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FREE RADICAL SUBSTITUTION IN ALIPHATIC COMPOUNDS. PART 36. THE CHLORINATION OF 1,1,1-TRIFLUORO-2-METHYLBUTANE

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SUMMARY

1,1,1-Trifluoro-2-methylbutane has been chlorinated in the gas and solvent phases. The trifluoromethyl group is known to exert a powerful electron attracting influence but chlorination of the 2-position is not particularly retarded. In order to explain the observed reactivity it is necessary to invoke steric effects, and in particular the release of steric compression associated with the abstraction of the hydrogen atom from the 2-position.

INTRODUCTION

The chlorination of alkanes containing trifluoromethyl groups was first investigated by Henne *et al.* [2]. Chlorination at sites adjacent to CF_3 and CF_2 groups was observed to be much retarded. The results were interpreted in terms of a powerful electron attracting effect of the CF_3-group. Later in the present series we described a study of the chlorination of 1,1,1-trifluoropentane and we reported that hydrogen abstraction from the 2-position was very restricted [3]. We followed Henne and attributed the low reactivity of the 2-position in terms of polarity, *i.e.* the electron attracting trifluoromethyl group resisting the formation of polar hydrogen chloride. At the time of our study of the chlorination of trifluoropentane we attributed the difference in reactivity between primary, secondary and tertiary sites to hydrogen abstraction in terms of hyperconjugation in the incipient radical [4]. More recent work has indicated that the contribution hyperconjugation makes is very small and a much more important factor is the release of steric compression associated with the abstraction of a hydrogen atom from a crowded position (*e.g.* a tertiary position) [5, 6].

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EXPERIMENTAL

1,1,1-Trifluoro-2-methylbutane: (Kindly supplied by I.C.I. Limited, Mond Division.)

The compound was carefully purified by preparative g.l.c. The purity was checked by examination of its n.m.r. spectrum. δ (ppm) 0.9 (t, 3H, J = 7 Hz); 1.15 (d, 3H, J = 7 Hz); 1.25 - 1.55 (complex, 2H); 1.6 - 2.25 (complex, 1H).

Procedure

The gas phase results were performed using a conventional vacuum line and the solution phase in the flasks described in previous papers [7]. The products were separated by g.l.c. and their identity as isomers $C_5H_8F_3Cl$ was confirmed by coupled g.l.c. m.s. The identity of the isomers was assumed by comparison with all the previous examples of the chlorination of 2-substituted butanes [1].

TABLE I

The Chlorination of 1,1,1-Trifluoro-2-methylbutane in Gas and Solvent Phase RS_4^x

Phase	T °C	CH_3 —	$\overset{CF_3}{CH}$ —	CH_2^* —	CH_3	No. of Runs
Gas Phase	55°	0.043±0.01	0.77±0.03	1.4 ±0.1 0.92±0.03	1.00	4
	105°	0.041±0.02	0.71±0.04	1.3 ±0.01 0.90±0.02	1.00	5
	155°	0.09 ±0.00	0.75±0.03	1.8 ±0.04 1.7 ±0.04	1.00	5
liquid "Neat"	25°	0.052±0.01	0.43±0.01	1.00±0.03 0.73±0.02	1.00	5
C_6H_6 (1:1) Solution	25°	0.063±0.00	0.44±0.01	1.5 ±0.04 0.94±0.04	1.00	5
CS_2 (1:1) Solution	25°	0.078±0.01	0.55±0.02	1.5 ±0.01 1.1 ±0.01	1.00	4

* *erythro/threo*

DISCUSSION

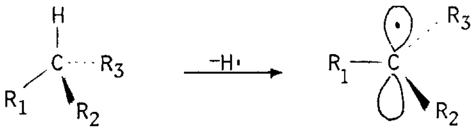
The previous studies have shown that in the gas phase a substituent in the 1-position of a monosubstituted butane has little influence on the rate of hydrogen abstraction from the 3- and 4-positions by chlorine atoms [1, 6]. Table II compares the chlorination of 1,1,1-trifluoropentane with the chlorination of 2-methyl-1,1,1-trifluorobutane in the gas phase and in solution. The table shows that the CF_3- group greatly retards hydrogen abstraction from the 2-position in 1,1,1-trifluoropentane and has a substantial but much less deactivating effect at the 3-position. In the chlorination of 2-methyl-1,1,1-trifluorobutane a very different selectivity was observed. Hydrogen abstraction by chlorine atoms from the 2-position to which the CF_3-group is attached is much faster than from the 2-methyl group. There is no doubt that the powerful electron attracting property of the trifluoromethyl group inhibits hydrogen abstraction by halogen atoms from adjacent sites and is responsible for the low reactivity of the 2-position in 1,1,1-trifluoropentane. The relative ease of hydrogen atom abstraction (from primary<secondary<tertiary alkanes) used to be attributed to hyperconjugation [4]. More recently the importance of steric effects has been appreciated. The formation of a tertiary radical by hydrogen abstraction from a tertiary position is accompanied by release of steric compression [5, 6].

TABLE II

The Relative Selectivities for the Chlorination of 1,1,1-Trifluoropentane [1, 3] and 2-Methyl-1,1,1-trifluorobutane in the Gas and Solvent Phases

	CH_3—	CH_2—	$\overset{\displaystyle CF_3}{\overset{\vert}{CH}}$—	CH_3	CH_3—	CH_2—	CH_2—	CH_2—CF_3
gas (50 and 75 °C)	1	2.3	0.77	0.04	1	4.4	1.2	0.04
liquid "Neat" 25°	1	1.7	0.43	0.05	1	2.6	0.83	0.01
liquid CS_2 (1:1) 25°	1	2.6	0.55	0.08	1	10.3	1.6	0.00
liquid C_6H_6(1:1) 25°*	1	2.5	0.44	0.06	1	4.9	0.99	0.00

*C_6H_5Cl was used in place of C_6H_6 for trifluoropentane



Hydrogen abstraction from the 2-position of 2-methyl-1,1,1-trifluorobutane is accompanied by the release of considerable steric compression and this partially accounts for the high reactivity of attack by chlorine atoms at the 2-position in spite of the unfavourable polar situation. The trifluoromethyl group is the archetype of electron attracting substituent, but its polar effect on reactivity can be modified by the steric situation.

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