necked, pear-shaped distilling flask (A), which was fitted with a 30-ml. dropping funnel containing 20 ml. of 0.11 *M* potassium dichromate in 18 *N* sulfuric acid, and a water cooled condenser. Four hundred milligrams of 2,4-dinitrophenylhydrazine in 15 ml. of 4 *N* sulfuric acid was placed in a 60-ml. pear-shaped receiving flask (B), which was connected to a carbon dioxide trap. A slow stream of nitrogen (2 to 3 bubbles per second) was passed through the apparatus and 10 ml. of the dichromate solution was added. The reaction mixture was maintained at room temperature for 10 to 15 minutes. Flask A was then heated at 70° by means of a water-bath. Within 5 to 10 minutes crystals of acetone 2,4-dinitrophenylhydrazone appeared in the receiving flask (B). To ensure complete oxidation an additional 10 ml. of dichromate solution was added to the reaction mixture and the reaction continued for an additional 15 minutes.

The hydrazone was collected on a filter paper and crystallized from 95% alcohol. The crystals were dissolved in petroleum ether and any insoluble residue removed by filtration. The petroleum ether solution was concentrated to dryness *in vacuo* and the hydrazone crystallized twice from 1:1 petroleum ether–diethyl ether mixture, yielding 20 mg. of needle-shaped crystals, m.p. 125–126°, no depression on admixture with an authentic sample of acetone 2,4-dinitrophenylhydrazone. The yield from sodium α,β-dimethylbutyrate was 8.5%. *Anal.* Calcd. for $C_9H_{10}O_4N_4$ (238): C, 45.42; H, 4.20; N, 23.50. Found: C, 45.47; H, 4.27; N, 23.47.

Twenty milligrams of the radioactive acetone 2,4-dinitrophenylhydrazone was diluted with an equal amount of nonradioactive hydrazone and dissolved in 2 *N* sulfuric acid solution. The hydrazone solution was slowly distilled and the distillate was trapped in 7.5 ml. 1 *N* sodium hydroxide solution. After about 15 ml. of distillate had been collected, the trap was detached and excess iodine solution added to the distillate.[15] The iodoform was collected by centrifugation, washed with distilled water and analyzed for its C^{14} content; specific activity, 0.00 c./min./mmole C. This iodoform was derived from both C_{26} and C_{27}.

The supernatant remaining after separation of the iodoform was made acidic with dilute sulfuric acid and the excess iodine was titrated with sodium thiosulfate. The mixture was steam distilled and the distillate was neutralized with 0.1 *N* sodium hydroxide. A salt of an acid was obtained. The free acid was identified as acetic acid by its Duclaux distillation constant; specific activity of sodium salt, 49.8 c./min./mg. or 2,040 c./min./mmole C.

Radioactivity Measurements.—The counting equipment consisted of a Tracerlab Autoscaler and Flow Gas Counter. The carbon 14 content of a sample was determined by counting either a direct mount of the material on copper or aluminum disks, or by combustion of the sample to CO_2 and conversion to barium carbonate, which was then counted in the usual manner. All samples were counted a sufficient length of time to ensure less than a 4% counting error.

SEATTLE 5, WASHINGTON

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

Reaction Rates by Distillation. IV. The Effect of Changes in Structure on the Rate of the Baeyer Condensation

BY ERNEST F. PRATT AND LARRY Q. GREEN[1]

RECEIVED JULY 17, 1952

It has been found that the Baeyer condensation proceeds smoothly in 80 to 90% yield when a benzene solution of an activated aromatic compound such as dimethylaniline or anisole, an aromatic aldehyde and *p*-toluenesulfonic acid is refluxed in an apparatus equipped with a Dean–Stark water trap. The reaction has been followed by observing the rate at which the by-product water collects and the rates of condensation of the *p*-$(CH_3)_2N$, CH_3O, CH_3, H, Cl and NO_2 benzaldehydes with dimethylaniline have been correlated quantitatively *via* Hammett's "ρ–σ" treatment. It is shown that the first of the two consecutive reactions involved in the Baeyer condensation is the rate-controlling one.

In previous papers of this series, it has been shown that etherifications, alkylations and Knoevenagel condensations may be carried out to advantage by refluxing a benzene solution of the reactants and catalyst in an apparatus equipped with a Dean–Stark trap to remove the by-product water as it forms.[2] These reactions may, furthermore, be followed quantitatively by observing the rate at which the water collects. The results of the extension of the method to the Baeyer condensation using *p*-toluenesulfonic acid as the catalyst are reported here. It is commonly considered that this condensation proceeds *via* the consecutive reactions[3,4]

$$p\text{-}RC_6H_4CHO + C_6H_5R' \longrightarrow p\text{-}RC_6H_4CHOHC_6H_4R'\text{-}p \quad (1)$$

$$p\text{-}RC_6H_4CHOHC_6H_4R'\text{-}p + C_6H_5R' \longrightarrow p\text{-}RC_6H_4CH(C_6H_4R'\text{-}p)_2 + H_2O \quad (2)$$

Dimethylaniline ($R' = N(CH_3)_2$) was found to react with various *p*-substituted benzaldehydes to give the expected products in high yield. The results of relative rate studies in which the *p*-substituent, R, was varied are shown in Table I.

TABLE I

THE CONDENSATION OF *p*-RC_6H_4CHO WITH $C_6H_5N(CH_3)_2$

R	$t_{0.5}$, min.	Yield,[a] %	$k \times 10^5$, l./mole/min.
NO_2	170	89	195 ± 4.0
Cl	475	83	69.8 ± 0.7
H	600	85	54.5 ± .8
CH_3	860	80	38.1 ± .8
CH_3O	1500	85	22.4 ± .5
$(CH_3)_2N$	5420	77	6.25 ± .1

[a] These are the yields of pure recrystallized product.

The tabulated rate constants were calculated on the assumption that the reactions are second order, *i.e.*, first order with respect to both the benzaldehyde and the dimethylaniline (see Experimental for details). In Fig. 1 it is shown that the increase in reaction rate with decrease in the ability of R

---

[1] From the Ph.D. thesis of L. Q. Green, September, 1948.

[2] For the preceding article in this series see E. F. Pratt and E. Werble, THIS JOURNAL, **72**, 4638 (1950). It is evident that the distillation method should be applicable to the quantitative determination of the wide variety of functional groups which have been shown to undergo a reaction to give the theoretical yield of water.

[3] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 348.

[4] G. E. K. Branch and M. Calvin, "The Theory of Organic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1944, pp. 482–483.

to release electrons may be quantitatively correlated by Hammett's "ρ–σ" treatment.[5] The value of ρ, *i.e.*, the slope of the line in Fig. 1, is 0.954. Hammett's list of reactions for which this correlation holds includes no examples which involve, as does the Baeyer condensation, reaction of a carbonyl group.

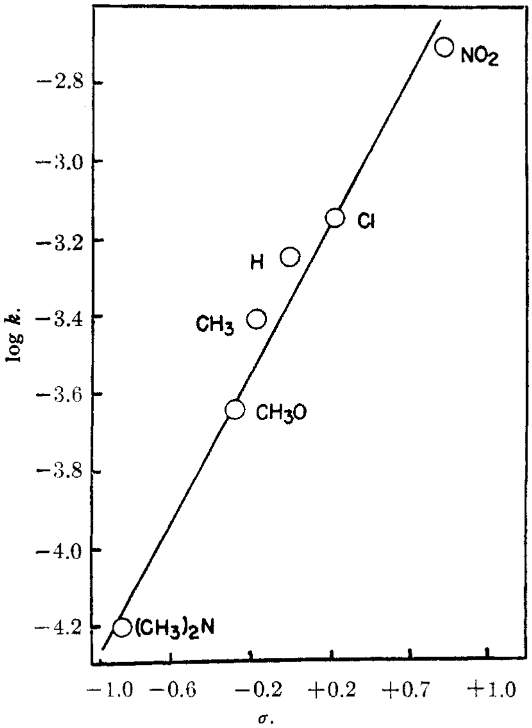
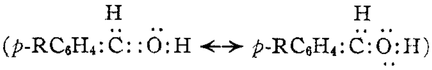


Fig 1.—Plot of the logarithm of the rate constants for the condensation of *p*-substituted benzaldehydes with dimethylaniline *versus* Hammett's σ-constants.

The increase in reaction rate with decrease in the electron-releasing ability of R shows that reaction (1) rather than (2) is rate controlling. This follows from the fact that a number of experiments with *p*-substituted benzhydrols[6] and benzyl alcohols[7] have shown that the rate of reaction (2) decreases rapidly with decrease in the electron-releasing ability of R.

A comparison of the rate of reaction (2) with the over-all rate of reactions (1) and (2) also shows that reaction (1) determines the rate. Thus *p*-methoxybenzhydrol (R = H, R′ = CH_3O) reacted with anisole (R′ = CH_3O) to give a 98% yield of water in less than 2% of the time required for the over-all reaction of benzaldehyde with anisole at the same catalyst concentration. Similarly *p,p*′-dimethylaminobenzhydrol reacted much more rapidly with dimethylaniline[6] than did *p*-dimethylaminobenzaldehyde (Table I) even though the catalyst concentration was one hundred times as high in the latter case; here both R and R′ are $(CH_3)_2N$. In all four of these experiments the expected products were isolated in 70 to 80% yields.

According to Hammett[3] the Baeyer reaction proceeds *via* the condensation of the oxonium–carbonium ion resonance hybrid



$$\left(p\text{-}RC_6H_4\!:\!\overset{H}{\ddot{C}}\!::\!\ddot{O}\!:\!H \longleftrightarrow p\text{-}RC_6H_4\!:\!\overset{H}{\ddot{C}}\!:\!\underset{\cdot\cdot}{\ddot{O}}\!:\!H\right)^{\oplus}$$

with the aromatic ring in typical Friedel–Crafts fashion.[8] It seems reasonable to consider that it is this discrete step of reaction (1) which determines the over-all rate since the coördination of the proton[9] with the benzaldehyde may well be rapid as are many other similar acid–base reactions. The changes in rates shown in Table I may be explainable on this basis since the positive charge at the reactive center and hence the reactivity of the oxonium–carbonium ion resonance hybrid would be expected to increase as the electron-releasing ability of R decreases. This interpretation is also consistent with the second-order reaction kinetics.

The foregoing interpretation is also in agreement with the fact that as the electron-releasing ability of R′ increased the reaction rate increased. Thus when anisole (R′ = CH_3O), phenetole (R′ = C_2H_5O) and butyl phenyl ether (R′ = $CH_3(CH_2)_3O$) were condensed with benzaldehyde the times required for the production of a 50% yield of water were 365, 250 and 175 minutes, respectively.[10] The expected products were isolated in about 75% yields. These results are supported by the findings that benzene (R′ = H) may be used as an inert solvent for the reaction of dimethylaniline (R′ = $(CH_3)_2N$) and that toluene (R′ = CH_3) reacts only very slowly while phenol (R′ = OH) reacts extremely readily with benzaldehyde. In the case of phenol, probably because of the occurrence of considerable *o*-substitution, only a very low yield of the expected product was isolated.

When attempts were made to condense chloral, cinnamaldehyde or heptanone-2 with dimethylaniline little if any of the expected products were obtained. Fairly satisfactory results were obtained, however, for the condensation of *n*-heptaldehyde and α-ethylbutyraldehyde with this amine.

Experimental[11]

Purification of Materials.—All starting materials were carefully purified by the usual methods. The physical constants for those compounds not used in the preceding in-

---

[5] Reference 3, pp. 188–197. We have used Hammett's σ-values which are based on the ionization constants determined by J. Dippy and co-workers (*J. Chem. Soc.*, 644 (1936)) except in the case of *p*-dimethylaminobenzoic acid. Since Dippy did not determine the ionization constant of this acid we have used the value 9.4×10^{-6} as found by J. Johnston, *Proc. Roy. Soc.*, (*London*), **A78**, 82 (1906). This gives a σ-value of 0.824 for the $(CH_3)_2N$ group which is not unreasonable compared to Hammett's value of 0.660 for the NH_2 group. Recent pertinent discussions are given by H. Gilman and G. E. Dunn, This Journal, **73**, 3404 (1951), and by E. Berliner and L. C. Monack, *ibid.*, **74**, 1574 (1952).

[6] E. F. Pratt and H. J. E. Segrave, to be published.

[7] E. F. Pratt, R. K. Preston and J. D. Draper, This Journal, **72**, 1367 (1950).

[8] For related discussions see J. von Braun, *Ann.*, **472**, 9 (1929), Schneller and Smith, This Journal, **70**, 4057 (1948); and Y. Ogata and M. Okano, *ibid.*, **72**, 1459 (1950).

[9] In these benzene solutions this coördination may involve formation of a hydrogen bond with a molecule of un-ionized *p*-toluenesulfonic acid rather than reaction with a proton.

[10] The second-order rate constants for these three reactions, calculated in the same way as for Table I, drifted upward from 15 to 25% over the first 60% of the reaction. It seems probable that with the relatively large amount of *p*-toluenesulfonic acid required here unless an excess of dimethylaniline is present the activity of the catalyst changes as the reaction progresses.

[11] All melting points are corrected.

vestigation[2] were as follows: dimethylaniline, $n^{21.5}\mathrm{D}$ 1.5696; anisole, $n^{23}\mathrm{D}$ 1.5160; phenetole, $n^{22}\mathrm{D}$ 1.5062; *n*-butyl phenyl ether, $n^{26}\mathrm{D}$ 1.4938; phenol, m.p. 41.0–41.2°; *p*-dimethylaminobenzaldehyde, m.p. 73.5–74.5°; *p*-methylbenzaldehyde, b.p. 94.3–95.0° (20 mm.); *n*-heptaldehyde, $n^{20}\mathrm{D}$ 1.4125; α-ethylbutyraldehyde, $n^{21}\mathrm{D}$ 1.4010; chloral, $n^{22}\mathrm{D}$ 1.4561; cinnamaldehyde, $n^{22}\mathrm{D}$ 1.6193; *p*-toluenesulfonic acid, m.p. 105–106°, neut. equiv. 190.5 (calcd. 190.2); *p*-methoxybenzhydrol, m.p. 66.5–67.5°. All these constants agree satisfactorily with the values in the literature except that the recorded refractive index for *n*-butyl phenyl ether is $n^{26}\mathrm{D}$ 1.5019.[12] The value listed above is for repurified Eastman Kodak Co. material. When this compound was prepared (80% yield) by heating a mixture of 1 mole of phenol, 1 mole of *n*-butyl bromide and 1.1 moles of sodium hydroxide on the steam-bath for 14 hours and carefully purified[13] the refractive index changed only very slightly to $n^{26}\mathrm{D}$ 1.4940. All the liquid aldehydes were redistilled immediately before use.

Reactions of Table I.—The precautions previously described[14] were taken and the same apparatus and procedure were used except for the following modifications. Sufficient benzene was added to 0.064 mole of *p*-toluenesulfonic acid monohydrate and 0.625 mole of dimethylaniline to give a total volume of 250 ml. minus the volume of the aldehyde (0.125 mole) to be added. The water separator was filled with additional benzene and the solution refluxed until all the water was removed from the catalyst. The aldehyde was then added with swirling and readings of time *versus* volume of water produced were begun.

After reaction was complete as evidenced by cessation of water evolution the mixtures were extracted with 100 ml. of 5% aqueous potassium hydroxide solution and then with water until the washings were free of alkali. The benzene was distilled off, the excess dimethylaniline removed under reduced pressure and the products isolated from the residue. Even with products readily crystallized it was often found that the yield was improved by distillation prior to the crystallization. The yields of water were 98 to 101% in all cases. The melting points of the products agreed closely with the recorded values except that the products from the *p*-chloro- and *p*-nitrobenzaldehydes melted at 105–106° and 182–183° while the literature values are 98–99°[15] and 176–177°,[16] respectively. Both the high (102°) and low (93°) melting forms of leucomalachite green were isolated; rapid crystallization of the higher melting form from hot alcohol converted it to the lower melting form.

It was necessary to use the rather high concentrations of reactants so that the reaction would proceed at a suitable rate. As a consequence of the decrease in concentration of total solutes as the reaction progressed there was a gradual fall in temperature of 0.6 to 1.0° over the first 60% of the reaction. It may be estimated on the basis of the rate in refluxing toluene (see below) that a 1° change in temperature would change the rate constant about 5%. This, of course, is not insignificant, but it does not seriously affect any of the conclusions reached. Among these reactions the initial temperature was 92.9 ± 0.3° and the temperature at 60% reaction was 92.2 ± 0.3°.

The rate constants in Table I as well as those given elsewhere were, unless otherwise noted, calculated on the assumption that the reactions are first order with respect to both the aldehyde and the dimethylaniline. The usual second-order equation was modified to allow for the fact that the dimethylaniline was consumed in both a slow (reaction (1)) and a fast (reaction (2)) step to give the result

$$k = \frac{2.30}{t(2a - b)} \log \frac{b(a - x)}{a(b - 2x)}$$

Here *a* is the original aldehyde concentration (in moles per liter), *b* the original amine concentration and *x* the decrease in aldehyde concentration in time *t*. Corrections were made for the expansion in volume (6% for benzene solutions and 9% for toluene solutions) which occurred upon warming from room temperature to the reflux temperature. Zero time was taken at the time of addition of the aldehyde and five successive *k* values were calculated from the data at 0 and 20% reaction, 0 and 30% reaction and so on up to 0 and 60% reaction. Above 60% reaction the *k* values began to rise significantly. The values given are the arithmetic mean of the five successive values plus or minus the average deviation of a single value from this mean.

Sufficient *p*-methylbenzaldehyde was not available for a second determination, but the rate constants for the other five reactions were readily checked to within 3 to 6% in repeat experiments.

A 150% excess of dimethylaniline was used in order to increase the rate and maintain constant catalyst activity. A consequence of this is that fairly satisfactory constants are also obtained if the calculations are made on the assumption that the reaction is first order with respect to the aldehyde only, *i.e.*, that the concentration of the dimethylaniline does not enter into the rate expression. In order to determine whether the concentration of dimethylaniline does affect the rate the experiment with benzaldehyde (Table I) was repeated except that the concentration of benzaldehyde was doubled. The rate constant under these conditions calculated from the second order equation above was 50.0 ± 0.8×10^{-5} l. per mole per min. with no significant drift in the constant as the reaction progressed. Calculation on the first-order basis gave "constants" which decreased steadily as the reaction progressed; the total decrease over the first 60% of the reaction was 22%.

These results were corroborated by the results of order calculations for two similar experiments in which toluene was the solvent in place of benzene. In the first of these 0.125 mole of benzaldehyde, 0.625 mole of dimethylaniline and 0.032 mole of catalyst were used with sufficient toluene to give 500 ml. of solution. The temperature fell from 118.7 to 117.8° over the first 60% of the reaction. On the second-order basis the rate constant was 113 ± 0.2×10^{-5} l. per mole per min. and on the first-order basis the constant was also fairly satisfactory with a downward drift of only about 5%. The second experiment was identical except that twice as much aldehyde was used. The temperature fell from 119.4 to 118.5°. Here the second-order constant was 82.5 ± 0.2×10^{-5} l. per mole per min. with no significant drift while the first-order "constant" decreased steadily; the total decrease over the first 60% of the reaction was 37%.

An idea of the effect of changes in temperature was gained by repeating the reaction of benzaldehyde and dimethylaniline (Table I) in refluxing toluene instead of benzene. An 85% yield of the pure product was isolated and the rate constant was 228 ± 5×10^{-5} l. per mole per min. The temperature decreased from 124.0 to 123.3° over the first 60% of the reaction. Upon completion of the reaction the catalyst was extracted into an excess of standard sodium hydroxide solution. Titration of the excess alkali showed that 99% of the catalyst remained at the end of the reaction. When this experiment in toluene was repeated with half as much *p*-toluenesulfonic acid the rate constant was 160 ± 5×10^{-5} l. per mole per min. With the excess of dimethylaniline present it is not surprising that a given decrease in the amount of acid does not cause an equivalent decrease in catalytic activity.

Alkylation of Anisole by *p*-Methoxybenzhydrol.—This study of the rate of reaction (2) (*cf.* Discussion) was designed to allow as close a comparison as possible with the companion study of the over-all rates of reactions (1) and (2) which is the first experiment of the group immediately below. A solution of 0.125 mole of *p*-methoxybenzhydrol, 0.500 mole of anisole, 0.064 mole of *p*-toluenesulfonic acid and sufficient benzene to give a total volume of 500 ml. was refluxed as usual. A 50% yield of water collected in 5 minutes and a 98% yield in 20 minutes. (The corresponding times for the related experiment immediately below were 365 and 1,440 minutes, respectively.) A 68% yield (26.0 g.) of pure *p,p'*-dimethoxytriphenylmethane was isolated, m.p. 99–100°.

Reactions of Other Aromatic Compounds with Benzaldehyde.—A solution of 0.625 mole of anisole, 0.125 mole of benzaldehyde and 0.064 mole of *p*-toluenesulfonic acid monohydrate with sufficient benzene to give a total volume of 500 ml. was refluxed in the usual fashion. A 70% yield (26.6 g.) of product distilling at 191–205° (0.8 mm.) was obtained. Crystallization from 1:1 methanol–chloroform gave 23 g. (60%) of *p,p'*-dimethoxytriphenylmethane, m.p. 98–100.6° (lit. m.p. 100–101°). The yield of pure product from a similar experiment except that no excess anisole was used was only 30%. From an experiment in

---

[12] R. Smith, THIS JOURNAL, **56**, 1419 (1934).

[13] We wish to thank Dr. Norman Sharpless for this preparation.

[14] E. F. Pratt and J. D. Draper, THIS JOURNAL, **71**, 2846 (1949).

[15] E. Noelting and P. Gerlinger, *Ber.*, **39**, 2049 (1906).

[16] O. Fischer, *ibid.*, **14**, 2520 (1881).

which 0.125 mole of benzaldehyde, 0.032 mole of catalyst and sufficient anisole to give a total volume of 250 ml. was used a 77% yield of pure product was obtained.

When phenetole was used in an experiment like that described first for anisole 32.0 g. (77%) of light orange distillate of b.p. 196–204° (0.5 mm.) was obtained. A negative test for solubility in aqueous alcoholic potassium hydroxide indicated the product was free of phenols. Attempts at crystallization were unsuccessful, but a redistilled sample (b.p. 196–197° at 0.5 mm.) analyzed satisfactorily for the expected *p,p'*-diethoxytriphenylmethane. This compound has not been reported previously.

Anal.[17] Calcd. for $C_{23}H_{24}O_2$: C, 83.10; H, 7.28. Found: C, 83.01, 83.11; H, 7.37, 7.33.

Similar results were obtained with *n*-butyl phenyl ether under the same conditions. The product distilled at 234–246° (1.0 mm.) and weighed 33.7 g. (70%). A redistilled sample (b.p. 225–227° at 0.5 mm.) analyzed satisfactorily for *p,p'*-di-*n*-butoxytriphenylmethane which has not been reported previously.

Anal. Calcd. for $C_{27}H_{32}O_2$: C, 83.46; H, 8.30. Found: C, 83.39, 83.18; H, 8.31, 8.26.

In the foregoing experiments with the three phenyl ethers under the same conditions the yield of water was 98 to 100%. In each case the temperature varied about 0.8° over the first 60% of the reaction; the median temperature with anisole was 86.3°, with phenetole 86.7° and with butyl phenyl ether 87.3°. The experiments for each of these three phenyl ethers were repeated and close checks on the rate (*cf.* Discussion) were obtained.

Excess toluene served as the solvent in a study of its reactivity. A solution of 0.125 mole of benzaldehyde and 0.128 mole of catalyst in sufficient toluene to give a total volume of 250 ml. was used. A 50% yield of water was obtained in 60 hours and a 98% yield in 130 hours. The temperature decreased from 115.9 to 115.2° as the reaction progressed. A 74% yield of product (25.2 g.) distilled at 156–157° (0.7 mm.). Crystallization from methanol gave a 38% yield (13.0 g.) of *p,p'*-dimethyltriphenylmethane, m.p. 48–49°. The low yield of crystals may be due to the presence of some *p,o'*-dimethyltriphenylmethane.

Phenol reacted rapidly to give a 50% yield of water in 3 hours and a 99% yield in 10 hours when a solution of 0.125 mole of benzaldehyde, 0.625 mole of phenol and 0.008 mole of catalyst in sufficient benzene to give a total volume of 500 ml. was refluxed in the usual fashion. Only a 14% yield of *p,p'*-dihydroxytriphenylmethane was isolated, m.p. 157–159.5°.

Reactions of Other Aldehydes with Dimethylaniline.—When *n*-heptaldehyde was treated with dimethylaniline using the procedure given above for the experiments of Table I an 83% yield of water was obtained in 120 hours. An 80% yield of 1,1-bis-(*p*-dimethylaminophenyl)-heptane distilled at 206–212° (0.5 mm.). Trituration with ethanol gave a 69% yield of crystals which melted at 58.5–59.0° (lit. m.p. 59.5°).

The same conditions were employed for the reaction of α-ethylbutyraldehyde except that 0.128 mole of catalyst was used. The reaction was stopped after refluxing two weeks at which time a 90% yield of water had been evolved. A 72% yield of crude 1,1-bis-(*p*-dimethylaminophenyl)-2-ethylbutyraldehyde distilled at 180–212° (0.8 mm.). Recrystallization five times from ethanol gave a 46% yield of white crystals which melted at 103.0–104.5°.

Anal. Calcd. for $C_{22}H_{32}N_2$: C, 81.43; H, 9.93; N, 8.64. Found: C, 81.70; H, 10.21; N, 9.07.

Attempts to find a basis of calculation which would give satisfactory rate constants for these two experiments were unsuccessful.

Acknowledgment.—It is a pleasure to thank du Pont de Nemours and Company for a fellowship (to L. Q. G.) and the Research Corporation for additional financial support.

COLLEGE PARK, MD.

---

(17) We wish to thank Professor Mary Aldridge and Mr. Byron Baer for the microanalyses.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

The Reaction of *n*-Butyllithium with Dibenzothiophene-5-dioxide and with Diphenyl Sulfone

BY HENRY GILMAN AND DONALD L. ESMAY

RECEIVED AUGUST 18, 1952

Dibenzothiophene-5-dioxide reacts with *n*-butyllithium at reduced temperatures (−20 to −30°) to yield after carbonation 4-carboxy- and/or 4,6-dicarboxydibenzothiophene-5-dioxide. Similarly diphenyl sulfone yields *o*-carboxy- and/or *o,o'*-dicarboxydiphenyl sulfone.

The metalation of dibenzothiophene has been accomplished with various organometallic compounds[1] yielding derivatives substituted in the 4-position in all cases except the apparently anomalous reaction with phenylcalcium iodide which yields 3-dibenzothiophenecarboxylic acid on carbonation.[1a] The first successful nuclear metalation of a sulfoxide was recently accomplished by treating dibenzothiophene-5-oxide with *n*-butyllithium at −10°.[2] The product obtained on carbonation was established as being 4-dibenzothiophenecarboxylic acid, thereby showing that reduction of the sulfoxide group occurred along with the nuclear metalation.[3]

Initial attempts to metalate dibenzothiophene-5-dioxide with *n*-butyllithium yielded only acidic gums after carbonation.[4] We are reporting the use of reduced temperatures (−20 to −30°) to successfully accomplish the metalation of dibenzothiophene-5-dioxide with *n*-butyllithium in diethyl ether. The use of one equivalent of *n*-butyllithium yielded after carbonation 4-carboxydibenzothiophene-5-dioxide. Similarly, two equivalents of the metalating agent gave mostly 4,6-dicarboxydibenzothiophene-5-dioxide along with some 4-carboxydibenzothiophene-5-dioxide, while

---

(1) (a) H. Gilman and A. L. Jacoby, *J. Org. Chem.*, **3**, 108 (1938); (b) H. Gilman and R. L. Bebb, THIS JOURNAL, **61**, 109 (1939); (c) H. Gilman, R. N. Meals, G. J. O'Donnell and L. A. Woods, *ibid.*, **65**, 268 (1943); (d) H. Gilman, A. H. Haubein, G. J. O'Donnell and L. A. Woods, *ibid.*, **67**, 922 (1945).

(2) H. Gilman and D. L. Esmay, *ibid.*, **74**, 266 (1952).

(3) H. Gilman and R. D. Nelson, *ibid.*, in press, have shown that 10-ethylphenothiazine-5-oxide undergoes a similar reaction.

(4) H. Gilman and F. J. Webb, *ibid.*, **71**, 4062 (1949).