sulfate and the solvent removed at reduced pressure. The clear yellow residue (10.6 g., 88% crude yield) appeared to contain ~90% of 1-thiophenoxy-3-methyl-1,2-butadiene and ~10% of 3-thiophenoxy-3-methyl-1-butyne on the basis of infrared. Distillation through a small helix column gave fair recovery of material, b.p. 70° (0.4 mm.), $n^{25}\text{D}$ 1.5954, which was mainly allenic (perhaps 3% of the acetylenic isomer as contaminant). An attempt at further purification by careful fractional distillation through a more efficient column gave mainly nonvolatile, polymeric products. The distillate was partly rearranged as shown by new infrared peaks at 810, 845, 942, 1307, and 1613 cm.$^{-1}$.

Reaction of V with Sodium Thiophenoxide.—A solution of 0.27 mole of sodium thiophenoxide prepared from 6.8 g. of sodium, 150 ml. of methanol and 30 g. of thiophenol was treated with 15 g. (0.10 mole) of V and allowed to stand at room temperature for 16 days. The solution was worked up as above to yield 14.0 g. (87% yield, crude) of a pale yellow product. Infrared showed no allenic material, but a small peak at 2107 cm.$^{-1}$ and a strong one at 3242 cm.$^{-1}$ indicated an acetylenic compound. There was also a strong peak at 1578 cm.$^{-1}$ and a weak one at 1657 cm.$^{-1}$ which may indicate conjugated diene. Fractionation through a small helix column gave a moderate yield of product believed to be 3-methyl-3-thiophenoxy-1-butyne, b.p. 52° (0.4 mm.), $n^{25}\text{D}$ 1.5505, $d^{20}{}_4$ 0.998.

Anal. Calcd. for $C_{11}H_{12}S$: C, 74.94; H, 6.86; S, 18.19. Found: C, 74.72; H, 6.65; S, 18.31.

Infrared spectrum: 684 (s), 735 (s), 780 (m), 833 (w), 912 (w), 935 (w), 998 (w), 1010 (m), 1021 (m), 1064 (m), 1072 (m), 1086 (m), 1122 (s), 1171 (m), 1211 (s), 1260 (m), 1301 (m), 1325 (w), 1357 (m), 1378 (m), 1437 (s), 1471 (s), 1578 (m), 1657 (w), 1745 (w), 1794 (w), 1871 (w), 1946 (w), 2107 (w), 2812 (m), 2820 (s), 3017 (m), and 3242 (s) cm.$^{-1}$. The peaks at 2107 and 3242 cm.$^{-1}$ were much stronger in the redistilled product and the peaks at 1578 and 1657 cm.$^{-1}$ much weaker.

Reaction Rates by Distillation. X. The Condensation of Anilines with Benzoins

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The acid-catalyzed condensation of aniline with benzoin in benzene containing dimethylaniline as a "leveller" has been found to be first order with respect to each reactant and the catalyst. Electron releasing groups *para* to the carbonyl group of the benzoin tend to decrease the rate. In a group of eleven anilines the rate increased consistently as the electron releasing ability of the *meta* or *para* substituent increased. The points for the less basic anilines fell on one straight line of a ρ–σ plot while those for the more basic anilines fell on a second straight line of decreased slope. Excellent yields of desylanilines were isolated in all cases. The results strongly favor reaction of the aniline with the carbonyl group rather than with the hydroxymethylene group of the benzoin. A mechanism analogous to that previously advanced for the condensation of aniline with benzaldehyde is evaluated.

The factors which determine the rate of reaction of anilines with benzoins have been studied by the distillation method previously employed for a variety of reactions which yield water as a by-product.[2]

$$\begin{array}{c}\text{ArC=O}\\ |\\ \text{Ar}'\text{CHOH}\end{array} + \text{PhNH}_2 \longrightarrow \begin{array}{c}\text{ArCHNHPh}\\ |\\ \text{Ar}'\text{C=O}\end{array} + H_2O$$

The standard conditions used are given at the top of Table I. When no dimethylaniline was employed (second experiment) the rate constants calculated at successive stages of reaction showed a distinct and consistent upward drift; this drift decreased to insignificance as the amount of dimethylaniline was increased (third and first experiments). The dimethylaniline "leveller" doubtlessly functions primarily to minimize changes in basicity of the reaction medium as the amount of unreacted aniline decreases.

TABLE I

REACTION OF ANILINE WITH BENZOIN

Standard conditions: 0.125 mole of aniline, 0.125 mole of benzoin, 0.0005 mole of PTS,[a] and 0.250 mole of dimethylaniline with benzene to give 500 ml.

Variable	$t_{50\%}$,[b] min.	$k \times 10^2$, l. mole^{-1} min.$^{-1}$
Standard conditions[c]	210	2.25 ± 0.02
No $C_6H_5N(CH_3)_2$	125	3.86 ± 0.21
Half std. amt. $C_6H_5N(CH_3)_2$[c]	148	3.12 ± 0.15
Half std. amt. PTS[a]	404	1.16 ± 0.01
Quarter std. amt. PTS[a]	780	0.61 ± 0.01
Double std. amt. $C_6H_5NH_2$	77	2.33 ± 0.03
Double std. amt. $C_6H_5COCHOHC_6H_5$	91	2.01 ± 0.02

[a] *p*-Toluenesulfonic acid monohydrate. [b] This is the time required for a 50% yield of water to collect. [c] For increased accuracy these experiments were double scale.

Comparison of the results for the last four experiments tabulated with those for the first experiment show that the reaction is first order with respect to the aniline, the benzoin, and the catalyst. First-order dependence on the aniline and benzoin is, of course, implicit in the fact that rate constants, calculated on the assumption of such dependence at successive stages of reaction showed no serious drift.

In Tables II and III are summarized the results for the condensation of eleven anilines with benzoin and five benzoins with aniline. The clear-cut nature of the reaction, a requirement for precise rate data, is emphasized by the high yields of products obtained and by the 98 to 102% yields of water collected in all cases; in most cases the yield of water was 99 to 101%. It would be difficult to improve on the facile distillation method as a preparative procedure. Since the reaction can be stopped as soon as complete, cyclization of the products to diarylindoles[3] is minimized.

A ρ–σ plot for the experiments of Table II is given in Fig. 1. It is suggested that since the dimethylaniline leveller is less basic than the most basic anilines employed, incomplete levelling resulted for those anilines for which the line of decreased slope is drawn. In support of this view the percent average deviation for the three most basic anilines (first three experiments of Table II) was greater than for the other anilines and in these three cases the rate constants calculated at successive stages of reaction showed an upward drift analogous to that encountered in the absence of a

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(1) From a portion of the Ph.D. thesis of M. J. Kamlet, March, 1954.

(2) For the preceding paper in this series, see E. F. Pratt and M. J. Kamlet, *J. Org. Chem.*, **26**, 4029 (1961).

(3) P. L. Julian, E. W. Meyer, and H. C. Printy, "Heterocyclic Compounds," Vol. 3, R. C. Elderfield, ed., J. Wiley and Sons, Inc., New York, N. Y., 1952, pp. 22-35.

Table II

Reaction of Substituted Anilines with Benzoin[a]

Substituent	$t_{50\%}$, min.	$k \times 10^2$, l. mole^{-1} min.$^{-1}$	Yield,[b] %
p-CH$_3$O	113	4.23 ± 0.07	89
3,4-di-CH$_3$	120	3.97 ± 0.07	84
p-CH$_3$	137	3.34 ± 0.06	89
m-CH$_3$	180	2.63 ± 0.02	84
H	210	2.25 ± 0.02	90
m-CH$_3$O	275	1.69 ± 0.02	84
3,4-C$_4$H$_4$[c]	314	1.50 ± 0.02	90
p-Cl	451	1.02 ± 0.01	87
m-Cl	1150	0.408 ± 0.003	87
p-COOEt	3700	0.127 ± 0.001	87
m-NO$_2$	7500	0.0633 ± 0.0008	84

[a] The standard conditions of Table I were used, but the scale was doubled for increased accuracy. [b] Yield of pure, recrystallized product. [c] β-Naphthylamine.

Table III

Reaction of Aniline with p-RC$_6$H$_4$COCHOHC$_6$H$_4$R′-p'[a]

R	R′	$t_{50\%}$, min.	$k \times 10^2$, l. mole^{-1} min.$^{-1}$	Yield,[b] %
H	H	210	2.25 ± 0.02	90
CH$_3$O	H	536	0.87 ± 0.01	70[d]
CH$_3$O	CH$_3$O	510	0.95 ± 0.01	87
CH$_2$O$_2$[c]	CH$_2$O$_2$[c]	840	0.56 ± 0.01	87
Cl	Cl	222	2.19 ± 0.03	71

[a] The standard conditions of Table I were used, but the scale was doubled for increased accuracy. [b] Yield of pure, recrystallized product. [c] 3,4,3′,4′-Bismethylenedioxybenzoin. [d] This was the yield of the unstable p'-methoxy isomer; a 2% yield of the stable p-methoxy isomer was also isolated.

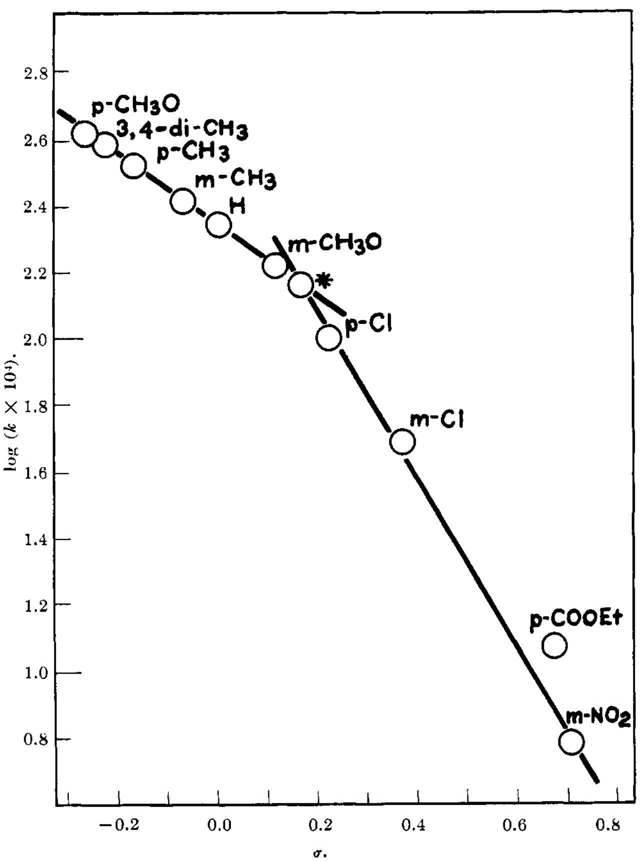

Fig. 1.—Plot of log ($k \times 10^4$) for the reaction of benzoin with substituted anilines *vs.* Hammett's σ-constants. *β-Naphthylamine.

leveller. Straight line plots relating the "levelling effect" or basicity of *para*-substituted acetophenones, ethyl benzoates and benzamides to the σ values of the substituents have been previously reported.[4,5] The line for the most basic anilines (Fig. 1) may well be the sum of a line showing the "levelling effect," or basicity, of these anilines and a line obtained by extrapolation of the line for the least basic anilines in Fig. 1. Inadequate levelling of the type considered here is a probable common cause of deviations in ρ–σ plots for reactions carried out in hydrocarbon or other solvents of negligible acidity or basicity as well as of deviations from integral order kinetics frequently encountered in such solvents.[6]

The σ-value for the *para*-carbethoxyl group employed in Fig. 1 is 0.678 as recommended for reactions of anilines and phenols.[7] Since this value is based on only two reactions it is less precisely known than most of the others which may explain why it does not fall on the line. The value of ρ calculated by the Jaffe method[7] for the five least basic anilines, excepting p-carbethoxylaniline, is −2.204; s, the standard deviation, is 0.052, and r, the correlation coefficient,[7] is 0.997. From this ρ value, a σ value of 0.628 for the *para*-carbethoxyl group, of anilines and phenols, may be calculated.

The data in Table II show that a strongly electron releasing methoxyl group *para* to the carbonyl group of benzoin greatly decreases the rate. Two methoxyl groups, at the *para* and *para* prime positions, or two methylenedioxy groups, at the 3,4- and 3′,4′-positions, also sharply reduce the rate. It is not clear why the methylenedioxy group has a greater effect than the methoxyl which has the larger σ-value[8] nor is it clear why two chlorine atoms at the 4- and 4′-positions slightly decreased the rate although they are electron attracting. It may be that a second substituent at the *para* prime position influences predictions based on a single substituent at the *para* position by altering the extent of intramolecular hydrogen bonding of the hydroxylic hydrogen with the carbonyl oxygen of the benzoin.

The results of this study strongly support those who believe the aniline attacks the carbonyl group[9] rather than the hydroxymethylene group[10,11] of the benzoin. Recently the factors determining the rate of reaction of anilines with benzaldehydes have been reported[2] and the parallelism with the results of the present study is extensive. In the condensation of anilines with both benzoins and benzaldehydes the rate depends on the first power of the concentration of the aniline, the carbonyl compound, and the catalyst and electron releasing *para* substituents in the aniline increase the rate while such groups *para* to the carbonyl group of the benzoin or benzaldehyde decrease the rate; the ρ-values obtained for reaction with the substituted

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(4) E. F. Pratt and K. Matsuda, *J. Am. Chem. Soc.*, **75**, 3739 (1953).

(5) E. F. Pratt and J. Lasky, *ibid.*, **78**, 4310 (1956).

(6) L. P. Hammett, "Physical Organic Chemistry, McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 288.

(7) H. H. Jaffe, *Chem. Rev.*, **53**, 191 (1953).

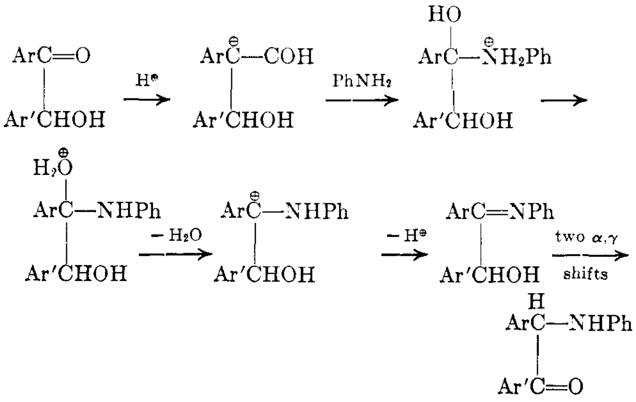
(8) Ref. 6, p. 188.

(9) R. M. Cowper and T. S. Stevens, *J. Chem. Soc.*, 347 (1940).

(10) A. Bischler and P. Fireman, *Ber.*, **26**, 1336 (1893).

(11) P. L. Julian, E. W Meyer, A. Magnani, and W. Cole, *J. Am. Chem. Soc.*, **67**, 1203 (1945).

anilines was −2.004 in the case of benzaldehyde and −2.204 in the case of benzoin. If the aniline attacked the hydroxymethylene group the most probable rate controlling step would be formation of the ArCOCHAr ion[12]; the rate would then be independent of both the concentration of, and the substituent on, the aniline and electron-releasing groups at the *para* and *para* prime positions of the benzoin would greatly increase rather than decrease the rate. A mechanism entirely analogous to that recently advanced[2] for the reaction of aniline with benzaldehyde is outlined below.



A 70% yield of *p*'-methoxydesylaniline ($C_6H_5COCH(NHPh)C_6H_4OCH_3$-*p*') and a 2% yield of the *p*-methoxydesylaniline were isolated from the reaction mixture for the second experiment of Table III. The minor product is the more stable[13] since in it the carbonyl carbon which bears a partial positive charge can more readily receive electrons from the methoxyl group. It appears, therefore, that because of the mild conditions of the distillation method it is well adapted to the preparation of the unstable isomers which may be rearranged to the stable forms under more rigorous conditions.[11,14-18]

Experimental[19,20]

General Considerations.—The *p*-toluenesulfonic acid monohydrate was Eastman's White Label grade. It was used as obtained since it was found to have close to the calculated neutralization equivalent. All other constituents of the reaction mixtures were purified by standard methods until their melting points or refractive indices agreed closely with the literature values.

The apparatus and procedure employed were entirely analogous to that previously described[2] for the reaction of aniline with benzaldehyde except that a nitrogen atmosphere was not used. Allowance was made in the calculations for the fact that 500- and 1000-ml. volumes of the benzene solutions at room temperature expand to 531 and 1062 ml. at the reflux temperature. The tabulated constants were calculated on the assumption the reactions were first order with respect to aniline and benzoin. In a given experiment successive rate constants were calculated from the time and water volume data at 10 and 20% reaction, then from the data at 10 and 30% reaction, and so on, to and including the data at 10 and 70% reaction. The tabulated values are the arithmetic mean of the six successive values plus or minus the average deviation of a single value from this mean.

Unless otherwise noted, the products were isolated as follows. When 1000 ml. of reaction mixture was used it was concentrated to 500 ml. before washing, by distilling benzene, while the 500-ml. reaction mixtures were washed without concentration. The benzene solutions were washed once with 100 ml. of water, twice with 30 ml. of concentrated hydrochloric acid in 70 ml. of water, and then three times more with 100 ml. of water. The benzene was removed by distillation using reduced pressure for the final stages and the products recrystallized from suitable solvents. New products were recrystallized to constant melting point while known compounds were recrystallized until their melting points agreed with the literature values.

Experiments of Table I.—The temperature range within an experiment was never more than ±0.2° for the 10 to 70% portion of the reaction. Proceeding downward in Table I the median temperatures were 83.5, 81.9, 82.8, 84.6, 83.9, 83.6, 84.5, and 84.5°. As might be expected, increasing the amount of dimethylaniline, aniline, or benzoin slightly increases the boiling point of the reaction mixtures.

The average yield of pure product was 89% for the four experiments of Table I for which the product was isolated. Except for the second experiment which was stopped at 77% water, the total yield of water was always 99.0 to 101.6%.

Three repetitions of the first experiment of Table I gave values for $k \times 10^2$ of 2.30 ± 0.03, 2.33 ± 0.04, and 2.20 ± 0.02 l. mole^{-1} min.$^{-1}$. Repetition of the second and last experiments gave values for $k \times 10^2$ of 3.80 ± 0.20 and 2.03 ± 0.03 l. mole^{-1} min.$^{-1}$.

Experiments of Table II.—For all of these experiments the temperature range was 83.1–83.7° for the 10 to 70% portion of the reaction; within a given experiment the maximum temperature variation was ±0.2°.

The product from the first experiment, desyl-*p*-anisidine, was recrystallized from cyclohexane and melted at 92–92.5°.

Anal. Calcd. for $C_{21}H_{19}O_2N$: C, 79.47; H, 6.03; N, 4.41. Found: C, 79.50; H, 5.90; N, 4.71; a repetition of this experiment gave a value for $k \times 10^2$ of 4.10 ± 0.06 l. mole^{-1} min.$^{-1}$.

Recrystallization of the product from the second experiment from aqueous ethanol and then from a mixture of ethanol, benzene, and water gave pure desyl-3,4-dimethylaniline which melted at 120.5–121.5°.

Anal. Calcd. for $C_{22}H_{21}NO$: C, 83.78; H, 6.71; N, 4.44. Found: C, 83.57; H, 6.61; N, 4.52.

The desyl-*m*-anisidine formed in the sixth experiment was recrystallized from cyclohexane, then from absolute ethanol, and then from methanol. It melted at 96–96.5°.

Anal. Calcd. for $C_{21}H_{19}NO_2$: C, 79.47; H, 6.03; N, 4.41. Found: C, 79.18; H, 5.84; N, 4.64.

A fluffy solid precipitated from the ethanolic mother liquors. Two recrystallizations of the 1.55 g., which melted at 190–200°, raised the melting point to 212–213°. The analytical results indicate it is 2,3-diphenyl-6-methoxyindole.

Anal. Calcd. for $C_{21}H_{17}NO$: C, 84.30; H, 5.73; N, 4.71. Found: C, 84.53; H, 5.88; N, 4.77.

The products of the experiments of Tables II and III not individually described are known compounds whose melting points agreed closely with the literature values.

The tenth experiment was repeated since the point for the *para* carbethoxy substituent does not fall on the line in Fig. 1. A value for $k \times 10^2$ of 0.130 ± 0.001 l. mole^{-1} min.$^{-1}$ was obtained.

Experiments of Table III.—With one minor exception the temperature range for the 10 to 70% portion of all these experiments was 83.2–83.8°; the temperature range within an experiment was ±0.15°.

A repetition of the second experiment of Table III gave a $k \times 10^2$ value of 0.89 ± 0.01 l. mole^{-1} min.$^{-1}$.

The 3,4,3',4'-bismethylenedioxydesylaniline obtained in the fourth experiment was recrystallized from hot ethanol. It melted at 135–135.5°.

Anal. Calcd. for $C_{22}H_{17}NO_5$: C, 70.38; H, 4.56; N, 3.73. Found: C, 70.56; H, 4.58; N, 4.03. A repetition of this experiment gave a $k \times 10^2$ value of 0.54 ± 0.1 l. mole^{-1} min.$^{-1}$.

A 3% yield of *p,p*'-dichlorobenzil was isolated along with the expected product from the last experiment of Table III. A repetition of this experiment gave a $k \times 10^2$ value of 2.15 ± 0.02 l. mole^{-1} min.$^{-1}$.

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(12) E. F. Pratt and P. W. Erickson, *J. Am. Chem. Soc.*, **78**, 76 (1956); E. F. Pratt and H. J. E. Segrave, *ibid.*, **81**, 5369 (1959).

(13) Ref. 3, p. 33.

(14) S. N. McGeoch and T. S. Stevens, *J. Chem. Soc.*, 1032 (1935).

(15) F. Brown and F. G. Mann, *ibid.*, 858 (1948).

(16) R. M. Cowper and T. S. Stevens, *ibid.*, 1041 (1947).

(17) Ref. 3, pp. 29, 30.

(18) K. LeRoi Nelson and R. L. Seefeld, *J. Am. Chem. Soc.*, **80**, 5957 (1958).

(19) All melting points are corrected.

(20) We wish to thank Dr. Mary Aldridge and Mrs. Raymond Baylouny for all microanalyses reported herein.