

606. *Molecular Rearrangements. Part II.* 2 : 6-Disubstituted N-Chloroacetanilides.*

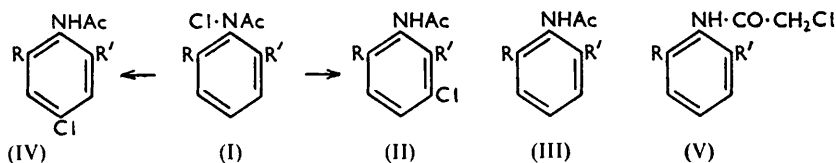
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meta-Migration of chlorine occurs when *N*-chloro-2 : 6-dimethyl- or -diethyl-acetanilide is heated in acetic acid. With *N* : 2 : 6-trichloroacetanilide under similar conditions, there is no substitution in the nucleus; instead the labile chlorine attacks the solvent and the acyl group, to give chloroacetic acid and the 2 : 6-dichloroanilides of mono- and di-chloroacetic acid. These observations, which are unexpected on the basis of an intramolecular course for the proton-catalysed rearrangement of *N*-chloroacylarylamines, are simply explained by assuming that this rearrangement is an intermolecular chlorination.

In contrast to the *meta*-migration induced by proton-catalysis, the rearrangement of *N*-chloro-2 : 6-dimethyl- and -diethyl-acetanilide promoted by benzoyl peroxide occurs with some difficulty and the chlorine is transferred to the *para*-position.

THE activating effect of an amino- or acetamido-group on the benzene ring is known to be diminished by substituents in the 2- and the 6-position,¹ *e.g.*, in 2 : 6-disubstituted *NN*-dialkylanilines the *para*-position is inert, or relatively so, towards nitrous acid, diazo-coupling, and condensation with aldehydes.^{2,3} Of special significance to the present investigation is the relatively high proportion of electrophilic substitution *meta* to the acetamido-group in 2 : 6-dimethylacetanilide: nitration gives 2 : 6-dimethyl-3-nitroacetanilide; ^{4,5,6} bromination yields a mixture of 3- and 4-bromo-compounds.^{5,6,7} It is now found that 2 : 6-dimethyl- and 2 : 6-diethyl-acetanilide are chlorinated in glacial acetic acid in the *meta*-position to the amido-group.

This provides a test of the view⁸ that the rearrangement of *N*-arylchloroacylamides is, not an intramolecular rearrangement, but an intermolecular chlorination. On this view the proton-catalysed change brought about by heating *N*-chloro-2 : 6-dimethylacetanilide



(I; R = R' = Me) in acetic acid should give 3-chloro-2 : 6-dimethylacetanilide (II; R = R' = Me), the same product as is obtained from 2 : 6-dimethylacetanilide by molecular chlorine in acetic acid. This has been verified experimentally and confirmed by the behaviour of *N*-chloro-2 : 6-diethylacetanilide (I; R = R' = Et) and of *N* : 2-dichloro-6-methylacetanilide (I; R = Me, R' = Cl) under similar conditions. In all these changes, the chlorine moves from the nitrogen to the position *meta* to the amido-group. The results are summarised in the Table.

The behaviour of *N* : 2 : 6-trichloroacetanilide (I; R = R' = Cl) is of special interest in that no migration of the *N*-chlorine to the nucleus has been observed when it is heated

* Part I, *J.*, 1957, 2981.

¹ Ingham and Hampson, *J.*, 1939, 981.

² Friedlander, *Monatsh.*, 1898, **19**, 627.

³ von Braun, *Ber.*, 1916, **49**, 1101; 1918, **51**, 282.

⁴ Nolting and Stocklin, *Ber.*, 1891, **24**, 568.

⁵ Nolting, von Braun, and Thesmar, *Ber.*, 1901, **34**, 2262.

⁶ Wepster, *Rec. Trav. chim.*, 1954, **73**, 810.

⁷ Dadswell and Kenner, *J.*, 1927, 1105.

⁸ Ayad, Beard, Garwood, and Hickinbottom, *J.*, 1957, 2981.

with acetic acid. Instead chlorination takes place in the acetyl group to give the 2 : 6-dichloroanilides of mono- and di-chloroacetic acid; chlorination of the solvent also takes place with the formation of chloroacetic acid. The simplest interpretation is that when the reactivity of the nucleus is reduced sufficiently, the *N*-chloroamido-group can chlorinate in other directions. This is indeed what is to be expected from other observations

Starting material (I)		Reactions of <i>N</i> -chloroacetanilides.	
R	R'	Products	
		Formed in AcOH	Formed under free-radical conditions
Me	Me	(II)	(III) 60%; (IV) 30%; (I) 10%
Et	Et	(II)	(III) 70%; (IV) 23%; <i>o</i> -C ₆ H ₄ Et·NHAc 7%
Me	Cl	(II) & (V)	(III) 75%; (I) 3%
Cl	Cl	{ (III) & (V) 2 : 6-C ₆ H ₃ Cl ₂ ·NH·CO·CHCl ₂ CH ₂ Cl·CO ₂ H	

reported in this paper and from our general conclusions⁸ on the nature of the reactions of *N*-chloroacetylarylamines in general.

Some free chlorine is indeed formed when *N* : 2 : 6-trichloroacetanilide is heated in acetic acid. The quantity is small and arises probably from a side reaction. Indeed chlorination of *p*-xylene or mesitylene in acetic acid by *N* : 2 : 4 : 6-tetrachloroacetanilide could not be halted by passing a stream of nitrogen through the solution: very little chlorine or hydrogen chloride is detected when the issuing nitrogen is passed through aqueous silver nitrate.

The rearrangement of *N*-chloro-2 : 6-dimethylacetanilide promoted by benzoyl peroxide should give, on our hypothesis, 4-chloro-2 : 6-dimethylacetanilide (IV; R = R' = Me) although the transference of the chlorine to the nucleus should be seriously hampered by the two *o*-alkyl groups which restrict conjugation of the acetamido-group with the nucleus. Indeed chlorine migrates to the *para*-position, though the yield is low and the product contains also 2 : 6-dimethylacetanilide (III; R = R' = Me) and a small proportion of 3-chloro-2 : 6-dimethylacetanilide (II; R = R' = Me). Under similar conditions, *N*-chloro-2 : 6-diethylacetanilide (I; R = R' = Et) gives a relatively poor yield of the expected chloro-compound (IV; R = R' = Et): the product is largely 2 : 6-diethylacetanilide (III; R = R' = Et) with, unexpectedly, a small amount of 2-ethylacetanilide. A search for 2-ethylaniline in the 2 : 6-diethylaniline used in this work established its absence, nor is it formed by acid hydrolysis of 2 : 6-diethylacetanilide; it is, indeed, a product of the reaction. There are at least two alternative schemes to account for its formation, but neither is offered as explanation until more experimental evidence is available.

EXPERIMENTAL

Rearrangement of N-Chloro-2 : 6-dimethylacetanilide.—(a) *In acetic acid.* *N*-Chloro-2 : 6-dimethylacetanilide⁹ melted at 112—113° (Found: active Cl, 17.8. Calc. for C₁₀H₁₂ONCl: Cl, 17.9%).

(i) A solution of it (3 g.) in acetic acid (30 c.c.) was stored at 50° in the dark. After a week, when there was no longer any positive reaction for active chlorine, the solution was diluted with water and the precipitate collected, washed, and dried. It consisted essentially of 3-chloro-2 : 6-dimethylacetanilide; the m. p. of the crude product was 138—145°, raised to 148—149.5° by three crystallisations from benzene.

The identity was established by direct comparison with a specimen prepared by acetylation of the amine (m. p. 71—72°; Dadswell and Kenner⁷ give m. p. 72—73°) obtained by hydrogenation of 4-chloro-2-nitro-*m*-xylene. The authentic acetyl derivative melted at 148.5—150° (Dadswell and Kenner⁷ give 146—147°).

(ii) For comparison, 2 : 6-dimethylacetanilide was chlorinated in glacial acetic by slowly evaporating into the solution, at 50°, the calculated amount of liquid chlorine. The product, after two crystallisations from benzene, had m. p. and mixed m. p. 149—150°.

⁹ Dewar and Scott, *J.*, 1955, 1845.

(iii) Chlorine was passed through a suspension of 2 : 6-dimethylacetanilide (16.3 g.) in boiling carbon tetrachloride till all the solid had dissolved. The solid residue obtained on evaporation was hydrolysed by boiling aqueous sulphuric acid (60% v/v) for 24 hr., and the resulting amines (10.5 c.c.) recovered by steam-distillation after basification. Distillation through a Haage spinning-band column gave the following main fractions: (a) 2 : 6-dimethylaniline, b. p. 113°/28.5 mm. (acetyl derivative, m. p. and mixed m. p. 180.5—181.5°); (b) 3-chloro-2 : 6-dimethylaniline, b. p. 148—150°/29 mm. (acetyl derivative, m. p. and mixed m. p. 148—149°); and (c) 4-chloro-2 : 6-dimethylaniline, m. p. 47—47.5°, b. p. 153°/29 mm. (acetyl derivative, m. p. and mixed m. p. 195.5—197°). It is estimated that the ratio of 4- to 3-chloro-2 : 6-dimethylacetanilide in the product is approximately 3 : 1.

(b) *With benzoyl peroxide.* A solution of *N*-chloro-2 : 6-dimethylacetanilide (49.4 g.) in carbon tetrachloride (125 c.c.) containing 0.6 g. of benzoyl peroxide was refluxed in the dark until there was a negative test for active chlorine (3 days). The solid remaining after evaporation was a mixture which could not be resolved satisfactorily by crystallisation. It was hydrolysed by boiling aqueous sulphuric acid (60% v/v) for 18 hr. and the amines obtained were distilled through a Haage spinning-band column, giving: (a) 2 : 6-dimethylaniline, b. p. 115.5°/37.5 mm. [acetyl derivative, m. p. and mixed m. p. 180.5—181.5° (Found: C, 73.6; H, 8.3; N, 8.6. Calc. for C₁₀H₁₃ON: C, 73.5; H, 8.0; N, 8.6%)] ; (b) 3-chloro-2 : 6-dimethylaniline, b. p. 144—148°/37.5 mm. (acetyl derivative, m. p. and mixed m. p. 148.5—150°); and (c) 4-chloro-2 : 6-dimethylaniline, b. p. 154—155°/37.5 mm. [acetyl derivative, m. p. and mixed m. p. 195.5—197.5° (Found: C, 61.0; H, 6.2; N, 7.0; Cl, 17.6. Calc. for C₁₀H₁₂ONCl: C, 60.7; H, 6.1; N, 7.1; Cl, 17.9%)] .

The approximate composition of the amine mixture deduced from the weights of the distillation fractions is given in the Table.

For the identification of 4-chloro-2 : 6-dimethylacetanilide, a specimen was made from the amine prepared by Dadswell and Kenner's method.⁷

Rearrangement of N-Chloro-2 : 6-diethylacetanilide.—2 : 6-Diethylaniline was a commercial sample, b. p. 109°/10.5 mm., n_D^{16} 1.5466; and its acetyl derivative melted at 139—140°. Ecke *et al.*¹⁰ give b. p. 235—236°, n_D^{20} 1.5461 (acetyl derivative, m. p. 135—136°).

N-Chloro-2 : 6-diethylacetanilide was prepared by shaking a suspension of finely powdered 2 : 6-diethylacetanilide (20 g.) with 0.45*N*-potassium hypochlorite (250 c.c.). After 2 hr., the suspended solid was removed in chloroform (30 c.c.) and shaken with two lots of 0.45*N*-hypochlorite (250 c.c.), each for 2 hr. Evaporation of the washed and dried chloroform solution left *N*-chloro-2 : 6-diethylacetanilide, m. p. 38.5—39.5° after crystallisation from light petroleum (b. p. <40°) (Found: C, 64.0; H, 7.1; N, 6.2; Cl, 15.5; active Cl, 15.6. C₁₂H₁₆ONCl requires C, 63.8; H, 7.1; N, 6.2; Cl, 15.7%).

(a) *In acetic acid.* A solution of the *N*-chloro-compound (5 g.) in acetic acid (12 c.c.) was stored at 70° in the dark. There was no positive test for active chlorine after 44 hr. The product precipitated by water was essentially 3-chloro-2 : 6-diethylacetanilide, m. p. 152—153° (from, successively, aqueous alcohol, benzene, and light petroleum) (Found: C, 63.6; H, 6.9; N, 6.1; Cl, 15.9. C₁₂H₁₆ONCl requires C, 63.8; H, 7.1; N, 6.2; Cl, 15.7%), identical with that obtained by chlorination of 2 : 6-diethylacetanilide in acetic acid (m. p. and mixed m. p. 152—153°). 3-Chloro-2 : 6-diethylaniline derived from it by hydrolysis with aqueous sulphuric acid (40% v/v) for 16 hr. boiled at 132—133°/11.5 mm. and had n_D^{17} 1.5617 (Found: C, 65.6; H, 7.6; N, 7.5; Cl, 19.4. C₁₀H₁₄NCl requires C, 65.4; H, 7.7; N, 7.6; Cl, 19.3%).

The orientation of the halogen in the amine was established by the diazo-reaction with hypophosphorous acid and subsequent oxidation of the resulting chlorodiethylbenzene with hot aqueous permanganate. 4-Chloroisophthalic acid, m. p. 296—298°, was obtained (Found: Cl, 18.2. Calc. for C₈H₆O₄Cl: Cl, 17.7%). Authentic 4-chloroisophthalic acid was prepared by the same reactions from 2-amino-4-chloro-*m*-xylene; it had m. p. and mixed m. p. 296—298° with some previous softening (Ullmann and Uzbachian^{11a} give m. p. 294°; Davies and Wood^{11b} give m. p. 295°; 5-chloroisophthalic acid melts at 278°).

(b) *With benzoyl peroxide.* The *N*-chloro-compound (37.6 g.), benzoyl peroxide (0.4 g.), and carbon tetrachloride (80 c.c.) were refluxed together in the dark. After 18 hr. there was a negative test for *N*-chloro-compound. Some hydrogen chloride and free chlorine were identified in the vapour above the boiling liquid. The mixed acetyl compounds left after

¹⁰ Ecke, Napolitano, Filbery, and Kolka, *J. Org. Chem.*, 1957, **22**, 640.

¹¹ (a) Ullmann and Uzbachian, *Ber.*, 1903, **36**, 1799; (b) Davies and Wood, *J.*, 1928, 1126.

evaporation were hydrolysed by boiling aqueous sulphuric acid (150 c.c.; 60% v/v) for 12 hr. The amines were separated by distillation through a Haage spinning-band column into the following three homogeneous fractions: (a) b. p. 87—96°/10.5 mm., n_D^{16} 1.5598 (acetyl derivative, m. p. 113—113.5°, not depressed on admixture with 2-ethylacetanilide); (b) b. p. 109°/10.5 mm., n_D^{16} 1.5462—1.5465 (acetyl derivative, m. p. 140—140.5°, not depressed on admixture with 2:6-diethylacetanilide); and (c) b. p. 136—138°/10.5 mm., n_D^{20} 1.5728 (acetyl derivative, m. p. 175—176.5°, identical with 4-chloro-2:6-diethylacetanilide described below). The distillation gave also a small amount of material, b. p. 109—136°/10.5 mm. It was not possible to isolate from it any homogeneous material by crystallisation of the acetyl derivatives, so that the 3-chloro-compound was present at most as a minor constituent. The composition of the product of the rearrangement, estimated from the weights of the distillation fractions and their refractive indices, was as shown in the Table.

4-Chloro-2:6-diethylacetanilide was prepared by acetylating the chlorination product of 2:6-diethylaniline. Its m. p. (175.5—176.5°) was not depressed on admixture with the rearrangement product (Found: C, 63.5; H, 7.1; N, 6.0; Cl, 15.8. $C_{12}H_{16}ONCl$ requires C, 63.8; H, 7.1; N, 6.2; Cl, 15.7%).

Rearrangement of N:2-Dichloro-6-methylacetanilide.—This compound was prepared from 2-chloro-6-methylacetanilide (20 g.), m. p. 165.5—167° (Bamberger¹² gives m. p. 165—165.5°) and 0.45N-potassium hypochlorite saturated with potassium hydrogen carbonate, as described for *N*-chloro-2:6-diethylacetanilide. The *N*-chloro-compound, recrystallised from light petroleum (b. p. 60—80°), melts at 74—74.5° (yield, 19.6 g.) (Found: C, 49.4; H, 4.2; N, 6.6; Cl, 32.9; active Cl, 16.2. $C_9H_9ONCl_2$ requires C, 49.5; H, 4.2; N, 6.4; Cl, 32.5; active Cl, 16.25%).

(a) *In acetic acid.* The change is relatively slow in acetic acid. A solution of 5 g. in 20 c.c. of acetic acid still contained some unchanged *N*-chloro-compound after a week at 75°; during this period some free chlorine was evolved. Heating, in a sealed tube at 116°, a solution of the *N*-chloro-compound (10 g.) in acetic acid (20 c.c.) caused loss of the reaction for active chlorine in 4 days. The product precipitated by water was a mixture. Crystallisation gave no useful separation; chromatography on fuller's earth with benzene–light petroleum for elution was more satisfactory. An acetyl derivative, m. p. 150.5—151.5° after repeated crystallisation from benzene, was obtained; it represented about 30% of the original mixture and was identified as 3:6-dichloro-2-methylacetanilide by comparison with an authentic specimen (see below) (Found: C, 50.0; H, 4.0; N, 6.2; Cl, 33.0. $C_9H_9ONCl_2$ requires C, 49.5; H, 4.2; N, 6.4; Cl, 32.5%).

Chromatography on alumina with benzene–light petroleum for elution separated 3:6-dichloro-2-methylacetanilide and a small amount of 2-chloro-*N*-chloroacetyl-6-methylaniline (5 mg. from 3 g.), m. p. 143—144.5°.

There remained finally a considerable amount of irresolvable material, presumably a mixture of dichloro-2-methylacetanilides and 2-chloro-6-methylacetanilide. For comparison a number of the possible rearrangement products were made.

2-Chloro-*N*-chloroacetyl-6-methylaniline. 2-Chloro-6-methylaniline (2.8 g.) in benzene (5 c.c.) was treated with chloroacetyl chloride (1.1 g.) in benzene (5 c.c.). There was a vigorous reaction and hydrogen chloride was evolved. The mixture was kept overnight after dilution with benzene; the *product*, after crystallisation from benzene and then aqueous alcohol, melted at 143.5—144.5° alone or mixed with the rearrangement product (Found: C, 49.9; H, 4.1; N, 6.1; Cl, 32.6. $C_9H_9ONCl_2$ requires C, 49.5; H, 4.2; N, 6.4; Cl, 32.5%).

3:6-Dichloro-2-methylacetanilide. 3-Chloro-2-methylacetanilide (55 g.; m. p. 159—160°; lit., 157—159°) was heated with chlorosulphonic acid (120 c.c.) on a steam-bath for 90 min. and poured into ice-water. Without purification except a short washing with ice-water, the sulphonyl chloride was converted into the sulphonamide by aqueous ammonia. Hydrolysis of this (21 g.) with boiling concentrated hydrochloric acid (30 c.c.) and water (30 c.c.) for 1 hr. gave 4-amino-2-chloro-3-methylbenzenesulphonamide, m. p. 248° (from acetone and then ethyl alcohol). It (4.4 g.) was chlorinated at 60° for 25 min. with concentrated hydrochloric acid (35 c.c.), water (35 c.c.), and 30% hydrogen peroxide (2 c.c.). The crude product was boiled with 75% w/v sulphuric acid (20 c.c.) for 2 hr. to remove the sulphonic group. Steam-distillation after dilution to 100 c.c. gave 3:6-dichloro-2-methylaniline. Its acetyl derivative, crystallised three times from benzene, melted at 150.5—151.5° (Found: C, 49.9; H, 4.1; N, 6.1; Cl, 31.9%).

¹² Bamberger, *Annalen*, 1925, **441**, 303.

2 : 3-Dichloro-6-methylacetanilide, m. p. 161.5—162.5°, was prepared from 5-chloro-2-methylacetanilide as just described. 2 : 4-Dichloro-6-methylacetanilide, m. p. 190.5—192°, (Found: C, 49.7; H, 4.2; N, 6.5; Cl, 32.2%), was obtained by chlorination of aceto-*o*-toluidide in acetic acid at 100°. In this and similar chlorinations it was convenient to allow the necessary amount of liquid chlorine to distil slowly into the solution.

(b) *With benzoyl peroxide.* *N* : 2-Dichloro-6-methylacetanilide (10.9 g.) was heated in carbon tetrachloride (25 c.c.) containing benzoyl peroxide (0.24 g.). After 14 days' refluxing in the absence of light, with a further addition of benzoyl peroxide (0.24 g.), no *N*-chloro-compound remained. The solid obtained by evaporation was chromatographed on alumina with benzene as eluant, to give 2-chloro-6-methylacetanilide (75%) and about 3% of chloroacetyl derivative, m. p. 143—144°, of 2-chloro-6-methylaniline. The remainder (22%) could not be resolved.

Rearrangement of N : 2 : 6-Trichloroacetanilide.—*N* : 2 : 6-Trichloroacetanilide, m. p. 80.5—81.5° (Found: C, 40.9; H, 2.8; N, 5.7; Cl, 44.8. $C_8H_6ONCl_3$ requires C, 40.3; H, 2.5; N, 5.9; Cl, 44.6; active Cl, 14.9%), was prepared by shaking finely powdered 2 : 6-dichloroacetanilide (10 g.) with 150 c.c. of bleaching powder solution (from 30 g. of bleaching powder, 500 c.c. of water, and 20 c.c. of acetic acid). After 20 min. 15 c.c. of chloroform were added, and the chloroform layer was separated after extraction of the organic matter was complete, then shaken with a further 150 c.c. of bleaching powder solution for 20 min. The operation was repeated once more. The chloroform solution was then freed from acid by repeated washing with sodium hydrogen carbonate solution, dried, and evaporated. The residue, crystallised from light petroleum (b. p. 60—80°), gave the pure *N*-chloro-compound in good yield.

(a) *In acetic acid.* The *N*-chloro-compound (9 g.) in acetic acid (27 c.c.) was heated in a sealed tube suspended in the vapour of boiling acetic acid. After 72 hr., the solution was deep bluish-purple; there was no gas pressure and all the *N*-chloro-compound had changed. The product precipitated by water was not amenable to separation by crystallisation. Partial resolution was achieved by chromatography on fuller's earth with benzene and benzene-ether as eluants. Three homogeneous fractions were obtained in the following order of elution: (a) 2 : 6-Dichloro-*N*-dichloroacetylaniline (0.1 g.), m. p. and mixed m. p. 171.5—173° (Found: C, 35.5; H, 1.8; N, 5.0; Cl, 51.5. $C_8H_5ONCl_4$ requires C, 35.2; H, 1.9; N, 5.1; Cl, 51.9%). (b) 2 : 6-Dichloro-*N*-chloroacetylaniline, m. p. and mixed m. p. 179—181° (0.1 g.) (Found: Cl, 44.0. C_8H_6ONCl requires Cl, 44.7%); (c) Impure fraction, m. p. 188—202° (~5 mg.); (d) 2 : 6-Dichloroacetanilide, m. p. and mixed m. p. 182—183° (0.8 g.).

For identification the 2 : 6-dichloroanilide of dichloroacetic acid was made by reaction of dichloroacetyl chloride with 2 : 6-dichloroaniline in benzene; it had m. p. 171—172° (Found: C, 35.4; H, 2.2; N, 4.9; Cl, 51.9%); the 2 : 6-dichloroanilide of chloroacetic acid, prepared similarly, had m. p. 178—180° (Found: C, 40.5; H, 2.1; N, 6.1; Cl, 44.7. $C_8H_6ONCl_3$ requires C, 40.3; H, 2.5; N, 5.9; Cl, 44.6%). Fraction (a), mixed with 2 : 3 : 4 : 6-tetrachloroaniline,¹³ m. p. 181—182° (lit., between 173° and 181°), melted at 137—165°. Fraction (b), mixed with 2 : 3 : 6-trichloroacetanilide, m. p. 175° (Huffer¹⁴ gives m. p. 171—173°), melted at 143—153°.

2 : 3 : 6-Trichloroaniline was obtained by hydrolysis of 1-amino-2 : 3 : 6-trichlorobenzene-4-sulphonamide, in turn obtained by chlorination of 1-amino-3-chlorobenzene-4-sulphonamide.

When it was established that chlorination could occur in the acetyl group, a search was made for chloroacetic acid in the solvent. The reaction mixture from the rearrangement of *N* : 2 : 6-trichloroacetanilide in acetic acid was diluted with light petroleum (b. p. 40—60°) to precipitate the bulk of the anilides, and the filtrate was concentrated by removal of the solvent and the bulk of the acetic acid. A brown liquid remained; it was diluted with water to precipitate all the anilide. The aqueous filtrate gave an abundant test for chloride ion after being boiled with alkali; the presence of chloroacetic acid was demonstrated by the formation of phenoxyacetic acid, m. p. and mixed m. p. 99—101°, by basifying and warming the solution with phenol.

The authors thank the Hydrocarbons Research Group of the Institute of Petroleum for support.

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[Received, January 28th, 1958.]

¹³ Willgerodt and Wilcke, *Ber.*, 1910, **43**, 275.

¹⁴ Huffer, *Rec. Trav. chim.*, 1921, **40**, 457.