Free Radical Substitution. Part 38.[1] The Effect of Solvent on the Atomic Chlorination and Bromination of 2-Substituted Butanes and the Importance of Steric Effects

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The relative selectivity of atomic halogenation of 2-substituted butanes is influenced by the phase and by solvents. There are solvents which increase the selectivity compared with the gas phase and solvents which decrease the relative selectivity. However the most striking feature of the halogenation (especially the bromination) of 2-substituted butanes is the high reactivity of the 2-position notwithstanding very unfavourable polar effects. This reactivity is attributed to the release of steric compression associated with the abstraction of the tertiary hydrogen atom. The halogenation of butan-2-ol esters is associated with some decomposition of 2-butyl radical [$CH_3CH_2\dot{C}(OCOR)CH_3$] and the chlorination of 2-phenylbutane with the formation of olefins 2-phenylbut-1-ene and 2-phenylbut-2-ene.

The halogenation of 2-substituted butanes has received very much less study than the analogous halogenation of 1-substituted butanes.[2,3] The halogenation of 2-halogenobutanes was reported in 1961.[4] The very striking feature of this work was the ease of abstraction of the hydrogen atom attached to the carbon atom which also carried the substituent halogen (*i.e.* the 2-position). In chlorination the 2-position was the most reactive site and in bromination almost all the attack occurred at this site. These results are in sharp contrast to the results obtained with the 1-halogenobutanes, where the substituted site (the 1-position) was the least reactive. The work described in this paper covers a study of the chlorination and bromination of 2-substituted butanes in general (not simply the halogenobutanes), and also extends the investigation to chlorination in different solvents as well as in the gas phase. The influence of solvent on the selectivity of chlorination has been the subject of recent papers from this laboratory.[5,6]

Before reporting the new results it should be emphasised that the chlorination of 1-phenylbutane and especially the chlorination of butanol derivatives C_4H_9OR (where R = CH_3, C_4H_9, COH, $COCH_3$, or $COCF_3$) were anomalous. Undoubtedly the bromination of these derivatives was associated with decomposition of the intermediate radical.[7,8]

Experimental

The experimental method has been described in detail in previous papers. In the gas phase the reactant proportions were 10 parts 2-substituted butane to 1 part halogen except in special cases when it was raised to 20 parts butane to 1 part halogen. The photolysis was continued until the halogen had been consumed.

(a) *Chlorination of 2-Chlorobutane.*—2-Chlorobutane was redistilled commercial material. The solvents were redistilled before use. The products of chlorination were separated and estimated by g.l.c.; their order of elution had been established previously.

(b) *Chlorination of 2-Bromobutane.*—Commercial 2-bromobutane was distilled and its purity checked by g.l.c. The products of chlorination were separated by preparative g.l.c. and their n.m.r. spectra and mass spectra were determined. The products in order of elution were: starting material, δ($CDCl_3$) 1.04 (3 H, t, *J* 7 Hz), 1.69 (3 H, d, *J* 7 Hz), 1.84 (2 H, m), and 4.14 (1 H, sextet, *J* 7 Hz); 2-bromo-2-chlorobutane, δ($CDCl_3$) 1.2 (3 H, t, *J* 7 Hz), 2.28 (2 H, q, *J* 7 Hz), 2.32 (3 H, s); *erythro*-2-bromo-3-chlorobutane δ($CDCl_3$) 1.68 (3 H, d, *J* 7 Hz), 1.85 (3 H, d, *J* 7 Hz), and 3.9—4.3 (2 H, m); *threo*-2-bromo-3-chlorobutane, δ($CDCl_3$) 1.60 (3 H, d, *J* 7 Hz), 1.75 (3 H, d, *J* 7 Hz), and 4.1—4.5 (2 H, m); 2-bromo-1-chlorobutane too small for n.m.r. but m.s. shows C_4H_8BrCl and structure deduced by process of elimination; the last peak was 2-bromo-4-chlorobutane, δ($CDCl_3$) 1.77 (3 H, *J* 7 Hz), 2.20 (2 H, q, *J* 7 Hz), 3.70 (2 H, t, *J* 7 Hz), and 4.30 (1 H, m).

Chlorination of 2-chlorobutane

Solvent phase	Temp. (°C)	CH_3	CH_2	CHCl	CH_3
Gas	25	1	1.7 ± 0.2 3.2 ± 0.5	4.1 ± 0.6	0.41 ± 0.03
Neat liquid	25	1	1.0 ± 0.2 1.7 ± 0.3	2.3 ± 0.3	0.32 ± 0.03
CCl_4 (1 : 1)	25	1	0.90 ± 0.11 1.6 ± 0.04	2.3 ± 0.3	0.29 ± 0.03
C_6H_6 (1 : 1)	25	1	1.1 ± 0.6 1.7 ± 0.1	3.9 ± 0.1	0.36 ± 0.03
CS_2 (1.7 : 1)	25	1	1.4 ± 0.3 2.7 ± 0.5	4.8 ± 0.7	0.34 ± 0.02

Reactivity per hydrogen, relative to position 4

Chlorination of 2-bromobutane

Solvent phase	Temp. (°C)	CH_3	CH_2	CHBr	CH_3
Gas	62	1	0.99 ± 0.09 2.2 ± 0.17	2.9 ± 0.1	0.22 ± 0.03
Neat	25	1	1.3 ± 0.1 2.3 ± 0.2	3.0 ± 0.4	0.46 ± 0.05
CCl_4 (1 : 1)	25	1	1.1 ± 0.1 2.2 ± 0.2	2.5 ± 0.5	0.40 ± 0.05
C_6H_6 (1 : 1)	25	1	1.3 ± 0.1 2.2 ± 0.1	4.5 ± 0.2	0.31 ± 0.05
CS_2 (1.7 : 1)	25	1	1.9 ± 0.1 2.8 ± 0.1	5.6 ± 0.3	0.19 ± 0.06

Reactivity per hydrogen, relative to position 4.

(c) *Bromination of 2-Bromobutane.*—Only one major product was isolated from the bromination of 2-bromobutane, and this had previously been identified by its n.m.r. spectrum to be 2,2-dibromobutane. There were two very small peaks which were assumed to be the *erythro*- and *threo*-2,3-dibromobutane.

(d) *Chlorination of 2-Cyanobutane.*—2-Cyanobutane was prepared from 2-methylpropanyl chloride which was con-

verted into 2-methylpropionamide by direct treatment with ammonia. The amide was refluxed with thionyl chloride for 1 h. After distillation the cyanobutane was purified by preparative g.l.c. The products of chlorination were separated by g.l.c. and their identity established by their n.m.r. spectra. The first product eluted was the unchanged starting material, δ($CDCl_3$) 1.07 (3 H, t, *J* 7 Hz), 1.30 (3 H, d, *J* 7 Hz), 1.61 (2 H, m), and 2.55 (1 H, sextet, *J* 7 Hz), followed by 2-chloro-2-cyanobutane, δ($CDCl_3$) 1.20 (3 H, t, *J* 7 Hz), 1.93 (3 H, s), 2.02 (2 H, m); *erythro*-2-chloro-3-cyanobutane, δ($CDCl_3$) 1.40 (3 H, d, *J* 7 Hz), 1.65 (3 H, d, *J* 7 Hz), 2.95 (1 H, m), and 4.04 (1 H, quintet, *J* 7 Hz); *threo*-2-chloro-3-cyanobutane, δ($CDCl_3$) 1.45 (3 H, d, *J* 7 Hz), 1.65 (3 H, d, *J* 7 Hz), 2.8—3.1 (1 H, m), and 3.8—4.3 (1 H, m); 1-chloro-2-cyanobutane, δ($CDCl_3$) 1.25 (3 H, t, *J* 7 Hz), 2.0—2.4 (2 H, m), 3.1—3.5 (1 H, m), and 3.85 (2 H, d, *J* 5 Hz); and 1-chloro-3-cyanobutane, δ($CDCl_3$) 1.35 (3 H, d, *J* 7 Hz), 1.8—2.2 (2 H, m), 2.90 (1 H, sextet, *J* 7 Hz), 3.67 (2 H, t, *J* 7 Hz).

Chlorination of 2-cyanobutane

Phase solvent	Temp. (°C)	CH_3-	CH_2	CH(CN)	CH_3
Gas	100	1	1.5 ± 0.1 2.1 ± 0.2	2.6 ± 0.2	0.20 ± 0.01
Gas	153	1	1.5 ± 0.1 2.2 ± 0.1	2.3 ± 0.2	0.20 ± 0.02
Gas	210	1	1.4 ± 0.2 2.0 ± 0.1	2.4 ± 0.4	0.26 ± 0.10
Neat liquid	25	1	1.1 ± 0.2 1.0 ± 0.1	2.9 ± 0.3	0.32 ± 0.05
CCl_4 (1 : 1)	25	1	1.1 ± 0.1 1.2 ± 0.1	1.4 ± 0.1	0.19 ± 0.01
C_6H_6 (1 : 1)	25	1	1.8 ± 0.1 1.9 ± 0.1	3.0 ± 0.1	0.47 ± 0.06
CS_2 (1 : 1)	25	1	2.1 ± 0.1 2.8 ± 0.1	3.0 ± 0.1	0.49 ± 0.02

The figures represent the mean value for four or five analytical determinations

Reactivity per hydrogen, relative to position 4

(e) *Bromination of 2-Cyanobutane.*—Only one major product was isolated and this proved to be 2-bromo-2-cyanobutane, δ($CDCl_3$) 1.22 (3 H, 7, *J* 7 Hz), 2.10 (3 H, s), and 2.25 (2 H, quartet, *J* 7 Hz).

(f) *Chlorination of 2-Methylbutanoyl Chloride and 2-Methylbutanoyl Fluoride.*—2-Methylbutanoyl chloride was prepared from the acid by treatment with thionyl chloride and 2-methylbutanoyl fluoride was prepared by refluxing the chloride over potassium fluoride. Both acid halides were redistilled before use and their purity checked by n.m.r. The products of chlorination were estimated by treating the reaction mixture with excess of methanol which converted unchanged starting material and the chloro-acyl halides into the corresponding methyl esters which were then identified by preparative g.l.c. and n.m.r. and qualitatively estimated by analytical g.l.c. The methyl esters in order of elution were methyl 2-methylbutanoate, δ($CDCl_3$) 0.90 (3 H, t, *J* 7 Hz), 1.15 (2 H, d, *J* 7 Hz), 1.52 (2 H, m), 2.35 (1 H, m), and 3.62 (3 H, s); methyl 2-chloro-2-methylbutanoate, δ($CDCl_3$) 0.99 (3 H, t, *J* 7 Hz), 1.72 (3 H, s), 2.00 (2 H, quartet, *J* 7 Hz), and 3.70 (3 H s); methyl *erythro*-3-chloro-2-methylbutanoate, δ($CDCl_3$) 1.30 (3 H, d, *J* 7 Hz), 1.53 (3 H, d, *J* 7 Hz), 2.65 (1 H, quintet, *J* 7 Hz), 3.71 (3 H, s), and 4.33 (1 H, quintet, *J* 7 Hz); methyl *threo*-3-chloro-2-methylbutanoate, δ($CDCl_3$) 1.22 (3 H, d, *J* 7 Hz), 1.51 (3 H, d, *J* 7 Hz), 2.77 (1 H, quintet, *J* 7 Hz), 3.70 (3 H, s), and 4.25 (1 H, quintet, *J* 7 Hz); methyl 2-(chloromethyl)butanoate, δ($CDCl_3$) 0.95 (3 H, t, *J* 7 Hz), 1.70 (2 H, m), 2.70 (1 H, quintet, *J* 7 Hz), 3.63 (2 H, m), and 3.73 (3 H, s); 4-chloro-2-methylbutanoate, δ($CDCl_3$) 1.20 (3 H, d, *J* 7 Hz), 1,60—2.5 (2 H, m), 2.70 (1 H, m), 3.55 (2 H, t, *J* 7 Hz), and 3.63 (3 H, s).

Chlorination of 2-methylbutanoyl chloride and fluoride

Phase solvent	Temp. (°C)	CH_3-	CH_2	CH(COCl)	CH_3
Gas	53	1	1.7 ± 0.4 2.0 ± 0.1	1.3 ± 0.2	0.22 ± 0.04
Gas	75	1	1.7 ± 0.4 2.3 ± 0.2	1.8 ± 0.1	0.26 ± 0.03
Gas	100	1	1.6 ± 0.2 2.2 ± 0.2	0.7 ± 0.3	0.27 ± 0.04
Gas	125	1	1.5 ± 0.1 1.9 ± 0.1	1.6 ± 0.1	0.24 ± 0.02
Neat liquid	25	1	0.89 ± 0.03 1.1 ± 0.04	0.69 ± 0.04	0.18 ± 0.01
CCl_4 (1 : 1)	25	1	0.90 ± 0.03 1.2 ± 0.06	0.74 ± 0.02	0.18 ± 0.01
C_6H_6 (1 : 1)	25	1	1.4 ± 0.10 1.7 ± 0.11	1.8 ± 0.20	0.26 ± 0.04
CS_2 (1 : 1)	25	1	1.7 ± 0.18 2.1 ± 0.22	1.7 ± 0.07	0.17 ± 0.04
				CH(COF)	
Gas	31	1	1.7 ± 0.3 2.1 ± 0.2	1.2 ± 0.3	0.19 ± 0.01
Gas	52	1	1.9 ± 0.2 2.6 ± 0.3	1.6 ± 0.4	0.25 ± 0.07
Gas	76	1	2.1 ± 0.1 2.7 ± 0.4	2.0 ± 0.3	0.21 ± 0.08
Gas	116	1	1.9 ± 0.2 2.3 ± 0.2	2.0 ± 0.3	0.27 ± 0.02
Neat liquid	25	1	0.96 ± 0.2 1.2 ± 0.1	0.62 ± 0.03	0.24 ± 0.02
CCl_4 (1 : 1)	25	1	0.95 ± 0.01 1.11 ± 0.04	0.74 ± 0.05	0.21 ± 0.02
C_6H_6 (1 : 1)	25	1	1.4 ± 0.01 1.6 ± 0.10	1.7 ± 0.1	0.21 ± 0.02
CS_2 (1 : 1)	25	1	1.8 ± 0.1 2.3 ± 0.1	1.8 ± 0.2	0.16 ± 0.05

Reactivity per hydrogen, relative to position 4

(g) *Bromination of 2-Methylbutanoyl Chloride and 2-Methylbutanoyl Fluoride.*—Only one major product ester (see above) was isolated from the bromination of 2-methylbutanoyl chloride. This was collected from several g.l.c. runs and identified as methyl 2-methylbutanoate by examination of its n.m.r. spectrum. The main product from the bromination of 2-methylbutanoyl fluoride had the same retention time on g.l.c. analysis and was assumed to be methyl 2-methylbutanoate.

(h) *Chlorination of 2-Phenylbutane.*—2-Phenylbutane was commercial material which was used without further purification. There were six peaks in the g.l.c. of the chlorinated product including the starting material which was eluted first. The next two peaks were olefins followed by two peaks attributable to both 2-chloro-3-phenylbutane and a final peak containing a mixture of 1-chloro-2-phenyl- and 1-chloro-3-phenyl-butane. 2-Phenylbut-1-ene had δ($CDCl_3$) 1.12 (3 H, t, *J* 7 Hz), 2.52 (2 H, q, *J* 7 Hz), 5.09 (1 H, m), 5.32 (1 H, m), and 7.2—7.5 (5 H, m); 2-phenylbut-2-ene,

δ($CDCl_3$) 1.78 (3 H, d, *J* 7 Hz), 2.05 (3 H, s), 3.8 (1 H, q, *J* 7 Hz), and 7.2—7.5 (5 H, m); *erythro*-2-chloro-3-phenylbutane, δ($CDCl_3$) 1.33 (3 H, d, *J* 7 Hz), 1.40 (3 H, d, *J* 7 Hz), 2.85 (1 H, quintet, *J* 7 Hz), 4.10 (1 H, quintet, *J* 7 Hz), and 7.1—7.4 (5 H, m); and *threo*-2-chloro-3-phenylbutane, δ($CDCl_3$) 1.38 (3 H, d, *J* 7 Hz), 1.43 (3 H, d, *J* 7 Hz), 3.10 (1 H, quintet, *J* 7 Hz), 4.28 (1 H, quintet, *J* 7 Hz), and 7.1—7.4 (5 H, m). 1-Chloro-2-phenyl- (1, 2-) and 1-chloro-3-phenylbutane (1, 3-) gave a mixture: peaks attributable to (1, 2-isomer, δ($CDCl_3$) 0.81 (3 H, t, *J* 7 Hz), 2.6 (2 H, quartet, *J* 7 Hz), 2.7—3.2 (1 H, m), 3.68 (2 H, d, *J* 7 Hz), and 7.0—7.5 (5 H, m); (1,3-isomer), δ($CDCl_3$) 1.28 (3 H, d, *J* 7 Hz), 2.02 (2 H, m), 3.40 (2 H, dt, *J* 7 Hz, 3 Hz), and 7.0—7.5 (5 H, m).

Chlorination of 2-phenylbutane

Phase solvent	Temp. (°C)	CH_3——CH_2——$C(C_6H_5)H$*——CH_3			
Gas	110	1	1.3 ± 0.1 1.7 ± 0.1	2.7 ± 0.2	0.76 ± 0.04
Gas	142	1	1.3 ± 0.1 1.8 ± 0.2	1.5 ± 0.1	0.82 ± 0.1
Gas	200	1	1.1 ± 0.1 2.7 ± 0.1	1.7 ± 0.1	0.65 ± 0.02
'Neat'	25	1	1.8 ± 0.1 2.4 ± 0.1	14.6 ± 1.6	0.55 ± 0.01
CCl_4 (1 : 1)	25	1	1.9 ± 0.2 2.6 ± 0.3	15.8 ± 1.4	0.55 ± 0.01

* No 2-chloro-2-phenylbutane was isolated in either the gas or liquid phases. The relative selectivity is calculated assuming all the olefins were formed from $CH_3(C_6H_5)\dot{C}CH_2CH_3$.

(i) *Bromination of 2-Phenylbutane.*—The bromination of 2-phenylbutane (1 part bromine : 25 parts phenylbutane) at 120° in the gas phase yielded only the two olefins obtained in the chlorination reactions. No bromo-derivatives were identified.

(j) *Chlorination of the Esters of Butan-2-ol.*—In the chlorination of 2-acetoxybutane seven product peaks were observed in the gas chromatogram. The first peak eluted was butanone followed by unchanged starting material. A small shoulder peak was 2-chloroacetoxybutane, identified by comparing its retention time with that of an authentic specimen. The remaining peaks were collected by preparative g.l.c. and identified by their ^1H n.m.r. These were in order of their elution. 2-Acetoxybutane, δ($CDCl_3$) 0.9 (3 H, t, *J* 7 Hz), 1.17 (3 H, d, *J* 7 Hz), 1.3—1.7 (2 H, m), 2.0 (3 H, s), and 4.72 (1 H, sextet, *J* 7 Hz); acetic acid; 1-chlorobutan-2-one, δ($CDCl_3$) 1.20 (3 H, t, *J* 7 Hz), 2.80 (2 H, quartet, *J* 7 Hz), and 5.80 (2 H, s); *erythro*-2-acetoxy-3-chlorobutane, δ($CDCl_3$) 1.26 (3 H, d, *J* 7 Hz), 1.48 (3 H, d, *J* 7 Hz), 2.08 (3 H, s), 4.10 (1 H, m), and 4.99 (1 H, m); and *threo*-2-acetoxy-3-chlorobutane, δ($CDCl_3$) 1.23 (3 H, d, *J* 7 Hz), 1.44 (3 H, d, *J* 7 Hz), 2.03 (3 H, s), 4.08 (1 H, m), and 5.03 (1 H, m). The next two products were eluted together but since the chloroacetate was only present in *ca.* 4% it could be distinguished from the major component 2-acetoxy-1-chlorobutane: 2-chloroacetoxybutane, δ($CDCl_3$) 1.07 (3 H, t, *J* 7 Hz), 1.25 (3 H, d, *J* 7 Hz), 1.55 (2 H, m), 4.05 (2 H, s), and 4.92 (1 H, sextet, *J* 7 Hz); 2-acetoxy-1-chlorobutane, δ($CDCl_3$) 0.09 (3 H, t, *J* 7 Hz), 1.5—2.0 (2 H, m), 2,07 (3 H, s), 3.6 (2 H, d, *J* 7 Hz), and 4.97 (1 H, quartet, *J* 7 Hz); and 2-acetoxy-4-chlorobutane, δ($CDCl_3$) 1.25 (3 H, d, *J* 7 Hz), 2.01 (3 H, s), 1.8—2.2 (2 H, m), 3.52 (2 H, t, *J* 7 Hz), and 5.01 (1 H, sextet, *J* 7 Hz).

In the chlorination of 2-trifluoroacetoxybutane, six products were separated by g.l.c. and their structures deduced from their n.m.r. spectra; the first peak eluted was the unchanged substrate, δ($CDCl_3$) 0.95 (3 H, t, *J* 7 Hz), 1.35 (3 H, d, *J* 7 Hz), 1.70 (2 H, quartet, *J* 7 Hz), and 5.07 (1 H, sextet, *J* 7 Hz), followed by the monochloro-products; 2-chloro-2-trifluoroacetoxybutane, δ($CDCl_3$) 1.10 (3 H, t, *J* 7 Hz), 2.03 (3 H, s), and 2.30 (2 H, quartet, *J* 7 Hz); *erythro*-3-chloro-2-trifluoroacetoxybutane, δ($CDCl_3$) 1.45 (3 H, d, *J* 7 Hz), 1.55 (3 H, d, *J* 7 Hz), 4.15 (1 H, m), and 5.20 (1 H, m); *threo*-3-chloro-2-trifluoroacetoxybutane, δ($CDCl_3$) 1.40 (3 H, d, *J* 7 Hz), 1.53 (3 H, d, *J* 7 Hz), 4.12 (1 H, m), and 5.22 (1 H, m); 1-chloro-2-trifluoroacetoxybutane, δ($CDCl_3$) 1.02 (3 H, t, *J* 7 Hz), 1.78 (2 H, m), 3.8 (2 H, d, *J* 7 Hz), and 5.2 (1 H, m); 4-chloro-1-trifluoroacetoxybutane, δ($CDCl_3$) 1.4 (3 H, d, *J* 7 Hz), 2.15 (2 H, m), 3.55 (2 H, t, *J* 7 Hz), and 5.35 (1 H, m).

Chlorination of esters of butan-2-ol

Phase solvent	Temp. (°C)	CH_3——CH_2——$CH(OCOCH_3)$*——CH_3			
Gas	90	1	1.4 ± 0.1 1.4 ± 0.1	22.1 ± 1	(0.01) 0.34 ± 0.15
Neat liquid	25	1	0.93 ± 0.11 0.95 ± 0.13	2.5 ± 0.5	(0.008) 0.20 ± 0.02

* Calculated from the 2,2 isomer plus the yields of CH_3CO_2H, $CH_3CH_2COCH_3$, and $CH_3CH_2COCH_2Cl$.

		CH_3——CH_2——$CH(OCOCF_3)$*——CH_3			
Gas	54	1	2.1 ± 0.1 2.4 ± 0.1	1.3 ± 0.1	0.16 ± 0.03
Gas	105	1	1.5 ± 0.1 1.9 ± 0.3	1.1 ± 0.4	0.14 ± 0.04
Gas	153	1	1.4 ± 0.1 1.7 ± 0.1	1.0 ± 0.1	0.15 ± 0.01
Gas	202	1	1.5 ± 0.1 1.7 ± 0.1	0.89 ± 0.12	0.20 ± 0.02
Gas	250	1	1.2 ± 0.1 1.3 ± 0.2	0.21 ± 0.10	0.25 ± 0.02
Neat liquid	25	1	0.80 ± 0.06 0.83 ± 0.04	0.32 ± 0.05	0.09 ± 0.01
CCl_4 (1 : 1)	25	1	0.83 ± 0.08 0.85 ± 0.07	0.21 ± 0.07	0.08 ± 0.04

*Attack at the 2-position was accompanied by some fragmentation and in the high temperature runs in the gas phase, acetic acid, butan-2-one, and 1-chlorobutanone were detected amongst the products.

(k) *Bromination of 2-Trifluoroacetoxybutane.*—There were three major product peaks and three small peaks in the gas chromatogram. The three large peaks were identified by their n.m.r.; 2-bromo-2-trifluoroacetoxybutane, δ($CDCl_3$) 1.12 (3 H, t, *J* 7 Hz), 2.15 (3 H, s), and 2.35 (2 H, quartet, *J* 7 Hz); *erythro*-3-bromo-2-trifluoroacetoxybutane, δ($CDCl_3$) 1.5 (3 H, d, *J* 7 Hz), 4.25 (1 H, m), and 5.3 (1 H, m); and *threo*-3-bromo-2-trifluoroacetoxybutane, δ($CDCl_3$) 1.45 (3 H, d, *J* 7 Hz), 1.65 (3 H, d, *J* 7 Hz), 4.15 (1 H, m), and 5.15 (1 H, m). These were the predominant peaks but quantitative estimation was not practical.

Discussion

A substituent in a terminal position of a straight chain alkane is usually regarded as having a maximum effect on free radical transfer reactions at the carbon atom to which it is attached. The influence of the substituent is then assumed to die away rapidly down the carbon chain. In gas-phase radical transfer reactions the substituent effect is usually insignificant after

Table 1. Chlorination of 1- and 2-substituted butanes in the gas phase

X	$\overset{\alpha}{CH_2X}$—$\overset{\beta}{CH_2}$—$\overset{\gamma}{CH_2}$—$\overset{\delta}{CH_3}$				Temp. (°C)	$\overset{\beta'}{CH_3}$—$\overset{\alpha}{CHX}$—$\overset{\beta}{CH_2}$—$\overset{\gamma}{CH_3}$				Temp. (°C)
H	1	3.9	3.9	1	35	1	3.9	3.9	1	35
F	0.9	1.7	3.7	1	78	<0.1	4.6	2.9	1	75
Cl *	0.8	2.1	3.7	1	78	0.2	3.7	3.6	1	75
Br	0.4		3.6	1	78	0.2	2.9	3.2	1	62
CN	0.2	1.7	3.9	1	90	0.2	2.6	3.6	1	100
CF_3	0.04	1.2	4.4	1	75	0.4	0.8	2.3	1	50
COF	0.08	1.6	4.2	1	65	0.2	1.2	3.9	1	31
COCl	0.2	2.1	4.0	1	55	0.2	1.3	3.7	1	53
NO_2	0.00		3.9	1	75	0.04	0.2	1.4	1	30

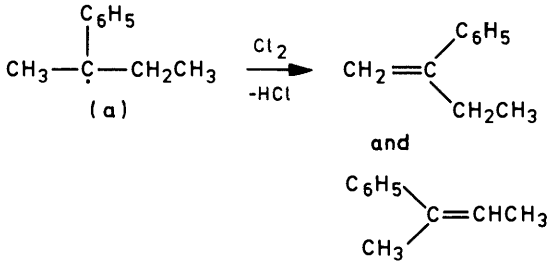
* From ref. 4, *cf.* slightly different values on p. 3.

Table 2. The chlorination of 2-substituted butanes in different solvents (25 °C)

X	$\overset{\beta'}{CH_3}$—$\overset{\alpha}{CHX}$—$\overset{\beta}{CH_2}$—$\overset{\gamma}{CH_3}$				
H	1	3.0	3.0	1	CCl_4
	1	5.1	5.1	1	C_6H_6
	1	9.3	9.3	1	CS_2
Cl	0.3	2.3	2.7	1	Neat liquid
	0.3	2.3	2.5	1	CCl_4 (1 : 1)
	0.4	4.0	2.8	1	C_6H_6 (1 : 1)
	0.3	4.8	4.1	1	CS_2 (1 : 1)
Br	0.5	3.0	3.6	1	Neat liquid
	0.4	2.5	3.3	1	CCl_4 (1 : 1)
	0.3	4.5	3.5	1	C_6H_6 (1 : 1)
	0.2	5.6	4.7	1	CS_2 (2 : 1)
CN	0.3	2.9	2.1	1	Neat liquid
	0.2	1.4	2.3	1	CCl_4 (1 : 1)
	0.5	3.0	3.7	1	C_6H_6 (1 : 1)
	0.5	3.0	4.7	1	CS_2 (1 : 1)
COCl	0.2	0.7	2.0	1	Neat liquid
	0.2	0.7	2.1	1	CCl_4 (1 : 1)
	0.3	1.8	3.1	1	C_6H_6 (1 : 1)
	0.2	1.7	3.8	1	CS_2 (1 : 1)
COF	0.2	0.6	2.2	1	Neat liquid
	0.2	0.7	2.1	1	CCl_4 (1 : 1)
	0.2	1.7	3.0	1	C_6H_6 (1 : 1)
	0.2	1.8	4.1	1	CS_2 (1 : 1)
CF_3	0.05	0.4	1.7	1	Neat liquid
	0.06	0.4	2.5	1	C_6H_6 (1 : 1)
	0.08	0.6	2.6	1	CS_2 (1 : 1)
NO_2	0.06	0.1	1.3	1	Neat liquid
	0.06	0.1	1.4	1	CCl_4 (1 : 1)
	0.08	0.7	1.3	1	C_6H_6 (1 : 1)
	0.07	0.5	2.0	1	CS_2 (1 : 1)

the β-position. Superficially these conclusions appear to be confirmed by the data in Table 1 for the chlorination of the 1-substituted butanes. However the data for the chlorination of the 2-substituted butanes show no such simplicity. The α (or 2) position is not greatly deactivated; indeed in 2-chloro- and 2-fluoro-butane it is the most reactive site. The β (or 3) position is hardly deactivated at all, while the β′ (or 1) position is deactivated appreciably by all substituents. The substituted sites (α positions) in both series of compounds follow the same trend, but the rate of attack is much the fastest at the α-position of the 2-substituted butanes.

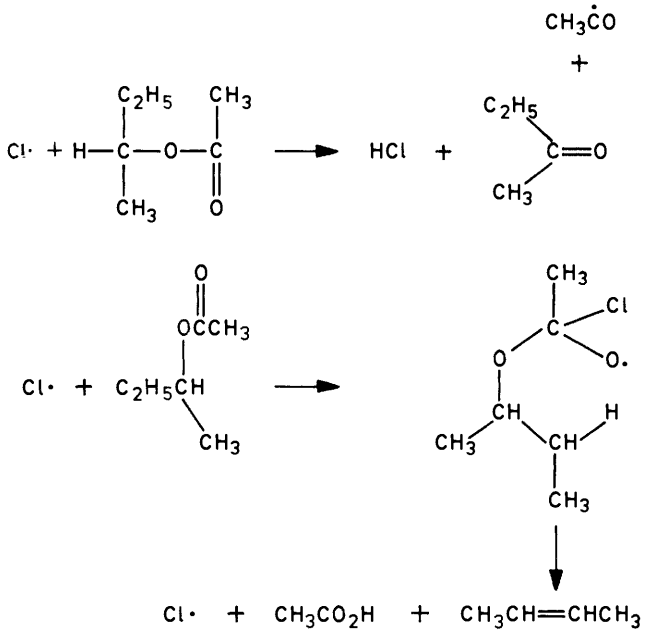
Rüchardt was the first to argue cogently that release of steric compression played an important part in determining the ease of formation of free radicals.[9] In general, release of steric compression will be most important in endothermic reactions which have late transition states, and we shall see below that in bromination it completely dominates all other directive effects. Table 1 shows however that even in exothermic chlorination reactions release of steric compression can overcome polar effects; the substituted α (2) position in the 2-substituted butanes is only appreciably deactivated when the substituent is both bulky and powerfully electron attracting (*e.g.* CF_3 and NO_2). The substituted α (1) position in the 1-substituted butanes is not greatly compressed and polar effects predominate. A significant feature of Table 1 is that the halogens show a regular progression (F < Cl < Br) in their influence on the site to which they are attached for both 1- and 2-halogeno-butanes. It seems likely that this is due to a quite different type of steric effect, namely classical 'steric hindrance'. The very bulky substituent bromine atom makes it difficult for the approaching chlorine atom to reach the hydrogens on the same carbon atom. The alternative explanation, namely the ability of the substituent halogen to 'hyperconjugate' with the new radical centre ($\dot{X}$–$\dot{C}$HR ↔ $\overset{+}{X}$=$\dot{C}$HR) seems unlikely. Such an interaction requires a 'late' transition state and the recent evidence is that this type of interaction is only of minor importance.



Scheme 1.

The bromination results are unequivocal: attack always occurs predominantly at the substituted α-position in the 2-substituted butanes. The bromination of the 2-halogeno, the 2-cyano, and even the 2-acyl fluoride yielded almost exclusively the 2,2-disubstituted product, *i.e.* the course of endothermic bromination is predominantly governed by the release of steric compression. The earlier studies of the bromination of 1-substituted butanes show the attack is not exclusively (or even predominantly) at the substituted position because hydrogen abstraction from a primary position results in much less release of steric compression.

Table 2 shows the effect of solvents on the chlorination of 2-substituted butanes. The important feature of Table 2 is that the concentration of 'solvent' was usually the same as the concentration of the 2-substituted butane, so that any effect implied a molecular interaction (not just a general medium effect). Just as with 1-substituted butanes we can distinguish between carbon tetrachloride, an unselective



Scheme 2.

solvent in which the product ratios are very similar to the ratio of the product of reactions performed in the ' neat ' liquid, and the solvents like benzene and carbon disulphide in which the chlorine atom is solvated. Solvation of the halogen atom has the effect of increasing the importance of bond strength (in particular steric compression), but reducing slightly the relative importance of polarity. This is exactly what we observe when benzene or carbon disulphide are the ' complexing ' solvents.

The experimental results for the chlorination and bromination of 2-phenylbutane and the esters of butan-2-ol show that some of the radicals formed initially were decomposing before they could react with molecular chlorine. Attack at the 2-position in 2-phenylbutane yields the resonance stabilised benzyl radical (a) which will react with molecular chlorine to give a conjugated olefin rather than the chloro-compound (Scheme 1).

The radicals formed by hydrogen abstraction from the esters of butan-2-ol clearly undergo a number of unimolecular transformations. The formation of acetic acid, butan-2-one, and 1-chlorobutan-2-one from the chlorination of 2-acetoxybutane indicates how complicated the reaction can be. Possible fragmentation pathways are indicated in Scheme 2. Re-examination of our earlier work shows that almost certainly the bromination of the esters of butan-1-ol was accompanied by decomposition. Even the data for chlorination suggests that some fragmentation of the initial radicals occurred.

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