581. *Molecular Rearrangements. Part I.* N-*Chloroacetanilide.*

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N-Chloroacetanilide rearranges to *o*- and *p*-chloroacetanilide in hot carbon tetrachloride in the absence of light, if a small quantity of benzoyl peroxide is present. *N*-Chloro-derivatives of *o*-, *m*-, and *p*-acetamidotoluene and of *o*-acetamidoethylbenzene similarly rearrange. 2-Acetamido-1-chloronaphthalene is formed when 2-acetamidonaphthalene and *N*-chloroacetanilide are warmed together in carbon tetrachloride containing some benzoyl peroxide. Homolytic fission of the N–Cl bond in these reactions is supported by chlorination of the side chain of alkylbenzenes by *N*-2 : 4 : 6-tetrachloroacetanilide if benzoyl peroxide is present : in acetic acid the aromatic nucleus is chlorinated. It is concluded that the formation of *o*- and *p*-chloroacetanilide from *N*-chloroacetanilide is due to intermolecular chlorination, whether it be catalysed by protons or by free radicals.

Since the first observations [1] on the formation of *o*- and *p*-chloroacetanilide from *N*-chloroacetanilide much has been done to determine how chlorine is transferred from nitrogen to the nucleus. The reaction promoted by hydrochloric acid is now generally recognised to depend on intermediate formation of molecular chlorine. This aspect, and the action of other aqueous acids, is reviewed by Hughes and Ingold,[2] with a bibliography. The rearrangement is also brought about by carboxylic acids in aprotic solvents [3] and may then be an intramolecular change.[4]

In addition to these proton-catalysed rearrangements, isomerisation can be brought about by heat [1a,b,5] or light.[6] A simple explanation is to assign to it a free-radical mechanism, and in this paper this suggestion is examined.

It is now found that *N*-chloroacetanilide is smoothly isomerised to *o*- and *p*-chloroacetanilide in hot carbon tetrachloride in the dark by a small proportion of benzoyl peroxide or azo*iso*butyronitrile; *o*-, *m*-, and *p*-*N*-chloroacetamidotoluene and *o*-*N*-chloroacetamidoethylbenzene are similarly rearranged. The Figure shows the amounts of *N*-chloro-compound remaining under the conditions described in the legend.

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[1] (*a*) Bender, *Ber.*, 1886, **19**, 2272; (*b*) Slosson, *Ber.*, 1895, **28**, 3265; (*c*) Chattaway and Orton, *J.*, 1899, **75**, 1046.

[2] Hughes and Ingold, *Quart. Rev.*, 1952, **6**, 35.

[3] Bell *et al.*, *Proc. Roy. Soc.*, 1934, *A*, **143**, 377; 1935, *A*, **151**, 211; *J.*, 1936, 1520; 1939, 1774.

[4] (*a*) Bell, *J.*, 1936, 1154; (*b*) Dewar, " Electronic Theory of Organic Chemistry," Oxford Univ. Press, 1949, p. 225.

[5] (*a*) Porter and Wilbur, *J. Amer. Chem. Soc.*, 1927, **49**, 2145; (*b*) Bradfield, *J.*, 1928, 351.

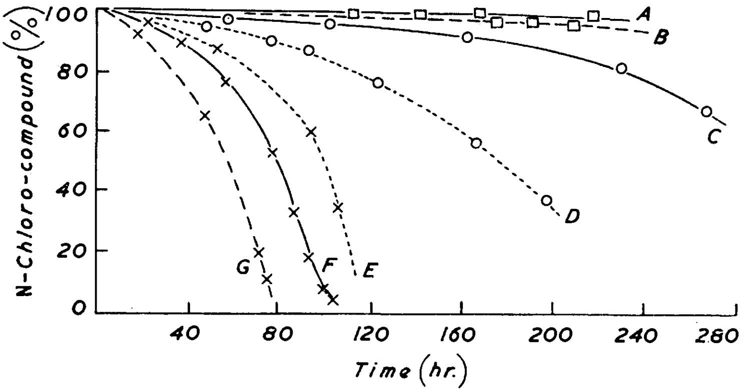
[6] (*a*) Blanksma, *Rec. Trav. chim.*, 1902, **21**, 366; (*b*) Matthews and Williamson, *J. Amer. Chem. Soc.*, 1923, **45**, 2574; (*c*) Hodges, *J.*, 1933, 240.

These observations provide a sound basis for the view that the rearrangement of *N*-chloroacetarylamides can be initiated by a free-radical mechanism. Other evidence of this type of N–Cl bond fission was sought in the behaviour of *N*-chloroacylarylamides which are incapable of rearrangement, *e.g.*, *N* : 2 : 4 : 6-tetrachloroacetanilide.

It is known that *N*-bromosuccinimide brominates the side chain of alkylbenzenes if benzoyl peroxide or azo*iso*butyric ester is present in small amounts.[7] There are also observations of side-chain halogenation of alkylbenzenes by *N*-halogenosuccinimides or *N*-bromophthalimide without specific reference to the use of peroxides, although it is probable that in these cases no precautions were taken to free the hydrocarbon from hydroperoxides arising from autoxidation.[8]

It seemed probable therefore that *N* : 2 : 4 : 6-tetrachloroacetanilide should chlorinate the side chain of alkylbenzenes in presence of benzoyl peroxide if homolytic fission of the N–Cl bond is possible. This has been realised (see Table). For comparison, the chlorinations were also carried out in acetic acid : substitution was then entirely in the nucleus and had all the characteristics of electrophilic substitution.

Decomposition of N-*chloro-amides.*



A, C, F, N-*Chloroacetanilide* (*A*) *alone,* (*C*) *with* azo*iso*butyronitrile, (*F*) *with benzoyl peroxide. B, D, E,* p-N-*Chloroacetamidotoluene,* (*B*) *alone,* (*D*) *with* azo*iso*butyronitrile, (*E*) *with benzoyl peroxide. G,* o-N-*Chloroacetamidotoluene with benzoyl peroxide.*

Chlorination of aromatic hydrocarbons by N : 2 : 4 : 6-*tetrachloroacetanilide.*

	Product			Product	
	in AcOH	with Bz_2O_2		in AcOH	with Bz_2O_2
PhMe	*o*- + *p*-Cl	Ph·CH_2Cl	α-$C_{10}H_7$Me	4-Cl	Ar·CH_2Cl
PhEt	*o*- + *p*-Cl	Ph·CHMeCl	Phenanthrene	9-Cl	—
m-Xylene	4-Cl	Ar·CH_2Cl	CH_2Ph_2	*	Ph_2CHCl
p-Xylene	2-Cl	Ar·CH_2Cl	$CHPh_3$	*	Ph_3CCl
Mesitylene	2-Cl	Ar·CH_2Cl	Acenaphthene	5-Cl	1-Cl

* Some nuclear chlorination.

It can reasonably be inferred that chlorination in acetic acid is due to heterolytic fission of the N–Cl bond and that the active agent is Cl^+. The effect when chlorination occurs in an excess of alkylbenzene containing benzoyl peroxide must be due to some other type of N–Cl bond fission ; a homolytic reaction seems the most likely of the possible alternatives and the one most in accord with other observations.

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[7] (*a*) Schmidt and Karrer, *Helv. Chim. Acta*, 1946, **29**, 573, 1144 ; (*b*) Newman and Kosek, *J. Org. Chem.*, 1949, **14**, 375 ; (*c*) Wenner, *ibid.*, 1952, **17**, 523 ; (*d*) Cope and Fenton, *J. Amer. Chem. Soc.*, 1951, **73**, 1668, 1673 ; (*e*) Ford and Waters, *J.*, 1952, 2240.

[8] (*a*) Pickering and Smith, *Rec. Trav. chim.*, 1950, **69**, 535 ; (*b*) Putokhin, *J. Gen. Chem. U.S.S.R.*, 1945, **15**, 332 ; *Chem. Abs.*, 1946, **40**, 3741 ; (*c*) Djerassi, *Chem. Rev.*, 1948, **43**, 288.

There is no reason to suppose that heterolytic or homolytic bond fission may not occur with *N*-chloroacetanilide. Indeed, it has been recorded[6a] that *N*-chloroacetanilide chlorinates solvents such as *cyclo*hexane on irradiation. In the present work chlorination of 2-acetamidonaphthalene by *N*-chloroacetanilide under the influence of benzoyl peroxide has been demonstrated. The formation of molecular chlorine when *N*-chloroacetanilide reacts with aqueous acid containing chloride ion is evidence of heterolytic fission of its N–Cl bond.[9]

These considerations suggest that *N*-chloroacetanilide may rearrange by either of two courses, the initial phases being formally represented by the following scheme, in which it is not necessarily implied that either Cl• or Cl$^+$ is kinetically free :

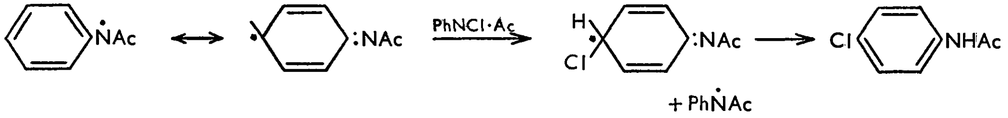
$$\mathrm{Cl\cdot} + \mathrm{Ph{\cdot}\dot{N}Ac} \longleftarrow \mathrm{Ph{\cdot}NClAc} \xrightarrow{\mathrm{H^+}} \mathrm{Ph{\cdot}\overset{+}{N}HClAc} \longrightarrow \mathrm{Ph{\cdot}NHAc} + \mathrm{Cl^+}$$

In the acid-catalysed reaction the protonated *N*-chloroamide is thus regarded as functioning as a source of Cl$^+$ (cf. Hickinbottom[9]). There does not appear to be any advantage in the suggestion[10] that the rearrangement in acetic acid involves the intermediate formation of acetyl hypochlorite, since this would presumably function merely as a carrier of Cl$^+$, and a molecule capable of accepting a chlorine cation from acetyl hypochlorite should interact directly with the protonated *N*-chloroamide. On the other hand, the conception of proton-catalysed isomerisation as dependent on Cl$^+$ provides, as far as our present knowledge goes, a satisfying picture of the reaction. It can moreover be extended simply and naturally to the rearrangement of *N*-bromo- and *N*-iodo-acylarylamides.

The rearrangement of *N*-chloroacetanilide, promoted by benzoyl peroxide in carbon tetrachloride, can be represented in general terms as nuclear chlorination by a homolytic process. The detailed mechanism cannot yet be defined with certainty, but from the observations of Ford, Hunt, and Waters,[11a] and of Ford,[11b] it is probable that the initial phase can be represented :

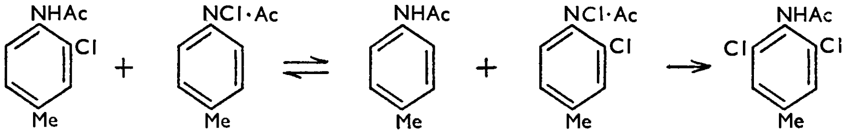
$$\mathrm{Ph{\cdot}NClAc} \xrightarrow{\mathrm{R\cdot}} \mathrm{Ph{\cdot}\dot{N}Ac} + \mathrm{RCl} \quad (\mathrm{R} = \mathrm{Ph\ or\ {\cdot}CMe_2{\cdot}CN})$$

Of the subsequent stages the following seems the most probable :



o-Chloroacetanilide can be derived by a similar mechanism.

Rearrangement of *p*-*N*-chloroacetamidotoluene catalysed by free radicals yields 4-acetamido-3 : 5-dichlorotoluene and *p*-acetamidotoluene in addition to the expected 4-acetamido-3-chlorotoluene. This indicates that the above scheme is incomplete, and requires an assumption that in a system containing an *N*-chloro-compound and an acetarylamide exchange can occur between NH and NCl :



An alternative scheme involving initial abstraction of *N*-hydrogen is as follows :

$$\mathrm{Ar{\cdot}\dot{N}Ac} + \mathrm{Ar'{\cdot}NHAc} \longrightarrow \mathrm{Ar{\cdot}NHAc} + \mathrm{Ar'{\cdot}\dot{N}Ac}$$
$$\mathrm{Ar'{\cdot}\dot{N}Ac} + \mathrm{Ar{\cdot}NClAc} \longrightarrow \mathrm{Cl(Ar'{-}H){\cdot}NHAc} + \mathrm{Ar{\cdot}\dot{N}Ac}$$

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[9] Hickinbottom, *J.*, 1934, 1702.

[10] Israel, Tuck, and Soper, *J.*, 1945, 547.

[11] (*a*) Ford, Hunt, and Waters, *J.*, 1953, 3529; (*b*) Ford, *J.*, 1955, 2529.

That the nuclear chlorination of a foreign amide by an *N*-chloro-compound does occur is shown by the formation of 2-acetamido-1-chloronaphthalene from *N*-chloroacetanilide and 2-acetamidonaphthalene under free-radical conditions.

Alternative but less probable mechanisms for these reactions involve initial abstraction of nuclear hydrogen, *e.g.* :

$$\mathrm{Ph{\cdot}NCl{\cdot}Ac + Ph{\cdot} \longrightarrow {\cdot}C_6H_4{\cdot}NClAc + PhH}$$
$$\mathrm{Ph{\cdot}NCl{\cdot}Ac + {\cdot}C_6H_4{\cdot}NClAc \longrightarrow ClC_6H_4{\cdot}NClAc + Ph{\cdot}\dot{N}Ac}$$
$$\mathrm{Ph{\cdot}\dot{N}Ac + Ph{\cdot}NClAc \longrightarrow Ph{\cdot}NHAc + {\cdot}C_6H_4{\cdot}NClAc}$$

The main objection to this type of mechanism is based on the fact that *N*-methylacetanilide, which has no *N*-hydrogen, undergoes homolytic chlorination by *N* : 2 : 4 : 6-tetrachloroacetanilide in carbon tetrachloride extremely slowly, the reaction not being complete even after 3½ weeks' refluxing, whereas under comparable conditions acetanilide is chlorinated in less than 40 hours.

EXPERIMENTAL

Rearrangement of N-*Chloroacetarylamides Promoted by Free Radicals.*—(a) N-*Chloroacetanilide.* (i) With benzoyl peroxide. A solution of *N*-chloroacetanilide (2·0 g.) in carbon tetrachloride (170 c.c.) was boiled in the dark after benzoyl peroxide (0·05 g.) had been added. No *N*-chloro-compound was detected after 100 hr. When the solution was concentrated, *p*-chloroacetanilide crystallised (m. p. and mixed m. p. 179°; 1·6 g.). The filtrate was washed with aqueous sodium carbonate, dried, and evaporated; the solid residue, on sublimation, gave *o*-chloroacetanilide, m. p. and mixed m. p. 87—88° (0·3 g.).

(ii) With αα'-azo*iso*butyronitrile. Under similar conditions but with azo*iso*butyronitrile, rearrangement occurred to give *o*- and *p*-chloroacetanilide, although the change was slower.

(iii) By irradiation. A solution of *N*-chloroacetanilide (4·27 g.) in carbon tetrachloride (50 c.c.) exposed to light from a mercury-vapour lamp for 3 days gave *p*-, m. p. 179° (3·3 g.), and *o*-chloroacetanilide, m. p. 87—88° (0·63 g.).

(iv) Rearrangement in presence of 2-acetamidonaphthalene. 2-Acetamidonaphthalene (3 g.), *N*-chloroacetanilide (2·7 g.), and benzoyl peroxide (0·1 g.) in carbon tetrachloride (500 c.c.) were heated under reflux for 40 hr. The active chlorine content fell to 1·5% of its original value. 2-Acetamido-1-chloronaphthalene, m. p. and mixed m. p. 149—150°, crystallised on cooling. The filtrate was evaporated under reduced pressure, and the solid residue taken up in ether, washed with aqueous sodium carbonate, dried, and recovered. Extraction with hot water left a solid from which *p*-chloroacetanilide was obtained (m. p. and mixed m. p. 179°) by chromatography on alumina with light petroleum (b. p. 60—80°)–benzene. The aqueous extracts, on concentration, gave a mixture of acetanilide and 2-acetamidonaphthalene, separated by fractional crystallisation, the components being identified by m. p.s and mixed m. p.s.

No accurate estimate could be made of the relative proportions of the products : acetanilide and 2-acetamido-1-chloronaphthalene were present in considerable amount.

(b) o-N-*Chloroacetamidotoluene.* This compound,[12] m. p. 41·5—42·5°, rearranged in boiling carbon tetrachloride in the dark after addition of 1·0 mole % of benzoyl peroxide, to give 2-acetamido-5-chlorotoluene, m. p. 143—144° (from benzene). This was identical with a specimen prepared by warming a solution of the *N*-chloro-compound in acetic acid at 50°.

(c) m-N-*Chloracetamidotoluene.* This *chloro-amide* was reported by Fontein [13] who did not record its m. p.; crystallised well from light petroleum (b. p. 60—80°), it had m. p. 70—72° (Found: Cl, 19·3. $C_9H_{10}ONCl$ requires Cl, 19·3%). Rearrangement under the conditions described for the *o*-isomer gave 3-acetamido-4-chlorotoluene, m. p. 90—91·5° after crystallisation from light petroleum and then aqueous alcohol, identical with the product obtained by warming the *N*-chloro-compound in acetic acid at 74°.

(d) p-N-*Chloroacetamidotoluene.* This was rearranged under the conditions described for the *o*-isomer. The solution was evaporated under reduced pressure and from the solid residue

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[12] Chattaway and Orton, *J.*, 1900, **77**, 790.

[13] Fontein, *Rec. Trav. chim.*, 1928, **47**, 635.

4-acetamido-3-chloro- and -3 : 5-dichloro-toluene were isolated by wasteful fractional crystallisation.

A more satisfactory method, based on that devised by Orton and Chattaway,[14] consisted in hydrolysing the product with 50% aqueous sulphuric acid and then steam-distillation after partial neutralisation. 2 : 6-Dichloro-*p*-toluidine (NH_2 = 1) distilled first, and then 2-chloro-*p*-toluidine when the acidity had been further reduced. *p*-Toluidine was collected by steam-distillation when the aqueous solution had been made alkaline. 2 : 6-Dichloro-*p*-toluidine was identified as its acetyl derivative, m. p. 207—208·5°, not depressed on admixture with a specimen prepared as described by Cohen and Dakin[15] (Found : C, 49·3; H, 3·9; N, 6·4; Cl, 32·7. Calc. for $C_9H_9ONCl_2$: C, 49·6; H, 4·2; N, 6·4; Cl, 32·6%). 2-Chloro-*p*-toluidine gave an acetyl derivative, m. p. and mixed m. p. 114—115°. *p*-Toluidine gave a hydrate, m. p. and mixed m. p. 45°, and an acetyl derivative, m. p. and mixed m. p. 147·5—149°.

(e) o-N-*Chloroacetamidoethylbenzene.* The method used for *o*-*N*-chloroacetamidotoluene gave the *ethyl analogue,* m. p. 27—28·5° [from light petroleum (b. p. < 40°)] (Found : C, 60·7; H, 6·3; N, 7·15; Cl, 17·8; active Cl, 17·9. $C_{10}H_{12}ONCl$ requires C, 60·7; H, 6·1; N, 7·1; Cl, 17·9%).

The product of its rearrangement in carbon tetrachloride containing some benzoyl peroxide was 2-*acetamido*-5-*chloro*-1-*ethylbenzene,* m. p. 136—136·5° after crystallisation from aqueous alcohol and then light petroleum, identical with a sample prepared by warming the *N*-chloro-compound in acetic acid (Found : C, 60·4; H, 6·1; N, 7·0; Cl, 17·9%).

Orientation of the halogen was established by conversion of the amine into dichloroethylbenzene by the diazo-reaction and then oxidation by permanganate to 2 : 5-dichlorobenzoic acid, m. p. and mixed m. p. 152—154°.

N : 2 : 4 : 6-*Tetrachloroacetanilide as a Chlorinating Agent.*—The following preparation gave more satisfactory yields than that described by Chattaway and Orton :[16] Acetic acid (10 c.c.) was added during 5 min. to a stirred mixture of 2 : 4 : 6-trichloroacetanilide (10 g.), chloroform (30 c.c.), and 2N-sodium hypochlorite (50 c.c.), and stirring continued till all the solid had dissolved. The chloroform solution was then separated, and washed with saturated sodium hydrogen carbonate solution and then several times with water. Evaporation, under reduced pressure, of the dried (Na_2SO_4) chloroform solution gave a pale yellow solid (10·7 g.) from which *N* : 2 : 4 : 6-tetrachloroacetanilide was obtained as plates, m. p. 75°, by crystallisation from light petroleum (b. p. 80—100°). Estimation of active chlorine gave a purity of 97%.

(a) *Chlorination in acetic acid.* (i) A solution of *N* : 2 : 4 : 6-tetrachloroacetanilide (40·9 g.) in acetic acid was diluted with an excess of toluene and kept in the dark at 60° for 24 hr. and then at 90° for a further 24 hr. 2 : 4 : 6-Trichloroacetanilide separated, having m. p. and mixed p. m. 209—210°; it was collected and a further amount was obtained by diluting the filtrate with water and neutralising it with sodium hydrogen carbonate. The excess of toluene and its chlorination products were removed with light petroleum and distilled, to give a mixture of *o*- and *p*-chlorotoluene, b. p. 55—75°/17 mm. (Found : C, 66·6; H, 5·7; Cl, 28·0. Calc. for C_7H_7Cl : C, 66·4; H, 5·6; Cl, 28·0%). This mixture contained no labile chlorine; oxidation with alkaline permanganate gave *p*-chlorobenzoic acid, m. p. and mixed m. p. 239—240°. The more soluble portions of the oxidation product were recrystallised further and then sublimed, to give *o*-chlorobenzoic acid, m. p. 140° after sintering from about 130°.

(ii) In similar chlorinations of other hydrocarbons (see Table) no attempts were made to determine the best conditions or the maximum yields. Analyses for total chlorine were supplemented by estimation of labile chlorine by boiling alcoholic silver nitrate, these results being given in parentheses.

Hydrocarbon	Conditions	Yield (g.)	C (%)	H (%)	Cl (%)
m-Xylene, 15·9 g.	50°, 24 hr. 85°, 3½ hr.	10·8	68·9	6·3	24·6 (0)
p-Xylene, 10·6 g.	80°, 2½ hr.	4·4	68·4	6·7	24·5 (0·35)
Ethylbenzene, 15·9 g.	42°, 3 days 93°, 8 hr.	9·2	68·4	6·6	25·0 (0·6)
Mesitylene, 9·5 g.	20°, ½ hr.	11·0	—	—	23·3 (1·5)
1-Methylnaphthalene, 21·3 g.	75°, 18 hr.	14·5	74·2	5·2	20·7 (2·0)

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[14] Orton and Chattaway, *J.*, 1900, **77**, 792.

[15] Cohen and Dakin, *J.*, 1902, **81**, 1337.

[16] Chattaway and Orton, *J.*, 1900, **77**, 136.

After 40 hr. at 62° phenanthrene gave unchanged hydrocarbon and 9-chlorophenanthrene, m. p. and mixed m. p. 51—52° (picrate, m. p. and mixed m. p. 113—114°).

Acenaphthene (4·84 g.) after 100 hr. at 20° gave 5-chloroacenaphthene (4·9 g.), m. p. and mixed m. p. 70·5° (picrate m. p. 138°).

In acetic acid a product was obtained from triphenylmethane containing triphenylmethyl chloride (hydrolysed by aqueous alkali to triphenylmethanol, m. p. and mixed m. p. 161—162°) and a mixture, b. p. 190—212°/10 mm. (Found : Cl, 9·2% ; no labile Cl).

From diphenylmethane, the main product boiled at 138—168°/11 mm. and consisted essentially of monochlorodiphenylmethanes with unchanged diphenylmethane (Found: C, 79·4; H, 5·8; Cl, 14·6. Calc. for $C_{13}H_{11}Cl$: C, 77·0; H, 5·5; Cl, 17·5.)

(b) *Homolytic chlorination.* (i) *N* : 2 : 4 : 6-Tetrachloroacetanilide (40·9 g.) and toluene (50 c.c.) were refluxed together for 5 hr. after addition of benzoyl peroxide (0·2 g.). The precipitate of 2 : 4 : 6-trichloroacetanilide was collected and the filtrate washed with aqueous sodium sulphite, dried, and distilled. Approximately pure benzyl chloride was collected at 80—83°/22 mm. (Found : C, 67·0; H, 5·9; Cl, 25·9; labile Cl, 24·4. Calc. for C_7H_7Cl : C, 66·4; H, 5·6; Cl, 28·0%) and converted by the Sommelet reaction into benzaldehyde (semicarbazone, m. p. and mixed m. p. 213—214·5°).

(ii) Homolytic chlorination of other alkylbenzenes was carried out by *N* : 2 : 4 : 6-tetrachloroacetanilide in boiling carbon tetrachloride containing 1·0 mol. % of benzoyl peroxide. The yields (see Table) represent approximately pure product isolated; the percentage of labile chlorine is given in parentheses. The identity of each product, except that from ethylbenzene, was established by conversion into the corresponding aldehyde by the Sommelet reaction and comparison of crystalline derivatives with authentic specimens. The product from ethylbenzene was converted into acetophenone by boiling aqueous copper nitrate.

Hydrocarbon	Time of reaction	Yield (g.)	C (%)	H (%)	Cl (%)
m-Xylene, 15·9 g.	5½ days	10·5	68·1	6·3	24·9 (24·9)
p-Xylene, 8·5 g.	,,	4	—	—	24·4 (24·5)
Ethylbenzene, 15·9 g.	,,	15·3	67·8	6·6	26·1 (22·5)
Mesitylene, 17·3 g.	30 hr.	17	—	—	22·4 (17·9)
1-Methylnaphthalene, 21·3 g.	5 days	17·4	77·9	5·4	16·6 (16·6)

Diphenylmethane gave diphenylmethyl chloride (good yield), b. p. 160—165°/13 mm. [Found : C, 76·7; H, 5·3; Cl, 17·5 (17·5). Calc. for $C_{13}H_{11}Cl$: C, 77·0; H, 5·5; Cl, 17·5%], characterised by the formation of bisdiphenylmethyl ether and of benzophenone.

Triphenylmethane (24·4 g.) gave triphenylmethyl chloride (25·7 g.), m. p. 110—111·5°.

Chlorination of acenaphthene in boiling carbon tetrachloride was complete after 70 hr. for 0·1 mol. quantities in 250 c.c. of solvent and 1·0 mole per cent of benzoyl peroxide. The bulk of trichloroacetanilide was removed by filtration and the remainder by passing a solution, in benzene–light petroleum, of the evaporated filtrate through silica. The less strongly adsorbed material was essentially 1-chloroacenaphthene, m. p. 5—15°, giving a strong test for labile chlorine and with boiling alcoholic potassium hydroxide giving acenaphthylene, m. p. and mixed m. p. 90° (picrate, m. p. 201—203°) (lit., m. p. 92—93°; picrate, m. p. 201—203°).

N : 2 : 4 : 6-Tetrachloroacetanilide, boiled for 10 days with an excess of *cyclo*hexane and benzoyl peroxide, gave *cyclo*hexyl chloride, b. p. 140—142°, in 40% yield, identified by conversion into *cyclo*hexanecarboxyanilide, m. p. and mixed m. p. 144—145° by reaction of the Grignard reagent with phenyl *iso*cyanate.

Neither fluorene nor phenanthrene was chlorinated under homolytic conditions.

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