703. *Vapour-phase Photochemical Chlorination and Bromination of 2,2,4,4-Tetramethylpentane.*

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2,2,4,4-Tetramethylpentane has been chlorinated and brominated in illuminated reactions at 135°. 1-Halogeno- and 3-halogeno-2,2,4,4-tetramethylpentane were found and there was no evidence for rearrangement of the carbon skeleton. Hydrolysis, with 80% aqueous ethyl alcohol, was used for the analysis of products, and this reaction was greatly accelerated by the addition of silver nitrate.

THE direct bromination of 2,2,4,4-tetramethylpentane was studied by Kharasch, Liu, and Nudenberg,[1] who reported that only a rearranged product, 2-bromo-2,3,4,4-tetramethylpentane, had been found. The free-radical mechanism postulated involves the migration of a methyl radical at an intermediate stage, and the evidence for this has been questioned by Walling,[2] who suspects a polar rearrangement of the expected, unrearranged, 3-bromo-2,2,4,4-tetramethylpentane. Liquid-phase chlorination of the hydrocarbon has been investigated by Davies,[3] who found only the expected substitution products, *viz.*, 1-chloro- and 3-chloro-2,2,4,4-tetramethylpentane.

Analyses of the products by Kharasch *et al.* and by Davies were markedly different. The former employed (*a*) hydrolysis with 75% aqueous ethyl alcohol and an excess of silver nitrate, (*b*) acetolysis in the presence of silver nitrate, and (*c*) reaction with silver 3,5-dinitrobenzoate to give 2,3,4,4-tetramethylpent-1-ene. Davies employed a kinetically controlled hydrolysis with 80% aqueous ethyl alcohol. The methods used by Kharasch *et al.* do not rule out the possibility that the bromo-compound formed during the reaction was the expected substitution product which subsequently underwent a silver-ion catalysed, carbonium-ion rearrangement.

I have re-investigated the bromination of the hydrocarbon in the vapour-phase, with illumination by mercury arcs, and also studied the chlorination under similar conditions. In both cases, the expected, unrearranged, substitution products were formed, *i.e.*, primary and secondary halides. The isomeric halides could not be separated by careful fractional distillation, and analysis was performed by a study of the kinetically-controlled hydrolysis with 80% aqueous ethyl alcohol. The structure of each component was deduced from the first-order rate coefficients. The structure, *i.e.*, primary, secondary, or tertiary, of an unknown alkyl halide can be deduced from this rate coefficient by comparison with that of a known compound, *e.g.*, t-butyl halide or isopropyl halide, under the same conditions.

With chlorination, no reaction took place at 25° during the first 47 hours and it was concluded that no tertiary, *i.e.*, rearranged, chloro-compound was present. At 100·4° a steady reaction took place during the first 100 hours but after this time the rate decreased considerably. First-order rate coefficients for these two reactions were $7{\cdot}68 \times 10^{-6}$ sec.$^{-1}$ and $1{\cdot}91 \times 10^{-8}$ sec.$^{-1}$. These values are in agreement with those obtained for the hydrolysis of the material from the liquid-phase chlorination of the hydrocarbon.[3] From the hydrolysis data it was calculated that 20% of the product was the secondary chloride, as would be expected from Hass, McBee, and Weber's " Rules for Chlorination." [4]

With the monobrominated product, hydrolyses were carried out at 25·0° and 73·05°. At 25° no reaction took place during the first five hours and it was concluded that no tertiary, *i.e.*, rearranged, bromo-compound was present. At 73·05° a steady reaction took place during the first 25 hours but after this time the reaction rate decreased considerably. First-order rate coefficients for these two reactions were $2{\cdot}93 \times 10^{-5}$ sec.$^{-1}$, and $3{\cdot}36 \times 10^{-8}$

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[1] Kharasch, Liu, and Nudenberg, *J. Org. Chem.*, 1954, **19**, 1150; 1955, **20**, 680.

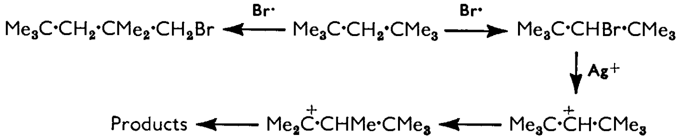
[2] Walling, " Free Radicals in Solution," John Wiley and Sons, Inc., New York, 1957, p. 373.

[3] Davies, Ph.D. Thesis, University of Wales, 1950.

[4] Hass, McBee, and Weber, *Ind. Eng. Chem.*, 1935, **27**, 1190; 1936, **28**, 333.

sec.$^{-1}$. Calculation showed that 82% of the product was secondary bromide. A hydrolysis carried out at room temperature, 21°, in the presence of an excess of silver nitrate proceeded rapidly, whereas in the absence of silver nitrate there was no reaction.

This indicates that when the unrearranged substitution products react in the presence of silver ions a carbonium-ion reaction takes place, leading to rearrangement. The over-all reaction may be represented as follows:—



$$\begin{tikzcd} Me_3C{\cdot}CH_2{\cdot}CMe_2{\cdot}CH_2Br & Me_3C{\cdot}CH_2{\cdot}CMe_3 \arrow[l, "Br^{\cdot}"'] \arrow[r, "Br^{\cdot}"] & Me_3C{\cdot}CHBr{\cdot}CMe_3 \arrow[d, "Ag^+"] \\ \text{Products} & Me_2\overset{+}{C}{\cdot}CHMe{\cdot}CMe_3 \arrow[l] & Me_3C{\cdot}\overset{+}{C}H{\cdot}CMe_3 \arrow[l] \end{tikzcd}$$

The relative proportions of secondary halide produced during the reaction, *i.e.*, 20% and 82% respectively for chlorination and bromination, were of the order expected after taking into consideration the variation of activation energies for halogen attack on primary and secondary C–H bonds. In the case of chlorination the activation energy for attack on a secondary C–H bond is approximately 650 cal. mole^{-1} lower than for the primary bond, whilst for bromination this decrease is greater and hence bromination is more specific. Halogenation of n-butane and isobutane in the gas phase has been studied by Anson, Fredricks, and Tedder [5] and the above values for the secondary halides agree with their " Relative Selection " values of chlorine and bromine for primary and secondary hydrogen atoms.

EXPERIMENTAL

The apparatus and technique for chlorination have been described previously.[6] For bromination, a vaporizer for the bromine, similar to that used for the hydrocarbon, replaced the apparatus used for drying and metering the chlorine. All experiments were carried out at atmospheric pressure.

Materials.—Chlorine was the middle fraction from a commercial cylinder and was dried before use. " AnalaR " bromine was used without further treatment.

2,2,4,4-*Tetramethylpentane.* Howard's method [7] was employed for the preparation of this hydrocarbon, b. p. 122·2—122·7°/752—768 mm., n_D^{25} 1·4450 (Found: C, 84·3; H, 16·0. Calc. for C_9H_{20}: C, 84·3; H, 15·7%), yield 44%.

Chlorination.—The hydrocarbon (144 ml.) was vaporized during 40 min., the rate of flow of the chlorine was 5·0 litres per hr. to give a hydrocarbon : chlorine ratio of 5·9, the reaction temperature was 135°, and the contact time about 22 sec. Fractional distillation under reduced pressure yielded unchanged hydrocarbon and 10 g. (yield 45%) of monochlorinated material, b. p. 38·5–39·0°/3·5 mm., n_D^{25} 1·4401. A similar experiment, with 500 ml. of the hydrocarbon, a contact time of about 34 sec. at 135°, and a hydrocarbon : chlorine ratio of 4·1, yielded 55·2 g. (yield 50%) of the monochlorinated material, b. p. 45·9°/5 mm., n_D^{25} 1·4402.

Hydrolyses.—Standard techniques were employed and the hydrogen chloride liberated was estimated by titration with standard sodium ethoxide solution, lacmoid being used as an indicator.

At 25° no reaction took place during the first 47 hr. *Reaction at* 100·4°. 0·7065 g. of the product was made up to 100 ml. with 80% aqueous ethyl alcohol [8] and 5·35 ml. samples were sealed up, immersed in a thermostat, and removed at suitable time intervals, and the hydrogen chloride content was determined:

Time (hr.)	0·0	1·0	3·0	5·0	8·42	21·5	25·0
Titre (ml.)	0·05	0·17	0·40	0·63	0·96	2·11	2·33
Time (hr.)	30·0	51·0	98·0	165·0	343·0	511·0	607·0
Titre (ml.)	2·60	3·38	4·04	4·15	4·34	4·42	4·65

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[5] Anson, Fredricks, and Tedder, *J.*, 1959, 918.

[6] Backhurst, Hughes, and Ingold, *J.*, 1959, 2742.

[7] Howard, *J. Res. Nat. Bur. Stand.*, 1940, **24**, 679.

[8] Grunwald and Winstein, *J. Amer. Chem. Soc.*, 1948, **70**, 852.

A plot of the titre against time showed that two reactions were proceeding, one of which was essentially complete after 100 hr.

Under the reaction conditions the reaction would be of first order, and rate coefficients were calculated accordingly. From the weight of chloride taken and the known concentration of the ethoxide solution, the titre after complete reaction, *i.e.*, infinity titre, was calculated to be 21·94 ml.; from the experimental data the titre of ethoxide solution equivalent to the " fast " (more readily hydrolysed) chloride was calculated to be 4·49 ml.; hence the monochlorinated material contained 20·5% of " fast " chloride. First-order rate coefficients for the " fast " chloride were calculated from the usual rate equation and also by Guggenheim's method.[9] A graphical method was used to calculate the rate coefficient for the " slow " (less readily hydrolysed) chloride.

Bromination.—The hydrocarbon (155 ml.) was vaporized and treated with bromine (29·3 g.) during 80 min.; the reaction temperature was 135°, the contact time 30 sec., and the hydrocarbon : bromine ratio 6·6. Unchanged hydrocarbon was recovered by fractional distillation and a second experiment carried out with 112 ml. of the hydrocarbon and 23·5 g. of bromine, contact time 26 sec., reaction temperature 135°, and hydrocarbon : bromine ratio 6·0. The unchanged hydrocarbon was recovered and the brominated product from both reactions fractionally distilled to yield 31·8 g. (yield 47%) of monobrominated material, b. p. 56·1—56·5°/5 mm., n_D^{25} 1·4692 (Found: C, 51·5; H, 9·1; Br, 39·8. Calc. for $C_9H_{19}Br$: C, 52·2; H, 9·2; Br, 38·6%); the residue from the distillation yielded white crystals which analysed correctly for a dibromide (Found: C, 37·3; H, 6·2; Br, 54·8. Calc. for $C_9H_{18}Br_2$: C, 37·8; H, 6·4; Br, 55·8%). Other experiments gave similar results.

Hydrolyses.—At 25° no reaction occurred during the first 5 hr. *Reaction at* 73·05°. 0·8347 g. of the product was made up to 100 ml. with 80% aqueous ethyl alcohol and 5·35 ml. samples treated as above:

Time (hr.)	0·0	0·5	1·0	1·5	2·5	3·0	4·0	6·0	8·0
Titre (ml.)	0·20	1·02	1·84	2·54	3·88	4·53	5·75	7·79	9·53
Time (hr.)	11·25	22·0	29·0	54·7	94·1	120·0	322·0	989·0	
Titre (ml.)	11·60	15·20	16·30	16·79	16·97	16·99	17·02	17·26	

By a method analogous to that used for the calculation of the composition of the product of chlorination, it was found that the product of bromination contained 82% of secondary bromide. First-order rate coefficients were calculated as before.

Hydrolysis of the Monobrominated Material, at Room Temperature, in the Presence of Silver Nitrate.—The product (0·1161 g.) was dissolved in 80% aqueous ethyl alcohol (50 ml.), and standard silver nitrate solution (10 ml. of 0·0963N) added. After the mixture had been shaken for 30 min. at room temperature (21°), the solid silver bromide was filtered off and washed with dilute nitric acid. The filtrate and washings were titrated with standard ammonium thiocyanate solution (31·11 ml. of 0·0212N were required), by Volhard's method.

It was calculated that 54% of the bromide had reacted, whereas in the absence of silver nitrate no reaction had taken place.

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[9] Guggenheim, *Phil. Mag.*, 1926, **7**, 538.