1076. *Kinetics and Mechanism of Substitution at the Central Carbon Atom of Tri*-p-*nitrophenylmethyl Chloride in Glacial and Aqueous Acetic Acid.*

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Tri-*p*-nitrophenylmethyl chloride did not react with pure acetic acid; but in this solvent the chloride undergoes exchange with the anion of salts such as mercuric chloride or acetate, lithium chloride, and silver acetate, and in the presence of a strong acid it was solvolysed. In aqueous acetic acid the chloride was solvolysed giving the corresponding alcohol. In the presence of an added salt in acetic acid the rate-determining step of a proposed mechanism involves the formation of an ionised complex of tri-*p*-nitrophenylmethyl chloride and the metallic salt followed by a fast collapse of the complex into the triarylmethyl derivative of one of the anions involved in the complex. The mechanism is essentially the same in the solvolyses studied. No chlorine of zero or positive valency was liberated during these reactions or in the presence of *N*-chlorosuccinimide or t-butyl hypochlorite in glacial or aqueous acetic acid.

SOLVOLYSIS of triphenylmethyl chloride and replacement of its chlorine in other reactions have been the subject of extensive investigations and of controversial theories.[1,2] In

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[1] Hughes, Ingold, Mok, Patai, and Pocker, *J.*, 1957, 1206—1279, and references quoted there.

[2] Swain, *J. Amer. Chem. Soc.*, 1948, **70**, 1119; Swain and Kreevoy, *ibid.*, 1955, **77**, 1122; Swain and MacLachlan, *ibid.*, 1960, **82**, 6095.

general it has been shown that the reaction is an S_N process[1] and relatively fast. It has also been found[3] that in nitromethane, chlorobenzene, benzene, acetic acid, etc., the ion pair $Ph_3C^+Cl^-$ is obtained in the presence of electrophilic catalysts such as mercuric chloride. Most of the mechanisms suggested for replacements in the triphenylmethyl halide series[1,2,4] rule out the possibility of a normal S_N2 process. The reluctance of 1-bromotrypticene to undergo an S_N reaction[5] indicates the improbability of an S_N2 process for triphenylmethyl halides, without inversion of configuration.

It was the aim of the present work to study the behaviour of a triarylmethyl halide of such an electronic structure that the ionisation of the carbon–halogen bond would not be facilitated, thus making an S_N1 mechanism improbable.

In tri-*p*-nitrophenylmethyl chloride, owing to the strongly electron-attracting substituents, the C–Cl bond will not undergo easy heterolysis into carbonium and chloride ions. Tri-*p*-nitrophenylmethyl bromide tends to undergo homolysis, *e.g.*, in basic media or in the presence of peroxides;[6] nevertheless it was hoped that the chloride would tend more towards heterolysis.

Although tri-*p*-nitrophenylmethylsodium in ether behaves as a strongly dissociated salt,[7] radical reactions such as oxidations were also observed.[6] Attempts to combine the postulated tri-*p*-nitrophenylmethyl anion with a carbonium ion such as the tri-*p*-methoxyphenylmethyl ion in order to produce a substituted hexaphenylethane with a carbon–carbon ion pair failed.[8]

RESULTS

Kinetic runs for the solvolysis and other exchange reactions of tri-*p*-nitrophenylmethyl chloride (Ar_3CCl) in glacial acetic acid or in water-containing acetic acid are summarised in Tables 1 and 2.

The kinetic runs were followed by measuring either the radioactivity of the chloride ions liberated from the organic chloride labelled with ^{36}Cl (method *a*), or by measuring the decrease in radioactivity of the labelled chloride and its derivatives obtained during the reaction (method *b*). The reproducibility of the results was good (compare runs 10—13, 14—15, 17—19, 29—31, 32—33, 34—36). Results in Table 1 conform well to first-order kinetics. Details of a typical kinetic run are given in Table 3.

Table 1 shows that no reaction * took place in acetic acid (runs 1, 2) or in this solvent in the presence of considerable concentrations of t-butyl hypochlorite, *N*-chlorosuccinimide, or lithium nitrate (runs 3—7). On the other hand, reaction took place in the presence of lithium chloride and of sulphuric acid (runs 8, 9).

The presence of water enhanced the reaction rate (compare runs 1,10, 29). In water-containing solutions the addition of a strong acid accelerated the reaction (runs 13, 24—28, 30, 32—33), although there was no acceleration for sulphuric acid concentrations higher than 0·07M and up to 0·18M. Added lithium chloride had an accelerating effect (runs 17—19). The results with added t-butyl hypochlorite in water-containing solutions showed an apparent slight slowing down in runs 20, 21, and an apparent slight acceleration in runs 22, 23. We believe that these small changes are caused solely by experimental errors when working with the volatile t-butyl hypochlorite. The Arrhenius activation energy of the solvolysis was calculated from runs 11, 14—16 as 20 kcal. mole^{-1}.

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* Unless otherwise stated the term " reaction " implies any change in the ^{36}Cl-labelled tri-*p*-nitrophenylmethyl chloride that enhances the radioactivity in the filtrate according to method *a*, or decreases the radioactivity in the precipitate according to method *b*.

[3] Evans, Price, and Thomas, *Trans. Faraday Soc.*, 1954, **50**, 568; 1955, **51**, 481; 1956, **52**, 332; *J.*, 1957, 4644; Bayles, Evans, and Jones, *J.*, 1955, 206, 3104; 1957, 1020; Cotter and Evans, *J.*, 1959, 2988.

[4] Read and Taylor, *J.*, 1939, 478.

[5] Bartlett and Lewis, *J. Amer. Chem. Soc.*, 1950, **72**, 1005.

[6] Leffler, *J. Amer. Chem. Soc.*, 1953, **75**, 3598.

[7] Ziegler and Wolschitt, *Annalen*, 1930, **479**, 123.

[8] Leffler, " The Reactive Intermediates of Organic Chemistry," Interscience Publ. Inc., New York, 1956, p. 17.

Table 2 records the second-order reaction coefficient found for the reaction with lithium chloride in acetic acid. It was impossible to carry out runs with initial concentrations differing much from those used, owing to the low solubility of tri-*p*-nitrophenylmethyl chloride in acetic acid on the one hand, and to very low reaction rates obtained with much lower initial concentrations of lithium chloride on the other.

TABLE 1.

First-order rate coefficients [a] for the solvolysis of tri-*p*-nitrophenylmethyl chloride in acetic acid at 30°.

Run	$10^3[\mathrm{Ar_3CCl}]_0$ (mole l.$^{-1}$)	Concn. of added substance (mole l.$^{-1}$)	10^2k (min.$^{-1}$)
In glacial AcOH			
1 [b]	2·36	—	0·00
2 [c]	5·92	—	0·00
3 [d]	3·02	0·20 Bu^{t}OCl	0·00
4 [a, e]	3·43	1·48 ,,	0·00
5 [f]	2·22	1·48 ,,	0·00
6 [g]	2·37	0·44 NCS [h]	0·00
7 [e]	1·16	0·177 $\mathrm{LiNO_3}$	0·00
8	2·14	0·426 LiCl	0·10
9	4·65	0·362 $\mathrm{H_2SO_4}$	0·20
Acid containing 20% v/v of water			
10	1·35	—	0·46
11	1·52	—	0·44
12	1·98	—	0·44
13	4·06	—	0·43
14, 15 [i]	2·37	—	1·52, 1·63
16 [j]	2·37	—	4·40
Acid containing 20% v/v of water			
17	1·53	0·426 LiCl	1·30
18	1·82	0·426 ,,	1·20
19	1·85	0·426 ,,	1·18
20	4·57	0·20 Bu^{t}OCl	0·34
21	6·04	0·20 ,,	0·40
22	4·02	0·74 ,,	0·47
23 [a]	3·86	0·74 ,,	0·48
24	2·88	0·0362 $\mathrm{H_2SO_4}$	0·88
25	2·88	0·0724 ,,	1·74
26	2·88	0·1086 ,,	1·74
27	2·88	0·1448 ,,	1·74
28	2·88	0·1810 ,,	1·74
Acid containing 30% v/v of water			
29	9·26	—	2·01
30	5·07	—	2·39
31	3·85	—	2·20
32	3·77	0·1448 $\mathrm{H_2SO_4}$	3·24
33	4·03	0·1448 ,,	3·42

[a] Sampling method *b* (see text) was used in runs 4, 22, and 23, in all others method *a*. [b] Run followed for 8 days. [c] Run followed for 3 weeks. [d] Run followed for 2·5 hr. [e] Run followed for 3 hr. [f] Run followed for 4 days. [g] Run followed for 6 days [h] *N*-Chlorosuccinimide. [i] At 40·3°. [j] At 50·3°.

TABLE 2.

Second-order [a] rate coefficients [b] for the reaction of tri-*p*-nitrophenylmethyl chloride and lithium chloride in glacial acetic acid at 40·3°.

Run	$10^3[\mathrm{Ar_3CCl}]_0$ (mole l.$^{-1}$)	$10^3[\mathrm{LiCl}]_0$ (mole l.$^{-1}$)	10^2k (l. mole^{-1} hr.$^{-1}$)
34	2·88	76·8	1·40
35	3·84	76·8	1·39
36	3·84	127·9	1·27

[a] First-order in each of $\mathrm{Ar_3CCl}$ and LiCl. [b] Determined by sampling method *a* (see text).

TABLE 3.

Kinetic details of run 13 (Table 1).

Sample	1	2	3	4	5	6
Time (min.)	2	10	26	43	63	87
Reaction (%)	1·2	3·1	10·4	16·5	24·5	30·6
10^2k (min.$^{-1}$)	0·5	0·3	0·42	0·42	0·44	0·43

Other qualitative experiments (see Experimental) gave the following results: Product analysis showed that in water-containing acetic acid the chloride was hydrolysed to tri-*p*-nitrophenylmethanol. It reacted slowly with silver acetate in acetic acid (giving silver chloride) and with mercuric chloride (undergoing chlorine exchange); when mercuric acetate was used instead of the chloride, chloride ions were liberated into the solution and the water-insoluble product was the organic acetate. The organic chloride underwent chlorine exchange with lithium chloride. No carbonium ions or ion pairs were formed in spectrophotometrically measurable concentrations when the chloride was dissolved in acetic acid containing various concentrations of mercuric chloride. In aqueous acetone it reacted with sodium hydroxide, liberating chloride ions; in this reaction colour changes occurred that are probably due to a homolytic process similar to those described by Leffler.[6] No reaction was detected in dry acetone or for a suspension in aqueous sodium hydroxide. No liberation of chlorine in a form capable of oxidizing iodide ions was detected during the solvolysis in aqueous acetic acid.

DISCUSSION

The following mechanism is proposed for the exchange reactions of tri-*p*-nitrophenylmethyl chloride in acetic acid:

$$\mathrm{RCl + MX} \underset{\substack{\text{Fast}\\(1)}}{\overset{\text{Slow}}{\rightleftharpoons}} \mathrm{R^+(ClMX)^-} \underset{\substack{\text{Slow}\\(2)}}{\overset{\text{Fast}}{\rightleftharpoons}} \mathrm{RX + MCl}$$

Step (1) represents the slow reaction with a metal salt [MX = $HgCl_2$, $Hg(OAc)_2$, LiCl, AgOAc], involving either ionisation of the organic chloride aided by electrophylic catalysis or possibly the formation of a quadruple ion composed of the organic chloride and the metal salt (see ref. 1, pp. 1265 *et seq.*). In either case the intermediate may collapse fast into the covalent form either by reversing step (1) or metathetically by step (2).

The following results support this mechanism: No reaction takes place by solvolysis in pure acetic acid, while in the same medium, in the presence of mercuric chloride (both the organic and the inorganic chloride in low concentrations), 70% exchange has been measured. In these conditions the solvolysis, if any, by acetic acid was less than 4%, *i.e.*, within the experimental error. We believe, therefore, that formation of ionised intermediates (ion pairs or quadrupoles) takes place, aided by the mercuric chloride, and that collapse of these leads to chlorine exchange. In other words, an ion pair of the form R^+Cl^- which is at least partially solvated by mercuric chloride gives returns to the organic halide molecule in which the chlorine may originate from the mercuric chloride, while practically no collapse to the corresponding acetate takes place notwithstanding the large excess of acetic acid in the vicinity. As mercuric acetate strongly catalyses the exchange of chlorine for acetate, it seems that the function of the metal atom is to aid distention of the C–Cl bond to a point where the collapse to the original molecule is not dominant but new C–Cl (in the case of $HgCl_2$) or C–OAc [in case of $Hg(OAc)_2$] bonds can be formed. The anions attached to the mercury atom will be in a preferential position for a nucleophilic attack on the central carbon atom. The second-order kinetics of the exchange with lithium chloride that was observed even with a large excess of the salt reinforce the argument for a slow rate of step (1). The failure to detect a measurable concentration of an ionised intermediate tends to show that its disappearance is faster than its formation.

The acceleration caused by added strong acid (run 9) can be explained similarly:

$$\mathrm{RCl + H^+} \underset{\text{Fast}}{\overset{\text{Slow}}{\rightleftharpoons}} \overset{\delta+}{\mathrm{R}}\,.\,.\,.\,\overset{\delta-}{\mathrm{Cl}}\,.\,.\,.\,\overset{\delta+}{\mathrm{H}} \xrightarrow[\text{Fast}]{\text{AcOH (Solvent)}} \mathrm{ROAc + HCl + H^+}$$

It is believed that the mechanism of solvolysis in aqueous acetic acid is essentially the same as that of the salt-catalysed exchange. On the basis of our experiments, we are unable to decide whether the alcohol is formed directly, owing to the preferential solvation by water, or through the acetate with subsequent hydrolysis, or by both routes simultaneously:

$$\mathrm{RCl + HOH} \underset{\text{Fast}}{\overset{\text{Slow}}{\rightleftharpoons}} \mathrm{R^+(ClH_2O)^-} \underset{\text{Fast}}{\overset{\text{Slow}}{\rightleftharpoons}} \mathrm{ROH + HCl}$$

The rate acceleration caused by larger amounts of water may be due to the enhancement of the dielectric constant of the solvent, thus aiding the separation of charges in the ionic intermediate. The observed acceleration by added lithium chloride may be caused by a positive salt effect as well as by the effect of the salt as an added nucleophilic reagent.

The proposed mechanism of reaction involves implications on the stereochemistry of the chlorine exchange: the reaction has to proceed without inversion of configuration, as the leaving and the entering group are placed on the same side of the molecule in respect to the phenyl groups.

Electrophilic catalysis by protons is probably the cause of the rate enhancement by added sulphuric acid in aqueous acetic acid. The sulphuric acid concentration is low enough not to change the medium essentially. A limit in the acid catalysis is reached with $2{\cdot}88 \times 10^{-3}$M-tri-*p*-nitrophenylmethyl chloride in 1 : 4 water–acetic acid when the sulphuric acid concentration is about 0·07M. The 25-fold concentration of sulphuric acid (as compared with that of the organic chloride) seems to supply sufficient protons to the solvation shell in the immediate vicinity of the reacting groups for higher acid concentrations to have no additional effect.

It has been postulated [6] that triaryl halides with electron-attracting substituents may ionise, $Ar_3CX \rightleftharpoons Ar_3C^- + X^+$. Our chloride does not react in presence of t-butyl hypochlorite as a possible source of positive or free chlorine,[9] in acetic acid or in 1 : 4 water–acetic acid, or in presence of *N*-chlorosuccinimide in acetic acid.[10] Thus our chloride has no tendency to undergo electrophilic or radical replacement at its central carbon atom in these conditions. Lack of reaction of potassium iodide with the mother liquors of the reaction also showed that our chloride does not liberate either free or positive chlorine.

EXPERIMENTAL

*Tri-*p*-nitrophenylmethyl Chloride*.—The synthesis was carried out in the apparatus shown in the Figure, under a hood. Tri-*p*-nitrophenylmethane [11] (4 g.) in a 200 ml. flat-bottomed flask (1) provided with a magnetic stirrer was dissolved in the minimal amount of dry pyridine by stirring and slight heating (infrared lamp). A stream of dry, oxygen-free nitrogen was passed continuously through tap (2), with all other taps closed. After cooling of flask (1), sodium (2 g.), dissolved in the minimum amount of absolute ethanol, was added through the funnel (3) with constant stirring during 2 min., giving a deep-blue suspension of tri-*p*-nitrophenylmethylsodium. Ether (100 ml.) was added through funnel (3) and the suspension stirred for 1 min. and left to settle for 10 min. About half of the ether layer was sucked out carefully through tap (4) into a trap connected to a vacuum, care being taken that no solid was carried over. The washing with ether was repeated until the ether became colourless or only very faintly blue after the sedimentation of the organosodium compound. The precipitate was a glistening copper-coloured solid. Part of the ether was sucked out, tap (4) closed, and the residue evaporated by increasing the nitrogen flow and heating the stirred suspension (infrared lamp) until the precipitate was almost dry. Drying was completed with the nitrogen stream alone. (This part of the procedure is a variation of the method given in ref. 12.) Dry carbon tetrachloride (120 ml.) was added through the funnel (3) and the mixture was vigorously stirred. With taps (5) and (6) open a stream of nitrogen was passed through tap (6) in order to expel all the air; tap (5) was closed, tap (7) opened, and a slow current of chlorine passed through tap (6) into the suspension. The nitrogen flow was stopped and a trap for chlorine (potassium iodide solution) attached to tube (8). The chlorine flow was maintained until the dark solid had all become yellow, then the mixture was left overnight. The solid was filtered off on sintered glass and washed with carbon tetrachloride. Recrystallisations from benzene give a light yellow powder, m. p. 196—198° (Found: C, 55·6; H, 3·0; Cl, 8·35; N, 9·85. Calc. for $C_{19}H_{12}ClN_3O_6$: C, 55·2; H, 2·9; Cl, 8·6; N, 10·2%), and a second fraction of efflorescent

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[9] Winkler and Hearne, *J. Org. Chem.*, 1960, **25**, 1835; Walling and Jacknow, *J. Amer. Chem. Soc.*, 1960, **82**, 6108, 6113.

[10] Robertson and Waters, *J.*, 1947, 492; Cosgrove and Waters, *J.*, 1949, 907; Hebbelynck and Martin, *Bull. Soc. chim. belges*, 1950, **59**, 193; 1951, **60**, 54.

[11] Shoesmith, Sosson, and Hetherington, *J.*, 1927, 2221.

[12] Ziegler and Boye, *Annalen*, 1927, **458**, 248.

orange crystals that melt at a low temperature, resolidify, and melt again at 195°; the latter form is believed to contain benzene of crystallisation, and recrystallisation from acetone gave yellow crystals, m. p. 208°, whose analysis and infrared spectrum coincided with those of the powder described above. The yield was 20—30%. A previous attempt to synthesise this compound was reported by Gomberg.[13]

To obtain the ^{36}Cl-labelled compound a modification of the method described by Brown *et al.*[14] was used: a suspension of " AnalaR " potassium persulphate (15 g.) in water (50 ml.) was placed in a flask (9) mounted in a water bath, taps (5), (10), and (11) were opened, and a vigorous nitrogen stream bubbled into flask (9) through tap (10). The water bath was heated to 70° and labelled 0·5N-hydrochloric acid (5 ml.) added through funnel (12). Tap (7) was opened and taps (2) and (5) were closed. Oxidation of the hydrochloric acid required 1—2 hr. Chlorination of the suspension in flask (1) was completed by stopping the nitrogen stream through tap (10), closing tap (11), and passing through tap (6) a slow current of chlorine as described above. The labelled compound was purified as described above.

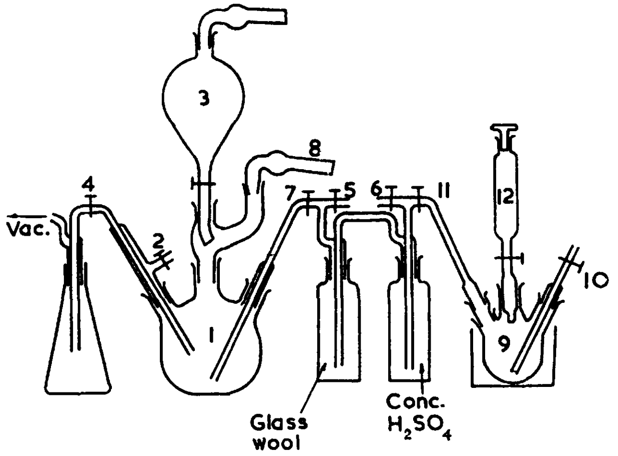

FIG. 1.

Other Materials.—Sulphuric and glacial acetic acid were analytical reagents. Distilled water was used. Lithium chloride (" AnalaR ") was powdered and then dried in an oven at 110° to constant weight. *N*-Chlorosuccinimide, silver acetate, mercuric chloride (all from B.D.H.), and mercuric acetate (Baker's " Analysed ") were used without purification. t-Butyl hypochlorite was prepared and purified as described by Teeter and Bell;[15] stock solutions in acetic acid were stable in tightly stoppered, all-glass bottles in the dark; the hypochlorite content was determined before use by iodometric titration.

Kinetic Runs.—Solutions of the reagents were kept in a water bath at the required temperature, then mixed, made up to volume, and placed in the water bath. Samples were processed by one of the following methods:

(*a*) The reaction mixture (3 ml.) was placed in a 10 ml. measuring flask, filled with water to the mark, shaken, and placed for several minutes in an ice–salt bath. A suspension of " Celite " filter aid (Johns-Manville) in water was filtered through a coarse sintered-glass funnel, to provide a layer of about 2 mm. The reaction mixture was filtered and the radioactivity of the filtrate was measured.

(*b*) The reaction mixture (5 ml.), in a 25 ml. measuring flask, was treated and filtered as in method *a* and the flask washed repeatedly with small amounts of cold water that were poured on the precipitate. The precipitate and " Celite " were transferred to the measuring flask, the funnel washed repeatedly with acetone into the flask, and the latter filled to the mark with

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[13] Gomberg, *Ber.*, 1904, **37**, 1626.

[14] Brown, Gillies, and Stevens, *Canad. J. Chem.*, 1953, **31**, 768.

[15] Teeter and Bell, *Org. Synth.*, 1952, **32**, 20.

the same solvent. The suspension was shaken and left to settle and 10 ml. of the overlying solution were taken for measurement.

Radioactivity measurements were carried out in a Geiger–Müller tube attached to a scaler (Ekco Electronics Ltd., type N529A). The background radiation and a suitable sample representing 0 or 100% reaction were measured each day.

Various.—Infrared spectra were determined in an " Infracord " Perkin-Elmer spectrophotometer. Ultraviolet spectra were determined in a Beckman DU spectrophotometer. M. p.s were determined on a Kofler heating stage.

The following experiments were also carried out (" organic chloride " refers to tri-*p*-nitrophenylmethyl chloride):

(I) The organic chloride (100 mg.) was refluxed for 5 hr. in acetic acid (120 ml.) containing 20% v/v of water; the product was precipitated with water, filtered, and recrystallised from acetic acid–ligroin; it had m. p. 186° and was identified as tri-*p*-nitrophenylmethanol by a mixed m. p. [lit., 188—189°, 189°, 193° (corr.); see refs. 16, 13, and 17] and by its infrared spectrum.

(II) $2{\cdot}36 \times 10^{-2}$M-Organic chloride (45 ml.) in acetic acid, mixed with a saturated solution (5 ml.) of silver acetate in the same solvent, was kept at 30°. After a few minutes the solution became turbid. After 2 days the precipitate was isolated and identified as silver chloride.

(III) $6{\cdot}21 \times 10^{-2}$M-Organic chloride in dry acetone gave no chloride or other water-soluble ion containing chlorine in 3 hr. at 30°.

(IV) The organic chloride (15 mg.) was refluxed for 1 hr. in suspension in 5% aqueous sodium hydroxide (100 ml.). No chloride ions were detected in the filtered solution by Volhard's method.

(V) $5{\cdot}22 \times 10^{-2}$M-Organic chloride in acetone containing 15% v/v of water and 1% w/v of sodium hydroxide gave after 1 hr. at 30° almost complete liberation of chloride and other water-soluble ions containing chlorine. The solution changed its colour in the first minutes of the reaction from colourless to green, then to dark blue; after 2 days' exposure to air the colour changed to red and finally to dark yellow.

(VI) The ultraviolet spectrum of the organic chloride was determined in acetic acid ($\lambda_{\text{max.}}$ 268 mμ, ε $3{\cdot}1 \times 10^4$). A 5×10^{-5}M-solution in a saturated solution of mercuric chloride in acetic acid was kept at 30° and the spectrum was determined after 2 hr. and after 2 days; in each case the spectrum coincided, within the limits of experimental error, with that of the organic chloride alone in acetic acid in the range 250—320 mμ. Similar results were obtained with more dilute solutions of mercuric chloride.

(VII) Various samples were taken by method *a* from runs 10, 11, 12, 13 (7, 12, 30, 41% reaction). When the filtrates were treated with aqueous potassium iodide solution, no iodine was liberated.

(VIII) An acetic acid solution $1{\cdot}92 \times 10^{-3}$M in labelled organic chloride and $2{\cdot}73 \times 10^{-3}$M in mercuric chloride was kept at 40·3°. Approximately 70% of the radioactive chlorine was liberated. The mixture with cold water gave a precipitate which melted at 195° and gave the correct chlorine analysis for the organic chloride (Found: Cl, 8·25%).

(IX) An acetic acid solution $3{\cdot}84 \times 10^{-3}$M in organic chloride and $2{\cdot}07 \times 10^{-3}$M in mercuric acetate was kept for 3 days at 40·3°. Tri-*p*-nitrophenylmethyl acetate, precipitated on addition of cold water, was filtered off and washed (m. p. 95—98°) (Found: Ac, 12·0. Calc. for $C_{21}H_{15}N_3O_8$: 1Ac, 11·9%).

(X) An acetic acid solution $3{\cdot}58 \times 10^{-3}$M in labelled organic chloride and 0·282M in lithium chloride was kept at 40·3°; after 7 days about 50% of the radioactive chlorine had been liberated. The solid precipitated on addition of cold water was filtered off and washed; it had m. p. 160° (Found: Cl, 7·3%); it was probably a mixture of about 85 mole-% of the organic chloride and 15 mole-% of the acetate.

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[*Received, July 4th,* 1961.]

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[16] Fischer and Fischer, *Annalen*, 1878, **194**, 242.

[17] Montagne, *Rec. Trav. chim.*, 1905, **24**, 127.