549. *Homolytic Substitution at a Saturated Carbon Atom. Part II.* Products of the Photoinduced Gaseous Chlorination of t-Butylbenzene.*

By J. D. Backhurst, E. D. Hughes, and Sir Christopher Ingold.

The test for intervention of alkyl radicals in aliphatic substitution, which uses t-butylbenzene as substrate, and relies on a formed 2-methyl-2-phenylpropyl (neophyl) radical to disclose itself by rearrangement, is verified by application to a reaction of known mechanism, namely, photoinduced chlorination in the gas phase. In theory, the test presupposes a radical life long enough to permit this activated rearrangement, and therefore it was for experimental determination whether it would be applicable to a mechanism providing only a short radical life, for example, a chain reaction, such as chlorination is known to be, of great chain length, where radical life is determined by the fast step of each unit process of chain-propagation. The rearrangement does occur in the gaseous chlorination of t-butylbenzene.

It is assumed that kinetics are not useful for exploring mechanism in the present studies of homolytic substitution, though they may later be for confirmation, and that the piecemeal establishment of single points of mechanism by *ad hoc* tests holds better prospects. In Part I, one such test, that for the intervention of free alkyl radicals, was successfully applied to a reaction of unknown mechanism, aliphatic nitration, but the validity of the test required to be checked by application to a reaction of known mechanism: chlorination was used.

As before, we took t-butylbenzene as substrate, so that the alkyl radical, if formed, would be 2-methyl-2-phenylpropyl (neophyl), which, uniquely among such simple radicals, would, in the length of life it has in some reactions, isomerise to give products which establish its intervention.[1] A certain length of life had to be provided, because rearrangement of the radical is somewhat slow, having an estimated activation energy of at least 8 kcal./mole.[2] Our problem was therefore to find out whether the 2-methyl-2-phenylpropyl radical, if an intermediate in a homolytic substitution, particularly one having a chain mechanism of numerous very rapid steps, would survive long enough to isomerise. In order to allow it a maximal opportunity so to do, we worked in the gas phase, and were prepared to go to low partial pressures.

The prototype of homolytic chlorination is the chlorine–hydrogen reaction, for which, on the basis of experiments by Bodenstein and others, Nernst proposed the first specific chain mechanism,[3] which all subsequent work has confirmed [4] ($R = H$):

$$Cl + HR \longrightarrow HCl + R; \quad R + Cl_2 \longrightarrow RCl + Cl$$

The chlorination of alkanes, whether thermally [5] or photochemically [6] induced, shows just the same kinetic characteristics, and must have an identical mechanism [7] ($R =$ alkyl). Chain-lengths are commonly 10^4—10^6. The first step (above) is rate-controlling, but is nevertheless very fast, having the activation energy 3·85 kcal./mole for methane, and lower values for other hydrocarbons.[8] The second step, which determines the life of the radical R, follows the first so very quickly that the first is not detectably reversed.

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* Part I, preceding paper.

[1] Urry and Kharasch, *J. Amer. Chem. Soc.*, 1944, **66**, 1438.

[2] Seubold, *J. Amer. Chem. Soc.*, 1953, **75**, 2532.

[3] Nernst, *Z. Elektrochem.*, 1918, **24**, 335.

[4] Hinshelwood, " Kinetics of Chemical Change in Gaseous Systems," Clarendon Press, Oxford, 1933, p. 100; Semenoff, " Chemical Kinetics and Chain Reactions," Clarendon Press, Oxford, 1935, p. 89.

[5] Pease and Walz, *J. Amer. Chem. Soc.*, 1931, **53**, 3728.

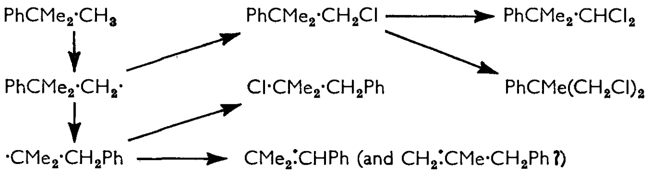
[6] Coehn and Cordes, *Z. phys. Chem.*, 1930, **89**, 1; Jones and Bates, *J. Amer. Chem. Soc.*, 1934, **56**, 2282; Tamura, *Rev. Phys. Chem. Japan*, 1941, **15**, 86; Ritchie and Winning, *J.*, 1950, 3579.

[7] Semenoff, ref. 4, p. 122; Steacie, " Atomic and Free Radical Reactions," Reinhold Publishing Corp., New York, 1954, p. 667; Walling, " Free Radicals in Solution," John Wiley and Sons Inc., New York, 1957, p. 352.

[8] Pritchard, Pyke, and Trotman-Dickinson, *J. Amer. Chem. Soc.*, 1955, **77**, 2629.

Unlike aliphatic nitration, aliphatic chlorination is not accompanied by degradation. Hass, McBee, and Weber have concluded [9] that, like nitration, chlorination is free from skeletal rearrangements, and also that every possible monochlorination product is always formed, the rates of hydrogen replacement, which are in the order tertiary > secondary > primary at lower temperatures, tending towards equality at higher. These general principles are confirmed in Walling's more recent and extensive collation [10] of data on relative rates and products of aliphatic chlorination.

In our experiments, preheated t-butylbenzene vapour and chlorine, in ratios between 3 : 1 and 10 : 1, were passed at atmospheric pressure, and at rates giving reaction times between 5 and 60 sec., through a Pyrex tube at some uniform temperature between 190° and 245°, and illuminated by mercury arcs. No clear difference of result was caused by packing the reaction tube with narrow tubes in order to increase 4-fold the surface area. The condensed product was fractionated, and, from the distillation graph, its composition was determined. The losses on distillation were usually not much more than 1%. Six products were identified, unchanged t-butylbenzene (283·5 g.), ωω-dimethylstyrene (2·0 g.), 1-benzyl-1-methylethyl chloride (14·3 g.), 2-methyl-2-phenylpropyl chloride (69·0 g.), ωω-dichloro-t-butylbenzene (5·0 g.), ωω′-dichloro-t-butylbenzene (4·0 g.). The yields shown are fairly typical, except that ωω-dimethylstyrene was not obtained from experiments at the lower temperatures. 2-Methyl-2-phenylpropyl chloride was always the main product, and 1-benzyl-1-methylethyl chloride was nearly always second in importance. The latter isomer is the chloride of the rearranged radical. ωω-Dimethylstyrene is a dehydrogenation product of the rearranged radical. 2-Methyl-2-phenylpropyl chloride underwent no conversion into 1-benzyl-1-methylethyl chloride under the conditions of production of these substances. However, the two dichlorides could be produced together by chlorination of 2-methyl-2-phenylpropyl chloride under similar conditions, and we therefore assume that they were produced from t-butylbenzene by way of this chloride. The following conversion scheme is, of course, partly hypothetical:



These experiments confirm what was certain from the kinetics of alkane chlorinations, namely, that the 2-methyl-2-phenylpropyl radical intervenes in the gaseous chlorination of t-butylbenzene. They show also, however, that the radical intervenes with a free life long enough to permit rearrangement, notwithstanding that the reaction involves long kinetic chains, in which even the slower propagation step is very fast, and radical life is determined by the faster propagation step. This conclusion justifies our using t-butylbenzene as a test for the intervention of alkyl radicals in aliphatic substitutions of unknown mechanism, as already illustrated in Part I with respect to nitration.

EXPERIMENTAL

Materials.—t-Butylbenzene, from benzene, t-butyl chloride, and ferric chloride, had b. p. 51°/10 mm., n_D^{25} 1·4905. 2-Methyl-2-phenylpropyl chloride, from benzene and 2-methylallyl chloride,[11] had b. p. 94—95°/9 mm., n_D^{25} 1·5227. It was characterised by nitration (fuming HNO_3) to its *p*-nitro-derivative, b. p. 142—143°/1·4 mm., m. p. 54°, which was reduced (Sn–HCl) to an amine whose acetyl derivative had m. p. 154°. 1-Benzyl-1-methylethyl chloride, from

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[9] Hass, McBee, and Weber, *Ind. Eng. Chem.*, 1935, **27**, 1190; 1936, **28**, 333.
[10] Walling, ref. 7, p. 356.
[11] Smith and Sellas, " Organic Syntheses," 1952, **32**, 90.

the alcohol (Part I), hydrogen chloride, and zinc chloride, had b. p. 85°/10 mm., n_D^{25} 1·5132. It was characterised by conversion, by treatment of its Grignard compound with phenyl isocyanate, into benzyldimethylacetanilide, m. p. 107·5°. ωω-Dimethylstyrene and its nitrosite are described in Part I.

Apparatus.—The system for supplying the reaction vessel with t-butylbenzene vapour at known flow-rate and temperature was as described in Part I. This vapour passed through the outer tube of the preheater; chlorine from a cylinder, dried ($CaCl_2$) and flow-metered, was passed along the inner tube. The chlorine was metered with a rotameter, consisting of a vertical tapered tube, up which it passed, lifting a Koramite float whose equilibrium position gave the rate of passage. A constriction in the outer tube of the preheater prevented back-diffusion. The outlet of the inner tube was so constructed that the outflow of chlorine was radial to the flow of hydrocarbon, thus ensuring efficient mixing in the reaction vessel, a 95 cm. length of Pyrex tube, 2·5 cm. in diameter, with an external heater winding surrounded by another Pyrex tube for thermal protection. Two mercury-discharge lamps, 15 cm. above the reaction vessel, provided the required irradiation, which was screened from the preheater, from the region of mixing of the gases, and from the condensing and collecting arrangements. The latter were similar to those described in Part I, except that strongly cooled traps proved unnecessary.

Method.—The required temperatures having been established, the apparatus was swept with oxygen-free nitrogen. The chlorine supply system was detached at the outlet end of the flow-meter, swept with chlorine, and reconnected. Meanwhile, the hydrocarbon supply system was started and regulated. When the hydrocarbon, having displaced the nitrogen in the preheater and reaction vessel, could be seen condensing, the chlorine supply was started and regulated. After a period sufficient for the attainment of steady conditions, the irradiation was started, and, after a further such period, the metering of supplies and collection of products were begun. At the end of the reaction period the apparatus was swept with nitrogen, which was also passed through the liquid condensate to carry off hydrogen chloride.

Separation of Products.—They were separated by distillation, under reduced but regulated pressure, with a long vacuum-jacketed column operating at high reflux ratio. Boiling points and refractive indices for one experiment are in the Table. Both sets of constants allow distillation curves to be constructed, which show the six components and provide a basis for their estimation.

Distillation results (*Run* 21).

Hydrocarbon : chlorine ratio 4·2; temp. 240°; time 29 sec.

Fract. No.	B. p. (10·0 mm.)	Wt. (g.)	n_D^{25}	Fract. No.	B. p. (10·0 mm.)	Wt. (g.)	n_D^{25}
1	50·0—51·0	195·1	1·4905	13	88·7—90·0	2·9	1·5155
2	50·0—51·0	82·3	1·4905	14	90·0—93·0	1·9	1·5172
3	51·0—52·0	4·3	1·4910	15	93·0—94·7	1·2	1·5202
4	52·0—60·0	3·2	1·4910	16	94·7—96·5	34·9	1·5228
5	60·0—65·0	0·6	1·5122	17	96·5	20·2	1·5228
6	67·8—69·2	1·0	1·5263	18	95·0	13·1	1·5230
7	69·2—72·0	0·8	1·5283	19	95·0—90·0	3·3	1·5243
8	72·0—81·0	0·7	1·5234		(4·0 mm.)		
9	81·0—86·0	1·8	1·5200	20	72·0—90·0	0·8	1·5343
10	86·0—87·3	2·4	1·5150	21	90·0—95·0	3·7	1·5378
11	87·3—87·0	1·8	1·5150	22	98·0—100·0	3·1	1·5465
12	87·0—88·7	2·4	1·5153	23	100·0—101·0	0·7	1·5482

Fractions 1—3 consisted of t-butylbenzene. Fraction 5 was unsaturated and had the odour of 2-benzylpropene; but this hydrocarbon, which we prepared, is not easy to characterise (*e.g.*, it seems not to form a crystalline nitrosite), and we were not able to confirm its presence here. Fraction 7 marks a sharp peak in the refractive-index curve of the distillate, and was identified as ωω-dimethylstyrene (Found: C, 91·0; H, 9·4. Calc. for $C_{10}H_{12}$: C, 90·9; H, 9·1%), by conversion into its nitrosite, m. p. 116° (Part I). Fractions 6 and 7, in combination with similar material from other experiments, when redistilled, gave material of b. p. 68°/10 mm., n_D^{25} 1·5350—1·5370. Fraction 11 was characterised as 1-benzyl-1-methylethyl chloride (Found: C, 71·5; H, 7·9; Cl, 20·9. Calc. for $C_{10}H_{13}Cl$: C, 71·2; H, 7·8; Cl, 21·0%) by conversion into benzyldimethylacetanilide, m. p. 107·5°. Fractions 10—13, on redistillation,

gave material of b. p. 85°/10 mm., n_D^{25} 1·5135. Fraction 17 was identified as 2-methyl-2-phenylpropyl chloride (Found: C, 71·5; H, 8·0; Cl, 21·2%) by conversion into 2-*p*-acetanilido-2-methylpropyl chloride, m. p. 154°. Fraction 21, on redistillation, gave a material of b. p. 98°/4·0 mm., n_D^{25} 1·5387, which was identified as 1,1-*dichloro-2-methyl-2-phenylpropane* (Found: C, 59·5; H, 6·1; Cl, 34·9. $C_{10}H_{12}Cl_2$ requires C, 59·1; H, 6·0; Cl, 34·9%) by comparison of its infrared spectrum with that of the same substance, prepared as described below. Fractions 22 and 23 on redistillation yielded a sample of b. p. 115°/4 mm., n_D^{25} 1·5475, which was identified as 1,3-*dichloro-2-methyl-2-phenylpropane* (Found: C, 58·9; H, 5·9; Cl, 35·6%) from its infrared spectrum (see below).

Chlorination of 2-Methyl-2-phenylpropyl Chloride.—For production of the two dichlorides on a preparative scale, 2-methyl-2-phenylpropyl chloride (300 g.), refluxing under 120 mm., and later under 150 mm., was treated with a stream of chlorine under irradiation from mercury arcs. A preliminary fractionation of the product through a short column gave a first fraction of unchanged chloride (77 g.), a fraction of b. p. 98—110°/4·0 mm. and n_D^{25} 1·536—1·542 (95 g.), and a fraction of b. p. 110—120°/4·0 mm. and n_D^{25} 1·545—1·552 (95 g.). The second of these fractions, on redistillation through a long vacuum-jacketed column at high reflux ratio, gave a compound (75 g.) of b. p. 98°/4·0 mm. and n_D^{25} 1·5376 (Found: C, 59·0; H, 6·0; Cl, 34·6%). The third, on similar treatment, gave a compound (55 g.) of b. p. 113°/4·0 mm. and n_D^{25} 1·5473. These two substances were identical (infrared spectra) with 1,1- and 1,3-dichloro-2-methyl-2-phenylpropane of the preceding paragraph.

1,1-*Dichloro-2-methyl-2-phenylpropane.*—2-Methylallyl chloride was isomerised by stirring with 80% sulphuric acid at 40° for 2·5 hr. to 2,2-dimethylvinyl chloride, b. p. 66—68°, which, on chlorination by chlorine at 0° in presence of excess of sodium hydrogen carbonate, was converted into 2-methylallylidene chloride, b. p. 108—112°, n_D^{25} 1·4550.[12] Following the method of conversion of 2-methylallyl chloride into 2-methyl-2-phenylpropyl chloride,[11] 2-methylallylidene chloride (0·18 mol.) was stirred with benzene (0·5 mol.) and sulphuric acid (2·0 ml.) for 30 hr. at 15°. The product, on fractionation, gave a material (1·25 g.) of b. p. 78°/0·7 mm., n_D^{25} 1·5350, which had infrared bands at 707, 724, 752, 775, 824, 858, 886, 939, 1052, 1100, 1110, and 1220 cm.$^{-1}$, identical in form and position with those of the above samples of 1,1-dichloro-2-methyl-2-phenylpropane.

1,3-*Dichloro-2-methyl-2-phenylpropane.*—It was necessary first to prepare 3-chloro-2-chloromethylprop-1-ene. Mooradian and Cloke's route [13] from pentaerythritol, through its trichlorohydrin, to the oxidation product of the latter, tris(chloromethyl)acetic acid, which should, by their account, have been easily decarboxylated and dehydrochlorinated with quinoline, was unsuccessful. We also tried the addition of hypochlorous acid to 2-methylallyl chloride, expecting to dehydrate the formed 1,3-dichloro-2-methylpropan-2-ol with sulphuric acid, phosphoric acid, or iodine; again, we tried chlorination of 2-methylallyl chloride by passing chlorine into the refluxing material, so obtaining a fraction of b. p. 135—140° as well as the expected 1,2,3-trichloro-2-methylpropane, b. p. 162—170°, which we attempted to dehydrochlorinate with quinoline. We were unable to develop well any of these processes, but almost all attempts gave some material boiling in the range 130—140°. As 1,3-dichloro-2-methylprop-1-ene is recorded [14] as having b. p. 132°, and 3-chloro-2-chloromethylpropene, b. p. 138°, we assumed this fraction to be a mixture of the two; as either isomer should give the required product in reaction with benzene, we used the whole fraction for this purpose. It was stirred with benzene and sulphuric acid, as in the similar preparation in the preceding paragraph. The product, on fractionation, gave a material (0·75 g.) of b. p. 116°/4 mm., n_D^{25} 1·5484, which had infrared bands at 717, 745, 766, 830, 872, 908, and 1001 cm.$^{-1}$, identical in form and position with those of the two already described samples of 1,3-dichloro-2-methyl-2-phenylpropane.

William Ramsay and Ralph Forster Laboratories,
University College, Gower St., London, W.C.1.

[*Received, March 18th*, 1959.]

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[12] Huntress, " Organic Chlorine Compounds," John Wiley and Sons, Inc., New York, 1948, p. 1042.
[13] Mooradian and Cloke, *J. Amer. Chem. Soc.*, 1945, **67**, 942.
[14] Huntress, ref. 12, pp. 727 and 732.