[CONTRIBUTION NO. 1591 FROM THE STERLING CHEMISTRY LABORATORY, YALE UNIVERSITY]

The Reaction of Thionyl Chloride with Benzilic and Chlorodiphenylacetic Acids. Interconversion of Chlorodiphenylacetic Acid Anhydride and Chlorodiphenylacetylbenzilic Acid Chloride[1]

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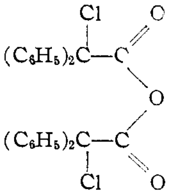
RECEIVED NOVEMBER 4, 1959

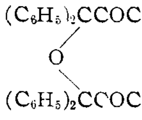
The reaction of thionyl chloride with chlorodiphenylacetic acid has been shown to form two isomeric products, $C_{28}H_{20}Cl_2O_3$, characterized as chlorodiphenylacetic acid anhydride and chlorodiphenylacetylbenzilic acid chloride. The two isomers are interconverted in the presence of acid catalysts, equilibration resulting in a mixture of 70% anhydride and 30% acid chloride.

In the course of studies on the pyrolysis of benzilic acid and its derivatives, reported earlier,[3] we had occasion to reinvestigate the reaction of benzilic acid with thionyl chloride. This reaction was first studied by Meyer,[4] who showed that benzophenone, carbon monoxide and sulfur dioxide were produced in the absence of solvents, while, somewhat later, Stollé claimed[5a] that other products could be obtained if the reagents were heated in solvents. This paper describes our studies on the characterization of these products, and on a novel reversible isomerization of chlorodiphenylacetic acid anhydride to an ester-acid chloride.

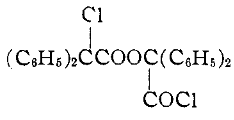
Stollé reported that product A, $C_{28}H_{20}Cl_2O_3$, m.p. 129°, could be obtained if benzilic acid and thionyl chloride were heated in refluxing carbon tetrachloride or ethyl acetate. He found that this material could also be obtained from the reaction of chlorodiphenylacetic acid with thionyl chloride, and assigned to A the anhydride structure I.



I



II



$(C_6H_5)_2\overset{Cl}{C}COO\underset{COCl}{C}(C_6H_5)_2$

III

This assignment was given some support by the fact that A could be converted with aniline in ether to anilinodiphenylacetic acid and anilinodiphenylacetanilide, although it may be noted that this evidence does not rule out other structures such as III. In some experiments, instead of A, an isomeric product B, m.p. 119°, was isolated, for which Stollé tentatively suggested, without confirmatory evidence, the diacid chloride structure II.

In our investigations, attempts to reproduce Stollé's results were, at first, unsuccessful. In fact, a 96% yield of benzophenone was recovered from the reaction of six moles of thionyl chloride with one mole of benzilic acid in dilute refluxing carbon tetrachloride solution. Using more concentrated solutions, other reactions occurred to an increasing extent, although benzophenone remained the major and only isolable product. It was found, however, that when chlorodiphenylacetic acid was used instead of benzilic acid, compounds A and B were readily obtained, and further attempts to duplicate the results of Stollé using benzilic acid were abandoned. It is probable that the experimental conditions used by Stollé were such that a substantial preliminary conversion of benzilic acid to chlorodiphenylacetic acid had occurred. This transformation is known to take place with thionyl chloride under mild conditions.[5]

From the reaction of 3.5 moles of thionyl chloride with one mole of chlorodiphenylacetic acid in refluxing carbon tetrachloride either A or B could be obtained depending on the conditions. When the reaction was followed spectroscopically, it was found that the 5.82 μ band of the starting acid was slowly replaced by two bands at 5.58 and 5.71 μ. If the reaction was stopped at the point of disappearance of the 5.82 μ band, compound B, m.p. 120–120.5°, could be isolated in 27% yield. With longer refluxing of the reaction solution, the bands at 5.58 and 5.71 μ were gradually and almost, completely replaced by two more at 5.48 and 5.69 μ. By working up the reaction when no further changes in the infrared spectrum were observed, a 25% yield of compound A, m.p. 129.5–130.5°, was obtained. The conversion of B to A under these conditions will be discussed later.

The properties of A were clearly compatible with the chlorodiphenylacetic anhydride structure I suggested by Stollé. (i) The infrared spectrum, showing bands at 5.49 and 5.70 μ ($CHCl_3$) was very similar to the spectrum of the model compound, diphenylacetic anhydride (bands at 5.51 and 5.72 μ); (ii) reaction of A with sodium methoxide followed by hydrolysis gave crude methoxydiphenylacetic acid in 98% yield; and, most conclusively, (iii) A was identical with authentic anhydride, synthesized from chlorodiphenylacetic acid at room temperature using methoxyacetylene, a very mild reagent for converting an acid to its anhydride.[6]

Compound B was shown not to be II, the structure suggested by Stollé. The two sharp and equally intense bands at 5.58 and 5.71 μ in the infrared spectrum of B do not fit the diacid chloride

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[1] Taken from the doctoral dissertation of P. S. Wharton, submitted to the Graduate School of Yale University in partial fulfillment of the requirements for the Ph.D. degree, June, 1959.

[2] Procter and Gamble Fellow, 1957–1958.

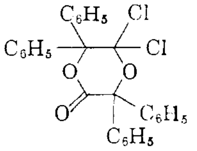
[3] H. H. Wasserman and H. E. Zimmerman, THIS JOURNAL, **72**, 5787 (1950); H. H. Wasserman, T.-C. Liu and E. R. Wasserman, *ibid.*, **75**, 2056 (1953); H. H. Wasserman, H. W. Ackerman, H. H. Wotiz and T-C. Liu, *ibid.*, **77**, 973 (1955).

[4] H. Meyer, *Monatsh. Chem.*, **22**, 777 (1901).

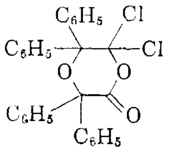
[5] (a) R. Stollé, *Ber.*, **43**, 2471 (1910); (b) S. A. Setlur and V. V. Nadkarny, *Proc. Indian Acad. Sci.*, **12A**, 266 (1940); *C. A.*, **35**, 1398 (1941).

[6] J. F. Arens and P. Modderman, *Proc. Koninkl. Ned. Akad. Wetenschap.*, **53**, 1163 (1950); *C. A.*, **45**, 6152 (1951); G. Eglinton, E. R. H. Jones, B. L. Shaw and M. C. Whiting, *J. Chem. Soc.*, 1860 (1954).

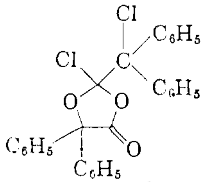
formulation but, rather, indicate two different carbonyl functions, one of which (5.58 μ) corresponds to an acid chloride, the other (5.71 μ) being in good accord with the absorption of an ester group. Of the possible structures (I-VI) which one may write for B, only the ester-acid chloride III fits the spectroscopic data. Further support for the ester-acid chloride structure is found in the chemical behavior of B. (a) First of all, drastic treatment of B with sodium methoxide, followed by hydrolysis yielded a mixture of benzilic acid (53%) and methoxydiphenylacetic acid (43%), thus showing the presence of an unrearranged α-substituted diphenylacetic acid skeleton in B. (b) Reaction of B with excess sodium methoxide under milder conditions yielded a product, showing carbonyl absorption at 5.72 μ only. The analysis of this material, assigned structure VII, indicated the replacement of only one chlorine atom by methoxyl. (c) Finally, on standing in aqueous acetone for several days, B was transformed to a non-crystalline product showing 5.71 and 5.82 μ absorption. The latter two reactions (b and c) thus correspond to the conversion of the acid chloride group to an ester and carboxylic acid, respectively.



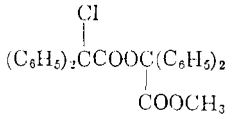
IV



V



VI



$$(C_6H_5)_2\overset{\displaystyle Cl}{\overset{|}{C}}COO\underset{\displaystyle COOCH_3}{\underset{|}{C}}(C_6H_5)_2$$

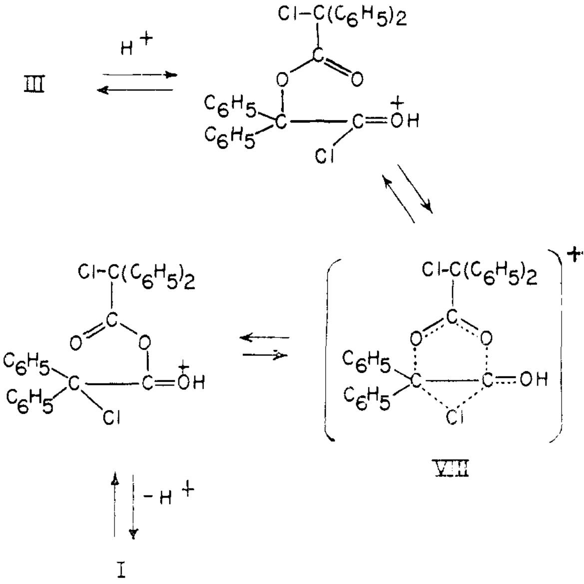
VII

One must now account for the interesting conversion of B(III) to A(I) discovered while observing the spectral changes in the reaction of thionyl chloride with chlorodiphenylacetic acid. It was shown that B is actually an intermediate in the formation of A by heating B in refluxing carbon tetrachloride solution. Isomerization to A readily took place in the presence of hydrogen chloride, boron trifluoride or even traces of water, although no reaction occurred in the absence of Lewis acids when both solvent and apparatus were thoroughly dried.

It was found that the isomerization did not go to completion. Instead, an equilibrium mixture of 70% A and 30% B was obtained, starting from either of the two components, as determined spectroscopically by comparison with standard mixtures. From the equilibrium mixture, compounds A and B could be recovered in 60 and 20% yields, respectively, and the residues, analyzed spectroscopically, consisted of a mixture of A and B in the expected ratio.

It was established that the isomerization does not occur through cleavage of A and B by hydrogen chloride to chlorodiphenylacetic acid and chlorodiphenylacetyl chloride, followed by recombination of these substances to form the observed equilibrium mixture. When an equimolar mixture of chlorodiphenylacetic acid and chlorodiphenylacetyl chloride was heated in refluxing carbon tetrachloride in the presence of hydrogen chloride, no appreciable amounts of A or B were formed. The acid chloride remained unaffected as shown by spectroscopic evidence (60% was actually recovered), while the acid underwent total decomposition to a carboxyl-free product, showing a broad maximum at 5.70 μ.[7]

It is suggested that the isomerization proceeds by an intramolecular rearrangement such as that shown, in which, it may be noted, the transition state VIII allows a considerable delocalization of charge. Related rearrangements have been well established. They include the interconversion of the *sym-* and *unsym*-phthaloyl chlorides,[8] the interchange of ester-acid chlorides of succinic and glutaric acids,[9] and the rearrangement of γ-alkoxybutyryl chlorides and γ- and δ-alkoxyvaleryl chlorides to the corresponding chloroesters.[10]



Experimental[11]

Chlorodiphenylacetic Acid.[12]—Benzilic acid (20.0 g., 0.088 mole), 8 ml. (0.12 mole) of acetyl chloride and 5 ml. of methylene chloride were mixed in a 50-ml. Skau tube. An air condenser and drying tube were attached to the Skau tube which was shaken at intervals. After 90 minutes the solid mass had changed to a clear, pale yellow, mobile liquid, which was left overnight. The crystals which had formed

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[7] By heating the acid alone in refluxing carbon tetrachloride, this product was shown to contain *ca* 12% of benzilide (the lactide of benzilic acid), the amorphous residue presumably consisting of polyester.

[8] E. Ott, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 528.

[9] B. H. Chase and D. H. Hey, *J. Chem. Soc.*, 553 (1952); J. Cason and R. D. Smith, *J. Org. Chem.*, **18**, 1201 (1953).

[10] V. Prelog and S. Heimbach-Juhász, *Ber.*, **74**, 1702 (1941) F. F. Blicke, W. B. Wright and M. F. Zienty, THIS JOURNAL, **63**, 2488 (1941); K. B. Wiberg, *ibid.*, **74**, 3957 (1952).

[11] All m.p.'s are uncorrected and were determined in soft glass capillary tubes in a Hershberg apparatus. Infrared spectra were recorded on a Perkin-Elmer model 21 spectrophotometer, calibrated against the spectrum of the atmosphere.

[12] *Cf.* E. L. Eliel, C. Herrmann and J. T. Traxler, THIS JOURNAL, **78**, 1193 (1956).

were broken up and centrifuged, the dry solid pulverized and allowed to stand over solid potassium hydroxide at *ca.* 1 mm. for 12 hours to remove the very persistent hydrogen chloride and acetic acid; yield 13.3 g. (62%), m.p. 119° dec., reported[13] 118–119° dec.

Chlorodiphenylacetic Anhydride.—The authentic anhydride was prepared by treating a stirred solution of 6.885 g. (0.028 mole) of chlorodiphenylacetic acid in 20 ml. of methylene chloride (cooled in ice-water) with a solution of 0.98 ml. (0.014 mole) of methoxyacetylene in 5 ml. of methylene chloride, added dropwise. The reaction mixture was allowed to stand overnight, the solvent was removed and the resulting solid crystallized from a mixture of 3 ml. of benzene and 10 ml. of hexane to give 4.69 g. (71%) of crude anhydride, m.p. 127–129°. Further crystallization from the same solvent raised the m.p. to 129.5–130.5°.

Compound A.—A solution of 500 mg. (2.0 mmoles) of chlorodiphenylacetic acid in 5 ml. of carbon tetrachloride and 0.5 ml. (6.9 mmoles) of thionyl chloride was refluxed until the infrared spectrum of the reaction solution changed inappreciably with time (*ca.* 40 hr.). The reaction solution was worked up as for compound B (below) to give 155 mg. (32%) of crude A, m.p. 120–127°. Crystallization at 5° from 0.3 ml. of a 1:1 mixture of benzene–hexane gave 120 mg. (25%) of purified A, m.p. 128.5–129.5°. Further crystallization from the same solvent gave analytical material, m.p. 129.5–130.5°; 5.49 and 5.70 μ ($CHCl_3$). This compound was indistinguishable from the authentic anhydride with respect to m.p. and infrared spectrum. A mixed m.p. of the two showed no depression.

Anal. Calcd. for $C_{28}H_{20}Cl_2O_3$: C, 70.74; H, 4.24; Cl, 14.92. Found: C, 70.94; H, 4.27; Cl, 14.54.

Compound B.—A solution of 60 g. (0.24 mole) of chlorodiphenylacetic acid in 600 ml. of carbon tetrachloride and 65 ml. (0.89 mole) of thionyl chloride was refluxed until the infrared spectrum of the reaction mixture showed that no free acid remained (*ca.* 6 hr.). The solvent was evaporated under reduced pressure at room temperature, the resulting oil dissolved in 100 ml. of hexane, and the solvent evaporated again. This procedure was repeated with successive lots of hexane until the solution deposited white crystals (a total of 500 ml. of hexane was used). After standing overnight at room temperature (cooling resulting in oiling out), the solid was centrifuged from the liquor, which then deposited more crystals on cooling to 5°. The two batches of crystals were mixed to give 35 g. (61%) of crude B, m.p. 100–112°. No further solid could be obtained by evaporation or cooling of the residual liquor. Crystallization of 23.8 g. of the crude product from 15 ml. of ethyl acetate (acetonitrile could also be used) at room temperature gave 10.7 g. (27% yield overall) of almost pure B, m.p. 117–119°. The analytical sample from benzene showed m.p. 120–120.5°; 5.58 and 5.71 μ (CCl_4), 5.59 and 5.76 μ (KBr).

Anal. Calcd. for $C_{28}H_{20}Cl_2O_3$: C, 70.74; H, 4.24; Cl, 14.92. Found: C, 70.86; H, 4.34; Cl, 14.71.

The Interconversion of Compounds A and B.—Preliminary experiments showed that the isomerization resulted in an equilibrium mixture of 70% A and 30% B, as determined by comparison with infrared spectra of standard mixtures of A and B. Further reactions were, therefore, stopped when the spectrum of the reaction solutions approximated this composition. The slowness of the isomerization in the absence of catalysts was demonstrated by heating a solution of B in carbon tetrachloride and acetonitrile in stoppered flasks at 70°. After 3 days, material of unchanged m.p. was recovered by evaporation of the solvent.

A solution of 500 mg. of compound A or B in 5 ml. of carbon tetrachloride was gently refluxed while hydrogen chloride was passed slowly through the system. After ca. 5 hr. the solvent was removed and the residue crystallized from 0.7 ml. of benzene and 1.0 ml. of hexane at room temperature. In one run this gave 250 mg. (51%) of pure A, m.p. 129–130°. The filtrate was left overnight at 5° and gave a further 30 mg. (6%) of A, m.p. 127–129°. Storing the filtrate at −20° for one week yielded 104 mg. (21%) of B, m.p. 118–120°. Other runs gave *ca.* 20% of B by crystallization of the evaporated filtrates from ethyl acetate or acetonitrile.

The m.p. of various mixtures of the two isomers were taken to see if m.p. alone was a good criterion of purity: 100% A, 129–130°; 93%, 120–127°; 81%, 103–125°; 56%, 102–111°; 21%, 102–110°; 5%, 112–117°; 0%, 119–120°.

Hydrolysis of Compound B.—A solution of 445 mg. of B in 10 ml. of acetone and 1 ml. of water was allowed to stand at room temperature for 9 days. Small samples were removed periodically and the solvent evaporated. The infrared spectra of the residue (CCl_4) showed the gradual replacement of the 5.58 μ band of B by absorption at 2.9–3.4 μ and 5.82 μ; the 5.71 μ band remained unchanged throughout. An attempt to obtain a crystalline product from the acetone solution was unsuccessful.

Action of Sodium Methoxide on Compound B. (a) Methyl Ester of Chlorodiphenylacetylbenzilic Acid.—To a solution of 91 mg. (4.0 mmoles) of sodium in 4 ml. of magnesium-dried methanol was added 921 mg. (1.94 mmoles) of B. The solution was refluxed for 3 hours, during which time the two-phase system which separated was agitated. Water was then added and the mixture extracted with ether. After drying, the ether layer was filtered and the solvent removed to give 685 mg. of an oil showing absorption at 2.9 and 5.72 μ (CCl_4). The oil was dissolved rapidly in hot methanol and the solution cooled quickly to room temperature. Chunky crystals developed gradually; yield 193 mg. (21%), m.p. 103–109°. Two crystallizations from large volumes of methanol at 5° gave excellent, large, compact crystals, m.p. 112–113°. Analytical material was obtained by crystallization from a small quantity of benzene, m.p. 113.5–114°; 5.72 μ (CCl_4) with no absorption at 2.9 μ.

Anal. Calcd. for $C_{29}H_{23}ClO_4$: C, 73.96; H, 4.92; Cl, 7.53. Found: C, 74.42; H, 4.90; Cl, 7.39.

(b) Formation of Benzilic and Methoxydiphenylacetic Acids.—To a tube containing a solution of 44 mg. (1.9 mmoles) of sodium in 1 ml. of magnesium-dried methanol, was added 119 mg. (0.25 mmole) of B. The tube was sealed and heated at 140° for 22 hours. After the addition of 0.8 ml. of water the tube was resealed and reheated at 140° for 3 hours. The contents were then washed into a separatory funnel with water and extracted with ether. After acidification, the water layer was again extracted with ether. Removal of volatiles from the combined ether extracts gave 75 mg. of an oil, crystallization of which from carbon disulfide at 5° gave 30 mg. (53%) of benzilic acid, m.p. 147–148°, raised to 149–150° by further crystallization from benzene. The carbon disulfide filtrate was evaporated and the residue crystallized from a small volume of carbon disulfide–pentane at 5° to give 26 mg. (43%) of methoxydiphenylacetic acid, m.p. 102–104°, characterized by conversion to methoxydiphenylacetanilide and comparison with authentic material.

Action of Sodium Methoxide on Compound A.—Treatment of 119 mg. of A in a manner similar to that described in in (b) above (except that the period of heating with methoxide was 3 hr.) gave 119 mg. (98%) of crude methoxydiphenylacetic acid as an oil which slowly solidified, m.p. 93.5–97.5°. Crystallization from carbon disulfide–pentane gave 70 mg. (58%) of excellent, large needles, m.p. 100–102°. A further 33 mg. (27%), m.p. 100–102°, was obtained by concentrating the filtrate and adding more pentane.

Methoxydiphenylacetic Acid.—The authentic acid, for which a variety of melting points ranging from 102° to 112° is recorded in the literature,[14] was prepared from the reaction of chlorodiphenylacetyl chloride with methanolic silver nitrate.[15] The acid chloride[16] (2.651 g., 10 mmoles), m.p. 51–52°, and 1.697 g. (10 mmoles) of silver nitrate in 10 ml. of magnesium-dried methanol, containing 1.161 g. (5 mmoles) of silver oxide, was refluxed for 18 hours. Water (10 ml.) was then added and the mixture extracted twice with 10 ml. of ether. The combined ether extracts were washed twice with 10-ml. portions of water (the second wash gave no precipitate with hydrochloric acid) and dried over sodium sulfate. The solvent was removed to give 2.15

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[13] A. Bistrzycki and C. Herbst, *Ber.*, **36**, 145 (1903).

[14] For example, F. F. Blicke and C. E. Maxwell, THIS JOURNAL, **64**, 431 (1942); K. Ziegler and F. Thielmann, *Ber.*, **56**, 1740 (1923); H. Staudinger and St. Bereza, *Ann.*, **380**, 243 (1911).

[15] *Cf.* H. Klinger, *ibid.*, **390**, 371 (1912).

[16] Prepared according to H. Staudinger, *ibid.*, **356**, 51 (1907); A. McKenzie and J. S. W. Boyle. *J. Chem. Soc.*, **119**, 1131 (1921).

g. of an oil which was saponified for 1.5 hours in a refluxing solution of 0.85 g. of 86% potassium hydroxide in 10 ml. of ethanol. The solvent was removed, water added and the solution acidified and extracted with ether. After drying, the ether was removed to give 1.760 g. (73%) of an oil which solidified completely after seeding and removing all volatiles, m.p. 103–104°. Crystallization from carbon disulfide–pentane raised the m.p. to 107–108°.

Methoxydiphenylacetanilide.[17]—A solution of 100 mg. (0.41 mmole) of methoxydiphenylacetic acid in 1 ml. of methylene chloride was treated with 0.5 ml. (7 mmoles) of methoxyacetylene. The reaction mixture was allowed to stand for one hour at room temperature, volatiles were removed, and the residue was heated at 90° for 2 hours with a slight excess (45 mg., 0.48 mmole) of freshly distilled aniline. The product was dissolved in methylene chloride and washed, first with acid, and then with water. The solid obtained by evaporating the methylene chloride was crystallized from methanol at 5° to give 41 mg. (31%) of methoxydiphenylacetanilide, m.p. 150.5–151.5°, reported[17] 149–150°; 2.95 and 5.88 μ (CCl_4).

Action of Thionyl Chloride on Benzilic Acid.—A solution of 500 mg. (2.2 mmoles) of benzilic acid in 15 ml. of carbon tetrachloride, containing 1.0 ml. (14 mmoles) of thionyl chloride, was refluxed for 40 hours. The solvent was then evaporated and the excess thionyl chloride removed by adding, and subsequently evaporating, two 5-ml. portions of hexane. The resulting oil was dissolved in hexane and passed through a column of silica gel (11 g.). Elution with 20-ml. portions of 5% ether–hexane yielded 381 mg. (96%) of benzophenone, m.p. 49–50°.

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[17] *Cf.* H. Klinger, *Ann.*, **389**, 253 (1912).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, OKLAHOMA STATE UNIVERSITY, STILLWATER, OKLA.]

Orientation and Relative Reaction Rate Factors in Aromatic Substitution by the Benzenesulfonimido Radical

BY JAMES F. HEACOCK AND MARVIN T. EDMISON

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The orientation and the relative reaction rates of homolytic aromatic substitution by the benzenesulfonimido radical have been studied. The benzenesulfonimido radicals were generated by decomposing benzenesulfonyl azide thermally at 105–120° in an excess of the aromatic substrate or substrates. The total and partial relative reaction rate factors were determined by using a competitive method with benzene as a reference solvent. Of the aromatic compounds which were studied, most of those with "*meta*-directing substituents" did not react to produce the expected substitution products. Orientation in the resultant compounds indicated electrophilic substitution and relative reaction rate values were indicative of radical substitution.

Benzenesulfonamidation, by decomposition of benzenesulfonyl azide in aromatic substrates, has previously been studied by Curtius and co-workers[1] and more recently by Dermer and Edmison.[2]

In this study,[3] the competitive method was used to determine the relative rate of benzenesulfonamidation of various aromatic substrates, using benzene as the reference solvent. In the course of this work, it became evident that quantitatively there was some discrepancy between the isomer ratios found by Dermer and Edmison[2] and the isomer ratios found in the competitive determinations. The isomer ratios were reinvestigated and analyzed by an analytical procedure that the authors believe to be superior considering the nature of the reaction products.

Recently, it has been found that an electronegative substituent in the *p*-position of a phenyl radical imparts to the radical an electrophilic character[4–6]; it then is reasonable to assume that the proximity of the strongly electronegative sulfonyl group in the benzenesulfonimido radical also should render it electrophilic. The results of this experimentation are consistent with this hypothesis.

Experimental

Analytical Method.—The analyses were accomplished by using an infrared technique similar to that of Augood, Hey and Williams.[7] A Perkin–Elmer, model 12-C infrared spectrophotometer, with a 0.1-mm. fixed-thickness sodium chloride cell, was used. Dioxane was employed as a solvent.

A solution of 0.5 g. in 5 cc. of dioxane was prepared for each component to be analyzed, and the spectrum of the solution was scanned between 9.5 and 14.5 mμ. A wave length, at which it had a higher absorbance than the other components, was selected for each component. The absorptions at these wave lengths were checked for deviations from the Beer–Lambert law. In every case, the selected wave length had a negligible deviation with the exception of the 11.0 mμ absorption used in the analysis of *p*-benzenesulfonamidobenzoic acid. In this case, a correction was applied by means of a calibration curve. The weight per cent. was then determined from the absorbance, of the unknown solution, at the five selected wave lengths. Knowns were used in each case to prove that the chemical interactions of the various components were not so great as to give erroneous results.

Synthesis of the Isomeric Benzenesulfonanilides.—Three methods were used in the synthesis of the benzenesulfonanilide derivatives. In all three procedures, the corresponding arylamine was treated with benzenesulfonyl chloride in the presence of a base. When possible, a 10% sodium hydroxide solution was used as the reaction medium, but in a number of syntheses, the alkali caused undesirable hydrolysis or side reactions. In these latter syntheses, pyridine and toluene were used as reaction media. The isomeric benzenesulfonamidoanilines were prepared by the reduction of the corresponding benzenesulfonamidonitrobenzene derivatives with iron and acetic acid. Table I lists the derivatives. The melting points agreed satisfactorily with those reported earlier.

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[1] T. Curtius, *J. prakt. Chem.*, **125**, 303 (1930).

[2] O. C. Dermer and M. T. Edmison, THIS JOURNAL, **77**, 70 (1955).

[3] J. F. Heacock, Ph.D. Thesis, Oklahoma State University, 1959; research program supported by a Frederick Gardner Cottrell grant from the Research Corporation of New York. Authors also gratefully acknowledge valuable assistance of Dr. O. C. Dermer, Head, Department of Chemistry, Oklahoma State University.

[4] J. I. G. Cadogan, D. H. Hey and G. H. Williams, *J. Chem. Soc.*, 1425 (1955); Chang Shih, D. H. Hey and G. H. Williams, *ibid.*, 1885 (1958); D. H. Hey, B. W. Pengilly and G. H. Williams, *ibid.*, 1463 (1956); Chang Shih, D. H. Hey and G. H. Williams, *ibid.*, 2600 (1958).

[5] R. L. Dannley and M. Sternfeld, THIS JOURNAL, **76**, 4543 (1954).

[6] D. F. De Tar and A. A. Kazimi, *ibid.*, **77**, 3842 (1955).

[7] D. R. Augood, D. H. Hey and G. H. Williams, *J. Chem. Soc.*, 44 (1953).