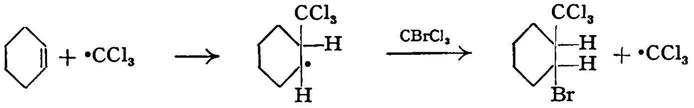
722. *The Reactivity of the α-Methylenic Carbon Atom of* cyclo*Hexene in Peroxide-catalysed Radical Reactions.*

By Shalom Israelashvili and Joseph Shabatay.

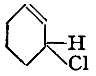
Two opposing mechanisms have been proposed for interaction of olefins with radicals : (*a*) abstraction of hydrogen from the α-methylenic carbon atom, followed by allylic substitution; (*b*) the Kharasch addition of radicals to the double bond. Investigation of the reaction of *cyclo*hexene with carbon tetrachloride, catalysed by benzoyl and acetyl peroxides, shows that both mechanisms operate simultaneously, and that reaction (*b*) occurs only with big radicals, which are excluded from allylic substitution by steric interference.

It has been shown by Farmer and Sundralingam (*J.*, 1942, 121), Farmer and Michael (*ibid.*, p. 513), Hermans and Van Eyk (*J. Polymer Sci.*, 1946, **1**, 407), Criegee (*Ber.*, 1939, **72**, 1799), Hock and Ganicke (*ibid.*, 1938, **71**, 1430), Waters (*Nature*, 1944, **154**, 772), and Ziegler *et al.* (*Annalen*, 1942, **551**, 80) that in *cyclo*hexene there are two possible sites for attack by radicals : the double bond, and the allylic carbon atom. Kharasch and Friedlander (*J. Org. Chem.*, 1949, **14**, 239, 538), however, formulated the addition of halogenated free methyl radicals, *e.g.*, trichloromethyl, to *cyclo*hexene as a chain reaction, thus :

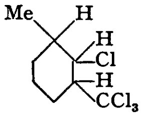


It is not clear why these two types of free-radical reactions should follow different mechanisms, and it seemed desirable to study the reactions of *cyclo*hexene with radicals more thoroughly in order to find reasons for the two alternative courses under different conditions. We now report a study of the reaction between *cyclo*hexene and carbon tetrachloride as catalysed (*a*) by benzoyl peroxide and (*b*) by acetyl peroxide.

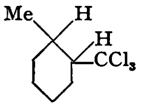
From the complex mixture of products obtained from *cyclo*hexene, carbon tetrachloride, and benzoyl peroxide, an approximately 10% yield of the expected 1 : 1-addition product was isolated. Its structure was proved by conversion through acid hydrolysis into *cyclo*hex-1-ene-1-carboxylic acid. A second product was formulated as $C_{19}H_{24}O_2Cl_2$ in view of its analysis and of the quantitative yield of 1 mol. of benzoic acid on alkaline hydrolysis, but its structure has not yet been conclusively established. From the volatile portion obtained in the fore-run of the distillation, a third product, 3-chloro*cyclo*hex-1-ene (I) was isolated.



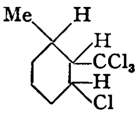
(I)



(II)



(III)

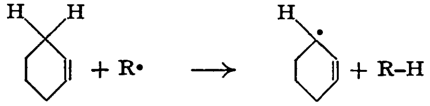


(IV)

From the interaction of *cyclo*hexene, carbon tetrachloride, and acetyl peroxide, a still more complex mixture was obtained. The products not only contained the elements of carbon tetrachloride, but in some of them an additional carbon atom was introduced as a methyl group. The following products have been identified : 3-chloro*cyclo*hex-1-ene (I), 2-chloro-1-methyl-3-trichloromethyl*cyclo*hexane (II), 1-methyl-2-trichloromethyl*cyclo*hexane (III), and 3-chloro-1-methyl-2-trichloromethyl*cyclo*hexane (IV). The chloro*cyclo*hexene (I) was identified by comparison of its properties with the compound obtained by Ziegler (*loc. cit.*) from *cyclo*hexene and *N*-chlorophthalimide, and also by its conversion into 3-acetoxy*cyclo*hex-1-ene. The other compounds (II, III, and IV) were hydrolysed to the corresponding carboxylic acids by 70% sulphuric acid. Compound (III) was thus converted into *trans*-2-methyl*cyclo*hexanecarboxylic acid, and (II) and (IV) into 3-methyl- and 6-methyl-*cyclo*hex-1-ene-1-carboxylic acid, respectively.

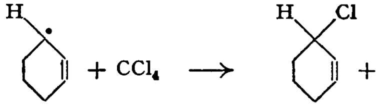
The different results obtained in the two reactions studied may be explained on the basis of the different reactivity of the peroxide catalysts used and the stability of the radicals produced from them. Benzoyl peroxide decomposes slowly, and the small amount of primary phenyl radicals supplied will react preferentially with solvent. Acetyl peroxide is applied in double the concentration and is readily decomposed, so that a relatively high concentration of methyl radicals is formed within a short time. Apart from this difference, the reaction mechanisms are similar. In the benzoyl peroxide-catalysed reaction, the trichloromethyl radical could abstract the hydrogen atom from the α-methylenic carbon atom—analogously to the allylic substitutions mentioned before—and thus produce the *cyclo*hexenyl radical (plus chloroform) (see Kooijman, *Rec. Trav. chim.*, **1950**, **69**, 492):

(1)



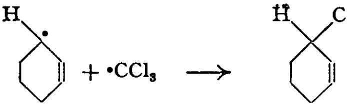
The radical thus obtained may then be stabilised in two ways:

(2)



(radical-transfer reaction)

(3)



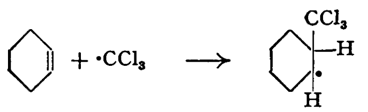
(chain termination)

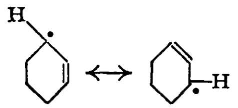
Reaction (3) has never been observed by us to occur with the trichloromethyl radical.

In addition, the simple 1 : 1-adduct corresponding to Kharasch's scheme was obtained, and this reaction may be represented thus:

(4) $$\text{Ph}\cdot + \text{CCl}_4 \longrightarrow \text{C}_6\text{H}_5\text{Cl} + \cdot\text{CCl}_3$$

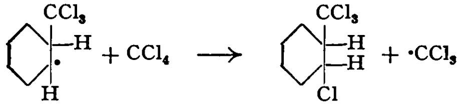
(5)





(*A*)

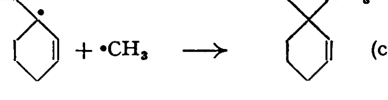
(6)



In the acetyl peroxide-catalysed reaction we may again assume the *cyclo*hexenyl radical to be the first intermediate, owing to the stabilising effect of resonance in the allylic radical, as in (*A*). As formulated above, the *cyclo*hexenyl radical should then give 3-chloro*cyclo*hex-1-ene, which was again isolated.

The *cyclo*hexenyl radical could also react with a methyl radical to give 3-methyl*cyclo*hex-1-ene:

(7)

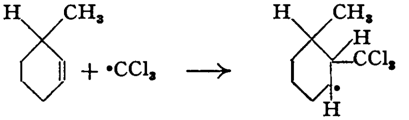


(chain termination)

So far this derivative has not been detected among the reaction products, probably owing to the difficulty of its separation from *cyclo*hexene.

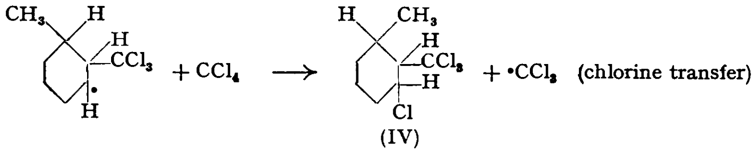
The double bond in 3-methyl*cyclo*hex-1-ene is much more susceptible to the peroxide-catalysed addition reaction of carbon tetrachloride than is the double bond in *cyclo*hexene, so one would expect that 3-methyl*cyclo*hex-1-ene would first add a radical in position 1. However, the yield of (IV) is much larger than that of (II), which shows that the trichloromethyl radical adds abnormally (in view of the mode of radical addition to propylene) mainly in one direction, *viz.*, ortho- to the methyl group :

(8)

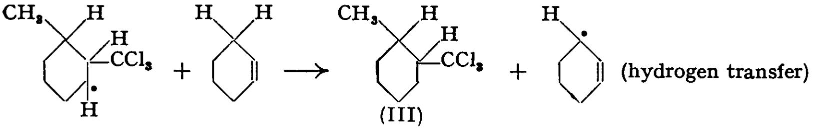


This intermediate radical can either react with carbon tetrachloride to yield (IV) or abstract hydrogen from *cyclo*hexene to give (III) :

(9)



(10)



Although we are still far from a complete picture of the reactions involved, this investigation yields one clear result : both free-radical mechanisms are operative with *cyclo*hexene, *viz.*, allylic substitution and addition to the double bond. However, it is clear that only certain radicals can effect the substitution reaction.

In view of these considerations, the question arises why reaction (5) take place at all. Tentatively, it can be assumed that in the molecule of *cyclo*hexene it is not possible for the trichloromethyl radical to approach the α-methylenic carbon atom closely enough, whereas the much smaller methyl radical can more easily be attached there. On the other hand, the double bond in *cyclo*hexene leaves much more space for the approach of bigger radicals, and therefore the Kharasch mechanism is operative for such groups as trichloromethyl and tribromomethyl. Thus, although the allylic radical is always more stable than the secondary radical produced by addition of a radical to the double bond, steric factors prevent the substitution reactions from occurring with big radicals like trichloromethyl and thus switch the reaction mechanism from substitution to addition.

In *cyclo*hexene both ethylenic carbon atoms are equally substituted. In open-chain olefins like oct-1-ene, carbon atom 1 is much less hindered for the combination with free radicals than carbon atom 2. In addition, the inductive effect of the aliphatic substituent at carbon atom 2 polarises the double bond in such a way that a higher electron density is produced at carbon atom 1; therefore the electron-deficient radical •CCl$_3$ attaches itself to the terminal carbon atom 1 (see Flory and Lautner, *J. Polymer Sci.*, 1948, **3**, 880). The approach of a big radical like trichloromethyl to the allylic position of oct-1-ene is also sterically hindered, although much less than in *cyclo*hexene. In any case our results with *cyclo*hexene indicate that even in the case of oct-1-ene the Kharasch reaction should produce partial substitution products, analogous to chloro*cyclo*hexene and to the allylic substitution product found by Bateman and Cunneen (*J.*, 1950, 941) in the reaction of oct-1-ene with *N*-bromosuccinimide.

EXPERIMENTAL.

M.p.s and b. p.s are uncorrected. Most of the microanalyses are by Drs. Weiler and Strauss, of Oxford.

Materials.—*cyclo*Hexene was distilled several times in a Vigreux column; it had b. p. 81°/690 mm., n_D^{22} 1·4450. Acetyl peroxide was prepared according to Gamberian's method (*Ber.*, 1909, **42**, 4010), but carbon tetrachloride was used as a solvent instead of ether. The concentration of the peroxide solution was determined iodometrically (Kokatnur and Jelling, *J. Amer. Chem. Soc.*, 1941, **63**, 1432). Commercial benzoyl peroxide was recrystallised from a small amount of warm chloroform, and had m. p. 104°.

Reaction between cyclo*Hexene and Carbon Tetrachloride in the Presence of Benzoyl Peroxide.*—In a three-necked flask fitted with a reflux condenser, a dropping funnel, a gas-inlet tube, and a thermometer, a mixture of *cyclo*hexene (41 g., 0·5 mole) and carbon tetrachloride (385 g., 2·5 moles) was refluxed for 18 hours under a continuous stream of dry carbon dioxide. At the beginning and also 9 hours later, benzoyl peroxide (2·4 g., 0·01 mole) was added. The mixture boiled initially at 78°, and after 18 hours at 82°. The yellow solution was washed three times with a 5% solution of sodium hydrogen carbonate and with water, and dried (Na_2SO_4). The low-boiling components of the reaction mixture were removed by distillation through a Vigreux column. The residual oil was fractionated *in vacuo*, the following fractions being isolated : (i) b. p. 60°/30 mm., n_D^{20} 1·4850 (3·0 g.), a colourless liquid (I); (ii) b. p. 95—100°/10 mm. (6 g.), a colourless oil; (iii) b. p. 150—155°/10 mm. (4 g.), a yellow oil; and (iv) undistillable residue, a viscous brown syrup (1 g.).

Identification of the products. Fraction (i) was identified as 3-chloro*cyclo*hex-1-ene. Fraction (ii) was found by bromate–bromide titration (Lucas and Pressman, *Ind. Eng. Chem., Anal.*, 1938, **10**, 140) to contain a small amount of olefin. It was purified by addition of the calculated amount of bromine in chloroform. The mixture was kept in the dark for 2 hours, washed with sodium hydrogen carbonate solution, and dried, and the chloroform residue distilled *in vacuo*. A colourless oil was obtained, b. p. 98—100°/10 mm., n_D^{20} 1·5232. The *product*, as indicated by analysis and by titration as before, still contained some unsaturated material (? $C_7H_9Cl_3$), probably formed by decomposition during distillation (Found : C, 37·0; H, 4·8; Cl, 58·55. $C_7H_{10}Cl_4$ requires C, 36·1; H, 4·3; Cl, 59·6%).

Acid hydrolysis of fraction (ii). Fraction (ii) (0·37 g.) was added to 70% sulphuric acid (15 c.c.), with vigorous stirring, and the mixture warmed in an oil-bath at 100° for 5 hours. The yellow solution first obtained gradually became brown and strongly evolved hydrogen chloride. The solution was cooled, an equal volume of cold water added, and the organic acid extracted from the ethereal layer with 10% sodium carbonate solution. The aqueous layer was acidified with dilute sulphuric acid, and the precipitate obtained was extracted with ether. The residue from the ether was left in an ice-box overnight. Yellow crystals (100 mg.) were thus obtained, m. p. 38—39° (identical with the value for *cyclo*hex-1-enecarboxylic acid; see Ruzicka and Brugger, *Helv. Chim. Acta*, 1926, **9**, 402; Berlingozzi, *Gazzetta*, 1927, **57**, 255; Boorman and Linstead, *J.*, 1935, 261) (Found : C 66·2; H 7·8. Calc. for $C_7H_{10}O_2$: C, 66·6; H, 7·9%).

Fraction (iii). On redistillation, this yielded a yellow oil, b. p. 155°/10 mm., n_D^{20} 1·5387, which was olefinic [Found : C, 63·3; H, 6·6; Cl, 19·5%; *M* (Rast), 350. $C_{19}H_{24}O_2Cl_2$ requires C, 64·2; H, 6·8; Cl, 20·0; *M*, 355] (Bromine titration : 1 g. absorbed 410 mg. Calc. : 450 mg.).

Alkaline hydrolysis of fraction (iii). Fraction (iii) (0·3 g.) in alcoholic 0·5N-sodium hydroxide (25 c.c.) was refluxed for 2 hours. Distilled water was added (25 c.c.), and a titration carried out with 0·5N-hydrochloric acid (phenolphthalein) : 97·44 mg. of alkali were consumed, equivalent to 3 moles per mole of fraction (iii) if it has *M*, 355. The solution obtained after the titration was evaporated to dryness on a water-bath, and the residue extracted with a solution of sodium hydrogen carbonate. About one-third of it dissolved. The aqueous layer was acidified with dilute sulphuric acid. The precipitate (100 mg.), recrystallised from water, yielded colourless crystals, m. p. 120° (mixed m. p. with benzoic acid, 120°). The remainder was dissolved in ether; the solution filtered, the solvent removed, and the residue triturated with ligroin. Colourless crystals, m. p. 52°, were obtained. These had a camphor-like smell, but after 24 hours in an open vessel they had almost completely evaporated.

Reaction between cyclo*Hexene and Carbon Tetrachloride in the Presence of Acetyl Peroxide.*—A mixture of *cyclo*hexene (82 g., 1 mole), carbon tetrachloride (708 g., 5 moles), and acetyl peroxide (0·4 g.) was refluxed in a continuous stream of carbon dioxide. At intervals of 6 hours additional portions of acetyl peroxide were added (total 2·4 g., 0·04 mole). The b. p. initially was 78°, and after 30 hours 86°. After purification of the product as described above, the reagents were removed by distillation, and the residue (36 g.) distilled *in vacuo*. A fore-run was lost owing to its low b. p. The following fractions were obtained : (i) b. p. 50—55°/20 mm., n_D^{20} 1·4853, d_4^{20} 1·028 (3·0 g.), a colourless liquid (I); (ii) b. p. 105—110°/18 mm., n_D^{20} 1·5014 (1·5 g.), a colourless oil; (iii) b. p. 112—114°/18 mm., n_D^{20} 1·5167 (1·5 g.), a yellow oil; (iv) b. p. 120°/18 mm., n_D^{20} 1·5197, d_4^{20} 1·299 (5 g.) (III), a yellow oil; (v) b. p. 160°/18 mm., n_D^{20} 1·5094 (a very small amount), a yellow oil; (vi) b. p. 120°/5 mm., n_D^{20} 1·5217, d_4^{20} 1·367 (7 g.) (II and IV), a yellow oil.

Identification of the fractions. Fraction (i) was identified as 3-chloro*cyclo*hex-1-ene as follows. It (Found : C, 61·4; H, 8·1; Cl, 30·7. Calc. for C_6H_9Cl : C, 61·8; H, 7·8; Cl, 30·4%) rapidly formed a precipitate with alcoholic silver nitrate; titration with bromate–bromide showed the existence of one double bond; comparison of the above physical data showed good agreement with those given by Berland (*Bull. Soc. chim.*, 1942, **9**, 644), *viz.*, b. p. 62°/35 mm.; n_D^{20} 1·4860; d_D^{20} 1·030.

Conversion of 3-*chloro*cyclo*hex*-1-*ene into* 3-*acetoxy*cyclo*hex*-1-*ene.* A mixture of fraction (i) (0·2 g.), anhydrous sodium acetate (0·25 g.), and glacial acetic acid (5 c.c.) was kept for 24 hours at room temperature, then extracted with ether; the extract was washed with water and a solution of 5% sodium hydrogen carbonate, and dried (Na_2SO_4). Evaporation of the ether left a small quantity of viscous, yellow oil. The 3-acetoxy*cyclo*hexene so obtained showed physical constants corresponding to those given by Berland (*loc. cit.*) : b. p. 83—84°/30 mm., d^{25} 1·003, n_D^{20} 1·4580 (Found : C, 68·8; H, 8·3. Calc. for $C_8H_{12}O_2$: C, 68·5; H, 8·5%).

Fraction (iv). This was identified as 1-*methyl*-2-*trichloromethyl*cyclo*hexane* (III) by analysis (Found : C, 44·9; H, 5·75; Cl, 49·1%; *M*, 218. $C_8H_{13}Cl_3$ requires C, 44·6; H, 6·0; Cl, 49·3%; *M*, 213) ($[R_L]_D$ 50·36. Calc. : 50·54), and by acid hydrolysis to 2-methyl*cyclo*hexanecarboxylic acid by the method described above. Yellow crystals, m. p. 52—54°, were obtained (cf. Goldschmidt, *Chem.-Ztg.*, 1902, **26**, 335; Gutt, *Ber.*, 1907, **40**, 2069) (Found : C, 67·3; H, 10·2%; equiv., 142·5. Calc. for $C_8H_{14}O_2$: C, 67·6; H, 9·9%; equiv., 142·0).

Fraction (vi). This fraction, which constituted about 40% of the total products of the reaction, is believed to be a mixture of (II) and (IV) (Found : C, 38·1; H, 4·85; Cl, 57·0%; *M*, 260. Calc. for $C_8H_{12}Cl_4$: C, 38·4; H, 4·8; Cl, 56·8%; *M*, 250) ($[R_L]_D$ 56·85. Calc. : 56·77); it was completely saturated towards perbenzoic acid and bromine.

Hydrolysis of fraction (vi). Fraction (vi) (1 g.) was added to 70% sulphuric acid (10 c.c.), with stirring, and the whole warmed on a steam-bath for 3 hours. The red solution first obtained became brown and evolved hydrogen chloride. It was then poured on chopped ice and extracted with ether, and the solvent removed. The residue was dissolved in carbon tetrachloride and chromatographed on activated silica gel (100 mesh). Two zones were obtained, which were separated by elution with ether–ethanol (1 : 1). After removal of the solvent from the separate percolates, the two products were isolated : (i) crystalline 6-methyl*cyclo*hex-1-ene-1-carboxylic acid (0·3 g.), m. p. 79° (cf. Mazza and Cremona, *Gazzetta*, 1927, **57**, 318) (Found : C, 68·2; H, 8·8%; equiv., 141. Calc. for $C_8H_{12}O_2$: C, 68·5; H, 8·5%; equiv., 140); (ii) a yellow oil which crystallised at 25° (100 mg.), identical with 3-methyl*cyclo*hex-1-ene-1-carboxylic acid (see Perkin and Tattersall, *J.*, 1905, **87**, 1095; Boorman and Linstead, *J.*, 1935, 264) (Found : C, 68·7; H, 8·6%; equiv., 139·2).

Fractions (ii) (Found : C, 54·7; H, 7·8; Cl, 30·55%), (3) (Found : C, 47·8; H, 6·1; Cl, 40·0%), and (v) (Found : C, 53·6; H, 6·9; Cl, 39·15%) are being investigated further. Fraction (v) represented 5% of the total reaction products.

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