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Free-radical Substitution in Aliphatic Compounds. Part XVIII.¹ The Gas-phase Chlorination of 1-Phenylpropane

By V. R. Desai, A. Nechvatal, and J. M. Tedder,* Chemistry Department, The University, Dundee

The chlorination of 1-phenylpropane has been studied in the gas phase from 90-200°. Attack is favoured at the 1-position, while the 2-position is deactivated in comparison to the secondary positions in butane. Appreciable yields of 1-phenylprop-1-ene are formed. The amount of olefinic product was reduced by the addition of an inert gas (SF₆). It is suggested that when an alkyl radical reacts with molecular chlorine a thermally excited alkyl chloride is formed which, in cases where elimination is favoured, may lose hydrogen chloride.

THE chlorination of alkylbenzenes has frequently been studied and recently a careful investigation of liquidphase photochlorination has been reported by Russell and his co-workers.² Our primary object was to extend our study of the halogenation of substituted butanes to 1-phenylbutane. In practice 1-phenylbutane is so involatile that most of the work involved 1-phenylpropane.

EXPERIMENTAL

Chlorination of 1-Phenylpropane.—A commercial sample of 1-phenylpropane which showed only one peak (g.l.c.) was used. Its gas-phase chlorination was carried out in a vacuum apparatus similar to that described.³

A mixture of 1-phenylpropane (10 parts) and chlorine (1 part) at a total pressure of approximately 80 mm. was illuminated with a 200w tungsten lamp for $1\frac{1}{2}$ hr. The contents of the reaction vessel were then condensed into a sample tube for analysis. The products were analysed on a Griffin and George D6 gas chromatograph (gas density balance detector) at 150° on a 6 ft. $\times \frac{3}{16}$ in. diam. column packed with 20% silicone oil on Celite (60-100 mesh) with nitrogen (60 ml./min.) as carrier gas. Five products were found, the three monochloro-1-phenylpropanes, 1-phenylprop-1-ene, and 1,2-dichloro-1-phenylpropane.

Analysis was complicated by the fact that 1-chloro-1-phenylpropane decomposed on the silicone oil column. 1-Chloro-1-phenylbutane decomposed similarly (Russell et al.²). The correlation between peak area of 1-chloro-1-phenylpropane and its molar concentration was determined by analysing mixtures of the 1-chloro- and 3-chloro-1-phenylpropanes of known composition, and applying the correction (Table 1) so obtained to the 1-chloro-isomer peak areas measured in the reaction product chromatograms. The results of the chlorination of 1-phenylpropane are expressed as relative selectivity values $(RS^{x,3})$ (Table 2) and

¹ Part XVII, J. M. Tedder and R. A. Watson, Trans. Faraday Soc., 1968, 64, 1304.

are calculated from the molar percentages of reaction products formed (Table 3).

TABLE 1

1-Chloro-1-phenylpropane in a mixture of 1-chloro- and 3-chloro-1-phenylpropane (%)

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Concn.	Molar	Concn.	Molar
measured	concn.	measured	concn.
(v/v)	obs.	(v/v)	obs.
25	13	67	49
33	18	75	57
50	31	52 (w/w)	30

TABLE 2 Relative selectivities $RS^{x,3}$ for the chlorination of 1 phanylpropage

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Temp.	C ₆ H ₅ CH ₂	C [*] ₂	——СН3
86°	$6 \cdot 5 \pm 0 \cdot 04$	1.0 ± 0.4	1
117	$6\cdot5 \pm 0\cdot2$	${1\cdot 3\over \pm0\cdot 3}$	1
145	$5\cdot7 \pm 0\cdot1$	${}^{1\cdot 2}_{\pm0\cdot 1}$	1
175	$5 \cdot 1 \\ \pm 0 \cdot 4$	$2 \cdot 0 \pm 0 \cdot 6$	1
202	$4 \cdot 9 \\ \pm 0 \cdot 1$	${1\cdot 3\over \pm0\cdot 3}$	1

* Approximate values calculated from: Σ 2-chloro- + 1.2dichloro-1-phenylpropane + 1-phenylprop-1-ene.

Chlorination of 1-Phenylpropane in the Presence of Sulphur Hexafluoride .- The reactions were carried out as in the previous series of experiments at two chosen temperatures, except that sulphur hexafluoride (340 mm.) was also present. The results are expressed as molar percentages of reaction products formed (Table 3).

Chlorination of 1-Phenylbutane.-The reactions were

² G. A. Russell, A. Ito, and D. G. Hendry, J. Amer. Chem. Soc., 1963, 85, 2976. ³ H. Singh and J. M. Tedder, J. Chem. Soc., 1964, 4737.

carried out analogously to the chlorination of 1-phenylpropane. At the end of a reaction, owing to the high b.p.s. of the chloro-1-phenylbutanes, the contents of the reaction vessel were condensed into a small tube joined to it, which was cut off for analysis. The products were analysed on two different columns; the 20% silicone oil column

TABLE 3

1 9 12:

						1,2-101-
					1-Phenyl-	chloro-
					prop-1-	1-phenyl-
	No. of	$C_6H_5CH_2-$	CH2-	$-CH_3$	ene	propane
Temp.	runs	(%)	(%)	(%)	(%)	(%)
86°	6	71.8	$8 \cdot 2$	16.5	$2 \cdot 3$	1.3
		±0·3 *	± 0.2	± 0.1	± 0.1	± 0.1
117	5	70.0	9.6	16.2	$3 \cdot 1$	1.0
		± 1.0	± 1.1	± 0.2	± 0.2	± 0.1
145	6	$68 \cdot 1$	6.5	17.8	$6 \cdot 1$	1.6
		± 0.2	± 0.1	± 0.2	± 0.5	± 0.04
145 +	5	69.3	7.8	18.3	4 ·0	0.6
		± 0.2	± 0.1	± 0.1	± 0.3	± 0.1
175	6	61.9	7.5	18.1	11.0	0.6
		± 0.8	± 0.1	± 0.3	± 0.3	± 0.1
198	8	$63 \cdot 4$	$7 \cdot 4$	19.5	$8 \cdot 7$	0.8
		± 0.2	± 0.4	± 0.2	± 0.2	± 0.1
192 +	6	64.8	9.4	19.2	$6 \cdot 1$	0.6
,		± 0.4	± 0.2	± 0.4	± 0.3	± 0.1
* 1	Gurana	nonrosont mag	n daw	ation	+ Chlorin	ation con

Errors represent mean deviation. † Chlorination conducted in the presence of sulphur hexafluoride (340 mm.).

 (150°) and one of 15% polyethylene glycol on Celite (60-100 mesh) (150°). The silicone column separated 4-chloro-1-phenylbutane and 1-phenylbut-1-ene, but did not separate the 1, 2-, and 3-chloro-1-phenylbutanes. The polyethylene glycol column separated the 1-, 2-, 3-, and 4-chloro-1-phenylbutanes and the 1-phenylbut-1-ene, but the 1-chloro-1-phenylbutane decomposed extensively on it. Very approximate RS values could be obtained [RS1,4: 7.4 (145°) ; 5.9 (175°) ; 4.3 (202°)] by combining the two sets of readings but although they showed the same overall trend as the 1-phenylpropane results, there was too much scatter to justify reporting them in detail.

Preparation of Authentic Reference Compounds.-1-Phenylpropan-1-ol (b.p. $210-211^{\circ}/750$ mm.)⁴ obtained by the reaction of benzaldehyde with ethylmagnesium bromide was treated with thionyl chloride in the presence of a trace of pyridine to yield 1-chlorophenylpropane (b.p. 77-80°/ 10 mm.),⁵ n.m.r. 9.27 (triplet, 3H, J 8 Hz CH₃); 7.7-8.4 (two superimposed quartets, 2H, CH₂); 5.38 (triplet, 1H, J 8 Hz, CHCl); 2.8 (broad singlet, 5H, C_6H_5). All n.m.r. spectra were measured at 60 MHz in carbon tetrachloride with tetramethylsilane as internal standard and are reported as τ values.

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⁵ P. A. Levene and L. A. Mikeska, J. Biol. Chem., 1926, 70, 361.

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2-Chloro-1-phenylpropane was prepared analogously. 1-Phenylpropan-2-ol (b.p. 110-112°/16 mm.)⁶ was treated with thionyl chloride in the presence of a trace of pyridine to give 2-chloro-1-phenylpropane (b.p. 89-90°/15 mm.);⁷ n.m.r. 8.65 (doublet, 3H, J 6 Hz, CH₃); a distorted octet centred at 7.08 (2H, CH₂); 5.85 (sextet, 1H, J 6 Hz, CHCl); 2.8 (broad singlet, 5H, C_6H_5).

1-Phenylpropan-3-ol (b.p. 110-111°/15 mm.)8 similarly gave 3-chloro-1-phenylpropane (b.p. 94-95°/11 mm.); n.m.r. 8.2 (quintet, 2H, J 9 Hz, -CH2-CH2Cl); 7.45 (triplet, 2H, J 9 Hz, CH₂C₆H₅); 6.8 (triplet, 2H, J 6 Hz, CH₂Cl); 3.0 (broad singlet, 5H, C_6H_5).

1-Phenylprop-1-ene (b.p. 175-178°/760 mm.)10 was obtained by dehydrating 1-phenylpropan-1-ol with concentrated sulphuric acid; 11 n.m.r. 8.16 (doublet, 3H, J 5 Hz, CH_3 ; 3.7-3.9 (multiplet, 2H, CH=CH); 2.82(broad singlet, 5H, C_6H_5).

1,2-Dichloro-1-phenylpropane, b.p. 110-114°/13 mm.¹² was prepared by the interaction of chlorine and 1-phenylprop-1-ene in carbon tetrachloride kept at room temperature for 20 hr.; n.m.r. 8.5 and 8.7 (two doublets, 8.6, 3H, J 6 Hz, CH₃); 5.74 (quartet, 1H, J 6 Hz, CHCl); 5.05-5.2 (multiplet, 1H, CHCl); 2.8 (broad singlet, 5H, $C_{6}H_{5}$).

1-Chloro-1-phenylbutane ¹³ (b.p. $70-72^{\circ}/3$ mm.) was prepared by the interaction of 1-phenylbutan-1-ol 14 (b.p. 110-112°/11 mm.) and thionyl chloride in the presence of a trace of pyridine; n.m.r. 9.1 (distorted triplet, J 6 Hz, CH_3 ; 8.5—8.9 (unresolved multiplet, CH_2CH_3); 7.8—8.4 (unresolved multiplet, CH₂CHCl); 5.35 (triplet, J 7 Hz, CHCl); 2.9 (broad singlet, C_6H_5).

2-Chloro-1-phenylbutane² (b.p. 63-65°/1 mm.) was prepared analogously to the 1-chloro-compound from 1-phenylbutan-2-ol¹⁵ (b.p. 63-64°/1 mm.); n.m.r. 9.0 (triplet, J = 6 Hz, 3H, CH_3); 8.0-8.7 (multiplet, 2H, $CH_{3}CH_{2}$; 7.1 (doublet, J 8 Hz, 2H, $C_{6}H_{5}CH_{2}$); 5.9-6.6 (multiplet, 1H, CHCl), 3.0 (broad singlet, 5H, C_6H_5).

The interaction of thionyl chloride and 1-phenylbutan-3-ol¹⁶ (b.p. 132°/14 mm.) in the presence of a trace of pyridine gave 3-chloro-1-phenylbutane (b.p. 80-82°/3 mm.)² which was shown to be only 78% pure (g.l.c.). From its n.m.r. spectrum could be identified the following absorptions: 8.56 (doublet, J 6 Hz, CH_3); 7.1-7.7 (multiplet, CH_2CH_2 ; 6.2 (multiplet, CHCl); 3.0 (broad singlet, C_6H_5).

4-Phenylbutan-1-ol (140°/14 mm.)¹⁷ treated as above gave 4-chloro-1-phenylbutane (b.p. 122°/12 mm.); ¹⁸ n.m.r. $8\cdot 1-8\cdot 4$ (multiplet, 4H, $CH_2CH_2CH_2Cl$), $7\cdot 4-7\cdot 8$ (multiplet, 2H, $C_6H_5CH_2$; 6.5—7.0 (multiplet, 2H, CH_2Cl); 3.1 (broad singlet, 5H, C_6H_5).

1-Phenylbutan-1-ol was passed over aluminium oxide heated to 300° to yield 1-phenylbut-1-ene (b.p. 70-72°/11 mm.); ¹⁹ n.m.r. 8.95 (triplet, J 7 Hz, 3H, CH₃); 7.5-8.1

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(multiplet, 2H, CH_2); 3.6-3.7 (multiplet, = $CHCH_2$ -), 3.4-3.6 (multiplet, $C_6H_5CH=$), the integral of these two absorptions comprising 2H; 2.9 (broad singlet, 5H, C_6H_5).

The n.m.r. spectrum also showed an absorption at τ 3 which indicated `that this compound is a mixture of the cis- and trans-isomers, although no separation was observed in the gas chromatogram.

The action of chlorine upon 1-phenylbut-1-ene in carbon tetrachloride gave 1,2-dichloro-1-phenylbutane, which was not distilled; n.m.r. 9.0 (triplet, 3H, J 6 Hz, CH₃) 7.8-8.4 (multiplet, 2H, CH_2CH_3), $5\cdot 6-6\cdot 1$ (multiplet, 1H, CHCICH₂); $4 \cdot 9 - 5 \cdot 2$ (distorted triplet, 1H, $C_6H_5CHClCHCl$; 2.9 (broad singlet, 5H, C_6H_5).

DISCUSSION

The relatively high reactivity of the 1-position (See Table 2) in the alkylbenzenes was expected,²⁰ although the phenyl group represents only the second substituent we have encountered which activates an adjacent methylene group to attack by chlorine atoms.²¹ A quantitative measure of the relative rates of attack at the 1- and 3-positions in 1-phenylpropane can be obtained by plotting the logarithm of the RS values against the reciprocal of the temperature [equation 1; subscript 2]

$$\log_{10} (\text{RS}^{1,3}) = \log_{10} \frac{A_2^1}{A_2^3} - \frac{E_2^1 - E_2^3}{2 \cdot 303 RT}$$
(1)

represents the reaction (2);

$$RH + Cl \cdot \xrightarrow{\kappa_2} R \cdot + HCl \qquad (2)$$

superscripts represent the positions.²²] By taking the average value for RS^{1,3} at each temperature we obtain $\log (A_2^{-1}/A_2^{-3}) = 0.39$ and $E_2^{-3} - E_2^{-1} = 0.85$ kcal. mole.⁻¹. If we assume that the rate of attack at the 3-position is identical with that at the terminal positions in butane we have $\log_{10}A_2^1 = 13.5$ l. mole⁻¹. sec.⁻¹ and $E_2^1 \simeq 0$ kcal. mole⁻¹ for attack at the 1-position. The high reactivity of the 1-position in 1-phenylpropane and presumably in other alkylbenzenes is thus due to a very low activation energy, a conclusion which is in accord with the usual picture of a resonance stabilised benzyl radical.

Unfortunately, Arrhenius parameters cannot be calculated for attack at the 2-position because of the approximate nature of the RS^{2,3} values owing to elimination. The temperature at which the present work was carried out is below the temperature at which appreciable thermal decomposition of 2-chloro-1-phenylpropane occurs. 2-Chloro-1-phenylpropane was heated in the

reaction vessel at 145° and also at 190° under the same illumination conditions as employed for the chlorinations, and then subjected to the same analytical procedure as the reaction products from a chlorination. No 1-phenylprop-1-ene was formed.

The reaction (3) between an alkyl radical and molecular chlorine is exothermic.²³ This energy will appear

$$R \cdot + Cl_2 \xrightarrow{\kappa_3} RCl + Cl \cdot;$$

$$\Delta H_3 = -20 \text{ kcal. mole}^{-1} \quad (3)$$

predominantly as vibration in the alkyl chloride molecule. It seems reasonable to suggest that in the case of the vibrationally excited 1-phenyl-2-chloroalkyl benzenes, the molecule may be sufficiently 'hot' for elimination to occur, as in reactions (4)—(8) where

$$C_{6}H_{5}CH_{2}\dot{C}HR + Cl_{2} \longrightarrow C_{6}H_{5}CH_{2}CHCIR^{*} + Cl \cdot (4)$$

$$C_{6}H_{5}CH_{2}CHCIR^{*} + M \longrightarrow$$

$$C_6H_5CH_2CHClR + M$$
 (5)

$$C_6H_5CH_2CHCIR^* \longrightarrow C_6H_5CH=CHR + HCl$$
 (6)

$$C_6H_5CH=CHR+Cl \rightarrow C_6H_5\dot{C}HCHClR$$
 (7)

$$C_{6}H_{5}\dot{C}HCHCIR + Cl_{2} \longrightarrow C_{6}H_{5}CHCICHCIR + Cl \cdot (8)$$

 $R=CH_3 \mbox{ or } C_2H_5.$ If this mechanism is correct, the ratio of 2-chloro-1-phenylalkane to the sum of the 1-phenylalk-1-ene plus the 1-phenyl-1,2-dichloroalkane present in the product should be pressure-dependent. Table 4 shows the effect of the addition of sulphur hexafluoride as an inert gas to the reaction mixture. These results strongly support the idea that vibrationally excited molecules formed in the reaction of the alkyl radicals with chlorine molecules are involved in the observed eliminations.

	Table 4	
Гетр.	SF_6 (mol.)	Ratio (see text)
145°	0	$1 : 1 \cdot 2$
145	4	1:0.6
192	0	1:1.3
192	4	1:0.7

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