

on Grade I neutral alumina (Woelm) with 1:4 ether-benzene gave 6.8 mg. (59%) of 9-phenylanthracene, m.p. 154–156° (reported¹⁵ m.p. 152°), identical by mixed melting point and ultraviolet analysis ($\lambda_{\text{max}}^{\text{C}_2\text{H}_5\text{OH}}$ 255 m μ , $\log \epsilon = 5.16$)¹⁶ with an authentic sample of XII prepared from anthrone and phenylmagnesium bromide.¹⁷

6,11-Diphenyl-5,12-naphthacenequinone (XVII) and 9-phenylanthracene (XIII). Sulfone IV (160 mg., 0.5 mmole) and 395 mg. (2.5 mmoles) of 1,4-naphthoquinone were mixed together in a test tube (0.8 × 5 cm.). The upper part of the test tube was then melted and drawn out into a fine capillary, which was left open. The tube was immersed up to its tip in a hot oil bath (250°) for 15 min., then cooled and wiped dry. Both the tube and its contents were ground to a fine powder in a mortar and extracted with two 20-ml.

(16) E. Clar and D. G. Stewart, *J. Am. Chem. Soc.*, **74**, 6237 (1952).

(17) J. W. Cook, *J. Chem. Soc.*, 2170 (1926).

portions of 1:4 ether-benzene. The extracts were combined and evaporated to dryness *in vacuo*. The residue was taken up in 10 ml. of 1:4 ether-benzene and chromatographed with the same solvent on Grade I neutral alumina (Woelm). The first fraction (blue-fluorescent) to leave the column consisted of 26 mg. (20%) of 9-phenylanthracene, m.p. 150–153°, identical in mixed melting point with an authentic sample prepared from anthrone.¹⁷ The second fraction (yellow) consisted of 86 mg. (42%) of 6,11-diphenyl-5,12-naphthacenequinone, m.p. 287–288°, identical in melting point and infrared spectrum with an authentic sample prepared from 1,3-diphenylisobenzofuran and 1,4-naphthoquinone.¹⁰

Acknowledgment. We wish to thank the Research Corporation for a grant supporting a part of this work.

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[CONTRIBUTION FROM THE RESEARCH DEPARTMENT, DIAMOND ALKALI COMPANY]

The Addition-Chlorination of Aniline

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Received January 26, 1960

The benzene ring of aniline has not undergone chlorination by addition in the past because the electron-releasing amine group enables substitution to take place too readily. The use of two electron-withdrawing acyl groups attached to the amine group in aniline did not enable addition-chlorination to take place. Instead, monoacetylation took place, followed by substitution-chlorination of the acetanilide to 2,4-dichloroacetanilide. The use of non-cleavable electron-withdrawing groups permitted addition-chlorination to take place readily. Thus, phenyl isocyanate and *N*-phenylimidocarbonyl chloride were chlorinated by addition in good yields. Hydrolysis of the addition products suggests that the major stable product from any attempted addition-chlorination of aniline would be 2,4,6-trichloroaniline.

In our previous paper on the addition-chlorination of phenol,¹ we demonstrated that the combination of the phenolic oxygen atom with groups exerting a negative inductive effect permits addition-chlorination of the benzene ring to take place readily. Thus, phenyl trichloroacetate was addition-chlorinated in near quantitative yields.

Aniline, like phenol, contains a strong electron-releasing atom, and readily undergoes substitution chlorination, even in the absence of catalysts. It was the purpose of this work to add chlorine to the benzene ring of an aniline derivative, and to determine the nature of the product of the addition-chlorination of aniline. The direct addition-chlorination of aniline was not attempted because of its ease of substitution, and because the expected product is a *gem*-chloroamine, II, an unstable structure which would not be identifiable.

It is known that the single acetylation of aniline diminishes the *ortho-para*-orienting power of the acetylated group, but does not reduce it sufficiently for *meta* orientation of an incoming group to take place. In another instance, it is known that the single acylation of nitrogen, as in aceto-*p*-toluidide, is not sufficient to reduce the orienting

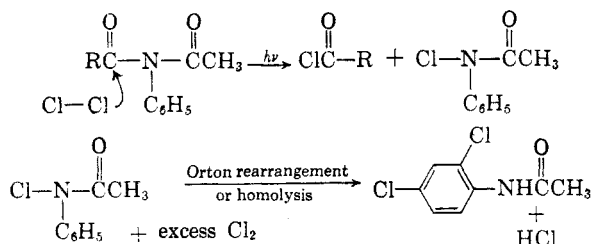
power of the acylamine group below that of the methyl group. However, double acylation is sufficient to enable the methyl group to take control.²

In view of the above information, it seemed likely that a doubly acylated amine group would be less *ortho-para* directing than the singly acylated group. It was expected that the deactivation of the nucleus would reduce the rate of the substitution chlorination reaction and permit addition-chlorination to take place more readily. Attempts were made to addition-chlorinate diacetanilide and α,α,α -trifluorodiacetanilide. It was hoped that the presence of the halogens on the acetyl group would also tend to reduce the *ortho-para* orientation by virtue of their added inductive effect in this system. The diacetanilide, together with carbon tetrachloride and the theoretical amount of chlorine for addition, was sealed in a borosilicate glass tube and exposed to ultraviolet irradiation. Some activation is needed for the reaction to take place; there is no reaction in the dark. With both starting materials, the same product, 2,4-dichloroacetanilide, was isolated in fair yields. It was assumed that this product was formed predominantly *via* the reaction scheme shown below, involving cleavage of an acyl group

(1) I. Rosen and J. P. Stallings, *J. Org. Chem.*, **24**, 1523 (1959).

(2) O. L. Brady, W. G. E. Quick, and W. F. Welling, *J. Chem. Soc.*, 127,2264 (1925).

and subsequent substitution of the benzene ring. The conversion of the *N*-chloroacetanilide to the ring chlorinated product can take place *via* the Orton rearrangement, or by a homolytic mechanism under the influence of light, or by both means.³



A diacylated aniline can be very readily cleaved to a monoacylated aniline.⁴ Once hydrochloric acid is formed in the reaction, some of the diacetanilide will be cleaved to acetanilide, which can then undergo a substitution reaction with chlorine.

Although one of the two acyl groups is readily cleaved, the remaining one is fairly stable. In order to avoid this cleavage and still try to maintain the reduced *ortho-para* directing power of the nitrogen atom, one of the acyl groups was replaced by a methyl group. The use of the compound, *N*-methyl, α, α, α -trichloroacetanilide, under conditions suitable for addition-chlorination, however, resulted only in a substitution reaction. For the conditions used, this means of achieving control over the nitrogen atom's electron-releasing properties proved ineffective.

In order to overcome the deficiencies in the preceding systems, it was apparently necessary to use a non-cleavable electron-withdrawing group attached to the amine. Thus, phenyl isocyanate was chosen as the next material for chlorination. The nitrogen atom in this molecule has a reduced *ortho-para* orienting power compared with that in aniline. Because of the decreased tendency for substitution in the benzene ring, it was hoped that the addition-chlorination could compete with the substitution-chlorination.

The benzene ring of phenyl isocyanate was readily addition-chlorinated in good yield. The addition-chlorinated product still possessed the isocyanate group intact. The product was identified by its elemental analysis and by its hydrolyzable chlorine content. The structure was confirmed by infrared analysis. The infrared spectrum of this product contained a strong absorption band at 2260 cm^{-1} for the isocyanate group, and no absorption bands for the benzene ring. The product was thus identified as 1,2,3,4,5,6-hexachlorocyclohexyl isocyanate.

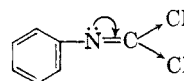
The by-product of this chlorination appeared to be *p*-chlorophenylcarbamoyl chloride. This material has been obtained previously by others by the

(3) E. D. Hughes and C. K. Ingold, *Quart. Revs.*, **6**, 34 (1952).

(4) E. J. Bourne, S. H. Henry, C. F. M. Tatlow, and J. C. Tatlow, *J. Chem. Soc.*, 4014 (1952).

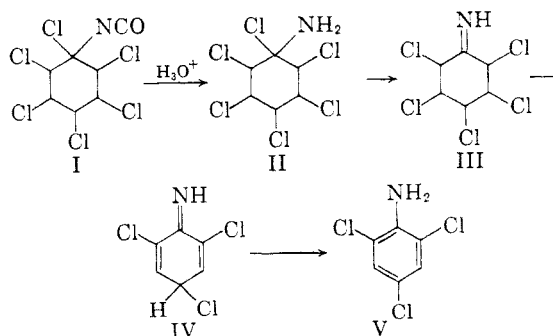
reaction of chlorine with phenyl isocyanate in both carbon tetrachloride and chloroform, but no physical properties were reported.^{5,6} The structure of the by-product was indicated by its elemental analysis and by its hydrolyzable chlorine content, and confirmed by infrared analysis. The infrared spectrum contained strong absorption bands at 1780 cm^{-1} and 1530 cm^{-1} , assignable to a carbonyl adjacent to an electronegative group, and to N—H stretch, respectively.

An extension of the above work on addition-chlorination involved the substitution of another electron-withdrawing group (chlorine) for the oxygen in the isocyanate. This change was made to determine if the *ortho-para* orienting power would still be reduced sufficiently to enable addition-chlorination to take place. The inductive effect of the two chlorine atoms should decrease the availability of the nitrogen electrons toward participation in ring activation. The *N*-phenylimidocarbonyl



chloride was prepared by a published method.⁷ It readily underwent the addition of chlorine to the benzene ring to yield 1,2,3,4,5,6-hexachlorocyclohexylimidocarbonyl chloride. This compound was identified by elemental and infrared analyses. The infrared spectrum contained a strong band at 1680 cm^{-1} for C=N stretch, and no absorption bands for the benzene ring.

In order to get some idea as to what the addition-chlorinated product of aniline might be, the 1,2,3,4,5,6-hexachlorocyclohexyl isocyanate was treated with dilute hydrochloric acid. Normally, the use of dilute acid converts an aromatic isocyanate into a mixture of aromatic amine and urea. The product which was obtained in our hydrolysis was 2,4,6-trichloroaniline (66% crude yield).



The proposed explanation for the formation of the 2,4,6-trichloroaniline rather than other isomers

(5) F. Gumpert, *J. prakt. Chem.*, (2), **32**, 278 (1885).

(6) N. S. Dokunikin, L. A. Gaeva, and I. D. Pletneva, *J. Gen. Chem. U.S.S.R.*, **24**, 177 (1954); *Zhur. Obshchei Khim.*, **24**, 174 (1954).

(7) R. S. Bly, W. L. Lewis, and G. A. Perkins, *J. Am. Chem. Soc.*, **44**, 289 (1922).

is represented by the above sequence of steps. In the first step, the isocyanate, I, should be hydrolyzed to the *gem*-chloroamine, II, which is the product of the addition-chlorination of aniline. The *gem*-chloroamine, II, then should undergo dehydrochlorination to the 2,3,4,5,6-pentachlorocyclohexylimine, III, and then probably to a dienimine such as IV. Finally, IV should rapidly undergo rearrangement to the product, V. An inference of the results is that if aniline were addition-chlorinated to II, II would probably undergo the same dehydrochlorination path and sequence of steps and yield V as the major stable product.

EXPERIMENTAL

Preparation of the N-substituted anilines. Diacetanilide. This compound was prepared in 65% yield by refluxing a mixture of acetanilide, acetic anhydride, and acetyl chloride for 12 hr. The compound was recrystallized from *n*-hexane, and had a m.p. of 39.0–40.5° (lit.⁸ m.p. 37.5°).

α,α,α -Trifluorodiacetanilide. This compound was prepared in 71% yield by refluxing a mixture of acetanilide and trifluoroacetic anhydride. The compound was purified by distillation, b.p. 78–82°/0.6–0.7 mm. (lit.,⁴ b.p. 121–125° (bath temperature)/12 mm.).

N-methyl, α,α,α -trichloromethyl acetanilide. This compound was prepared in 70% yield by refluxing a mixture of *N*-methylaniline and trichloroacetyl chloride in ether. The compound was purified by distillation, b.p. 120–122°/0.7 mm., m.p. 50–51° (lit.,⁹ m.p. 55°).

N-phenyl imidocarbonyl chloride. This compound was prepared in 83% yield from the reaction of chlorine with phenyl isothiocyanate. The compound was purified by distillation, b.p. 110°/33 mm. (lit.,⁷ b.p. 104–106°/30 mm.).

Eastman White Label grade phenyl isocyanate was used in this work. It was distilled prior to use.

Addition-chlorination of the substituted anilines. Preparation of 1,2,3,4,5,6-hexachlorocyclohexyl isocyanate (I). In a thick-walled borosilicate glass tube of 2.5 cm. i.d. were placed 11.0 g. (0.095 mole) of phenyl isocyanate and 30 ml. of carbon tetrachloride. Chlorine gas was bubbled into the solution until the slight exothermic reaction ceased. The tube was then cooled and 24.7 g. (0.348 mole) of chlorine added. The tube was sealed and placed adjacent to a black light fluorescent lamp (General Electric Co. catalog No. F15T8-BL) for 22 hr. When the tube was opened, no hydrogen chloride was detected. A solid which had formed inside the tube was filtered. The solid was recrystallized from benzene, yielding white needles, m.p. 127° dec. The yield was 2.0 g. (12%) of a by-product, *p*-chlorophenyl-carbamoyl chloride.

Anal. Calcd. for $C_7H_5Cl_2NO$: C, 43.25; H, 2.67; hydrolyzable Cl, 18.7. Found: C, 43.92; H, 2.87; hydrolyzable Cl, 18.9.

The infrared spectrum of this compound was obtained using the potassium bromide pellet technique. The spectrum contains the following assignable bands: 3350 cm^{-1} , N—H stretch; 1780 cm^{-1} , carbonyl stretch in an acid chloride;

1530 cm^{-1} , N—H deformation; 1600 cm^{-1} , skeletal benzene ring; and 3050 cm^{-1} , CH stretch in benzene. There was no band for the R—NCO stretch. This evidence indicates the compound is probably *p*-chlorophenylcarbamoyl chloride, previously reported prepared by the reaction of chlorine with phenyl isocyanate in chloroform.^{5,6}

The filtrate of the original reaction mixture was evaporated under vacuum to remove the carbon tetrachloride. The amber oil which remained weighed 23.6 g. (84%), but decomposed on attempted distillation at 0.1 mm. The infrared spectrum of the oil contained a very strong absorption band at 2260 cm^{-1} , assignable to the —NCO group. The spectrum also contained no evidence of aromatic character. A weak absorption at 1780 cm^{-1} indicated that a carbamoyl chloride impurity was present in the oil, probably as a hexa- or heptachlorocyclohexylcarbamoyl chloride.

Anal. Calcd. for $C_7H_5Cl_6NO$ (hexachlorocyclohexyl isocyanate): C, 25.30; H, 1.51; Cl, 64.0; hydrolyzable Cl, 32.0. Found: C, 25.25; H, 1.41; Cl, 61.8; hydrolyzable Cl, 31.4.

Preparation of 1,2,3,4,5,6-hexachlorocyclohexylimidocarbonyl chloride. In a thick-walled borosilicate glass tube of 2.5 cm. i.d. were placed 23.8 g. (0.137 mole) of phenyl imidocarbonyl chloride, 20 ml. of carbon tetrachloride, and 42.6 g. (0.60 mole) of chlorine. The tube was sealed and placed adjacent to the black light fluorescent lamp for 18 hr. A solid formed in the tube during this time. The tube was cooled in Dry Ice and vented. The remaining chlorine was removed with the aid of a vacuum. The mixture was filtered. The crude solid weighed 23.9 g. The carbon tetrachloride was removed from the filtrate under the vacuum of a water aspirator. The amber oil which remained weighed 20.8 g. The total yield of solid and oil was 44.7 g. (84%). The crude solid was recrystallized twice from *n*-hexane, m.p. 138–143°.

Anal. Calcd. for $C_7H_5NCl_6$ (hexachlorocyclohexylimidocarbonyl chloride): C, 21.75; H, 1.30; Cl, 73.4. Calcd. for $C_7H_4NCl_6$: C, 19.94; H, 0.95; Cl, 75.8. Found, Crystals: C, 21.1; H, 1.5; Cl, 74.4. Found, Oil: C, 21.4; H, 1.3; Cl, 74.3.

The infrared spectra of the crystals and oil contain the following assignable bands: 1680 cm^{-1} , C=N stretch; and 2960 cm^{-1} , aliphatic C—H stretch. There was no evidence of aromaticity in the spectra.

Acid hydrolysis of 1,2,3,4,5,6-hexachlorocyclohexyl isocyanate (I). Into a 50-ml. one-necked round bottomed flask fitted with a magnetic stirrer and reflux condenser were placed 1.000 g. (0.0030 mole) of I, 18 ml. of 6*N* aqueous hydrochloric acid, and 18 ml. of 95% ethanol. Upon warming, a homogeneous solution was obtained. After refluxing for 3 hr. the solution had turned deep red and a small amount of sediment had accumulated. The mixture was cooled and filtered. The filtrate was made basic with 1*N* sodium hydroxide and extracted with three 50-ml. portions of ether. The ether extracts were combined, dried, and evaporated. The residue weighed 0.371 g. and was recrystallized from *n*-hexane. The crystals of 2,4,6-trichloroaniline weighed 0.257 g. (44%), m.p. 77.5–79.0°. Mixture with an authentic sample of 2,4,6-trichloroaniline did not depress the melting point.

Acknowledgment. The authors wish to thank J. J. Mannion and T. S. Wang of the Diamond Alkali Company Analytical Section for their aid in obtaining the infrared spectra.

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(9) L. Spiegel and P. Spiegel, *Ber.*, **40**, 1730 (1907).