588. *The Synthesis and Reactions of Branched-chain Hydrocarbons. Part XVII.** N-*Chlorosulphonamides as Chlorinating Agents*

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The photochlorination of some n- and some iso-alkanes is compared with the peroxide-initiated chlorination by sulphuryl chloride by some *N*-chloro-*N*-alkylsulphonamides, and by trichloromethanesulphonyl chloride. The ratio of reactivity of secondary to primary hydrogens in the n-alkanes is 2·1 for photochlorination, 3·5 for sulphuryl chloride, and 4·3 for *N*-chloro-*N*-t-butylbenzenesulphonamide; a similar value is obtained with *N*-chloro-*N*-n-butyl- and *N*-chloro-*N*-t-butyl-toluene-*p*-sulphonamides; *N*-chloro-*N*-t-butylmethanesulphonamide gives a ratio of 3·0.

The relative reactivity at primary, secondary and tertiary positions in the isoalkanes is modified by steric factors. Chlorination at secondary carbons may also be influenced by polar effects.

In an earlier Paper[1] it was shown that the rate of free-radical chlorination of alkanes and cycloalkanes is influenced by the structure of the hydrocarbon. Further, the ratio of reactivities of primary, secondary and tertiary hydrogens for any one chlorinating agent is not the same for all hydrocarbons.[2] The study of the effect of structure on chlorination is now continued by an examination of the free-radical chlorination of n- and iso-alkanes by some *N*-chloro-*N*-alkylsulphonamides and also by sulphuryl chloride and by chlorine. The ratio of reactivity of secondary to primary hydrogens towards such chlorinating agents is given in Table 1.

Table 1

Relative reactivity of secondary to primary hydrogen towards chlorination

	Chlorinating agent						
	I	II	III	IV	V	VI	VII
n-Heptane		3·7	2·8	4·5	4·2	4·3	*c*
n-Octane	2·0	3·4	2·8	4·3	4·0	3·6	
n-Decane	2·1	3·4	3·4	4·1	4·8	4·1	*c*
n-Dodecane	2·1	3·3	3·2	4·3	5·4	4·1	
n-Hexadecane	2·8	3·5	*a*	4·2	*b*	4·3	
2-Methylheptane	2·2	3·2	2·8	4·3	3·6	3·4	
3,3-Diethylpentane	2·0	2·6	1·4	0·6	1·3	2·4	
Methylcyclohexane	2·0	3·7	4·1	4·4	6·5	4·5	

I: Cl_2 at 20° (light initiated).
II: SO_2Cl_2 at 85°.
III: $MeSO_2\cdot NClBu^t$ at 85°.
IV: $PhSO_2\cdot NClBu^t$ at 85°.
V: p-$Tol\cdot SO_2\cdot NClBu^n$ at 85°.
VI: p-$Tol\cdot SO_2\cdot NClBu^t$ at 85°.
VII: $CCl_3\cdot SO_2Cl$.

(*a*) The results were not consistent, probably due to low solubility of the chlorinating agent. (*b*) No chlorination observed. (*c*) The product in each case was essentially a mixture of secondary chlorides, the proportion of primary chloride being about 2%.

The value of 2·0 to 2·2 for the ratio of the reactivity of secondary to primary hydrogens towards chlorination in the liquid phase at 20° is near to that given by Cerny and Hajeck[3] (2·4 at 20°); Blouri *et al.*[4] give 2·4 at 40°. The value reported by Hass *et al.*[5] (3·7 at 40°) is almost certainly too high by reason of the presence of dichloro-compounds in the product and uncertainties in the method of analysis. The high value of 3·4 reported by Asinger and Geiseler[6] is probably due to difficulties in the analysis of the product.

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* Part XVI, J. R. B. Boocock and W. J. Hickinbottom, *J.*, 1963, 1319.

[1] J. R. B. Boocock and W. J. Hickinbottom, *J.*, 1963, 1234.

[2] A. E. Fuller and W. J. Hickinbottom, *Proc. Chem. Soc.*, 1963, 147.

[3] O. Cerny and J. Hajek, *Coll. Czech. Chem. Comm.*, 1961, **26**, 2624.

[4] B. Blouri, C. Cerceau, and G. Lanchec, *Bull. Soc. chim. France*, 1963, 304.

[5] (*a*) H. B. Hass, E. T. McBee, and P. Weber, *Ind. Eng. Chem.*, 1936, **28**, 333; (*b*) C. Walling, " Free Radicals in Solution," John Wiley and Sons, Inc., New York, 1957, p. 358 *et seq.*

[6] (*a*) G. Geiseler and F. Asinger, *Ber.*, 1957, **90**, 1786; (*b*) F. Asinger, *Ber.*, 1942, **75**, 668.

It has been widely accepted that halogenation by *N*-bromosuccinimide and other *N*-halogeno-amides occurs by halogen abstraction from the *N*-halogeno-amide by an alkyl radical, as represented by the scheme: [7]

$$\mathrm{SNBr + Alk\cdot \longrightarrow AlkBr + SN\cdot} \qquad \text{(i)}$$
$$\mathrm{SN\cdot + AlkH \longrightarrow Alk\cdot + SNH} \qquad \text{(ii)}$$
$$(\mathrm{SN} = \text{succinyl, } \mathrm{RCO{\cdot}NAlk,\ RCO{\cdot}NAr})$$

An alternative view, now current, is that halogenation depends on the formation of a low concentration of halogen derived by the action of halogen hydride on the *N*-halogeno-amide, according to the scheme:

$$\mathrm{Br\cdot + AlkH \longrightarrow HBr + Alk\cdot} \qquad \text{(iii)}$$
$$\mathrm{HBr + SNBr \longrightarrow SNH + Br_2} \qquad \text{(iv)}$$
$$\mathrm{Alk\cdot + Br_2 \longrightarrow AlkBr + Br\cdot} \qquad \text{(v)}$$

Evidence for this view is derived almost entirely from the side-chain halogenation of alkylbenzenes by *N*-chloro- and *N*-bromo-succinimides. Bromine and *N*-bromosuccinimide have the same reactivity towards alkylbenzenes and the isotope effect is almost the same for each of these halogenating agents.[8] These halogenations are all light-induced and have been concerned only with the alkylbenzenes. The application of the hypothesis to alkanes and cycloalkanes is on a less secure experimental basis. Apart from the work reported in the following Paper, the only other experimental evidence is that due to Cerny and Hajeck [3] on the light-initiated chlorination of n-hexane by a series of *N*-chloro-compounds. It is certain that under these conditions chlorine is not an intermediate in most of the chlorinations, since substitution occurs at secondary hydrogens without any substitution of the primary hydrogens.

The results given in Table 1 show that the peroxide-induced chlorination of the n-alkanes by *N*-chlorosulphonamides does not depend on the formation of chlorine. The following scheme represents the most probable course of chlorination:

$$\mathrm{RSO_2{\cdot}NClBu + B\cdot \longrightarrow RSO_2{\cdot}\dot{N}Bu + BCl} \qquad \text{(vi)}$$
$$\mathrm{RSO_2{\cdot}\dot{N}Bu + AlkH \longrightarrow RSO_2{\cdot}NHBu + Alk\cdot} \qquad \text{(vii)}$$
$$\mathrm{Alk\cdot + R{\cdot}SO_2{\cdot}NClBu \longrightarrow AlkCl + RSO_2{\cdot}\dot{N}Bu} \qquad \text{(viii)}$$
$$(\mathrm{B\cdot = Ph\cdot \text{ or } PhCO_2\cdot})$$

Further it is evident from Table 1 that chlorination by sulphuryl chloride does not depend on hydrogen abstraction by Cl· as represented by the scheme: [8c, 9]

$$\mathrm{AlkH + Cl\cdot \longrightarrow Alk\cdot + HCl} \qquad \text{(ix)}$$
$$\mathrm{Alk\cdot + SO_2Cl_2 \longrightarrow AlkCl + \cdot SO_2Cl} \qquad \text{(x)}$$
$$\mathrm{\cdot SO_2Cl \longrightarrow SO_2 + Cl\cdot} \qquad \text{(xi)}$$

The most probable course is:

$$\mathrm{AlkH + \cdot SO_2Cl \longrightarrow Alk\cdot + HCl + SO_2} \qquad \text{(xii)}$$
$$\mathrm{Alk\cdot + SO_2Cl_2 \longrightarrow AlkCl + \cdot SO_2Cl} \qquad \text{(xiii)}$$

Blouri [4] reported that the photochlorination of n-heptane in the liquid phase gives more 2-chloroheptane than the 3-chloro-compound. The effect is more pronounced with bromination.[4] The peroxide-initiated chlorination of n-heptane by trichloromethanesulphonyl chloride is also selective in that more 2-chloroheptane is formed than either the 3- or 4-chloro-compounds; the amount of 1-chloroheptane in the product is almost negligible.[10]

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[7] G. F. Bloomfield, *J.*, 1944, 114.

[8] (*a*) G. A. Russell, C. DeBoer, and K. M. Desmond, *J. Amer. Chem. Soc.*, 1963, **85**, 365; (*b*) R. E. Pearson and J. C. Martin, *ibid.*, p. 1963, **85**, 354; (*c*) K. B. Wiberg and L. H. Slaugh, *ibid.*, 1958, **80**, 3033; (*d*) F. L. J. Sixma and R. H. Reim, *Verhandel. k. ned. Akad. Wetenschap.*, Afd. Natuurk., 1958, **61**, *B*, 183; (*e*) B. P. McGrath and J. M. Tedder, *Proc. Chem. Soc.*, 1961, 80.

[9] G. A. Russell and H. C. Brown, *J. Amer. Chem. Soc.*, 1955, **77**, 4031.

[10] B. Fell and L. H. Kung, *Angew. Chem.* (*International Edn.*), 1963, **2**, 99.

In this work, the separation of the products from the n-alkanes was not sufficient to permit an accurate assessment of the abundance of each chloro-compound in any one product. In the chlorination of n-decane, however, using *N*-chloro-*N*-t-butylsulphonamides considerably more 2- and 3-chlorodecanes were formed than the 4- and 5-chlorodecanes. No such difference was observed for photochlorination or for peroxide-initiated chlorination by sulphuryl chloride.

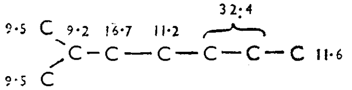

FIGURE 1. Percentage distribution of monochloro-compounds in the product from the photochlorination of 2-methylheptane

In the chlorination of 2-methylheptane and of 2,3,4-trimethylpentane the abundance of each chloro-compound in the product could be assessed accurately. The percentages of monochloro-compounds in the product of the photochlorination of 2-methylheptane are given in Figure 1, it being assumed that the two methyl groups of the isopropyl group are equally reactive. The values for other chlorinating agents are given in Table 2. There are some unexpected features about these results. The terminal 7-methyl group is more reactive than those of the isopropyl group, and this holds for all the chlorinations examined. The low reactivity at C-4 is noteworthy when comparison is made with reactivity at other secondary positions.

TABLE 2

Chlorination of 2-methylheptane

Chlorinating agent *	% Distribution of chloro-2-methylheptane					
	1-	2-	3-	4-	5- & 6-	7-
I	19·1	9·2	16·7	11·2	32·4	11·6
II	14·0	13·0	18·9	11·6	34·1	8·5
III	14·4	11·5	14·1	10·5	38·8	10·8
IV	8·6	8·8	6·4	10·6	55·4	10·2
V	11·9	20·0	14·3	10·7	35·6	7·1
VI	13·0	11·5	12·7	11·0	43·0	9·1

* See Table 1.

Selective halogenation also occurs in the photochlorination of 2,3,4-trimethylpentane (see Figure 2). The three tertiary hydrogens do not have the same reactivity, although Russell and Brown [9] have reported to the contrary. Further, one of the methyl groups is less reactive than the other four; this applies to all chlorinations except that by trichloromethanesulphonyl chloride (see Table 3).

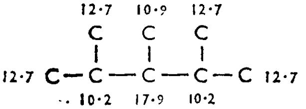

FIGURE 2. Percentage distribution of monochloro-compounds in the product from the photochlorination of 2,3,4-trimethylpentane

TABLE 3

Chlorination of 2,3,4,-trimethylpentane

Chlorinating agent *	% Monochloro-2,3,4-trimethylpentanes			
	1-	2-	3-	3'-
I	50·8	20·4	17·9	10·9
II	40·2	24·0	26·1	9·7
III	52·6	19·1	19·2	9·1
IV	63·5	14·8	13·4	8·3
V	45·5	21·1	24·4	9·0
VI	50·7	19·4	20·4	9·5
VII	4·9	71·3	23·8	—

* See Table 1.

TABLE 4

Chlorination of methylcyclohexane

Chlorinating agent *	% Monochloromethylcyclohexanes			
	1-	2-	3- & 4-	1'-
I	7·7	15·8	64·6	11·9
II	15·1	18·3	60·2	6·4
III	6·8	13·9	73·0	6·3
IV	3·9	14·2	75·8	6·1
V	18·9	12·1	65·4	3·6
VI	6·7	15·2	72·4	5·8
VII	50·9	7·5	41·6	—

* See Table 1.

With methylcyclohexane, although complete separation was not obtained, there was a clear difference in reactivity between the 2- and the 3-, 4-, and 5-positions (see Table 4).

Selectivity in chlorination of the methyl groups of 3-methylheptane and of 3,4-dimethylhexane was also observed. Table 5 compares the reactivities of two differently situated methyl groups in these hydrocarbons toward chlorination. For comparison, 2-methylheptane and 2,3,4-trimethylpentane are included to give other examples of selectivity in chlorination.

A simple explanation of some of these observations is based on steric effects. Thus in 3,3-diethylpentane (Tables 1 and 6) the ratio of reactivity of secondary to primary in photochlorination is the same as in the n-alkanes, but with other bulkier chlorinating agents the ratio falls much below the value obtained with n-alkanes. It is also clear from an inspection of models of 3,3-diethylpentane that the secondary hydrogens are shielded from attack by a bulky reagent. The relatively low reactivity of the primary hydrogens of an isopropyl group is probably due to the same cause.

The high reactivity of position 3 in 2,3,4-trimethylpentane is less easy to account for on purely steric grounds, and suggests that other factors are involved. The combined inductive effects of two adjacent isopropyl groups is a likely explanation, which could also account for the enhanced reactivity of the 2-position in the n-alkanes toward relatively inactive halogenating agents (as in the bromination of n-heptane or its chlorination by trichloromethanesulphonyl chloride).

TABLE 5

Relative reactivities of methyl groups towards chlorination

		Chlorinating agent *					
Positions		I	II	III	IV	V	VI
2-Methylheptane	7 : 1	1·2	1·2	1·5	1·1	1·4	1·2
	3 : 4	1·5	1·6	1·3	0·6	1·2	1·3
3-Methylheptane	3' : 1	0·8	0·85	0·6	0·4	0·75	0·6
3,4-Dimethylhexane	3' : 1	0·8	0·8	0·6	0·4	0·75	0·6
2,3,4-Trimethylhexane	3' : 1	0·85	1·0	0·7	0·5	0·8	0·75
	3 : 2	1·75	2·2	2·2	1·8	2·1	2·3

* See Table 1.

TABLE 6

Chlorination of 3,3-diethylpentane

Chlorinating agent *		I	II	III	IV	V	VI
% Chlorination at position	1-	42·7	36·6	57·4	71·7	53·3	38·7
	2-	57·3	63·4	49·0	28·3	46·7	61·3

* See Table 1.

EXPERIMENTAL

Free-radical Chlorination of Alkanes by N-*Chloroamides*.—The *N*-chloroamide (*ca.* 0·08 mole) and benzoyl peroxide (*ca.* 0·004 mole) in the hydrocarbon (50 c.c.) were kept at 85° and stirred till there was no positive test for active chlorine. The mixture was then cooled and diluted with light petroleum (b. p. $<40°$). The precipitated amide was washed with light petroleum. The combined filtrate and washings were freed from solvent and distilled. No attempt was made to obtain the maximum yield.

(*a*) *n-Heptane.* A mixture of monochloroheptanes (48%), b. p. 44—47°/15 mm., n_D^{20} 1·4238—1·4244 (Found: C, 62·8; H, 11·4; Cl, 26·0. Calc. for $C_7H_{15}Cl$: C, 62·5; H, 11·1; Cl, 26·3%) was obtained using *N*-chloro-*N*-methylmethanesulphonamide.

Similar products were obtained using *N*-chloroacetamide, *N*-chloro-*N*-t-butylmethanesulphonamide, *N*-chloro-*N*-butyltoluene-*p*-sulphonamide, *N*-chloro-*N*-t-butyltoluene-*p*-sulphonamide and *N*-chloro-*N*-t-butylbenzenesulphonamide as chlorinating agents. The purity of each product was established by its physical constants and by analyses for C, H, and Cl.

(*b*) *n-Decane.* Chlorination by *N*-chloro-*N*-t-butyltoluene-*p*-sulphonamide gave a mixture of monochlorodecanes, b. p. 94—95°/11 mm., n_D^{20} 1·4365—1·4369 (Found: C, 68·0; H, 11·9; Cl, 20·1. Calc. for $C_{10}H_{21}Cl$: C, 68·0; H, 11·9; Cl, 20·1%).

N-Chloro-*N*-t-butylmethanesulphonamide and *N*-chloro-*N*-butyltoluene-*p*-sulphonamide also gave a mixture of monochlorodecanes.

(*c*) *Cyclohexane.* Reaction with *N*-chloroacetamide gave chlorocyclohexane (51%), b. p. 34—35°/13 mm., n_D^{20} 1·4616 (Found: C, 60·8; H, 9·7; Cl, 29·4. Calc. for $C_6H_{11}Cl$: C, 60·7; H, 9·3; Cl, 29·9%). Its identity was established by reaction of the Grignard reagent, derived from it, with α-naphthyl isocyanate, to give the α-naphthalide of cyclohexanecarboxylic acid, m. p. and mixed m. p. 188—190°.

In all these chlorinations the pure amide was isolated in 85—90% yield as the other product of the reaction, except when *N*-chloro-*N*-butyltoluene-*p*-sulphonamide was used; this gave an oily product, probably because of concurrent self-chlorination.

Analysis of the Products of Chlorination.—A Pye Argon unit with an ionisation detector was used for vapour-phase chromatography. The column packings were: A, 10% Reoplex-110 on Celite (60—80 mesh); B, 15% Apiezon-L on Celite (110—120 mesh); C, 10% polyethylene glycol adipate.

The product of the peak height and retention time was used as a measure of the proportion of a component in the mixture, after it had been established that the standard deviation σ of Bartlett and Smith [11] is proportional to the retention time. The results were checked against those from cutting and weighing [12] and also from triangulation.[13]

Some of the hydrocarbons were gifts from British Petroleum Co. Ltd. Before use they were distilled in nitrogen from sodium through a 10-cm. column packed with Fenske helices. Hydrocarbons purchased from Eastman Kodak were passed through a column of silica gel and then distilled in nitrogen from sodium through a 30-cm. column packed with Dixon gauzes. All the hydrocarbons were examined by vapour-phase chromatography; each gave only one peak except n-octane and 2-methylheptane. These two contained less than 2% of impurities, which could not be removed.

Not all the *N*-chloroamides listed above were suitable for quantitative studies of chlorination. Complete solubility of the *N*-chloroamide in the hydrocarbon is necessary if reproducible results are to be obtained. Thus *N*-chloroacetamide (which is only sparingly soluble in alkanes) gave consecutive results which varied by as much as 50%. *N*-Chloro-*N*-methyltoluene-*p*-sulphonamide and *N*-chloro-*N*-methylmethane sulphonamide were not used for a similar reason. *N*-Chloro-*N*-s-butyltoluene-*p*-sulphonamide decomposes slowly at 0° and as its purification is unsatisfactory it was not used. *N*-Chloro-*N*-butyltoluene-*p*-sulphonamide also decomposes slowly at 0° but it can be purified easily and it gave reproducible results.

The chlorinating agents used are listed in Table 1.

For benzoyl-peroxide initiated chlorinations, the following procedure was adopted. The hydrocarbon was deoxygenated by boiling it under reflux while a stream of nitrogen was passed through it; it was cooled in an atmosphere of nitrogen. A standard solution of benzoyl peroxide ($3{\cdot}6 \times 10^{-4}$ mole) in the hydrocarbon (12 c.c.) was divided into six equal parts, and each was added by a micro-funnel to 3×10^{-3} mole of the chlorinating agent in a Pyrex tube which was warmed till a homogeneous solution was obtained. The tubes were then flushed

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[11] J. C. Bartlet and D. M. Smith, *Canad. J. Chem.*, 1960, **38**, 2057.

[12] A. I. M. Keulemans, " Gas Chromatography," Reinhold, New York, 1957, p. 32.

[13] G. Dijkstra, J. G. Keppler, and J. A. Schols, *Rec. Trav. chim.*, 1955, **74**, 805.

with argon, sealed, covered with tin foil, and kept at 85° ± 0·1° for 2 hr. The contents were then examined by gas–liquid chromatography.

Chlorination by trichloromethanesulphonyl chloride was also carried out by this method except that the concentration of benzoyl peroxide was increased to 5 moles % on the chlorinating agent.

For photochlorination, nitrogen was passed through the hydrocarbon at 25° ± 0·1° in a 50 c.c. two-necked flask, then chlorine (0·5 g.) was introduced in a stream of nitrogen. These operations were carried out in weak light. Reaction was started by a short exposure to weak ultra-violet light and was complete, in general, in 2—3 min.; the product was examined directly.

		Chlorinating agent						
		I	II	III	IV	V	VI	VII
n-Heptane	Primary		13·9	17·5	11·8	12·6	12·2	2·5
	Secondary		86·1	82·5	88·2	87·4	87·8	97·5
n-Octane	Primary	20·1	13·0	15·0	10·5	11·2	12·2	
	Secondary	79·9	87·0	85·0	89·5	88·8	87·8	
n-Decane	Primary	15·1	9·9	9·8	8·4	7·2	8·4	1·5
	Secondary	84·9	90·1	90·2	91·6	92·8	91·6	98·5
n-Dodecane	Primary	12·8	8·3	8·4	6·5	5·3	7·0	
	Secondary	87·2	91·7	91·6	93·5	94·7	93·0	
n-Hexadecane	Primary	7·1	5·7		4·8		4·7	
	Secondary	92·9	94·3		95·2		95·3	

The results for n-alkanes are given below as percentages of primary and secondary chlorides in the product. The Roman numerals refer to the reagent used (see Table 1). The same results are expressed in a different way in Table 1.

N-*Chloro*-N-*alkylsulphonamides*.—Acetic acid (55 c.c.) was added dropwise (1 hr.) to a stirred suspension of the sulphonamide (0·53 mole), dissolved in chloroform (100 c.c.), in sodium hypochlorite (200 c.c., 10% available chlorine). After being stirred for a further hour the chloroform solution was separated, washed with water, dried ($MgSO_4$), and evaporated.

		Found (%)				
	M. p.	C	H	Cl	Active Cl	Note
N-Chloro-*N*-methylmethanesulphonamide ...	32°	16·3	4·1	25·2	24·5	*a*
N-Chloro-*N*-t-butylmethanesulphonamide ...	3	32·1	7·0	19·6	18·8	*b*
N-Chloro-*N*-t-butylbenzenesulphonamide......	58	48·5	5·8	14·6	14·1	*c*
N-Chloro-*N*-methyltoluene-*p*-sulphonamide ...	79					*d*
N-Chloro-*N*-butyltoluene-*p*-sulphonamide ...	44	50·2	6·1	13·1	13·4	*e*
N-Chloro-*N*-s-butyltoluene-*p*-sulphonamide ...	32—36	50·8	6·0	14·6	15·4	*e*
N-Chloro-*N*-t-butyltoluene-*p*-sulphonamide ...	88	50·0	6·4	14·1	13·4	*e*

(*a*) $C_2H_6{\cdot}ClNO_2S$ requires C, 17·1; H, 4·2; Cl, 24·7%. (*b*) $C_5H_{12}ClNO_2S$ requires C, 32·1; H, 7·0; Cl, 19·1%. (*c*) $C_{10}H_{14}ClNO_2S$ requires C, 48·5; H, 5·7; Cl, 14·3%. (*d*) Murakama and Nashima[14] give m. p. 80°. (*e*) $C_{11}H_{16}ClNO_2S$ requires C, 50·5; H, 6·1; Cl, 13·6%.

The sulphonamides required for the preparation of the *N*-chloro-compounds were obtained by reaction of the appropriate amine with the sulphonyl chloride in chloroform and pyridine. N-*t-Butylmethanesulphonamide*, had b. p. 72—76°/0·15 mm., m. p. 44—45° (Found: C, 39·9; H, 8·3; N, 9·3. $C_5H_{13}NO_2S$ requires C, 39·9; H, 8·6; N, 9·3%); *N*-t-*butylbenzenesulphonamide*, m. p. 79—80° (Found: C, 56·0; H, 6·9; N, 6·3. $C_{10}H_{15}NO_2S$ requires C, 56·3; H, 7·0; N, 6·6%); *N*-butyltoluene-*p*-sulphonamide, m. p. 43° (lit.,[15] m. p. 43°); *N*-s-butyltoluene-*p*-sulphonamide b. p. 144°/0·1 mm., m. p. 58° (lit.,[16] m. p. 61·5—62·5°); and *N*-t-butyltoluene-*p*-sulphonamide, m. p. 114° (lit.,[16] m. p. 115—115·5°).

Chloro-hydrocarbons.—The 1-chloro-derivatives of hexane, heptane, octane, decane, dodecane, and hexadecane were pure commercial samples. The s-chloro-derivatives of hexane, heptane, octane, and decane were prepared from the corresponding alcohols by reaction with thionyl chloride in dimethylaniline. Their constants agreed with those in the literature and their

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[14] M. Murakami and T. Nashima, *Chem. Abs.*, 1955, **49**, 6864.
[15] L. Demény, *Rec. Trav. chim.*, 1931, **50**, 51.
[16] W. D. Emmons and J. P. Freeman, *J. Amer. Chem. Soc.*, 1955, **77**, 6061.

purity was confirmed by vapour-phase chromatography. The compounds listed below were prepared similarly and appear to be new.

	B. p./mm.	n_D^{20}	Found (%) C	H	Cl	Note
2-*Chlorododecane*	56°/0·1	1·4404	70·3	12·2	17·3	*a*
3-*Chlorododecane*	51—53/0·05	1·4413	70·4	12·2	16·7	*a*
4-*Chlorododecane*	52—53/0·05	1·4407	70·6	12·2	17·3	*a*
5-*Chlorododecane*	51—52/0·05	1·4406	70·7	12·3	17·2	*a*
4-*Chlorohexadecane* *	90—95/0·1	1·4504	73·9	12·8	13·0	*b*
1-*Chloro-2-methylheptane*	51—52/11	1·4299	64·6	11·3	23·7	*c*
4-*Chloro-2-methylheptane*	43—44/13	1·4248	64·9	11·7	23·8	*c*
5-*Chloro-2-methylheptane*	46—47/13	1·4265	64·8	11·7	23·8	*c*
6-*Chloro-2-methylheptane*	45—46/11	1·4248	64·7	11·6	23·7	*c*
7-*Chloro-2-methylheptane*	61—62/17	1·4285	64·5	11·5	23·6	*c*
1-*Chloro-3-methylheptane*	61/17	1·4311	64·7	11·5	23·7	*c*
5-*Chloro-3-methylheptane*	54—56/17	1·4290	64·7	11·5	23·6	*c*
6-*Chloro-3-methylheptane*	45/11	1·4282	64·6	11·4	23·9	*c*
7-*Chloro-3-methylheptane*	53/10	1·4314	64·5	11·5	23·6	*c*
3-(*Chloromethyl*)*heptane*	62/16	1·4321	64·8	11·7	23·3	*c*
1-*Chloro-3,4-dimethylhexane*	53/12	1·4368	64·8	11·4	23·9	*c*
3-*Chloro-3,4-dimethylhexane*	44—45/13	1·4390	64·9	11·6	23·8	*c*
3-(*Chloromethyl*)-3-*methylhexane*	49—50/13	1·4377	64·9	11·4	23·8	*c*
3-(*Chloromethyl*)-2,4-*dimethylpentane*	51—52/15	1·4388	64·6	11·4	24·0	*c*

(*a*) $C_{12}H_{25}Cl$ requires C, 70·4; H, 12·3; Cl, 17·3%. (*b*) $C_{16}H_{33}Cl$ requires C, 73·7; H, 12·8; Cl, 13·6%. (*c*) $C_8H_{17}Cl$ requires C, 64·6; H, 11·5; Cl, 23·9%.

* From vapour-phase chromatography this was only 95% pure; the impurities did not correspond with any of the other chlorohexadecanes.

Attempts to prepare 3-chloro-2-methylheptane from the alcohol, thionyl chloride, and dimethylaniline gave a product consisting of 2-chloro-2-methylheptane (75%), and other s-chloro-2-methylheptanes. Similarly, an attempted preparation from the toluene-*p*-sulphonate of 2-methylheptan-2-ol and lithium chloride in alcohol gave a mixture of which 58% was 2-chloro-2-methylheptane and 38% s-chloro-2-methylheptanes.

Reaction of 2,3,4-trimethylpentan-2-ol with concentrated hydrochloric acid gave a mixture of 2-chloro-2,3,4-trimethylpentane (83%) with 11% of the 3-chloro-compound and some unidentified material (5%). Similarly 2,3,4-trimethylpentan-3-ol with hydrochloric acid gave the corresponding 3-chloro-compound with 40% of the isomeric 2-chloro-compound.

1-*Chloro*-2,3,4-*trimethylpentane*, had b. p. 54—56°/16 mm., n_D^{20} 1·4396 (Found: C, 64·8; H, 11·6; Cl, 23·7. $C_8H_{17}Cl$ requires C, 64·7; H, 11·5; Cl, 23·9%); 1-*chloro*-3-*methylcyclohexane*, b. p. 39·5—40°/13 mm., n_D^{20} 1·4588 (Found: C, 63·5; H, 9·8; Cl, 27·1. $C_7H_{13}Cl$ requires C, 63·4; H, 9·9; Cl, 26·8%); 1-*chloro*-4-*methylcyclohexane*, b. p. 39—40°/12 mm., n_D^{20} 1·4592 (Found: C, 63·4; H, 9·8; Cl, 26·8%); cyclohexylmethyl chloride, b. p. 45·5—46°/13 mm., n_D^{20} 1·4638 (Found: C, 63·7; H, 10·1; Cl, 26·7%).

Treatment of 2-methylcyclohexanol with thionyl chloride and dimethylaniline gave a poor yield of methylcyclohexyl chlorides containing 40% of 1-chloro-1-methylcyclohexane.

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