The crude product (5.0 g.) was suspended in 30 ml. of dry acetone containing 0.5 ml. of water and the mixture was heated under reflux until practically complete solution was effected. Norite was added and 70 ml. of hot benzene was added to the clear filtrate. On standing overnight in the cold, the compound (3.0 g.) crystallized in cubes as the trihydrate, m.p. 176–179°. This compound is insoluble in dry acetone and was recrystallized twice more for analysis.

Anal. Calcd. for $C_{11}H_9O_6P \cdot 3H_2O$: P, 9.63; neut. equiv., 107.3. Found: P, 9.66; neut. equiv., 108.0.

When 0.4080 g. of the trihydrate was heated *in vacuo* over P_2O_5 for 4 hours at 60° and then at 80° constant weight was obtained in *ca.* 15 hours. The anhydrous material melted at 177–179°; calcd. for loss of 3 moles of water: 0.0674 g., found 0.0667 ± 0.0004.

Anal. Calcd. for $C_{11}H_9O_6P$: C, 49.27; H, 3.38; P, 11.55; neut. equiv., 89.3. Found: C, 49.67; H, 3.48; P, 11.63; neut. equiv., 89.6.

Determination of Ionization Constants.—The determination of the second and third ionization constant were performed, as previously described[2a,b] on solutions which were 0.01 *M* in acid, and to which sufficient KCl was added to bring the ionic strength to $\mu = 0.1$; the first ionization constants were obtained on solutions 0.1 *M* in acid. Since β-naphthyl phosphate was not soluble enough at the latter concentration, the determinations were made in solution containing 10% dioxane. Since both phenyl and α-naphthyl phosphate show an increase of 0.1 *p*H unit on determination of the first ionization constant in 10% dioxane over water, this correction was subtracted from the value in dioxane in the case of the β-compound.

Buffers and Mole Fractions.—The buffer solutions were the same as those used in our previous report.[2a,b] However, at *p*H values of 6 and above, the observed rates showed marked drifts. This effect we attribute to the ineffectiveness of the veronal buffer at 80°. Therefore, these *p*H values were achieved by adding the requisite amount of NaOH to the acid, and under these conditions the observed rate constants showed but small drifts during the progress of the reaction. We term these solutions self-buffered; they are indicated by superscript b in the tables. As a further check, the specific rate constants also were determined with self-buffered solutions at those *p*H values where phthalate buffers were used and the two derived rates checked within experimental error. The mole fractions, M_1, M_2, etc., present at any *p*H were evaluated as previously described, employing the semi-classical ionization constants determined in this work.

Determinations of Rates of Hydrolysis.—The rates of hydrolysis were determined essentially by the method already described,[2a,b] and the specific rate constants (k_1 and k_2) were evaluated from an average of at least 4 runs, at the *p*H's discussed and noted in Table II. The method was modified only to the extent that aliquots of stock solutions containing the acid (1.291×10^{-3} mole per liter) and the requisite amount of buffer and KCl to bring the ionic strength to $\mu = 0.1$ and the desired *p*H were placed in well stoppered tubes and heated in a constant temperature bath for at least 15 minutes to ensure thermal equilibrium. These aliquots then were removed at appropriate intervals and plunged into an ice-bath. Samples were removed and the liberated phosphate determined as previously described. Blanks and solutions containing known amounts of inorganic phosphate were run under identical conditions in parallel experiments, to eliminate any day to day variations in the colored development with the molybdate reagent. The deviation in any particular run was no greater than 3% and the results in repeated runs were the same within experimental error.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF KANSAS]

Relative Rates of Migration of Aryl Groups in the Schmidt Reaction of Benzhydrols[1]

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A series of five *m*- and *p*-substituted benzhydrols has been prepared and subjected to the Schmidt rearrangement. Product ratios have been determined and relative participation aptitudes assigned to the various aryl groups. These results have been correlated by a suitable adaptation of the Hammett equation.

Introduction

In recent years, mechanism studies have been carried out on Schmidt rearrangements of carboxylic acids,[3] ketones,[4] aldehydes[5] and olefins.[6] Relatively little is known concerning the Schmidt rearrangement of reactive alcohols, however, such reactions having been attempted only with menthol,[7] borneol,[7] benzhydrol,[7,8] fluoren-9-ol,[8] *p*-methylbenzhydrol,[9] triethylcarbinol,[10] and methyldiphenylcarbinol.[6b] Partly to extend the scope of such reactions, but principally for theoretical reasons to be discussed in the following paragraphs, the Schmidt rearrangement of several unsymmetrically substituted benzhydrols has now been investigated.

Experimental[11]

Preparation of Benzhydrols.—*m*-Chlorobenzhydrol, m.p. 38.4–39.6°, was prepared by reduction of *m*-chlorobenzophenone by aluminum isopropoxide (60% yield); reported

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[1] From part of a thesis submitted by Raymond F. Tietz in partial fulfillment of the requirements for the degree of Doctor of Philosophy, University of Kansas, 1954.

[2] Du Pont Fellow, 1953–1954.

[3] (a) L. H. Briggs and J. W. Lyttleton, *J. Chem. Soc.*, 421 (1943); (b) M. S. Newman and H. L. Gildenhorn, THIS JOURNAL, **70**, 317 (1948); (c) C. Schuerch and E. H. Huntress, *ibid.*, **71**, 2233 (1949); (d) C. L. Arcus, J. Kenyon and S. Levin, *J. Chem. Soc.*, 407 (1951); (e) G. M. Badger, R. T. Howard and A. Simons, *ibid.*, 2849 (1952); (f) C. L. Arcus and M. M. Coombs, *ibid.*, 3698 (1953).

[4] (a) P. A. S. Smith, THIS JOURNAL, **70**, 320 (1948); (b) P. A. S. Smith and B. Ashby, *ibid.*, **72**, 2503 (1950); (c) P. A. S. Smith and J. P. Horwitz, *ibid.*, **72**, 3718 (1950); (d) J. R. Dice and P. A. S. Smith, *J. Org. Chem.*, **14**, 179 (1949); (e) P. A. S. Smith, THIS JOURNAL, **76**, 431 (1954); (f) H. Shechter and J. C. Kirk, *ibid.*, **73**, 3087 (1951); (g) J. K. Sanford, F. T. Blair, J. Arroya and K. W. Sherk, *ibid.*, **67**, 1941 (1945); (h) R. D. Westland and W. E. McEwen, *ibid.*, **74**, 6141 (1952); (i) S. C. Bunce and J. B. Cloke, *ibid.*, **76**, 2244 (1954).

[5] W. E. McEwen, W. E. Conrad and C. A. VanderWerf, *ibid.*, **74**, 1168 (1952).

[6] (a) W. E. McEwen, M. Gilliland and B. I. Sparr, *ibid.*, **72**, 3212 (1950); (b) L. P. Kuhn and J. Di Domenico, *ibid.*, **72**, 5777 (1950); (c) S. N. Ege and K. W. Sherk, *ibid.*, **75**, 354 (1953); (d) D. R. Nielsen and W. E. McEwen, *ibid.*, **76**, 4042 (1954); (e) W. E. McEwen and N. B. Mehta, *ibid.*, **74**, 526 (1952).

[7] K. F. Schmidt and W. Klavehn, German Patent 583,565 (Sept. 21, 1933); *C. A.*, **28**, 1047 (1934).

[8] C. L. Arcus and R. J. Mesley, *J. Chem. Soc.*, 178 (1953).

[9] C. L. Arcus and R. J. Mesley, *Chem. and Ind.*, 701 (1951).

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[11] All m.p.'s are corrected and all b.p.'s are uncorrected.

m.p.'s are 38°[12] and 40°.[13,14] *p*-Bromobenzhydrol, m.p. 62–63°, was prepared by reduction of *p*-bromobenzophenone by aluminum isopropoxide (73% yield); reported m.p.'s are 61–62°,[15] 63.5°[16] and 65°.[12] *p*-Chlorobenzhydrol, m.p. 60–61°, was prepared by reduction of *p*-chlorobenzophenone both by zinc dust and alcoholic sodium hydroxide (56% yield) and aluminum isopropoxide (49% yield); reported m.p.'s are 60–61°,[17] 62°[18] and 67.5°.[12] *p*-Methylbenzhydrol, m.p. 52–53°, was prepared by reduction of *p*-methylbenzophenone by zinc dust and alcoholic sodium hydroxide (85% yield); reported m.p.'s are 48°,[12] 52–53°,[19] 53–54°[20] and 58°.[21] *p*-Methoxybenzhydrol, m.p. 65–66°, was prepared by reduction of *p*-methoxybenzophenone both by sodium borohydride (88% yield) and zinc dust and alcoholic sodium hydroxide (82% yield); reported m.p.'s are 60°,[12] 59–60°,[22] 66–68°[23] and 68°.[24]

Schmidt Reaction of *m*-Chlorobenzhydrol. (a) Normal Procedure.—A 500-ml., 3-necked flask was equipped with a dropping funnel, a mercury sealed stirrer and a reflux condenser, to the top of which was attached in series a safety bottle and a bubbler filled with sodium hydroxide solution. In the flask were placed 100 ml. of chloroform and 32.5 g. (0.50 mole) of sodium azide. While this was cooled in an ice-bath, 75 ml. (1.4 moles) of concentrated sulfuric acid was added dropwise with stirring. The flask was then removed from the ice-bath and placed in an unheated oil-bath at room temperature (26°). A solution containing 55.0 g. (0.25 mole) of *m*-chlorobenzhydrol in 100 ml. of chloroform was added during 10 minutes. Nitrogen was evolved, and an orange solid gradually formed. After an hour at room temperature, the bath temperature was slowly raised, reaching 55° at the end of 2 hours. To hydrolyze the reaction mixture, 300 g. of ice was added with stirring. The chloroform layer was separated from the acidic aqueous layer, and the aqueous layer was washed with several portions of chloroform. Distillation of the combined chloroform solution, first to remove solvent, then through a short Vigreux column *in vacuo*, gave three fractions: (1) b.p. 86–90° (28 mm.), 1.0 g.; (2) b.p. 91–104° (28 mm.), 0.9 g.; (3) b.p. 104–111° (26 mm.), 10.5 g.

The infrared spectra of fractions (1) and (3) showed, in addition to absorption peaks characteristic of an aromatic aldehyde, a pronounced peak at 2245 cm.$^{-1}$, indicative of an aromatic nitrile. Sodium fusion tests also showed the presence of nitrogen in each fraction. An analysis[25] of fraction (3) indicated the presence of about 28% of *m*-chlorobenzonitrile (based on the assumption that fraction (3) was a binary mixture of *m*-chlorobenzaldehyde and *m*-chlorobenzonitrile). The presence of substantial amounts of nitriles indicates that the primary products of the reaction react further when excess hydrazoic acid is present. It has been shown[5,26] that aldehydes react under the Schmidt conditions to give nitriles and formamides.

Oxidation of fraction (2) with hydrogen peroxide gave a small amount of *m*-chlorobenzoic acid, m.p. 152–153° after three recrystallizations from benzene (reported[27] m.p. 154.5°). Benzoic acid also was obtained.

The acidic aqueous layer from the original reaction mixture was made basic with sodium hydroxide and extracted thoroughly with chloroform. Distillation of the chloroform followed by fractionation of the residue through a Vigreux column gave 12.1 g. (0.130 mole) of aniline, b.p. 81–85° (28 mm.) and 3.4 g. (0.0266 mole) of *m*-chloroaniline, b.p. 118–120° (28 mm.) as the two main fractions. The aniline was characterized as benzanilide, m.p. 159–160° after one crystallization from ethanol. The entire 3.4 g. of *m*-chloroaniline was dissolved in anhydrous ether and its hydrochloride quantitatively precipitated by passing anhydrous hydrogen chloride into the ether solution.

Anal. Calcd. for $C_6H_7NCl_2$: neut. equiv., 164. Found: neut. equiv., 165.

The molar ratio, *m*-chloroaniline/aniline, was therefore calculated to be 0.20 and the yield of mixed amines to be 63%.

(b) Modified Procedure.—A solution of 9.90 g. (0.045 mole) of *m*-chlorobenzhydrol and 24.3 g. of trichloroacetic acid in 25 ml. of chloroform was added to 65 ml. of a 1.4 *M* chloroform solution of hydrazoic acid (0.091 mole).[28] After having stood at room temperature for 24 hours, during which period of time no nitrogen was evolved, the chloroform solution was washed thoroughly with water to remove trichloroacetic acid and excess hydrazoic acid. The chloroform solution was dried over anhydrous sodium sulfate. The resulting clear, light yellow solution of *m*-chlorobenzhydryl azide was then added dropwise during ten minutes to 15 ml. of concentrated sulfuric acid, at room temperature and with vigorous mechanical stirring. After about 20 minutes, nitrogen evolution ceased, and 150 ml. of ice-water was added to the solution. The chloroform and aqueous layers were separated, and the aqueous solution was extracted with fresh chloroform. The infrared spectrum of the chloroform solution indicated that no nitriles were formed in this modified Schmidt reaction. The combined chloroform solution was distilled to remove the solvent, and the residue was oxidized by silver oxide essentially according to a procedure which has been used for the quantitative analysis of aldehydes in the presence of other neutral compounds.[29]

To the distillation residue was added 17 g. (0.10 mole) of silver nitrate dissolved in 25 ml. of water. The mixture was cooled in an ice-bath and stirred vigorously as a solution of 8 g. of sodium hydroxide in 25 ml. of water was added gradually. After all the sodium hydroxide solution had been added, the mixture was stirred another 10 minutes, then filtered. The filter cake was washed thoroughly with hot water and dilute sodium hydroxide solution. The combined filtrate and washings was extracted with chloroform. The aqueous solution was then acidified by addition of 6 *M* sulfuric acid, and the liberated acids were extracted by twenty 20-ml. portions of chloroform. Evaporation of the chloroform and drying of the residue *in vacuo* gave 3.66 g. of mixed benzoic and *m*-chlorobenzoic acids. This was redissolved in anhydrous acetone and a trace of inorganic material removed by filtration. An aliquot of the acetone solution was evaporated and the residue dried *in vacuo*.

Anal. Found: Cl, 18.67,[30] 18.69.[31]

The molar ratio, benzaldehyde/*m*-chlorobenzaldehyde (actually, benzoic acid/*m*-chlorobenzoic acid), was therefore calculated to be 0.27, and the yield of mixed aldehydes (acids) to be 53%.

Modified Schmidt Reaction of *p*-Bromobenzhydrol. Run No. 1.—A solution of *p*-bromobenzhydryl azide was prepared by mixing 100 ml. of a 1.15 *M* chloroform solution of hydrazoic acid, a solution of 28 g. of trichloroacetic acid in 50 ml. of chloroform and 15.0 g. (0.052 mole) of *p*-bromobenzhydrol, then stirring for one hour at room temperature. After having been washed thoroughly with water and dried over anhydrous sodium sulfate, the solution was added dropwise to 15 ml. of concentrated sulfuric acid at room temperature and stirred until evolution of nitrogen ceased. After hydrolysis with ice and water, the chloroform layer was separated and the aqueous layer extracted with several portions of fresh chloroform. The combined chloroform solution was extracted thoroughly with sodium bisulfite solution. The bisulfite solution was acidified by addition of hydrochloric acid and extracted thoroughly with chloroform. Distillation of the chloroform left a residue of benzaldehyde

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(13) P. J. Montagne and J. M. Van Charante, *ibid.*, **31**, 298 (1912).

(14) S. A. Koopal, *ibid.*, **34**, 115 (1915).

(15) C. F. Winans, THIS JOURNAL, **61**, 3564 (1939).

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(17) R. H. Baker and L. E. Linn, THIS JOURNAL, **71**, 1399 (1949).

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(24) R. Adams, W. V. Wirth and H. E. French, *ibid.*, **40**, 424 (1918).

(25) *Anal.* Found: N, 2.82, 2.92 (Weiler and Strauss, Microanalytical Laboratory, Oxford, England).

(26) K. F. Schmidt, British Patent 252,460 (Feb. 27, 1925); *C. A.*, **21**, 2273 (1927).

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(28) See H. Wolff, "The Schmidt Reaction," "Organic Reactions," Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1946, p. 327.

(29) H. Siegel and F. T. Weiss, *Anal. Chem.*, **26**, 917 (1954).

(30) Analysis by Clark Microanalytical Laboratory, Urbana, Illinois.

(31) Analysis by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

and *p*-bromobenzaldehyde. The aldehydes were mixed with 10 g. of sodium bicarbonate and 50 ml. of a saturated aqueous solution of potassium permanganate, and the mixture was stirred at room temperature for 30 minutes. After acidification with sulfuric acid, the excess permanganate and manganese dioxide were reduced by addition of sodium bisulfite. The mixed acids were taken up in chloroform and extracted from the chloroform solution by sodium bicarbonate solution. Acidification of the sodium bicarbonate solution, thorough extraction with chloroform and evaporation of the solvent gave 1.762 g. of a mixture of benzoic acid and *p*-bromobenzoic acid. The acids were dissolved in anhydrous acetone and an aliquot removed. Evaporation of the solvent and drying of the residue *in vacuo* provided a sample which was analyzed.

Anal. Found: Br, 29.35.[31]

The molar ratio, benzoic acid/*p*-bromobenzoic acid, was calculated to be 0.58, and the yield of mixed acids to be 20%.

Run No. 2.—A chloroform solution of *p*-bromobenzhydryl azide was prepared from 11.8 g. (0.045 mole) of *p*-bromobenzhydrol as described in run no. 1, with the exception that the reaction mixture was stirred for 12 hours before being washed with water. The azide was added to sulfuric acid and the mixture hydrolyzed as in run no. 1. The chloroform solution of the neutral (and acid) fraction of the reaction mixture was not extracted with sodium bisulfite solution in this run. Instead, the chloroform was removed by distillation and the residue oxidized by silver oxide as described in the modified Schmidt reaction of *m*-chlorobenzhydrol. After filtration of the basic solution and washing of the filter cake with hot water and fresh sodium hydroxide solution, the combined filtrate and wash solutions was extracted with chloroform and acidified with dilute sulfuric acid. A voluminous precipitate was obtained which was collected by filtration in a tared sintered glass crucible and dried *in vacuo*. The dried precipitate was washed with two 40-ml. portions of anhydrous benzene (in which *p*-bromobenzoic acid is insoluble) and dried again *in vacuo*. The residue weighed 4.176 g. (after subtracting a 0.014 g. residue which was found to be insoluble in sodium bicarbonate solution) and was identified as *p*-bromobenzoic acid by its m.p. and that of its methyl ester derivative, m.p. 77.5–78.5° (reported[32] for methyl *p*-bromobenzoate, m.p. 78°). An authentic sample of methyl *p*-bromobenzoate, m.p. 77.5–78.5°, showed no depression of m.p. upon admixture with the derivative.

By extraction of the solution from which the solid acids had been precipitated with twenty 20-ml. portions of chloroform, combination of these with the benzene used to wash the solid acids, and evaporation of the solvents, 1.466 g. of benzoic acid was obtained, identified by its m.p. and that of its anilide derivative.

Thus 0.0208 mole of *p*-bromobenzoic acid and 0.0120 mole of benzoic acid were obtained, corresponding to a molar ratio of 0.58 and a yield of mixed acids of 73%. The increased yield over run no. 1 was due solely to the greater reaction period for formation of the azide.

By making the aqueous layer from the original rearrangement reaction mixture basic with sodium hydroxide solution, extraction with chloroform and distillation of the solvent, a residue of amines was obtained. No attempt was made to determine the composition of this mixture quantitatively, but distillation yielded one fraction, b.p. 70–72° (15 mm.), identified as aniline by formation of its tribromo derivative, m.p. 118° (reported for 2,4,6-tribromoaniline, m.p. 118°,[33] 122°[34]). When the residue from the distillation was dissolved in hot ethanol and cooled, slightly brown crystals of *p*-bromoaniline were obtained, m.p. 63–64° (reported[34] m.p. 66°).

Modified Schmidt Reaction of *p*-Chlorobenzhydrol. Run No. 1.—The procedure paralleled that described for run no. 1 of the modified Schmidt reaction of *p*-bromobenzhydrol. The mixture of benzoic acid and *p*-chlorobenzoic acid was analyzed for chlorine.

Anal. Found: Cl, 15.48,[30] 15.42.[31]

The molar ratio, benzoic acid/*p*-chlorobenzoic acid was therefore calculated to be 0.60 and the yield of mixed acids to be 29%.

Modified Schmidt Reaction of *p*-Chlorobenzhydrol. Run No. 2.—The preparation of the azide and its rearrangement in contact with sulfuric acid was carried out as in run no. 1. The crude neutral (and acid) fraction was not extracted with sodium bisulfite this time, but was oxidized with silver oxide as described for the modified Schmidt reaction of *m*-chlorobenzhydrol. The resulting acids were analyzed as described below for the control oxidation of a known mixture of benzaldehyde and *p*-chlorobenzaldehyde. There was obtained from an original 9.90 g. (0.045 mole) of *p*-chlorobenzhydrol 0.954 g. (0.00781 mole) of benzoic acid and 1.620 g. (0.01034 mole) of *p*-chlorobenzoic acid. This corresponds to a molar ratio, benzoic acid/*p*-chlorobenzoic acid, of 0.75 and a yield of 41% of the mixed acids.

Aniline and *p*-chloroaniline were isolated from the acid solution, after neutralization, and identified by the preparation of derivatives. No attempt was made to effect a quantitative separation of the amines.

Control Oxidation of Benzaldehyde and *p*-Chlorobenzaldehyde in the Presence of *p*-Chlorobenzhydrol.—In a 100-ml. flask fitted with a mechanical stirrer were placed 1.0866 g. (0.01023 mole) of benzaldehyde, 1.8199 g. (0.01296 mole) of *p*-chlorobenzaldehyde and 2.0 g. of *p*-chlorobenzhydrol. A small amount of thiophene-free benzene was used to wash in these samples. To this solution was added 13.6 g. (0.08 mole) of silver nitrate dissolved in 25 ml. of water. While this mixture was cooled in an ice-bath and stirred vigorously, 6.4 g. (0.16 mole) of sodium hydroxide dissolved in 25 ml. of water was added dropwise during ten minutes. After an additional ten minutes of stirring, a black precipitate which had formed was filtered off and washed thoroughly with hot water. The somewhat cloudy filtrate and wash solutions were combined and extracted with four portions of chloroform, then filtered once again through a sintered glass funnel. Acidification with 25 ml. of 4 *M* sulfuric acid gave a voluminous precipitate which was filtered through a tared sintered glass crucible and dried *in vacuo*. The dried acids (2.53 g.) were washed with two 40-ml. portions of anhydrous benzene and the insoluble residue dried again. There remained 1.977 g. (0.01262 mole, 97.4%) of pure *p*-chlorobenzoic acid.

By extraction of the acidic aqueous filtrate with twenty 10-ml. portions of chloroform, combination of these extracts with the 80 ml. of benzene wash solution and evaporation to dryness, there was obtained 1.243 g. (0.01018 mole, 99.5%) of benzoic acid.

The original mixture simulated a product ratio, *p*-chlorobenzaldehyde/benzaldehyde, of 0.79, while the experimentally obtained ratio was 0.81.

Modified Schmidt Reaction of *p*-Methylbenzhydrol. Run No. 1.—A solution of *p*-methylbenzhydryl azide was prepared by mixing 175 ml. of a 1.36 *M* chloroform solution of hydrazoic acid, a solution of 50 g. of trichloroacetic acid in 100 ml. of chloroform and 20.0 g. (0.101 mole) of *p*-methylbenzhydrol, then stirring for two hours at room temperature. After washing thoroughly with water and drying the chloroform solution over anhydrous sodium sulfate, the solution was added dropwise during a period of 20 minutes to 30 ml. of concentrated sulfuric acid. No cooling bath was employed during this period, and the mixture became hot enough to cause mild refluxing of the chloroform for a minute or two. Addition of 100 g. of ice caused formation of a yellow precipitate of amine sulfates which was collected by filtration and washed thoroughly with chloroform. The chloroform layer from the reaction mixture was combined with the wash solution, and the aqueous layer from the reaction mixture was washed with fresh chloroform. The combined chloroform solution was shaken vigorously with 50 ml. of saturated sodium bisulfite solution for 10 minutes. A precipitate which formed was collected and added to the aqueous bisulfite solution. The chloroform solution was extracted once again with 10 ml. of saturated sodium bisulfite solution. Acidification of the combined bisulfite solutions containing the precipitate with hydrochloric acid, followed by thorough extraction with chloroform and distillation of the chloroform through a fractionating column, left a residue of mixed aldehydes. This was oxidized as described below for the control oxidation of a mixture of benzaldehyde and *p*-tolualdehyde. There was obtained 2.429 g. (0.0146 mole) of terephthalic acid (identified by its m.p. and that of the dimethyl ester, m.p. 138.5–139°) and 6.300 g. (0.0516 mole) of benzoic acid (identified by its m.p. and that of its amide), corresponding to a molar ratio,

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[32] J. J. Sudborough, *J. Chem. Soc.*, **67**, 587 (1895).

[33] W. Koerner, *Gazz. chim. ital.*, **4**, 305 (1874).

[34] W. Fuchs, *Monatsh.*, **36**, 113 (1915).

benzaldehyde/*p*-tolualdehyde (actually benzoic acid/terephthalic acid) of 3.53 and a yield of 66% of mixed aldehydes (acids).

Aniline and *p*-toluidine were qualitatively identified as components of the amine fraction of the reaction mixture.

Run No. 2.—On repetition of the above experiment the azide was formed by allowing the trichloroacetic acid, hydrazoic acid and *p*-methylbenzhydrol to stand for 12 hours. Rearrangement of the azide was effected as described above. In working up the hydrolyzed products, however, enough water was added to dissolve all of the amine sulfates and the subsequent extraction of the neutral products was from a clear solution.

Oxidation with potassium permanganate was carried out as before, and there was obtained 3.069 g. (0.0185 mole) of terephthalic acid and 7.571 g. (0.0620 mole) of benzoic acid, corresponding to a molar ratio, benzaldehyde/*p*-tolualdehyde, of 3.35 and a yield of 80%.

Control Oxidation of a Mixture of Benzaldehyde and *p*-Tolualdehyde.—In a 500-ml. flask were placed 4.677 g. (0.0441 mole) of benzaldehyde and 1.026 g. (0.00854 mole) of *p*-tolualdehyde. To the aldehydes were added 20 g. of sodium bicarbonate and 13.3 g. of potassium permanganate dissolved in 200 ml. of water, and the mixture was heated to 70° and maintained at that temperature for four hours. The solution was decolorized by acidification with sulfuric acid and treatment with sodium bisulfite. The precipitate which had formed was collected by filtration, dried, digested with 100 ml. of anhydrous ether and filtered through a tared sintered glass crucible. There was obtained 1.346 g. (0.00810 mole, 95%) of terephthalic acid.

The aqueous filtrate was extracted with twenty 10-ml. portions of chloroform. The chloroform extracts were combined with the ether solution and evaporated to dryness, giving 5.192 g. (0.0425 mole, 96%) of benzoic acid. The control mixture simulated a molar product ratio, benzaldehyde/*p*-tolualdehyde, of 5.16, while the experimental results indicated a ratio of 5.25.

Modified Schmidt Reaction of *p*-Methoxybenzhydrol. Run No. 1.—A solution of *p*-methoxybenzhydryl azide was prepared by the slow addition of 330 ml. of a 1.6 *M* chloroform solution of hydrazoic acid (0.528 mole) to a stirred solution of 49.7 g. (0.232 mole) of *p*-methoxybenzhydrol and 98 g. of trichloroacetic acid in 300 ml. of chloroform. After having been allowed to stand at room temperature for 12 hours, the solution was thoroughly extracted with water, then dried over anhydrous sodium sulfate. The solution was then added dropwise during a period of four hours to 55 ml. of concentrated sulfuric acid with vigorous stirring. After nitrogen evolution had ceased, 400 g. of ice was added to the reaction mixture. The aqueous layer was separated from the chloroform layer and washed several times with fresh chloroform. The chloroform solutions were combined.

The combined chloroform solution was thoroughly extracted with saturated sodium bisulfite solution. The combined solid bisulfite addition compounds and bisulfite solutions were acidified with hydrochloric acid, and the liberated aldehydes were extracted with chloroform. After distillation of the chloroform the residue was oxidized by being stirred in a mixture with 24.8 g. of potassium permanganate, 10 g. of sodium hydroxide and 300 ml. of water for one hour. After acidification with sulfuric acid and decolorization of the solution by addition of sodium bisulfite, chloroform was used to exhaustively extract the acids present. The chloroform solution was extracted in several portions by 250 ml. of 5% sodium bicarbonate solution. Acidification of the basic extract, extraction of the resulting solution with chloroform and evaporation of the chloroform afforded 13.1 g. of a mixture of benzoic and *p*-anisic acids.

Anal. Found: % CH_3O, the average of six methoxyl determinations on the products of three different runs was 1.56 ± 0.26.[30,31]

By calculation, the molar product ratio, benzoic acid/*p*-methoxybenzoic acid, was 15.0 and the yield of mixed acids 46%. By means of a control experiment (see below), it was found that only 41% of the anisaldehyde initially present in a known mixture of benzaldehyde and anisaldehyde could be recovered in the form of *p*-anisic acid after treatment with warm sulfuric acid, followed by oxidation with potassium permanganate as described above. The apparent molar ratio, benzoic acid/*p*-methoxybenzoic acid, was found to be 13.9 in a control run on a known mixture having a molar ratio, benzaldehyde/*p*-anisaldehyde, of 5.8. Therefore a better estimate of the molar product ratio, benzaldehyde/anisaldehyde, from the modified Schmidt reaction is obtained by multiplying the experimental value, 15.0, by a correction factor, 5.8/13.9. The corrected product ratio equals 6.3. A more convincing value was obtained by reducing the concentration of sulfuric acid in the rearrangement step of the modified Schmidt reaction.

Aniline and *p*-anisidine were qualitatively identified as components of the amine fraction of the reaction mixture.

Run No. 2.—A solution of *p*-methoxybenzhydryl azide was made in the usual manner from 9.6 g. (0.045 mole) of *p*-methoxybenzhydrol, 24.3 g. of trichloroacetic acid and 65 ml. of a 1.4 *M* chloroform solution of hydrazoic acid (0.091 mole) in a 12-hour reaction period. After thorough extraction with water and drying over sodium sulfate, the solution was added dropwise to 11 ml. of 91% sulfuric acid. After oxidation of the aldehyde fraction of the reaction mixture as described below in a control experiment, there was obtained 2.134 g. of a mixture of benzoic and *p*-methoxybenzoic acids.

Anal. Found: CH_3O, 3.04,[30] 3.15.[31]

By calculation, it was determined that the molar product ratio, benzoic acid/anisic acid, was 7.0. Multiplication by a correction factor of 5.8/6.2, obtained from the results of a control run (see below), reduced the ratio to 6.5.

Control Experiments with Known Mixtures of Benzaldehyde and *p*-Methoxybenzaldehyde.—To a solution of 3.909 g. (0.0372 mole) of benzaldehyde and 0.874 g. (0.00642 mole) of *p*-methoxybenzaldehyde in 50 ml. of chloroform was added 16 ml. of 91% sulfuric acid, and the mixture was stirred for 15 minutes. Ice was added and the chloroform layer separated from the aqueous layer. The aqueous layer was thoroughly extracted with fresh portions of chloroform, and the solvent was distilled from the combined chloroform solution through a fractionating column. To the residue was added a solution of 17 g. (0.10 mole) of silver nitrate in 30 ml. of water. The mixture was stirred vigorously while a solution of 8 g. of sodium hydroxide in 20 ml. of water was added slowly. After two hours of stirring the mixture was filtered and the precipitate washed thoroughly with hot water and hot dilute sodium hydroxide solution. The combined filtrate and wash solution was acidified with 6 *M* sulfuric acid. The mixture of benzoic and *p*-anisic acids was isolated as described in run no. 1 for the Modified Schmidt Reaction of *p*-methoxybenzhydrol.

Anal.[31] CH_3O, 3.26, 3.52.

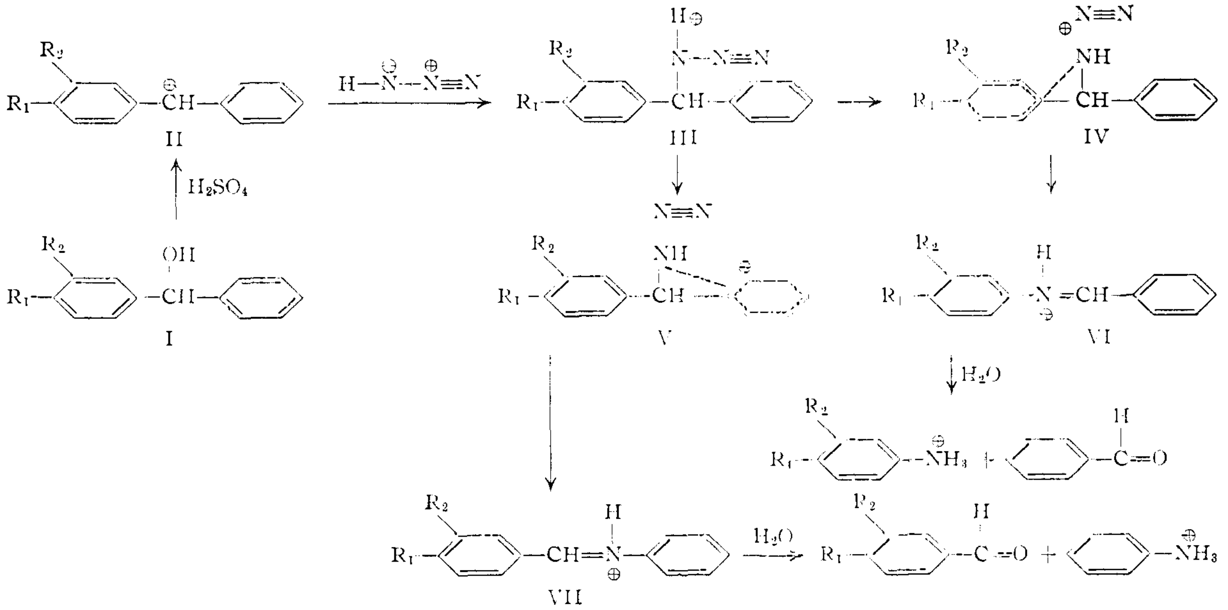
By calculation, it was determined that the molar ratio, benzoic acid/*p*-anisic acid, was 6.2, as compared to the molar ratio, benzaldehyde/*p*-methoxybenzaldehyde, of 5.8 in the original known mixture. The yield of mixed acids was 5.29 g. (about a 97% yield of benzoic acid and a 91% yield of anisic acid).

When a control experiment was carried out using 15 ml. of concentrated sulfuric acid instead of 91% sulfuric acid in the initial treatment of the aldehydes, only 41% of anisic acid was obtained, together with 97% of benzoic acid.

In order to further prove that loss of potential *p*-anisic acid occurred in the treatment of the aldehydes with sulfuric acid rather than in the oxidation step, a mixture of 1.2109 g. (0.00889 mole) of *p*-methoxybenzaldehyde and 0.7 g. of *p*-methoxybenzhydrol was oxidized with silver oxide as described above. There was obtained 1.289 g. (0.00847 mole, 95.3%) of *p*-anisic acid.

Discussion

Treatment of a *m*- or *p*-substituted benzhydrol (I) with sulfuric and hydrazoic acids gives, after hydrolysis of the reaction mixture, benzaldehyde, a *m*- or *p*-substituted benzaldehyde, the anilinium ion and a *m*- or *p*-substituted anilinium ion. On the basis of other mechanisms which have been proposed for the various Schmidt reactions,[3-6] it may be assumed that I reacts with concentrated sulfuric acid to form the carbonium ion, II, which then combines with hydrazoic acid to form the conjugate acid, III, of the *m*- or *p*-substituted benzhydryl



azide. Rearrangement of III *via* the transition states, IV and V, gives rise to the conjugate acids, VI and VII, of two Schiff bases. Upon subsequent hydrolysis, VI and VII give the ultimate products of the reaction.

In some of the earlier runs, with *p*- and *m*-chlorobenzhydrol and *p*-methoxybenzhydrol, a solution of the *m*- or *p*-substituted benzhydrol in chloroform was dropped into a mixture of hydrogen azide, sulfuric acid and chloroform. After completion of the reaction, including the hydrolysis step, the neutral fraction of the reaction mixture was subjected to distillation *in vacuo* to separate the aldehydes. An infrared examination of the respective aldehyde fractions indicated significant contamination by nitriles, however, these arising from subsequent Schmidt reactions involving the aldehydes[5] or their precursors, the Schiff bases.

Since these side reactions would render the quantitative determination of product ratios for the aldehyde fraction of the reaction mixture extremely difficult, another method[6c] of carrying out the Schmidt reactions was tried. The *m*- or *p*-substituted benzhydryl azide was first prepared and subsequently rearranged under the influence of sulfuric acid. Since no free hydrogen azide was present during the rearrangement step, it would not be possible for the products of rearrangement to undergo partial conversion to nitriles, and the infrared spectra of the crude neutral fractions showed that no nitriles were formed under these conditions.

A number of different methods for determining product ratios were explored initially, but it was finally determined that the simplest and most reliable procedure for many of the cases studied was to oxidize the aldehydes in the crude neutral fraction to acids by means of silver oxide and then analyze the acids by some appropriate procedure, which varied from one case to another. A limited number of control experiments with known mixtures of aldehydes, both in the presence and absence of the appropriate benzhydrol, showed that the general method was probably reliable. However, because of the complex multistep procedures used in the various analyses, we cannot claim that product ratios were determined with great accuracy. At best, the product ratios are probably accurate to within ± 10% of the true values.

In view of our previously reported success in correlating relative rates of migration of *m*- and *p*-substituted groups in the Schmidt reaction of unsymmetrical diarylethylenes by means of a suitable adaptation of the Hammett equation,[6d,e] we also made a plot, shown in Fig. 1, of log molar product ratio, benzaldehyde/*m*- or *p*-substituted benzaldehyde, *vs.* the various σ-values. The values for the product ratios on which the plot was based are given in Table I, with the exception of the value for the *p*-nitrobenzhydrol reaction. The molar product ratio, benzaldehyde/*p*-nitrobenzaldehyde, was found by Mr. Joseph Scherrer of these laboratories to be 0.047 for this reaction; the experimental details will be given in a subsequent article. A linear relationship was found to prevail (see Fig. 1), and analysis of the data by the "least squares" method gave as the equation of the line

$$\log \text{product ratio} = -2.03\sigma + 0.237$$

TABLE I

PRODUCT RATIOS IN THE ACID-CATALYZED REARRANGEMENT OF BENZHYDRYL AZIDES

Benzhydryl azide, $XC_6H_4-\underset{N_3}{CH}-C_6H_5$ X	Molar product ratio, benzaldehyde/*m*- or *p*-substituted benzaldehyde
m-Chloro	0.27
p-Bromo	0.58
p-Chloro	0.67
p-Methyl	3.44
p-Methoxy	6.50

Although the amines formed in each of these reactions were qualitatively identified, no effort was made to determine accurate product ratios of the amine fractions resulting from any of the modified (prior formation of the organic azide, followed by treatment with sulfuric acid) Schmidt reactions.

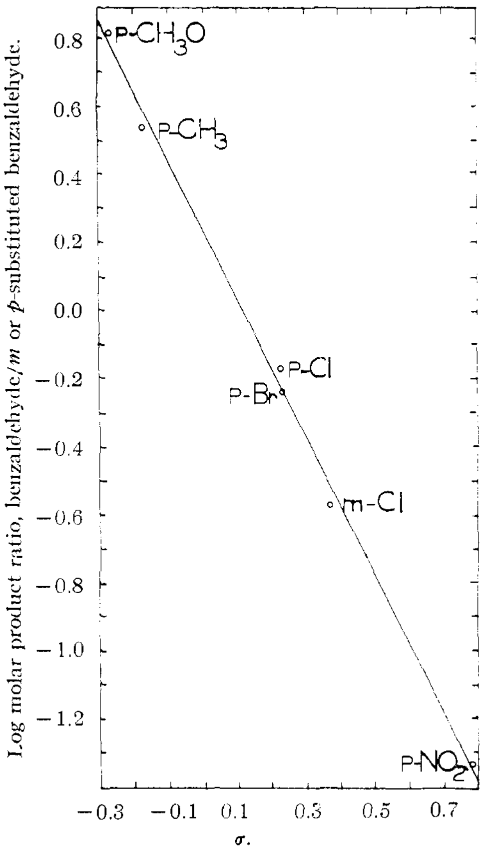
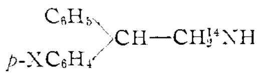


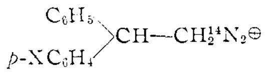
Fig. 1.—The Hammett equation applied to the Schmidt reaction of *m*- and *p*-substituted benzhydrols.

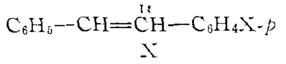
In a few cases, moderately precise product ratios of the amine fractions resulting from normal (carried out in the presence of excess hydrazoic acid) Schmidt reactions were determined. These ratios tended to be somewhat lower than those found by analysis of the aldehyde fractions as described above. These deviations are probably due to the fact that small and unpredictable amounts of amines are formed, together with nitriles and formamides, in the secondary reactions of the aldehydes or their precursors, the Schiff bases, with the excess hydrazoic acid present.

A number of significant articles dealing with the theory of rearrangement reactions have recently appeared in the literature. Winstein and co-workers,[35] for example, have provided evidence that there is a driving force due to participation by neighboring carbon in the rate-determining step of Wagner–Meerwein rearrangements. It may also be concluded that, in competitive rearrangements such as those discussed in this article, it is possible to consider relative rates of migration of various aryl groups as a measure of relative participation aptitudes of these groups. In the product-determining step of the Schmidt rearrangement of *p*-methoxybenzhydrol, for example, the fact that there is a greater degree of *p*-anisyl migration than phenyl migration may be interpreted to mean that the electron cloud associated with the *p*-anisyl group is more effective in aiding the departure of molecular nitrogen than is the electron cloud associated with the phenyl group. In other words, due to the electron-releasing properties of the methoxyl group, the transition state, IV (R_1 = OCH_3, R_2 = H), for *p*-anisyl migration is of lower energy than the transition state, V (R_1 = OCH_3, R_2 = H), for phenyl migration. Therefore, the rate of *p*-anisyl migration is greater than that of phenyl migration.

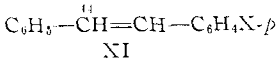
Some recent work by Burr and Ciereszko,[36] however, needs to be considered in the light of the above ideas. By reaction of a series of α-C-^{14}β,β-diarylethylamines (VIII) with nitrous acid, a competitive rearrangement occurred, presumably *via* the diazonium cation, IX, to give as final products the isomeric stilbenes, X and XI.


VIII


IX


C_6H_5—CH=$\overset{14}{C}$H—C_6H_4X-*p*

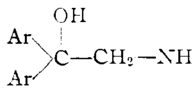
X

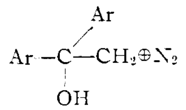

C_6H_5—$\overset{14}{C}$H=CH—C_6H_4X-*p*

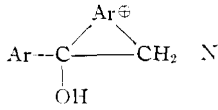
XI

Burr and Ciereszko found that there was little or no difference in the relative rates of migration of phenyl, *p*-tolyl and *p*-biphenylyl groups, while the relative rate of migration of the *p*-anisyl group was only slightly greater than that of the phenyl group. The interpretation of this result would seem to be that molecular nitrogen, having an abnormally large heat of formation, departs with extraordinary facility and without demanding aid in the form of a "push" by the migrating group in these reactions.

Curtin and Crew[37] have determined migration ratios in the rearrangements of a variety of 2-amino-1,1-diarylethanols (XII), brought about by the action of nitrous acid. The migration ratio of *p*-anisyl/phenyl was found to be 1.5, of *p*-tolyl/phenyl to be 1.3 and of *p*-chlorophenyl/phenyl to be 0.9. These workers concluded that resonance structures such as XIII rather than XIV make a relatively large contribution to the transition state for each rearrangement reaction in this series since "relatively little driving force by aryl migration is required for reaction."


XII


XIII


XIV

This immediately poses the question as to why there is a distinct order of relative participation aptitudes in the Schmidt rearrangement of benzhydrols (and 1,1-diarylethylenes). The departing group is also molecular nitrogen in these reactions. The answer would obviously seem to be related to the one difference in this system and that studied by Burr and Ciereszko,[36] the respective atoms from

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(35) S. Winstein, B. K. Morse, E. Grunwald, K. C. Schreiber and J. Corse, THIS JOURNAL, **74**, 1113 (1952).

(36) J. G. Burr and L. S. Ciereszko, *ibid.*, **74**, 5426 (1952).

(37) D. Y. Curtin and M. C. Crew, *ibid.*, **76**, 3719 (1954).

which the molecular nitrogen departs. In the β,β-diarylethylamine series this atom is carbon, and in the Schmidt rearrangement series this atom is nitrogen. Since carbon has a lower ionization potential than nitrogen, it would be an easier process, energetically, for molecular nitrogen to depart from a carbon atom than from a nitrogen atom. Therefore in the β,β-diarylethylamine and 2-amino-1,1-diarylethanol series the molecular nitrogen can depart without demanding aid in the form of a "push" by the migrating group, but in the Schmidt series participation by neighboring carbon is demanded for departure of the molecular nitrogen.

Another point of theoretical interest is the fact that the value of ρ for the Schmidt reaction of 1,1-diarylethylenes ($\rho = -2.11$)[6e] is not much different from the value of ρ for the Schmidt reaction of benzhydrols. In fact, the migration ratios of *p*-anisyl/phenyl, of *p*-chlorophenyl/phenyl and of *p*-bromophenyl/phenyl are nearly the same in both series, but the migration ratio of *p*-tolyl/phenyl in the 1-phenyl-1-*p*-tolylethylene reaction appears to be somewhat higher than that in the *p*-methylbenzhydrol reaction.[6] This is more likely due to accumulative errors in the analytical methods employed rather than to any real differences in reactivity.[38]

An examination of the literature revealed that rate studies have been made on the Hofmann rearrangement of *m*- and *p*-substituted N-bromobenzamides[39] and the Lossen rearrangement of the potassium salts of *m*- and *p*-substituted O-benzoylbenzhydroxamic acids.[40] The rate data for these rearrangements could also be correlated by use of the Hammett equation (see Fig. 2). Perhaps the most valid comparison of these reactions with Schmidt reactions would be with the Schmidt reaction of *m*- and *p*-substituted benzoic acids. It was previously shown[6e] that a suitable adaptation of the Hammett equation could be used to correlate the relative rate data supplied by Briggs and Lyttleton[3a] for the Schmidt reaction of *m*- and *p*-substituted benzoic acids. The values of ρ for the Hofmann (-2.58) and Lossen (-2.51) rearrangement series are more negative than the value of ρ for the Schmidt (-1.76)[41] rearrangement series. This may be explained on the basis that nitrogen departs more readily than either the bromide ion or the benzoate ion. Therefore there is less demand for a "push" by the migrating aryl group in the Schmidt reaction than in the Hofmann and Lossen reactions.

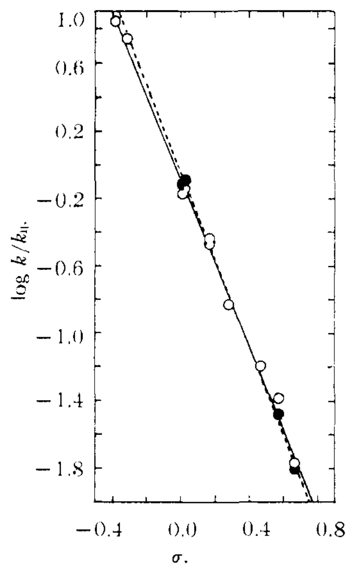

Fig. 2.—The Hammett equation applied to the Hofmann rearrangement of *m*- and *p*-substituted N-bromobenzamides (-----) and the Lossen rearrangement of *m*- and *p*-substituted O-benzoylbenzhydroxamic acids (——).

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LAWRENCE, KANSAS

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[38] Ege and Sherk[6c] have reported a migration ratio of *p*-tolyl/phenyl of 4.0 in the Schmidt reaction of 1-phenyl-1-*p*-tolylethylene in contrast to a vaue of 5.0 reported by McEwen, Gilliland and Sparr.[6a] The former value agrees fairly well with the value, 3.44, found in the present paper for the Schmidt reaction of *p*-methylbenzhydrol. For a reaction series in which the presence of a β-methyl group does markedly influence the relative extents of aryl participation by the *p*-anisyl and phenyl groups see S. Winstein, C. R. Lindegren, H. Marshall and L. L. Ingraham, THIS JOURNAL, **75**, 147 (1953).

[39] C. R. Hauser and N. B. Renfrow, Jr., *ibid.*, **59**, 121 (1937).

[40] R. D. Bright and C. R. Hauser, *ibid.*, **61**, 618 (1939).

[41] This value was incorrectly reported to be -1.97 in a previous article.[6b]