EXPERIMENTAL

Oxidation of anisole. A solution of trifluoroperoxyacetic acid[5] (110 ml., 2.1 *M*) in methylene chloride was added dropwise over a two-hour period to a stirred solution of anisole (21.6 g.; 0.2 mole) in 100 ml. of methylene chloride maintained at 15–20°. Stirring was continued at 25° for thirty minutes at which time 95% of the peroxy acid had been consumed. The mixture was diluted with methylene chloride and washed with a 10% sodium bicarbonate solution. After drying the solvent was removed by distillation. The residual liquid was distilled through a semimicro Vigreux column to give anisole, 12.0 g., b.p. 51–53° (20 mm.) and fraction 2, 4.0 g., b.p. 55–90° (3 mm.).

Analysis of fraction 2 by gas-liquid chromatography at 190° on a column packed with DC 710 on firebrick indicated the presence of three components. Comparison of the chromatogram with those of authentic specimens showed that the constituents were anisole (4%), *o*-methoxyphenol (73–77%), and *p*-methoxyphenol (18–23%).

Fractional distillation of fraction 2 through a micro spinning band column at 4 mm. pressure yielded *o*-methoxyphenol, b.p. 53–55°, and *p*-methoxyphenol, b.p. 85–87°. The latter isomer was recrystallized from methylene chloride-hexane to give white plates, m.p. and mixed m.p. 53–54°.

Anal. Calcd. for $C_7H_8O_2$: C, 67.7; H, 6.48; phenolic acidity, 0.805 eq./100 g. Found for *o*-methoxyphenol: C, 67.5; H, 6.51; phenolic acidity, 0.80 eq./100 g. Found for *p*-methoxyphenol: C, 67.6; H, 6.53; phenolic acidity, 0.81 eq./100 g.

Oxidation of diphenyl ether. Trifluoroperoxyacetic acid in methylene chloride (110 ml. of 2.1 *M* solution) was added dropwise over a ninety-minute period to a stirred solution of diphenyl ether (34.4 g., 0.2 mole) in 120 ml. of methylene chloride at 20–25°. Fifteen minutes after the addition was complete 95% of the peroxy acid had been consumed. The dark brown mixture was washed with 10% sodium bicarbonate, dried, and the methylene chloride removed under vacuum. Unreacted diphenyl ether, 19.0 g.; b.p. 102–104° (7 mm.), was recovered by distillation through a Vigreux column.

The residual solid was fractionally sublimed at 60–80° and 0.5 mm. pressure. Each fraction was analyzed by gas-liquid chromatography at 200° on a column packed with DC-11 on firebrick at a helium flow-rate at 60 ml./min. Comparison of each chromatogram with those of authentic samples showed that the total sublimate (8.1 g.) contained *o*-phenoxyphenol (5.7 g.), *p*-phenoxyphenol (1.9 g.), and diphenyl ether (0.5 g.).

The first few fractions of sublimate were triturated with cold *n*-hexane and filtered. The insoluble crystalline material was recrystallized from *n*-hexane to give white needles melting at 103–104°. The melting point was undepressed on admixture with an authentic sample of *o*-phenoxyphenol.

Anal. Calcd. for $C_{12}H_{10}O_2$: C, 77.5; H, 5.42; phenolic acidity, 0.537 eq./100 g. Found: C, 77.8; H, 5.48; phenolic acidity, 0.525 eq./100 g.

The last few fractions melted at 77–81° and were recrystallized from *n*-hexane to give white plates melting at 82–83°. The melting point was undepressed on admixture with an authentic sample of *p*-phenoxyphenol.

Anal. Calcd. for $C_{12}H_{10}O_2$: C, 77.5; H, 5.42; phenolic acidity, 0.537 eq./100 g. Found: C, 77.9; H, 5.35; phenolic acidity, 0.54 eq./100 g.

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[5] W. D. Emmons and G. B. Lucas, *J. Am. Chem. Soc.*, 77, 2287 (1955). *Warning:* as used in the preparation of trifluoroperoxyacetic acid, a suspension of 90% hydrogen peroxide in methylene chloride could be detonated by a modification of the drop weight test method of F. Bellinger, *et al., Ind. Eng. Chem.*, **38,** 310 (1946). (See Tech. Bull. SC:-59-44, p. 17, Shell Chemical Co., for description of apparatus.)

The Decarbonylation of α-Anilino-α,α-diphenylacetic Acid by *p*-Toluenesulfonyl Chloride and Pyridine

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We have observed a novel decarbonylation of α-anilino-α,α-diphenylacetic acid (I), by the action of *p*-toluenesulfonyl chloride and pyridine, leading to the formation of benzophenone anil (II). The by-products (carbon monoxide and pyridinium *p*-toluenesulfonate) suggest that the reaction proceeds by formation of an unusual mixed anhydride, followed by a base-catalyzed elimination.

The reaction was discovered during an attempt to prepare the *N*-*p*-toluenesulfonyl derivative of the amino acid I. The acid was recovered unchanged after treatment with *p*-toluenesulfonyl chloride and aqueous sodium hydroxide (even under forcing conditions), but reacted smoothly when anhydrous pyridine was employed as the base. However, the reaction products were those described above; none of the expected tosyl derivative was isolated.

The base-catalyzed decomposition of α-(arylsulfonamido)carboxylic acids and acid chlorides has been reported previously by Wiley and his coworkers.[1–3] In the case of the free acids the decomposition products were aldehydes, disulfides, and carbon dioxide[2]; the acid chlorides gave aldehydes, sulfonamides, and carbon monoxide.[3] A cyclic mechanism was suggested to account for these transformations.[1]

The formal analogy between these observations and our results led us to postulate that the *N*-toluenesulfonyl derivative was formed first and subsequently underwent a rapid decomposition to the anil, carbon dioxide, and *p*-toluenesulfinic acid (as the pyridinium salt). However, the gaseous by-products of the reaction gave no precipitate when passed through aqueous barium hydroxide and, in fact, proved to be exclusively carbon monoxide as determined by infrared methods. In addition, the solid by-product was identified as pyridinium *p*-toluenesulfonate by comparison of the *S*-benzylthiuronium salt with an authentic sample. As sulfinic acids are relatively stable in the salt form,[4] it is unlikely that pyridinium *p*-toluenesulfonate could have arisen from previously formed *p*-toluenesulfinate.

These results suggest that the present reaction pursues a different course from that of the simpler

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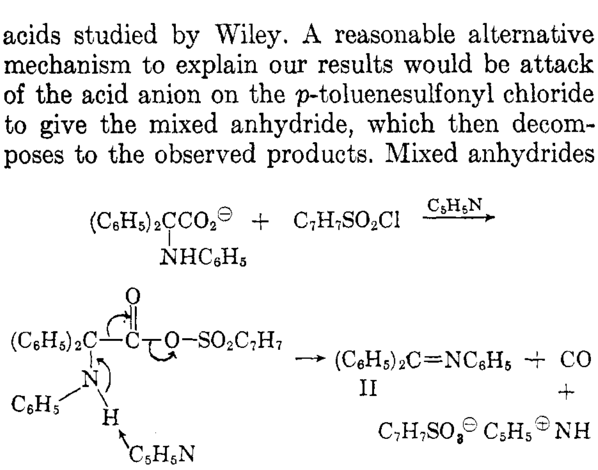
[1] R. H. Wiley and R. P. Davis, *J. Am. Chem. Soc.*, **76,** 3496 (1954).

[2] R. H. Wiley and N. R. Smith, *J. Am. Chem. Soc.*, **73,** 4719 (1951).

[3] R. H. Wiley, H. L. Davis, D. H. Gensheimer, and N. R. Smith, *J. Am. Chem. Soc.*, **74,** 936 (1952).

[4] W. C. Truce and A. M. Murphy, *Chem. Revs.*, **48,** 69 (1951).

acids studied by Wiley. A reasonable alternative mechanism to explain our results would be attack of the acid anion on the p-toluenesulfonyl chloride to give the mixed anhydride, which then decomposes to the observed products. Mixed anhydrides



of p-toluenesulfonic acid are known[5] and have been proposed[6] as highly reactive intermediates in acylation reactions. Apparently the reduced basicity of the amino group and steric factors favor reaction at the carboxyl group in this case.

EXPERIMENTAL[7]

α-Anilino-α,α-diphenylacetic acid (I).[8a,b] To a cooled (10°) solution of 1.2 ml. (1.22 g., 0.013 mole) of freshly distilled aniline in dry benzene was added, dropwise, a benzene solution of 1.4 g. (0.0057 mole) of α-chloro-α,α-diphenylacetic acid.[9] After the addition was complete (one-half hour) the reaction mixture was stirred at room temperature for an additional one-half hour. Aniline hydrochloride was removed by filtration and the combined benzene fractions were washed with water, dried (magnesium sulfate), and concentrated to one-quarter volume. Upon cooling, 1.36 g. of solid, m.p. 165–170°, was obtained. Addition of petroleum ether to the mother liquor and cooling afforded a second crop. The total yield of crude acid was 1.6 g. (93%). After a single recrystallization from benzene–petroleum ether the m.p. was 178–180° (lit.[8b] m.p. 174–175°). The acid obtained in this way was identical to a sample prepared by the somewhat more laborious procedure of Klinger and Standke.[8a]

Reaction of α-anilino-α,α-diphenylacetic acid (I) *with p-toluenesulfonyl chloride and pyridine.* To a suspension of 1 g. (0.0032 mole) of α-anilino-α,α-diphenylacetic acid (I) and 0.8 g. (0.0047 mole) of p-toluenesulfonyl chloride in 30 ml. of sodium-dried benzene was added 2.5 ml. of dry pyridine. The resulting light yellow solution was refluxed for seven hours. As the reaction progressed, the gas produced was swept from the reaction vessel in a slow stream of nitrogen, passed through a drying tube containing Drierite and Anhydrone, and collected in a gas cell. The infrared spectrum of the collected gases demonstrated that carbon monoxide (characteristic doublet at 2120 cm.$^{-1}$ and 2160 cm.$^{-1}$, identical to that of an authentic sample[10]) was the only gas present (other than the nitrogen diluent).

After the removal of the gases, the reaction mixture was cooled to room temperature. The pyridinium salts were removed by filtration and washed with benzene. The combined benzene extracts were washed with dilute acid, dilute base, and water and dried. After evaporation of the solvent and crystallization from methanol 0.53 g. (62.4%) of benzophenone anil (II), m.p. 109–112° (lit.[11] m.p. 112°), was obtained. The melting point was not depressed upon admixture with authentic benzophenone anil.[11] The infrared spectrum was identical with that of the authentic sample.

Addition of phenylhydrazine to an alcoholic solution of the crude residue after the methanol crystallization afforded the phenylhydrazone of benzophenone, m.p. 138–139° (lit.[12] m.p. 137°), not depressed by admixture with an authentic sample.

S-Benzylthiuronium salt. To a chilled aqueous solution of the crude salt mixture from the reaction described above was added an aqueous solution of S-benzylthiuronium chloride. The resulting heavy precipitate was collected by filtration and recrystallized from ethanol. The m.p. was 183–184° (lit.[13] m.p. for the corresponding derivative of p-toluenesulfonic acid, 181–182°) and the sample did not depress the m.p. of an authentic sample prepared from sodium p-toluenesulfonate.

The crude salt mixture failed to form a sulfone with 1-chloro-2,4-dinitrophenol, in the characteristic test for sulfinic acids.[14]

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(5) See, for example, H. P. Kaufmann and L. S. Huang, *Ber.*, **75B**, 1214 (1942).

(6) J. H. Brewster and C. J. Ciotti, *J. Am. Chem. Soc.*, **77**, 6214 (1955).

(7) Melting points are corrected. The authors are indebted to Mrs. N. Alvord for the infrared spectra.

(8) (a) H. Klinger and O. Standke, *Ber.*, **22**, 1212 (1889). (b) W. Schlenk, J. Appenrodt, A. Michael, and A. Thal, *Ber.*, **47**, 484 (1914).

(9) J. Klosa, *Arch. Pharm.*, **288**, 42 (1955).

(10) G. Jacini, *Chimica e Industria*, **29**, 204 (1947); *Chem. Abstr.*, **44**, 9844 (1950).

(11) E. Knoevenagel, *J. prakt. Chem.*, (2) **89**, 37 (1914).

(12) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, *The Systematic Identification of Organic Compounds*, Wiley, New York, 1956, p. 318.

(13) E. Chambers and G. W. Watt, *J. Org. Chem.*, **6**, 376 (1941).

(14) J. P. London, *J. Chem. Soc.*, 537 (1935).

The Reaction of Aldoximes with Alkali[1]

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During the course of another investigation[2] it was found that phenylacetaldoxime, when subjected to the action of alkali at 170°, was converted in 78% yield to phenylacetic acid. This reaction seemed to have sufficient potential as a synthetic tool to merit further investigation, and its application to a variety of aldoximes is the subject of the present report.

The only similar case of such a conversion of an aldoxime to an acid by means of hot alkali[3] involved the conversion of benzaldoxime and several substituted benzaldoximes, as well as fur-

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(1) Sponsored in part by the United States Atomic Energy Commission.

(2) H. Rapoport and W. Nilsson, *J. Am. Chem. Soc.*, **83**, 4262 (1961).

(3) E. Jordan and C. R. Hauser, *J. Am. Chem. Soc.*, **58**, 1304 (1936).