[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MARYLAND]

# Reaction Rates by Distillation. VII. The Relative Basicities of Selected Amides[1]

BY ERNEST F. PRATT AND JACK LASKY[2]

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The effects of 56 selected carboxy- and sulfonamides on the rate of self-etherification of benzhydrol in the presence of *p*-toluenesulfonic acid in benzene solution have been determined. Changes in rate of nearly one hundred-fold resulted as the structure of the amide was varied at a concentration of 0.0156 molar. Good correlation was obtained between the decrease in rate of etherification and the decrease in the electron attracting ability of R as R was varied among $NO_2$, Cl, H, $CH_3$ and $CH_3O$ in the following types of amides: *p*-$RC_6H_4CONH_2$, *p*-$RC_6H_4CONHCH_3$, *p*-$RC_6H_4CON(CH_3)_2$, *p*-$RC_6H_4CONHC_6H_5$, $C_6H_5CONHC_6H_4R$-*p*, *p*-$RC_6H_4CONHC_6H_4R$-*p*, *p*-$RC_6H_4SO_2NHC_6H_5$ and $C_6H_5SO_2NHC_6H_4R$-*p*. The large decreases in etherification rate observed with most of the amides are ascribed to their ability to coördinate with and thereby deactivate the acid catalyst. All of the benzenesulfonamides and most of the chloro- and nitrobenzanilides, however, markedly increased the etherification rate. Since these amides were found to be too weakly acidic to catalyze the etherification in the absence of the *p*-toluenesulfonic acid alternative explanations for their accelerating effects are briefly considered.

Relative basicities for a number of ketones, esters and ethers were previously determined by measuring the ability of these oxygen bases to coördinate with and thereby deactivate the *p*-toluenesulfonic acid used to catalyze the self-etherification of benzhydrol.[3,4] In the present investigation the effects of 56 selected carboxy- and sulfonamides on the rate of the etherification were similarly investigated. One liter of a benzene solution containing 0.250 mole of benzhydrol, 0.001 mole of *p*-toluenesulfonic acid and 0.0156 mole of the amide was heated under reflux. The reaction, which is first order in the benzhydrol, was followed by observing the rate at which the by-product water collected in a Dean-Stark trap. It is apparent from the data in Table I that a nearly one hundred-fold variation in rate constant occurred as the structure of the amide was varied. This contrasts sharply with the results of the earlier study[3] in which the rate constant varied only about fourfold although the concentration of the oxygen bases in that study was eight times the concentration of the amides in this one.

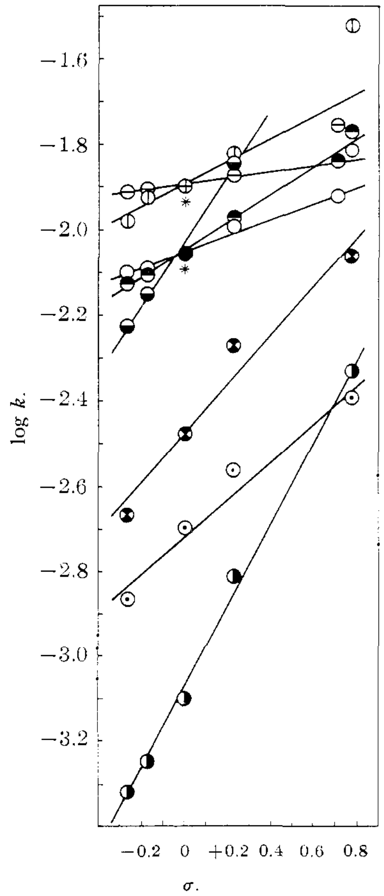
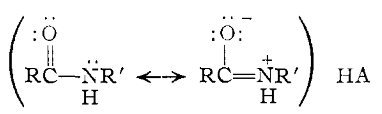


Fig. 1.—Plot of the logarithm of the rate constants for etherification in the presence of: $RC_6H_4SO_2NHC_6H_5$, ⊖; $C_6H_5SO_2NHC_6H_4R$, ⦶; $RC_6H_4CONHC_6H_5$, O; $C_6H_5CONH$-$C_6H_4R$, ◓; $RC_6H_4CONHC_6H_4R$, ◒; $RC_6H_4CONHCH_3$, ⧓; $RC_6H_4CON(CH_3)_2$, ⊙; $RC_6H_4CONH_2$, ◑; (from Table I) *versus* Hammett's *sigma* constants. *, the point, ⊕, is for $C_6H_5SO_2NHC_6H_5$ and the point, ●, is for $C_6H_5CONHC_6H_5$.

A high degree of correlation between an increase in rate of etherification and an increase in the electron attracting ability of either substituent[5] on the –CONH– or –$SO_2$NH– group is apparent throughout Table I. In Fig. 1 it is shown that most of the results for the first eight groups of amides tabulated can be quantitatively correlated with the acidities of the corresponding benzoic acids as expressed by Hammett's $\sigma$ constants.[6,7] Such correlations would be the expected result of deactivation of the *p*-toluenesulfonic acid *via* association with the amides. For the present purposes the complex may be indicated as I since there is disagreement concerning whether the *p*-toluenesulfonic acid (HA) would be coördinated pre-



$$\left(\mathrm{R\overset{O}{\overset{\|}{C}}-\underset{H}{N}R'} \longleftrightarrow \mathrm{R\overset{O^-}{\overset{|}{C}}=\underset{H}{\overset{+}{N}}R'}\right)\ \mathrm{HA}$$

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[1] For the preceding article in this series see E. F. Pratt and P. W. Erickson, THIS JOURNAL, **78**, 76 (1956).

[2] From the Ph.D. thesis of Jack Lasky, June, 1955.

[3] E. F. Pratt and Ken Matsuda, THIS JOURNAL, **75**, 3739 (1953).

[4] L. A. Wiles and E. C. Baughan, *J. Chem. Soc.*, 933 (1953), give valuable data on the basicity of ketones and diketones. Their paper was unavailable in this country when the manuscript of reference 3 was submitted. A recent summary of some of the extensive pioneering work of R. P. Bell and co-workers in this field may be found in "Advances in Catalysis," Vol. IV, Ed. by W. G. Frankenburg, V. I. Komarewsky and E. K. Rideal, Academic Press, Inc., New York, N. Y., 1952, pp. 201–207.

[5] Revised values for the relative electron attracting abilities of a variety of groups are given by H. H. Jaffé, *Chem. Revs.*, **53**, 191 (1953).

[6] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., New York, N. Y., 1940, p. 188.

[7] It will be noted that the points for two of the three benzanilides and benzenesulfonanilides tested which have a nitro group in either of the *para* positions lie markedly above the straight lines of Fig. 1.

TABLE I

EFFECT OF AMIDES ON RATE OF SELF-ETHERIFICATION OF BENZHYDROL

| Compound | $k \times 10^4$, min.$^{-1}$ |
|---|---|
| Blank | 98.7 |
| $RC_6H_4SO_2NHC_6H_5$ | |
| $p$-$CH_3OC_6H_4SO_2NHC_6H_5$ | 123 |
| $p$-$CH_3C_6H_4SO_2NHC_6H_5$ | 125 |
| $C_6H_5SO_2NHC_6H_5$ | 126 |
| $p$-$ClC_6H_4SO_2NHC_6H_5$ | 134 |
| $m$-$O_2NC_6H_4SO_2NHC_6H_5$ | 176 |
| $C_6H_5SO_2NHC_6H_4R$ | |
| $C_6H_5SO_2NHC_6H_4OCH_3$-$p$ | 105 |
| $C_6H_5SO_2NHC_6H_4CH_3$-$p$ | 121 |
| $C_6H_5SO_2NHC_6H_5$ | 126 |
| $C_6H_5SO_2NHC_6H_4Cl$-$p$ | 147 |
| $C_6H_5SO_2NHC_6H_4NO_2$-$p$ | 302 |
| $C_6H_5SO_2N(CH_3)C_6H_4NO_2$-$p$ | 107 |
| $RC_6H_4CONHC_6H_5$ | |
| $p$-$CH_3OC_6H_4CONHC_6H_5$ | 79.6 |
| $p$-$CH_3C_6H_4CONHC_6H_5$ | 81.4 |
| $C_6H_5CONHC_6H_5$ | 87.9 |
| $p$-$ClC_6H_4CONHC_6H_5$ | 102 |
| $m$-$O_2NC_6H_4CONHC_6H_5$ | 120 |
| $p$-$O_2NC_6H_4CONHC_6H_5$ | 156 |
| $p$-$O_2NC_6H_4CON(CH_3)C_6H_5$ | 68.1 |
| $C_6H_5CONHC_6H_4R$ | |
| $C_6H_5CONHC_6H_4OCH_3$-$p$ | 74.6 |
| $C_6H_5CONHC_6H_4CH_3$-$p$ | 78.4 |
| $C_6H_5CONHC_6H_5$ | 87.9 |
| $C_6H_5CONHC_6H_4Cl$-$p$ | 107 |
| $C_6H_5CONHC_6H_4NO_2$-$m$ | 145 |
| $C_6H_5CONHC_6H_4NO_2$-$p$ | 170 |
| $RC_6H_4CONHC_6H_4R$ | |
| $p$-$CH_3OC_6H_4CONHC_6H_4OCH_3$-$p$ | 59.5 |
| $p$-$CH_3C_6H_4CONHC_6H_4CH_3$-$p$ | 70.8 |
| $C_6H_5CONHC_6H_5$ | 87.9 |
| $p$-$ClC_6H_4CONHC_6H_4Cl$-$p$ | 145 |
| $RC_6H_4CONHCH_3$ | |
| $p$-$CH_3OC_6H_4CONHCH_3$ | 21.5 |
| $C_6H_5CONHCH_3$ | 33.4 |
| $p$-$ClC_6H_4CONHCH_3$ | 53.2 |
| $p$-$O_2NC_6H_4CONHCH_3$ | 86.5 |
| $RC_6H_4CON(CH_3)_2$ | |
| $p$-$CH_3OC_6H_4CON(CH_3)_2$ | 13.6 |
| $C_6H_5CON(CH_3)_2$ | 20.2 |
| $p$-$ClC_6H_4CON(CH_3)_2$ | 27.4 |
| $p$-$O_2NC_6H_4CON(CH_3)_2$ | 40.4 |
| $RC_6H_4CONH_2$ | |
| $p$-$CH_3OC_6H_4CONH_2$ | 4.79 |
| $p$-$CH_3C_6H_4CONH_2$ | 5.65 |
| $C_6H_5CONH_2$ | 7.95 |
| $p$-$ClC_6H_4CONH_2$ | 15.5 |
| $p$-$O_2NC_6H_4CONH_2$ | 46.5 |
| $RCONHC_6H_5$ | |
| $CH_3CONHC_6H_5$ | 44.8 |
| $CH_3(CH_2)_4CONHC_6H_5$ | 56.2 |
| $CH_3CH_2CONHC_6H_5$ | 57.6 |
| $C_6H_5CH_2CONHC_6H_5$ | 68.0 |
| $t$-$C_4H_9CONHC_6H_5$ | 79.4 |
| $ClCH_2CONHC_6H_5$ | 89.7 |
| $Cl_2CHCONHC_6H_5$ | 108 |
| $Cl_3CCONHC_6H_5$ | 108 |
| $C_6H_5CONHR$ | |
| $C_6H_5CONHCH_3$ | 33.4 |
| $C_6H_5CONHC_4H_9$-$n$ | 39.7 |
| $C_6H_5CONHC_4H_9$-$t$ | 50.0 |
| $C_6H_5CONHCH_2C_6H_5$ | 51.4 |
| Other amides | |
| $CH_3(CH_2)_4CONH_2$ | 3.38 |
| $CH_3(CH_2)_4CON(CH_3)_2$ | 9.08 |
| $C_6H_5CON(C_4H_9$-$n)_2$ | 21.0 |
| $CH_2CH_2CONHCO$ | 72.3 |
| $o$-$C_6H_4CONHCO$ | 89.1 |
| $o$-$C_6H_4COCONCH_3$ | 92.2 |
| $o$-$C_6H_4COCONH$ | 152 |

dominantly at the nitrogen of the un-ionized or at the oxygen of the ionized form.[8] An analogous complex for the sulfonamides seems reasonable.[9]

It is of considerable interest that all of the benzenesulfonamides and most of the chloro- and nitrobenzanilides, in sharp contrast to all of the ketones, esters and ethers of the previous study,[3] markedly increased the rate of etherification over that of the blank with no amide present. Although it might at first glance be considered that these amides are acting simply as acid catalysts, such an interpretation is invalidated by the fact that none of the amides were effective catalysts by themselves. In each determination the benzene solution of benzhydrol and amide was allowed to reflux for at least 1 hr. to remove any traces of water before the $p$-toluenesulfonic acid was added, and etherification never occurred during this period.

In an attempt to elucidate further the characteristics of the accelerating effect the influence, at two concentrations of $p$-toluenesulfonic acid, of changing the concentrations of benzenesulfon-$p$-nitroanilide, benz-$p$-nitroanilide and benzanilide was studied (Table II). It is evident that doubling the concentration of $p$-toluenesulfonic acid enhances the accelerating effect of a given amount of either of the nitroamides showing again that they are not functioning simply as acid catalysts. At both concentrations of $p$-toluenesulfonic acid, the accelerating effect of the nitroamides is approximately proportional to the amount of amide added while with benzanilide the retarding effect of successive equal portions tends to decrease. If the amount of any of the three amides is held constant doubling the concentration of $p$-toluenesulfonic acid approximately triples the rate.

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[8] It has been concluded that amides are not ordinarily enolized to a significant extent and that they are best represented as the resonance hybrid of the forms shown in parentheses (L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954, pp. 175–198). Amides have been shown to be almost exclusively monomeric in benzene solution at the concentrations used here (M. E. Hobbs and W. W. Bates, THIS JOURNAL, **74**, 746 (1952)). Formerly coördination of acids at the oxygen of amides was preferred (N. V. Sidgwick, "The Organic Chemistry of Nitrogen," University Press, Oxford, 1942, p. 144), but limited recent evidence favors coördination at the nitrogen (S. Mizushima, "Structure of Molecules and Internal Rotation," Academic Press, Inc., New York, N. Y., 1954, pp. 118–119).

[9] (a) E. A. Fehnel and M. Carmack, THIS JOURNAL, **71**, 235 (1949); (b) W. von E. Doering and A. K. Hoffman, *ibid.*, **77**, 521 (1955), and preceding papers in this series.

TABLE II

EFFECT OF VARYING THE CONCENTRATION OF CERTAIN AMIDES AT 0.001 AND 0.002 MOLAR CONCENTRATIONS OF *p*-TOLUENESULFONIC ACID

| 0.001 mole PTS[a] | | 0.002 mole PTS[a] | |
|---|---|---|---|
| Concn. [b] | $k \times 10^4$, min.$^{-1}$ | Concn.[b] | $k \times 10^4$, min.$^{-1}$ |
| | Blanks | | |
| 0 | 98.7 | 0 | 293 |
| | $C_6H_5SO_2NHC_6H_4NO_2$-*p* | | |
| 4 | 146 | 1 | 322 |
| 8 | 199 | 2 | 365 |
| 16 | 302 | 4 | 444 |
| 24 | 393 | 8 | 595 |
| | $C_6H_5CONHC_6H_4NO_2$-*p* | | |
| 4 | 116 | 1 | 315 |
| 8 | 133 | 2 | 338 |
| 16 | 170 | 4 | 378 |
| | | 8 | 459 |
| | $C_6H_5CONHC_6H_5$ | | |
| 16 | 87.9 | 16 | 266 |
| 32 | 78.5 | 32 | 226 |
| 64 | 62.6 | 64 | 199 |
| 128 | 50.0 | | |

[a] *p*-Toluenesulfonic acid. [b] Unit concentration of amide equals 1/1024 molar; thus a concentration of 16 units equals the standard concentration of 1/64 molar.

The simplest interpretation which appears to be consistent with the foregoing data is that the amides increase the etherification rate by increasing the polar character of the benzene medium. In addition to its function as an acid catalyst the *p*-toluenesulfonic acid itself appears to exert a similar effect since doubling its concentration more than doubles the rate (Table II and reference 3). Related effects are frequently encountered in aprotic solvents.[10] All the amides might be expected to exert such a rate increasing effect, but it might also be expected that with only the least basic amides would it predominate over the above described catalyst deactivating effect.

The foregoing data also appear to be consistent with the interpretation that the free amide increases the etherification rate by functioning as a basic catalyst by pushing on the carbon of the benzhydrol from which the acid catalyst is pulling the hydroxyl group. Evidence in support of such concerted processes for a number of related reactions in benzene has been presented.[11] Since a detailed analysis of why, with the least basic amides, their influence as basic catalysts predominates over their influence as deactivators of the acid catalyst, while with the most basic amides the reverse is true, would be complicated and perhaps premature, it will not be attempted at this time. It should be noted, however, that as might be expected, the hydrogen on the nitrogen of the complex I, above, appears to be sufficiently acidic to be catalytically active (see following paragraph). It is reasonable to suggest that the maximum etherification rate is reached only when the proper balance exists between the pull by the complex and the push by the corresponding free amide and that the ideal balance is more closely approached as the basicity of the amide decreases.[12]

It will be noted (Fig. 1) that a change of the amino group of benzamides to the methylamino group caused an increase in rate. If, as seems probable, the deactivating effect on the *p*-toluenesulfonic acid is the chief factor to be considered, the steric effects of the methyl group predominate over its electron releasing effect. A further change of the methylamino group to the dimethylamino group, however, caused a decrease in rate and a very striking decrease also resulted when the hydrogen on the nitrogen of *p*-$NO_2C_6H_4CONHC_6H_5$, $C_6H_5SO_2NHC_6H_4NO_2$-*p* and *o*-$C_6H_4COCONH$ was replaced by a methyl group (Table I). Since the rate decreasing effect appears only when the last hydrogen on the nitrogen is replaced, it is indicated that these hydrogens in complexes such as I are sufficiently acidic to catalyze the etherification to a significant extent.[13] As noted above these hydrogens in the free amide do not catalyze the etherification.

A change of substituent on the anilino group of benzanilides and benzenesulfonanilides (Fig. 1) had a greater effect on the rate of etherification than did a corresponding change on the benzoyl or benzenesulfonyl group; in fact a change on the benzenesulfonyl group usually had a scarcely significant effect. Among the benzanilides the effect of changing both substituents at once was slightly greater than the sum of the effects of changing one at a time. It is of interest that the rates with benzanilides were closer to those for the sulfonanilides than they were to those for the benzamides of the methylamines and ammonia (Fig. 1).

A change of R in the $RCONHC_6H_5$ and $C_6H_5CONHR$ amides of Table I from methyl to *n*-butyl or *n*-amyl causes an increase in rate and a further change to *t*-butyl produces a larger further increase. Again the steric effects of the alkyl groups appear to predominate over their electron releasing effects. Within the same two groups of amides a change of R from *n*-alkyl to benzyl to phenyl causes an increase in rate which might be expected from both the electronic and steric standpoints. A similar interpretation appears valid for the results of a change in R of the $RCONHC_6H_5$ amides from mehtyl to chloromethyl to dichloromethyl, but for some unknown reason a further change to trichloromethyl did not further increase the rate.

In the last group of amides tabulated it is of interest that isatin and the isomeric *o*-phthalimide gave markedly different rates, and that of all the amides tested *n*-caproamide, a representative aliphatic amide, gave the lowest rate.

## Experimental[14]

**Preparation and Purification of Materials.**—All constituents of the reaction mixture were prepared where necessary

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[10] Reference 6, pp. 288–290.

[11] C. G. Swain and M. M. Kreevoy, THIS JOURNAL, **77**, 1122 (1955), and earlier papers from their Laboratory.

[12] C. G. Swain and W. P. Langsdorf, Jr., *ibid.*, **73**, 2816 (1951), have pointed out that steric effects may be extreme. The steric requirements within a series of *para*-substituted amides such as are considered here, would, however, remain constant.

[13] It is pertinent to note in this regard that S. Mizushima in discussing amides states that ". . .the hydrogen atom of the NH group tends to form a strong hydrogen bond . . ."

[14] All melting points are corrected.

and carefully purified by standard methods until the melting points or refractive indices agreed closely with the literature values with the following exceptions.

Although N-*n*-butylbenzamide has been reported as a solid[15] melting at 41–42°, attempts at crystallization were unsuccessful. This amide was readily prepared by slowly mixing ether solutions of one equivalent of benzoyl chloride and two equivalents of *n*-butylamine. The amine hydrochloride was filtered off and the ether solution washed with aqueous alkali, then with aqueous acid and finally with water until neutral to litmus. Distillation of the dried ether solution gave the product at 128° (0.5 mm.), $n^{25}_D$ 1.5327.

*Anal.*[16] Calcd. for $C_{11}H_{15}NO$: C, 74.54; H, 8.53. Found: C, 75.08; H, 8.35.

N,N-Di-*n*-butylbenzamide which appears to be a new compound was prepared by the same general procedure. The amide distilled at 118–120° (0.5 mm.), $n^{25}_D$ 1.5050.

*Anal.* Calcd. for $C_{15}H_{23}NO$: C, 77.20; H, 9.93. Found: C, 77.50; H, 9.87.

*p*-Chlorobenzanilide, prepared by the same general procedure, melted at 199.5–200.0° which is significantly above the literature value of 194°.

The melting point of N-methyl-*p*-chlorobenzamide could not be raised above 152–153° although the literature value is 161°.[17]

*Anal.* Calcd. for $C_8H_8ClNO$: C, 56.70; H, 4.75. Found: C, 56.77; H, 4.46.

**Standard Procedure.**—The standard procedure was identical with that previously described[3] except that 0.0156 mole of amide replaced the 0.125 mole of ketone, ester or ether. All precautions of the earlier study were taken and the results calculated in the same way. The value of 98.7 min.$^{-1}$ for $k \times 10^4$ for the control is the average of five values, the extremes among which were 98.3 and 98.9; the agreement with the value of 109.9 obtained in the previous study[3] is fairly satisfactory. Duplicate determinations on many of the amides showed that the rate constants could readily be checked to within ±2%. In the great majority of the cases the plot of log $a/(a - x)$ *versus* $t$ gave a straight line for at least the 20 to 80% portion of the reaction. Only in the cases of N,N-dimethylanisamide and *n*-caproamide which gave linear portions of about 45% was the linear portion appreciably less than 50%. In over 80% of the determinations the yield of water was 99 ± 1%, and except in the cases of *p*-nitrobenzamide and *n*-caproamide which gave 102.5 and 95% yields, respectively, the yield was always 99 ± 2%. Within a given experiment the temperature variation for the 10 to 80% range of the reaction was not more than ±0.1°; among all the experiments the temperature was 82.5 ± 0.5°.

When a representative compound of the previous study,[3] namely, di-*n*-butyl ether, was checked using 0.125 mole as before the value of $k \times 10^4$ was 45.0 min.$^{-1}$ which checks almost exactly with the earlier value of 45.6. With 0.0156 mole of di-*n*-butyl ether (corresponding to the standard amount of amide in the present study) the value of $k \times 10^4$ was 90.7 min.$^{-1}$.

It is fortunate that such small amounts of amides were effective since difficulties arising from their limited solubility were thus largely eliminated. Several amides, however, namely, oxamide, malonamide, fumaramide, cyanoacetamide, 2,5-piperazinedione, γ-hydroxypyridine, saccharin and *p,p'*-dinitrobenzanilide were not studied because they were not completely soluble under the standard conditions.

Any changes required in the standard procedure for the experiments of Table II are readily apparent from the tabulated data.

**Consideration of Possible Side Reactions.**—Since 0.125 mole of dibenzhydryl ether was present together with the 0.0156 mole of amide at the end of the determination quantitative recovery of the amide was ordinarily impractical. Because of their solubility in alkali or unusually low solubility in benzene, however, the following amides were recovered in at least 85% yields: benzanilide, *p*-nitrobenzanilide, benzenesulfon-*p*-nitroanilide, benzenesulfon-*p*-methylanilide and *p*-methoxybenzenesulfonanilide. When the determination of the basicity of benzenesulfonamide was attempted, excess water was evolved. Upon cooling the reaction mixture, a small amount of a white solid which melted at 185–185.5° was obtained. The literature melting point for N-diphenylmethylbenzenesulfonamide is 182°. It was found possible to prepare the pure solid in 62% yield by refluxing a solution of 0.031 mole of benzhydrol, 0.031 mole of benzenesulfonamide, 0.0025 mole of *p*-toluenesulfonic acid and 250 ml. of benzene for 24 hr. at which time a 97% yield of water, calculated for N-alkylation, was obtained. It appears that N-alkylation by benzhydrol interferes significantly only with amides which have no alkyl or aryl groups on the nitrogen[18] and which give an unusually strong acid upon hydrolysis. Most of the amides used in this study had an alkyl or aryl group on the nitrogen. The above noted 2.5% excess of water obtained with *p*-nitrobenzamide suggests that N-alkylation may have occurred here to an appreciable extent, but in no additional cases was there a significant excess of water or any other evidence of N-alkylation.

When attempts were made to determine the rates of etherification in the presence of formamide and formanilide hydrolysis of the amides occurred as indicated by the precipitation of the *p*-toluenesulfonates of ammonia and aniline. In both cases water was evolved much more slowly than in any of the experiments of Table I and water evolution stopped at less than a 25% yield. In no other determinations was precipitation of the amine salts or any other indication of hydrolysis encountered.

**Acknowledgment.**—It is a pleasure to thank du Pont de Nemours and Company for a fellowship (to J. L.) which greatly aided the progress of this work.

COLLEGE PARK, MARYLAND

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[15] H. W. Grimmel, A. Guenther and J. F. Morgan, THIS JOURNAL, **68**, 539 (1946).

[16] We wish to thank Dr. Mary Aldridge and Miss Kathryn Gerdeman for the microanalyses.

[17] J. Tafel and C. Enoch, *Ber.*, **23**, 104 (1890).

[18] R. F. Phillips and B. M. Pitt, THIS JOURNAL, **65**, 1355 (1943).