400 (1948); C. M. Welch and H. A. Smith, *ibid.*, **72**, 4748 (1950).

(5) A. Bistrzycki and E. Reintki, *Ber.*, **38**, 839 (1905); A. Bistrzycki and L. Mauron, *ibid.*, **43**, 2883 (1910); H. R. Dittmar, *J. Phys. Chem.*, **33**, 533 (1929).

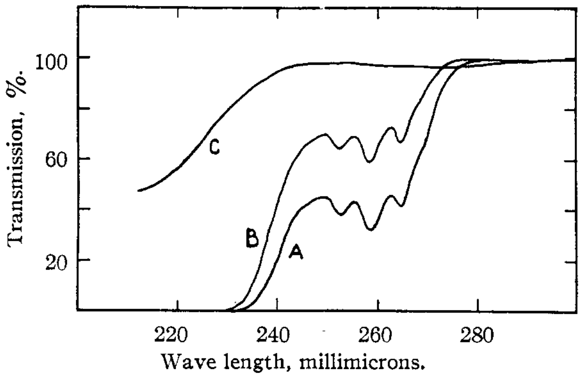


Fig. 1.—Spectral transmission curves for benzilic (A), phenylcyclohexylglycolic (B) and dicyclohexylglycolic (C) acids; concentration = 0.001 *M* (in 95% ethanol).

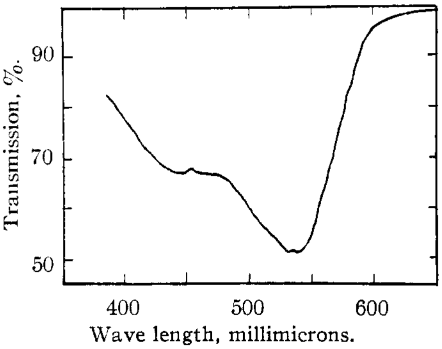
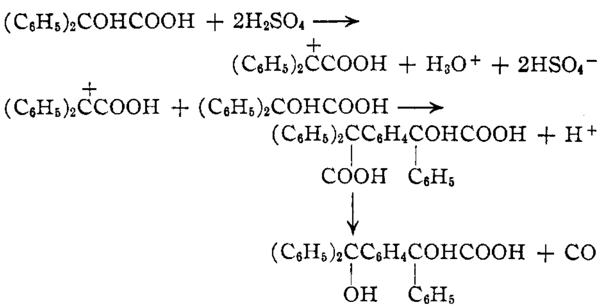


Fig. 2.—Spectral transmission of benzilic acid in sulfuric acid; concenrration = 5.0 micrograms per milliliter.

teristics of the solution are primarily those of solutions made from pure benzilic acid. However, if the crystals are dissolved in an inert solvent, the solvent evaporated, and sulfuric acid added, the solutions are different from those of pure benzilic acid, but like those of the products of partial hydrogenation. It seems probable that the reaction which takes place is



$$(C_6H_5)_2COHCOOH + 2H_2SO_4 \longrightarrow (C_6H_5)_2\overset{+}{C}COOH + H_3O^+ + 2HSO_4^-$$

$$(C_6H_5)_2\overset{+}{C}COOH + (C_6H_5)_2COHCOOH \longrightarrow (C_6H_5)_2\underset{COOH}{C}C_6H_4\underset{C_6H_5}{C}OHCOOH + H^+$$

$$\downarrow$$

$$(C_6H_5)_2\underset{OH}{C}C_6H_4\underset{C_6H_5}{C}OHCOOH + CO$$

Further ionization and polymerization are, of course, probable. Evidence for this type reaction may be found in the literature.[6] The phenyl group of phenylcyclohexylglycolic acid would also undergo reaction with the carbonium ion formed from benzilic acid, leading to polymeric ions which would contain cyclohexyl groups in place of phenyl groups, and might be expected to greatly influence the color of the solutions. The reaction is probably complicated to some extent by sulfonation and side reactions.

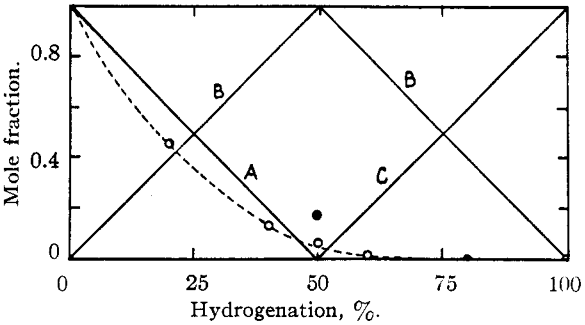


Fig. 3.—Variation in mole fraction of A, B and C for reaction $A \xrightarrow[Pt]{H_2} B \xrightarrow[Pt]{H_2} C$ if $T_A \gg T_B$. O.....O gives variation of benzilic acid mole fraction with percentage. Hydrogenation as determined by comparison with standard solutions of benzilic acid in sulfuric acid. ● represents corrected result.

Kinetic Results.—The hydrogenation of benzilic acid, and certain other compounds containing two benzene rings, takes place in two steps

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

where A and C are the unhydrogenated and totally hydrogenated materials and B is the intermediate with one ring saturated; k_1 and k_2 are first order rate constants.[7] For a homogeneous reaction, the composition of the reaction mixture at any time, t, depends on the relative magnitudes of k_1 and k_2. In catalytic hydrogenations of the type studied, the composition depends on the relative adsorption tendencies, T_A and T_B, of A and B on the platinum catalyst. It is assumed that T_C is negligible. If $T_A \gg T_B$, the course of the reaction is that shown in Fig. 3. This is the behavior found for diphenylacetic acid and diphenylmethane.[1] If $T_A \ll T_B$, the concentration of B is negligible, and C is formed at the same rate that A disappears. For an intermediate situation, one may calculate the ratio T_A/T_B by the following method.

The equilibrium existing on the catalyst surface is assumed to be

$$\text{adsorbed A} + \text{B} \rightleftarrows \text{adsorbed B} + \text{A}$$

The hydrogenation reactions of A and B by themselves are zero order with respect to the concentration of the hydrogen acceptor, so that all of the catalyst sites should be covered with A or B throughout the reaction. Furthermore, since both hydrogenation reactions involve the saturation of the phenyl group, it is assumed that the same total number of sites is available to either A or B, and it is already known that the rate constants are the same for hydrogenation of either compound.[1]

The equilibrium constant for the adsorption is $K = \sigma_B C_A/\sigma_A C_B$ where σ_A and σ_B are the fractions of catalyst sites occupied by adsorbed benzilic and phenylcyclohexylglycolic acids. Also, the rates of consumption of A and of accumulation of B are

$$-dC_A/dt = k\sigma_A p_{H_2}$$

and

$$dC_B/dt = k(\sigma_A - \sigma_B)p_{H_2}$$

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[6] A. Bistrzycki and L. Mauron, ref. 5; A. Bistrzycki and W. Niederberger, *Helv. Chim. Acta*, **11**, 261 (1928).

[7] H. A. Smith, D. M. Alderman and F. W. Nadig, THIS JOURNAL, **67**, 272 (1945).

from which it may be readily shown that

$$\frac{\mathrm{d}C_B}{\mathrm{d}C_A} = \frac{KC_B}{C_A} - 1$$

This may be integrated to obtain the expression

$$\log \frac{C_A}{C^0_A} = \frac{1}{K - 1} \log \left[1 - (K - 1)\frac{C_B}{C_A}\right]^{8}$$

where C^0_A is the initial concentration of benzilic acid.

Since analysis of the half-hydrogenated mixture gave 65% B, 17.5% A and 17.5% C, starting with 100% A, one may calculate K from these data. The result gives $K = 0.22$, and T_A/T_B (which equals σ_A/σ_B when $C_A = C_B$) = 4.6. Thus it appears that benzilic acid is 4.6 times more readily adsorbed on the platinum catalyst than phenylcyclohexylglycolic acid.

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(8) The mathematical steps are: $\mathrm{d}\frac{C_B}{C_A} = \frac{C_A\mathrm{d}C_B - C_B\mathrm{d}C_A}{C^2_A}$ whence $\frac{\mathrm{d}C_B}{\mathrm{d}C_A} = \frac{C_A\mathrm{d}\frac{C_B}{C_A}}{\mathrm{d}C_A} + \frac{C_B}{C_A} = \frac{KC_B}{C_A} - 1$. Rearranging $\frac{\mathrm{d}C_A}{C_A} = \frac{\mathrm{d}\frac{C_B}{C_A}}{(K - 1)\frac{C_B}{C_A} - 1}$. When this is integrated, and C_B set equal to zero when $C_A = C^0_A$, the expression given in the text is obtained.

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF S. B. PENICK & COMPANY]

The Glycosides of the Seeds of *Strophanthus amboensis* E. and Pax

BY M. R. SALMON, ROBERT FOPPIANO AND W. G. BYWATER

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The seeds of *Strophanthus amboensis* E. and Pax were found to contain sarveroside, intermedioside, panstroside and a new glycoside that has not previously been found in *Strophanthus*. We also obtained Reichstein's crystallizate 790.

Continuing our examination of the glycosides of *Strophanthus*[1] we wish to report our investigations of the seeds of another species which has not previously been described in detail. The seeds were collected in the extreme south of Angola. The collection was supervised and samples identified as *Strophanthus amboensis* E. and Pax by John Gossweiler, botanist, Service of Agriculture, Luanda, Angola, whom we wish to thank for his coöperation.

The seeds were processed as previously described. We obtained 0.69% crude glycosides from the ether extract and 4.48% of crude product from the chloroform extract. The ether soluble fraction yielded sarveroside[2] and intermedioside (formerly Reichstein's substance 761).[3] The chloroform extract yielded intermedioside and panstroside (formerly Reichstein's substance 762)[4] and a new glycoside which has not previously been found in *Strophanthus* seeds, as well as a crystallizate 790. We obtained 0.3% of sarveroside, 0.6% of intermedioside, 0.4% of panstroside, 0.1% of crystallizate 790 and 0.05% of the new glycoside.

Crystallizate 790 has recently been described by Euw, Hess, Speiser and Reichstein[4b] as a mixture of three to five difficultly resolvable components which simulate sarmentocymarin in properties. Sarmentocymarin differs from crystallizate 790 in carbon analysis and ultraviolet absorption spectrum and by crystallizing as a high melting form from acetone and ether.

The new glycoside melted at 232–240° and had a rotation of $[\alpha]_D$ −25.2° The Keller–Kiliani test was negative and Legal test positive. The ultraviolet absorption spectrum showed the maximum at 216–218 mμ which is characteristic of the unsaturated lactone ring of the cardiac glycosides. The analysis does not distinguish between several possible formulas.

We believe that this glycoside is different from substance 792 isolated by Euw and Reichstein[5] from the seeds of *S. petersianus*. The rotations of the two substances are the same but they differ in melting point, carbon analysis and the color test with 84% sulfuric acid. We failed to obtain a lower melting form by recrystallization from water which appears to be characteristic of substance 792.

In addition to *S. amboensis*, sarveroside, intermedioside and panstroside have been found in *S. schuchardti*,[1b] *sarmentosus*,[6] *courmontii*[7] and *gerrardi*[8] and the latter two glycosides are also found in *S. intermedius*.[1,4b] The occurrence of intermedioside in *S. amboensis* has previously been mentioned briefly.[3]

Experimental

The light brown seeds had 4.1% moisture and 26% fat. Slices of seeds treated with 84% sulfuric acid became tan (2 min.), brown (5 min.), and then purple (30 min.).

The seeds (200 g.) were extracted and sarveroside, intermedioside and panstroside were isolated, purified and characterized as previously described.[1] The yield and physical constants of these glycosides are shown in Table I. Each of these glycosides showed no melting point depression when mixed with the corresponding glycosides isolated from *S. sarmentosus* or *S. intermedius* and the color tests with 84% sulfuric acid were identical with those previously described.

A major portion of the intermedioside and panstroside crystallized when the chloroform soluble fraction was taken up in acetone. The mother liquor from these crystals was

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(1) (a) M. R. Salmon, Eric Smith and W. G. Bywater, THIS JOURNAL, **73**, 3824 (1951); (b) Robert Foppiano, M. R. Salmon and W. G. Bywater, *ibid.*, **74**, 4537 (1952).

(2) A. Buzas, J. v. Euw and T. Reichstein, *Helv. Chim. Acta*, **33**, 465 (1950).

(3) J. P. Rosselet and A. Hunger, *ibid.*, **34**, 1036 (1951).

(4) (a) J. v. Euw and T. Reichstein, *ibid.*, **33**, 522 (1950); (b) J. v. Euw, H. Hess, P. Speiser and T. Reichstein, *ibid.*, **34**, 1821 (1951).

(5) J. v. Euw and T. Reichstein, *ibid.*, **33**, 1551 (1950).

(6) (a) Sarveroside: J. v. Euw, A. Katz, J. Schmutz and T. Reichstein, *Pharm. Acta Helv.*, **24**, 178 (1949), and reference 2; (b) *panstroside:* J. v. Euw and T. Reichstein, *Helv. Chim. Acta*, **33**, 2153 (1950); (c) intermedioside: mentioned briefly in reference 3 and confirmed by Smith and Salmon (unpublished).

(7) J. v. Euw and T. Reichstein, *ibid.*, **33**, 1006 (1950).

(8) J. v. Euw and T. Reichstein, *ibid.*, **33**, 522 (1950).