589. *The Synthesis and Reactions of Branched-chain Hydrocarbons. Part XVIII.* Chlorination of 2,2,4-Trimethylpentane*

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Chlorination of 2,2,4-trimethylpentane in an excess of hydrocarbon by some *N*-alkyl-*N*-chlorosulphonamides and by sulphuryl chloride initiated by benzoyl peroxide is compared with that brought about by chlorine activated by a weak source of ultraviolet light. With the exception of sulphuryl chloride, the product has the same composition whatever chlorinating agent is used. Furthermore, the reactivity of the tertiary hydrogen is unexpectedly low, being less than that of the secondary hydrogens.

The possible causes of these effects are discussed. It is concluded that the chlorination by *N*-chlorosulphonamides occurs mainly through the formation of chlorine.

The low reactivity of the tertiary position can be satisfactorily explained if it is assumed that only a fraction of 2,2,4-trimethylpentane has a conformation permitting free access of the chlorinating agent at the tertiary position and that interconversion of the possible conformations is hindered.

The substitution reactions of 2,2,4-trimethylpentane are reported to be anomalous when compared with other alkanes. Thus Chambers and Ubbelohde,[1] studying the chlorination of hydrocarbons in the vapour phase, observed that the reaction rate of 2,2,4-trimethylpentane was less than that expected by comparison with other alkanes. More recently Boocock and Hickinbottom,[2] in a study of the peroxide-induced chlorination of hydrocarbons by *N*,2,4,6-tetrachloroacetanilide, established that 2,2,4-trimethylpentane and some similarly substituted alkanes undergo substitution at a notably slow rate. With t-butoxy-radicals [3] the rate of reaction is also less than that calculated from other alkanes. Similar effects are reported for autoxidation [4] and for oxidation by chromic acid.[5]

Brook [3] and also Wibaut and Strang [4] interpret their results as due to a masking of the reactive tertiary hydrogen by the adjacent t-butyl group. Such an explanation is supported by the relatively low reactivity of similarly constituted hydrocarbons, such as 2,2,4,4,6-pentamethylheptane.[2]

It was the purpose of the work now described to test this hypothesis by a comparison of the behaviour of 2,2,4-trimethylpentane towards a range of chlorinating agents of different effective bulk. The relative proportions of substitution at primary, secondary and tertiary positions were determined for photochlorination and for peroxide-induced chlorinations by sulphuryl chloride and by *N*-alkyl-*N*-chlorosulphonamides of the general formula $RSO_2{\cdot}NCl{\cdot}Alk$ (R = Me, Ph, or *p*-Tol; Alk = Bu^n or Bu^t).

Experimental

2,2,4-Trimethylpentane,[6] b. p. 99·0°, n_D^{20} 1·3913, was distilled and passed through a column of activated silica. It was stored in full bottles in the dark. Immediately before use it was distilled from sodium in an atmosphere of nitrogen.

Chlorination.—2,2,4-Trimethylpentane (250 c.c.) mixed with sulphuryl chloride (45 g.) and benzoyl peroxide (1·6 g.) was kept at 85—90° under nitrogen. After 3 hr. it was treated with water and sodium hydrogen carbonate, then dried and distilled. A mixture of monochlorotrimethylpentanes (28 g.) was collected at 42—50°/15 mm., n_D^{20} 1·4288 (Found: C, 64·9;

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* Part XVII, preceding Paper.

[1] G. Chambers and A. R. Ubbelohde, *J.*, 1955, 285.

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

[3] J. H. T. Brook, *Trans. Faraday Soc.*, 1957, **53**, 327.

[4] J. P. Wibaut and A. Strang, *Verhandel. k. ned. Akad. Wetenschap., Afd. Natuurk.*, 1951, **54**, *B*, 229.

[5] G. Foster and W. J. Hickinbottom, *J.*, 1960, 680.

[6] A. L. J. Beckwith, *J.*, 1962, 2248.

H, 11·6; Cl, 23·6. Calc. for $C_8H_{17}Cl$: C, 64·7; H, 11·5; Cl, 23·9%). A residue (1 g.) remained undistilled, and even if this were all dichloro-compounds they would form less than 4% of the total product.

All the four monochlorotrimethylpentanes were shown to be present by converting the distillate into the Grignard derivative, followed by aerial oxidation of this to the corresponding mixture of alcohols, which were identified by their individual peaks and retention times on the gas–liquid chromatograms after comparison with those of authentic materials.

Chlorination by *N*-chloro-*N*-t-butyl benzenesulphonamide, initiated by benzoyl peroxide, or by chlorine, initiated by exposure to a weak source of ultraviolet light, gave similar results. In no chlorination did the undistilled residue amount to more than 3% of the product.

Analysis of the Chlorination Products.—The procedure was that described in the previous Paper, the products being analysed directly by vapour-phase chromatography on column A at 50° and column B at 75°. column A gave individual peaks for 4-chloro- and 3-chloro-2,2,4-trimethylpentanes and a third peak for a mixture of the primary chlorides. Column B gave separate peaks for the 1- and 4-chloro-compounds and a peak for a mixture of the 3- and 5-chloro-compounds. By combining the results from both chromatograms, regular and consistent values were obtained. The Table summarises the results in tems of substitution at the primary, secondary and tertiary positions and the ratios of reactivity at these positions.

	Monochloro-compound, %			Ratio of reactivity		
Chlorinating agent	primary	secondary	tertiary	primary	secondary	tertiary
Cl_2	62	27·5	10·5	1	3·3	2·5
SO_2Cl_2	58	31·5	10·5	1	4·1	2·7
$MeSO_2$·$NClBu^t$	65	25	10	1	2·9	2·3
$PhSO_2$·$NClBu^t$	64	27	9	1	3·2	2·2
p-Tol·SO_2·$NClBu^t$	62	28	10	1	3·4	2·4
p-Tol·SO_2·$NClBu^n$	63	28	9	1	3·3	2·1

Chlorination by trichloromethanesulphonyl chloride (using benzoyl peroxide) gave a poor yield of product containing 63% of monochlorotrimethylpentanes; the composition of the latter was 22% primary, 11% secondary, and 66% tertiary.

*Preparation of Chloro-*2,2,4-*trimethylpentanes.*—2,2,4-Trimethylpentan-1-ol,[7] b. p. 63—64°/10 mm., n_D^{20} 1·4300 (lit.,[7] b. p. 166—166·5, n_D^{20} 1·4300) on reaction with chlorotrimethylsilane in benzene–quinoline [8] gave *trimethyl*(2,2,4-*trimethylpentyloxy*)*silane*, b. p. 64—66°/14 mm., n_D^{20} 1·4114 (Found: C, 65·3; H, 12·8. $C_{11}H_{26}OSi$ requires C, 65·3; H, 12·9%). This (0·068 mole) reacted violently with thionyl chloride (0·1 mole) in the presence of quinoline hydrochloride; [8] the mixture was then boiled for 20 hr. to give a poor yield (1 g.) of 1-chloro-2,2,4-trimethylpentane, b. p. 47—48°/14 mm., n_D^{20} 1·4285 (*ca.* 90% pure) (Found: C, 65·4; H, 11·6; Cl, 20·2. Calc. for $C_8H_{17}Cl$: C, 64·7; H, 11·5; Cl, 23·9%). In the gas–liquid chromatogram the major peak was distinct from that of either 4- or 5-chloro-2,2,4-trimethylpentanes: it corresponded to one of the peaks in the chlorination product of 2,2,4-trimethylpentane. The identity of the compound was established by converting it into 2,2,4-trimethylpentan-1-ol through the Grignard reagent.

The main product from the above reaction with thionyl chloride was the corresponding *dialkyl sulphite*, a yellow oil, b. p. 102°/0·1 mm., n_D^{20} 1·4463 (Found: C, 63·1; H, 11·4; S, 10·0. $C_{16}H_{34}O_3S$ requires C, 62·8; H, 11·1; S, 10·5%).

Attempts to prepare 3-chloro-2,2,4-trimethylpentane were unsuccessful. Reaction of the corresponding alcohol with thionyl chloride in *NN*-dimethylaniline gave 4-chloro-2,2,4-trimethylpentane. From trimethyl(2-methyl-1-t-butylpropoxy)silane and thionyl chloride, a mixture of four chlorides was obtained, none being the one required. Reaction of the alcohol with triphenyl phosphite and benzyl chloride, treatment of its methanesulphonate with lithium chloride, and attempted preparation through the ethyl ether were also unsuccessful.

4-Chloro-2,2,4-trimethylpentane, b. p. 45—46°/17 mm., n_D^{20} 1·4304 (lit., b. p. 44°/16 mm., n_D^{20} 1·4307) was made from di-isobutene and hydrogen chloride, and 5-*chloro*-2,2,4-*trimethylpentane*, b. p. 48—49°/17 mm., n_D^{20} 1·4295 (Found: C, 64·7; H, 11·2; Cl, 24·2%) from the corresponding alcohol by reaction with thionyl chloride and dimethylaniline in chloroform.

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[7] K. C. Brannock, *J. Amer. Chem. Soc.*, 1959, **81**, 3379.

[8] L. H. Sommer, H. D. Blankman, and P. C. Miller, *J. Amer. Chem. Soc.*, 1954, **76**, 803.

DISCUSSION

A striking feature of the results summarised in the Table is that the ratio of the reactivities of primary, secondary and tertiary hydrogens is approximately the same for all chlorinating agents except sulphuryl chloride. This suggests that the course of chlorination of 2,2,4-trimethylpentane by *N*-chlorosulphonamides is not the same as with the n-alkanes, where the reactivity of the primary and secondary hydrogens differs markedly from those for photochlorination. The most likely explanation is that the active chlorinating agent is the same whether chlorine or *N*-chlorosulphonamides are used, and that it is the chlorine atom. This might arise from *N*-chlorosulphonamides by initial homolytic dissociation of the *N*-chlorosulphonamide according to the following scheme:

$$RSO_2{\cdot}NClBu^t \longrightarrow RSO_2{\cdot}\dot{N}Bu^t + Cl{\cdot} \qquad (i)$$

$$Cl{\cdot} + AlkH \longrightarrow Alk{\cdot} + HCl \qquad (ii)$$

This is unlikely: if homolytic dissociation had any serious part in the reaction it would have been noticed in the chlorination of the n-alkanes, where, under the same conditions, *N*-chlorosulphonamides give a ratio of reactivity of primary to secondary which is distinct and different from that from photochlorination.

Alternatively, the *N*-chlorosulphonamide might react with hydrogen chloride as represented by the scheme:

$$HCl + RSO_2{\cdot}NClBu^t \longrightarrow RSO_2{\cdot}NHBu^t + Cl_2 \qquad (iii)$$

$$Cl_2 + Alk{\cdot} \longrightarrow AlkCl + Cl{\cdot} \qquad (iv)$$

$$Cl{\cdot} + AlkH \longrightarrow Alk{\cdot} + HCl \qquad (v)$$

This is similar to that suggested by Adam *et al.*,[9] and subsequently adopted to represent the course of halogenation of alkylbenzenes by *N*-chloro- and *N*-bromo-succinimides. The hydrogen chloride needed is not formed directly from *N*-chlorosulphonamides since it is not present in the reaction with n-alkanes. Its formation is so far peculiar to 2,2,4-trimethylpentane. The most likely explanation is that it arises from 4-chloro-2,2,4-trimethylpentane, which is formed in the preliminary phase of the chlorination by the normal free-radical process; elimination of hydrogen chloride with the formation of di-isobutene seems a more likely source than hydrolysis by traces of water.

It is commonly accepted that the order of reactivity of hydrogen in the alkanes is tertiary > secondary > primary.[10] This holds for thermal and photochlorination, for free-radical chlorinations by sulphuryl chloride and *N*-chloroamides, for bromination, and for oxidation. It is remarkable therefore that in 2,2,4-trimethylpentane this order is changed to: primary < tertiary < secondary, with mean values of 1 : 2·3 : 3·3. Sulphuryl chloride gives the same order but with different values, 1 : 2·7 : 4·1.

It is not sufficient to ascribe these results to the removal of 4-chloro-2,2,4-trimethylpentane from the reaction product by hydrolysis; the amount of water required to bring about such an effect makes such an explanation improbable. The elimination of hydrogen chloride from the tertiary chloride probably occurs but the amount needed is small and is not sufficient to alter the ratio of primary to tertiary so drastically. Indeed if the elimination of hydrogen chloride occurred to any extent, it would have been detected in the products.

An explanation based on the shielding of the tertiary hydrogen from free access of the chlorinating agent is in itself not sufficient. Account must also be taken of the enhanced reactivity of the secondary positions with respect to the primary, 3·3 : 1 compared with 2·1 : 1 in the n-alkanes. An inspection of molecular models shows that two conformations

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[9] J. Adam, P. A. Gosselain, and P. Goldfinger, *Nature*, 1953, **171**, 704; *Bull. Soc. chim. belges*, 1956, **65**, 523.

[10] (*a*) K. B. Wiberg and L. H. Slaugh, *J. Amer. Chem. Soc.*, 1958, **80**, 3033; (*b*) G. A. Russell, C. DeBoer, and K. A. Desmond, *ibid.*, 1963, **85**, 365; (*c*) R. E. Pearson and J. C. Martin, 1963, **85**, 354; (*d*) J. M. Tedder, *Quart. Rev.*, 1960, **14**, 339; (*e*) G. A. Russell and H. C. Brown, *J. Amer. Chem. Soc.*, 1955, **77**, 4031.

are the most stable and that interconversion is restricted by the bulk of the t-butyl group. Only one of these conformations permits free access to the tertiary hydrogen and it is from this form that 4-chloro-2,2,4-trimethylpentane is derived. The two secondary hydrogens are open to attack in either conformation while the primary hydrogens of the t-butyl group are partially shielded by mutual interference.

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