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THE BENZOYL PEROXIDE INITIATED ADDITION OF CARBON TETRACHLORIDE TO OLEFINS ¹⁾

BY

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The initiation, propagation and termination steps of the benzoyl peroxide initiated addition of carbon tetrachloride to olefins are described.

Initiation follows two main routes, viz. a) addition of benzoate and of phenyl radicals to the olefinic double bond, followed by chlorine abstraction from carbon tetrachloride by the new radicals and b) formation of trichloromethyl radicals from carbon tetrachloride and phenyl radicals.

The propagation mechanism proposed by *Kharasch* et al. ²⁾ is confirmed and the extent of telomer ^{*}) formation estimated for the case of cetene.

Chain termination consists in the formation of stable allyl-type radicals, which are incapable of starting a new chain; in the case of cyclohexene, these radicals were found in the form of their dimer 3,3'-dicyclohexenyl.

Supporting evidence is based on detailed analyses of the reaction mixtures, peroxide decomposition products and other by-products being isolated and identified. Further arguments follow from the influence of retarders and the results obtained with olefins of a special structure.

Introduction and Survey.

In most free radical chain reactions the average kinetic chain lengths are very large. As a result, only very small proportions of groupings or products arising from the initiation and termination steps are formed; their nature is therefore generally difficult to establish. In the case of vinyl polymerisation, recourse has even been had to tracer methods with a view to ascertaining the incorporation of peroxide fragments into the polymers formed ³⁾.

In the addition of carbon tetrachloride to normal alpha olefins about 20 to 60 moles of addition product are formed per mole of

¹⁾ Preliminary communication: *E. C. Kooyman*, *Rec. trav. chim.* **69**, 492 (1950).

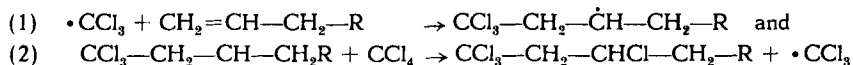
^{*}) Compounds containing more than one molecule of olefin per molecule of carbon tetrachloride.

²⁾ *M. S. Kharasch* et al., *J. Am. Chem. Soc.* **69**, 1100, 1105 (1947).

³⁾ Cf. *C. C. Price* in „Reactions at carbon-carbon double bonds”. Interscience New York 1946, p. 76 sqq.; *W. Kern* and *H. Kämmerer*, *J. prakt. Chem.* **161**, 81 (1942).

peroxide decomposed *). Therefore, the amounts of products formed in the initiation and termination steps should constitute as much as several per cent molar of the total reaction product. In consequence a more detailed study of these steps should be feasible than in most other reactions of this type.

In a preliminary communication ¹⁾ some results were reported on the mechanism of the chain breaking steps. The present paper deals with the above addition process as a whole. "Initiation" (Section A) will be used to indicate reactions or reaction sequences producing the chain carrying CCl_3 radical, other than by way of the propagation cycle (Section B). According to *Kharasch* et al. ²⁾, this consists of

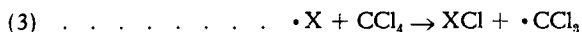


"Termination" or "chain breaking" (Section C) will be used in the kinetic sense, i.e. to indicate reactions of active free radicals leading to products incapable of starting a new chain; "active" are those radicals which are capable to do so. Section D deals with termination reactions caused by foreign compounds: retardation. The isolations and identifications of reaction products are described in the experimental part; this also gives experimental details on our preliminary communication.

In all experiments, temperatures of 77—100° C were used; at 90° C the half-life of benzoyl peroxide is of the order of one hour ⁴⁾. At higher temperatures, interactions of the initiating radicals might occur, whereas the decomposition of the peroxide is very slow below 75° C. Carbon tetrachloride was always used in excess with respect to olefin (3 : 1 molar).

A. Initiation.

The formation of trichloromethyl radicals obviously involves the abstraction of a chlorine atom from carbon tetrachloride by a free radical:



*) Ref. ²⁾ and unpublished experiments on a series of normal alpha olefins by one of the present authors (K.).

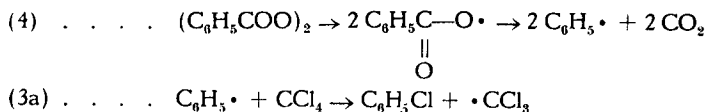
⁴⁾ Kinetics of the decomposition of benzoyl peroxide:

a. *P. D. Bartlett and K. Nozaki*, *J. Am. Chem. Soc.* **68**, 1495 (1946).

b. *B. Barnett and W. E. Vaughan*, *J. Phys. and Colloid Chem.* **51**, 936 and 942 (1947).

The radicals X will arise from the peroxide, either directly or indirectly.

The decomposition of benzoyl peroxide in *carbon tetrachloride* has been reported to yield chlorobenzene, carbon dioxide and hexachloroethane as the main products⁵⁾ *). This indicates the formation of phenyl radicals, which abstract a chlorine atom from carbon tetrachloride, leaving the resulting CCl₃ radicals to dimerize:



The decomposition of benzoyl peroxide in *cyclohexene* was studied by *Farmer and Michael*⁶⁾ at 140° C. The authors found a variety of saturated and unsaturated products; from their results they concluded that the alpha methylenic positions rather than the double bonds formed preferential points of free radical attack. (Cf. Section A-3).

Equation (3a) was proposed by *Kharasch* and his coworkers²⁾ to account for chain starting. However, radicals X (eq. 3) might further consist of radicals formed by addition of peroxide fragments to the double bond; thus, both phenyl and benzoate radicals are known to be incorporated into polymers when using benzoyl peroxide as the initiator³⁾.

A-1. Results.

Table I gives a survey of the experimental results with various olefins. Cyclohexene was especially chosen because of its low reactivity with respect to addition of CCl₄, the small amounts of addition products facilitating detailed analyses of by-products. The formation of the reaction products tabulated in the last column has no direct bearing on initiation and will be discussed in sections B and C.

A-2. Discussion of results.

a) *Cyclohexene*. 2-Chlorocyclohexyl benzoate is apparently formed

⁵⁾ Discussion on the decomposition of benzoyl peroxide: *W. A. Waters* in „The chemistry of free radicals”, Clarendon Press, Oxford 1948, p. 166 sqq.

*) Upon repeating this experiment we also found some phosgene, *symm.* diphenyl urea being formed when sweeping the gaseous reaction products through an aqueous solution of aniline by means of nitrogen. (M.p. and mixed m.p. with authentic sample 235° C). Cf. ref. ^{4b)}.

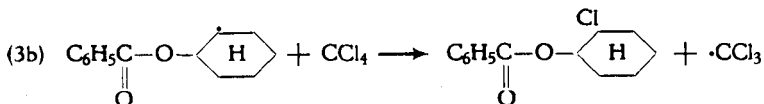
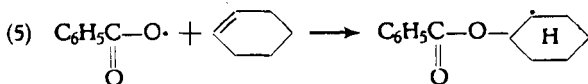
⁶⁾ *E. H. Farmer and S. E. Michael*, J. Chem. Soc. 1942, 513; *E. H. Farmer*, Trans. Faraday Soc. 38, 341 (1942); J. Soc. Chem. Ind. 66, 86 (1947). Cf. ref. 5, p. 168.

Table I.
Decomposition of benzoyl peroxide in CCl₄/olefin mixtures.

| Olefin | Moles of CCl ₄ , olefin and peroxide, respectively | Temperature | Aromatic decomposition products (% molar based on phenyl groups) | | | | | | | Other reaction products *) (% molar based on phenyl groups) | |
|--|---|-------------|--|----------------|--------------|---------------------------|---------------------------|-----------------|-------------------|---|---|
| | | | Benzene | Chloro-benzene | Benzoic acid | 2-chloroalkyl-1-benzoates | 1-phenyl-2-chloro alkanes | Accounted for | | | |
| | | | | | | | | Phenyl radicals | Benzoate radicals | | Total |
| Cyclohexene | 11.4 : 3 : 0.145 | 78—80°C | 8 | 10 | 12 | 55 + 6 (unidentified) | ? | 18 | 73 | 91 | carbon dioxide 19 chloroform 95 3-chlorocyclohexene 11 3,3'-dicyclohexenyl 60 1-chloro-2-tri-chloro methyl cyclohexane 89 |
| n-Heptene-1 | 3 : 1 : 0.02 | 85—90°C | 10 | 25 | 10 | 21 (unidentified) | ? | 35 | 31 | 66 | chloroform 65 1,1,1-trichloro octane ? 1,1,1,3-tetrachloro octane 2300 Telomers |
| Propene (28 ⁰ / ₀ C ₃ H ₆ 70 ⁰ / ₀ C ₃ H ₈ 2 ⁰ / ₀ C ₂ and C ₄ hydro-carbon) | 41 : 17 : 0.4 | 90—95 °C | 5 | 32 | 12 | 20 (unidentified) | 7 | 44 | 32 | 76 | Isopropylchloride 15 chloroform 65 1,1,1-trichlorobutane 6 1,1,1,2-tetrachloro-butane 1150 tetrachloroheptane (telomer) 115 |

*) Carbon dioxide was determined only in the case of cyclohexene.

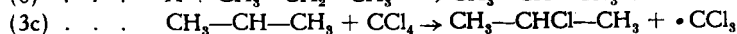
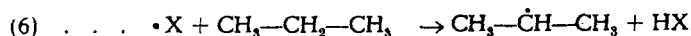
by addition of a benzoate radical to the double bond, followed by a type (3) reaction:



This compound contains fragments of three different molecules (a chlorine atom from CCl_4 , an aromatic fragment from the peroxide and a cyclohexyl group from the olefin), which leaves little doubt as to its mode of formation.

b) *n*-Heptene-1. Experimental difficulties were caused by the large excess of tetrachlorooctane formed and the high boiling points of most reaction products, which led to poor separations during distillations. Attempts at isolating phenyl chloroheptane or benzoic esters failed.

c) *Propene*. The use of a commercially available mixture of propene and propane enabled us to employ fairly large intakes; this facilitated the isolation of small amounts of by-products. 1-Phenyl-2-chloropropane was probably formed by reactions analogous to (5) and (3b) viz. addition of a (phenyl) radical to the double bond, followed by interaction of the new radical with carbon tetrachloride. Benzoic esters could not be isolated in a pure state. The isopropyl chloride may have been formed from propane by reactions (6) and (3c):

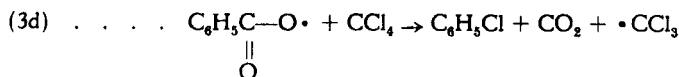


A-3. Conclusions.

From the high percentages of peroxide accounted for, it follows that the main decomposition products have been detected.

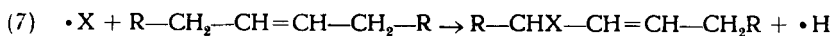
The main initiation steps are seen to consist in a) addition of benzoate or phenyl radicals to the double bond, followed by type (3b) reactions and b) reactions (3a). In view of recent results of *Edwards and Mayo*⁷⁾ with respect to the decomposition of diacetyl peroxide in carbon tetrachloride and other halides, chlorobenzene may also have been formed by a direct interaction of a benzoate radical and CCl_4 :

⁷⁾ *W. Edwards and F. R. Mayo, J. Am. Chem. Soc. 72, 1265 (1950).*

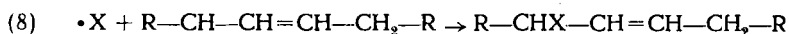


The formation of isopropyl chloride suggests that initiation may also occur by the formation of active secondary alkyl radicals (eq. (6) and (3c); cf. Section C-3).

The absence of unsaturated products containing peroxide fragments may indicate that no direct substitutions occur. Contrary to this, *Farmer* and *Michael* (l.c.) assumed this type of reaction to account for the formation of unsaturated compounds in the decomposition of benzoyl peroxide in cyclohexene at 140° C:



This reaction involves the expulsion of a free hydrogen atom, which is known to possess a high free energy; it was even proposed to occur for X = cyclohexenyl, an allyl type radical. In view of the very rapid generation of radicals from benzoyl peroxide at 140° C *), it would seem to be more likely that the unsaturated reaction products had been formed by recombination of a radical X with an allyl-type radical previously formed by hydrogen abstraction at the alpha methylenic group:



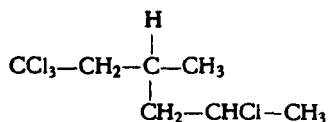
As for the quantitative aspects of the present results, the shift from products containing the benzoate grouping towards products containing only a phenyl grouping when passing from cyclohexene to propene is quite considerable (73, 31, 32 % and 18, 35 and 44 %, respectively). This shift is probably mainly caused by the increasing reaction temperature employed, decomposition of benzoate radicals into phenyl plus carbon dioxide being favoured by a higher temperature 4^{b)} 5).

B. Propagation.

The mechanism of the main propagation cycle (reactions (1) and (2)) is analogous to that obtaining for "abnormal" addition of hydrogen bromide as well as many related reactions such as the addition of mercaptans and of sodium bisulphite ⁸⁾). The structures of the 1:1 addition products of carbon tetrachloride and olefins were established by *Kharasch* and coworkers ²⁾ to be 1,1,1,3-tetrachloro alkanes. Contrary to their statement that olefins con-

*) At this temperature, the half-life of the peroxide is of the order of one minute.

⁸⁾ Survey in ref. 3, p. 62 sqq.



With the other olefins, no telomers could be isolated in a pure state because of the very high boiling points.

B-2. Quantitative determinations of telomerization with cetene.

In order to obtain information on the rate of (9) as compared with (2), a number of experiments were made with cetene. The low volatility of this compound enables one to determine the total amount (A) of carbon tetrachloride bound to olefin simply by evaporating the excess CCl_4 and weighing the residue, olefin intake being known. The quantity A was found to be smaller than the number of millimoles of olefin converted as determined by titration with bromine (ΔO). Assuming telomerization not to proceed beyond the (olefin) $_2\text{CCl}_4$ stage *) and neglecting olefin consumed in the initiation reaction (5) as well as unsaturates consumed and formed in the termination reactions (Section C), A equals the sum of 1:1 addition products (M, for Monoaddition product) and 2:1 addition products (D, for Dimer addition product). $A = M + D$ and $\Delta\text{O} = A + D$; therefore $M = 2A - \Delta\text{O}$ and $D = \Delta\text{O} - A$.

Graph A represents a plot of $D = f(M)$ based on the above mentioned simplifying assumptions. Varying amounts of peroxide were used in order to obtain varying conversions.

At complete conversion of the olefin, telomerization amounted to about 11 % molar based on cetene. As might be anticipated, telomerization decreases at an increasing conversion of the olefin. By combining equations (9) and (2), assuming all trichloroalkyl radicals (T.) eventually to give either D or M molecules, one obtains

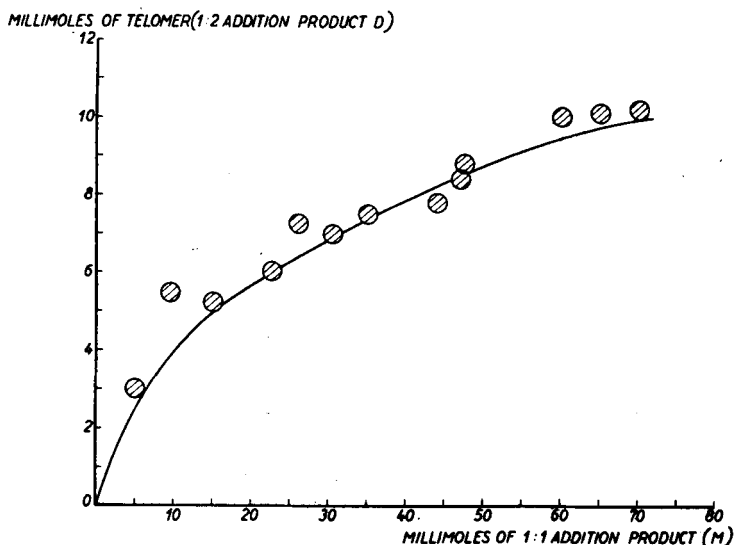
$$\frac{dD}{dM} = \left(k_9 \times \frac{[\text{T.}] \times [\text{CCl}_4]}{[\text{T.}] \times [\text{O}]} \right) = k \cdot \frac{\text{O}}{\text{CCl}_4}$$

in which k represents the ratio of the rate constants of (9) and (2), respectively, and O and CCl_4 represent the amounts of cetene and of carbon tetrachloride as both reactions are of the same order.

The rather poor experimental accuracy merely suffices to give some idea about the order of magnitude of the constant k. From the smooth curve drawn through the experimental points, k is calculated

*) Kharasch et al.²⁾ have shown that this assumption is not generally valid, substituted olefins sometimes giving predominantly (olefin) $_2\text{CCl}_4$, with smaller amounts of (olefin) $_3\text{CCl}_4$ and 1:1 addition products.

to be about 0.7. This fairly high value suggests that the tendency for trichloroalkyl radicals to add on olefin is quite considerable and that a large excess of carbon tetrachloride should be employed if one wants to avoid appreciable telomerization. This conclusion was



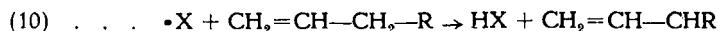
(graph A)

confirmed by experiments with an initial molar ratio of 1:1. Furthermore, chloroform gives larger amounts of telomers as compared with carbon tetrachloride²⁾; the hydrogen atom in chloroform is less reactive towards radicals than the chlorine atoms in CCl_4 , which leads to a higher value of k .

In experiments with 3.3-dimethylbutene, telomerization was found to be only 4% molar at complete conversion of the olefin when using the same initial molar ratio of halide and olefin as in the experiments with cetene (3:1). This may have been caused by mutual steric repulsion of the bulky tertiary butyl groups in the olefin and the trichloroalkyl radical.

C. Chain termination.

Some arguments have already been given¹⁾ which indicate that these reactions involve hydrogen abstraction at the alpha methylenic groups:



Reactions involving chlorine abstraction from carbon tetrachloride are known to require a fairly reactive radical; primary as well as secondary alkyl radicals react quite readily, whereas tertiary alkyl radicals and benzyl radicals fail to do so⁹). It seems likely, therefore, that allyl-type radicals — which have a resonance energy comparable to that of benzyl radicals — will also be incapable to give this abstraction reaction.

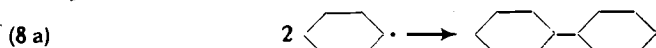
If (10) were to represent the only possible route of disappearance of active radicals, one would have to expect the formation of hydrides (HX) derived from all radicals present in the system, specifically: chloroform, trichloroalkanes, benzene, benzoic acid, alkylbenzoates, alkylbenzenes and "trichlorotelomers". Their sum total should equal the intake of phenyl groups from the peroxide. The allyl-type radicals should be present in the form of special reaction products such as dimerisation or disproportionation products (diolefins, allene-type or acetylene type compounds).

C-1. Results.

Table II gives the reaction products which may have a bearing on reaction (10); it applies to the same experiments as table I. In addition, an experiment with 3,3-dimethylbutene-1 and one with a mixture of dimethylbutene and cetene has been tabulated in order to emphasize the difference between olefins with and without alpha methylenic hydrogen atoms with respect to termination.

C-2. Discussion of results.

a) *Cyclohexene*. Most of the compounds anticipated on the basis of (10) were found. 3,3'-Dicyclohexenyl is an important product, as it is probably formed from two stable cyclohexenyl radicals:



Farmer and Michael (l.c.; cf. Section A-3) attributed the formation of this compound to a type (7) reaction involving a cyclohexenyl radical and cyclohexene. In our case, the expelled hydrogen atom would be capable of starting a new chain by abstracting a chlorine atom from CCl_4 . Chloroform, benzene and benzoic acid were found whereas trichloromethylcyclohexane may also have been present but could not be definitely identified.

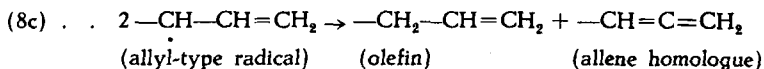
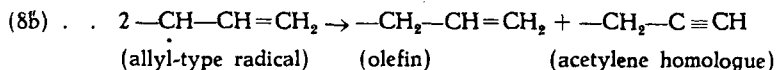
The formation of a small amount of 3-chlorocyclohexene is difficult to explain. Perhaps, the cyclohexenyl radical is somewhat more reactive than an open-chain allyl-type radical.

⁹) M. S. Kharasch et al., J. Am. Chem. Soc. 64, 1621 (1942); 65, 2428 (1943).

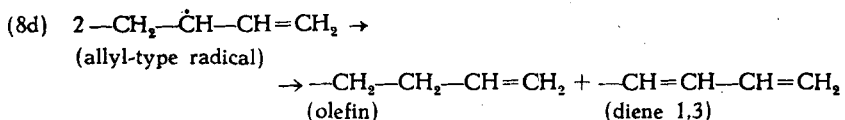
Table II.
Products conceivably formed in the termination step.

| Olefin | Yields of possible termination products (reaction 10) (% molar based on intake of phenyl groups) | | | | | Dimerisation products of free radicals | Other products |
|--|---|--------------|------------|---------------------------------|------------------------------|---|---|
| | Benzene | Benzoic acid | Chloroform | Trichloroalkene | Total percentage of hydrides | | |
| Cyclohexene | 8 | 12 | 95 | probably a few percent | 115 | 3,3'-dicyclohexenyl 60 no C ₂ Cl ₆ | Cf table I |
| n-Heptene-1 | 10 | 10 | 65 | probable | 85 | no C ₂ Cl ₆ | Cf table I |
| Propene | 5 | 12 | 65 | 6 (1,1,1-trichloro-n-butane) | 88 | no C ₂ Cl ₆ | Cf table I and section B |
| 3,3-Dimethyl-butene-1 olefin/peroxide ratio 800 : 1 | — | trace | — | — | — | C ₂ Cl ₆ (trace) | nearly complete conversion of olefin to addition product |
| 3,3-dimethyl-butene-1 + ce'ene (1 : 1) olefin/peroxide ratio 100 : 1 | — | 10 | — | — | — | no C ₂ Cl ₆ | Incomplete conversion of both olefins (cetene 60 0/0, d methyl butene 35 0/0) |

b) *n*-Heptene-1 and propene. Chloroform, benzene and benzoic acid were found, whereas propene gave also trichlorobutane. The formation of trichlorooctane from heptene could not be definitely established, although the tetrachlorooctane fraction contained a small amount of a lower boiling halogen compound. The fate of the allyl radicals presumably formed could not be traced. With propene, diallyl was definitely absent. It may be significant that cyclohexene, which is the only olefin incapable of giving allene or acetylene derivatives by disproportionation of allyl radicals *), yielded an appreciable quantity of a dimer of cyclohexenyl radicals, viz. dicyclohexenyl. The presence of acetylene or allene homologues could not be established; both types of compounds should boil within the same range as the unreacted olefins. Their formation could be represented as follows:



The allyl radicals from heptene could also disproportionate to olefin plus heptadiene 1,3; this would be impossible with propene:



Although the above arguments are based on negative evidence, they tend to show that the experimental results do not invalidate the proposed termination scheme expressed by reaction (10).

c) *3,3*-Dimethylbutene-1. Although this olefin required only one tenth of a percent molar of peroxide based on olefin to give nearly complete conversion to the carbon tetrachloride addition product, traces of hexachloroethane could be isolated and identified. In all other experiments, hexachloroethane could not be detected, although much larger amounts of peroxide were employed. This suggests that the dimerisation of trichloromethyl radicals is a possible route of their disappearance (i.e. constitutes a chain-breaking step!) only in the absence of alpha methylenic hydrogen atoms. This is in line with (10).

*) Six-membered rings containing triple bonds or allene groupings seem to be non-existent, probably because of steric strain.

C-3. Conclusions.

The overall picture is in satisfactory agreement with equation (10). Chloroform forms the major quantity of possible hydrides. Trichloroalkanes were identified with certainty only in the case of propene, although they were probably also formed from the other olefins.

The formation of isopropyl chloride (Section A-2,3) indicates hydrogen abstraction to occur also at other than alpha methylenic groups. Therefore, the hydrides found may have originated both from (6) and (10). According to West and Schmerling¹⁰, reactions (6) — involving a CCl_3 radical — and (3c) are responsible for the formation of chloroalkanes when heating benzoyl peroxide with carbon tetrachloride and paraffins at 130° C. However, the overall kinetic chain lengths were found to be rather short (below 12), which would suggest that these reactions could not readily occur at our reaction temperatures. In line with this, we found a considerable amount of hexachloroethane but little chlorination when heating benzoyl peroxide with n-hexadecane and carbon tetrachloride at 90° C.

If type (6) reactions would not occur the sum total of the hydrides should equal 100 % based on phenyl groups. The experimental figures for propene and heptene were nearly 90 %. With cyclohexene, where a more accurate analysis was feasible, we found 115 %. This suggests a small proportion of the hydrides to have originated from reactions (6). It would seem probable that phenyl radicals will have little preference for loosely bound hydrogen or chlorine atoms, being extremely reactive⁵); therefore, the phenyl radicals probably furnished the major contribution to (6) as they are the most reactive radicals present in our system.

It should be noted that no indications were obtained as regards type (10) reactions producing alkylbenzoates or alkyl benzenes.

Summing up, our results suggest chain termination mainly to occur by reactions (10) involving trichloromethyl radicals. Trichloroalkyl, benzoate and phenyl radicals probably give minor contributions decreasing in the order mentioned.

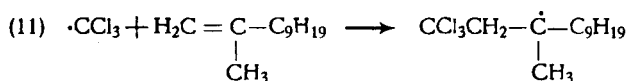
D. Retardation.

On the basis of the proposed termination mechanism a decrease in yield of addition products on the basis of the same amount of peroxide decomposed should be caused by the presence of foreign compounds containing alpha methylenic groups. Using the system

¹⁰ J. P. West and L. Schmerling, J. Am. Chem. Soc. 72, 3525 (1950).

carbon tetrachloride-cetene (molar ratio 3, temperature $91\frac{1}{2}^{\circ}$ C) as a basis of comparison, marked decreases in yield were actually found to occur when adding ethylbenzene, n-heptene-3 and many other compounds of this type; no retardation was caused by tert. butylbenzene or 2,2,5,5-tetramethylhexene-3, which do not possess alpha methylenic groups *).

An interesting case formed 2-methyl-undecene-1, which also acted as a strong retarder. This may be interpreted as follows. A similar compound, viz. 2-ethylbutene-1 was found by *Kharasch and Sage*¹¹⁾ to add on bromotrichloromethane 1.4 times more readily than octene-1, which proves that reaction (1) (addition of a trichloromethyl radical to the double bond) is somewhat faster for the branched olefin. Like all tertiary radicals, the radical formed in this reaction will be incapable of abstracting a chlorine atom from CCl_4 ⁹⁾ although it readily abstracts the very loosely bound bromine atom from CBrCl_3 ²⁾. Thus, when using CCl_4 the formation of a stable radical is responsible for termination:



Hydrogen abstraction at the alpha methylenic groups of methylundecene will proceed much more slowly than the above "addition retardation", otherwise the olefin could not add on bromotrichloromethane more rapidly than octene-1, trichloromethyl radicals being operative in step (1) in both cases. A similar example of retardation by an olefin which is more reactive in the first step and unreactive in the second step has been recently described by *Kharasch and Friedlander*¹²⁾, viz. the inhibition of bromotrichloro methane addition to olefins by styrene at temperatures below 40° C. At this low temperature, the substituted benzyl radical is even incapable of abstracting a bromine atom from CBrCl_3 .

The above facts are thus furnishing examples of retardation by foreign compounds by the formation of stable radicals, both by hydrogen abstraction reactions and by addition reactions.

*) These retardation reactions have been employed as a tool in determining alpha methylenic reactivity in various compounds. (E. C. Kooyman, Disc. Faraday Soc. on Hydrocarbons, April 1951, in press).

¹¹⁾ M. S. Kharasch and M. Sage, J. Org. Chem, **14**, 537 (1949).

¹²⁾ M. S. Kharasch and H. N. Friedlander, J. Org. Chem. **14**, 239 (1949).

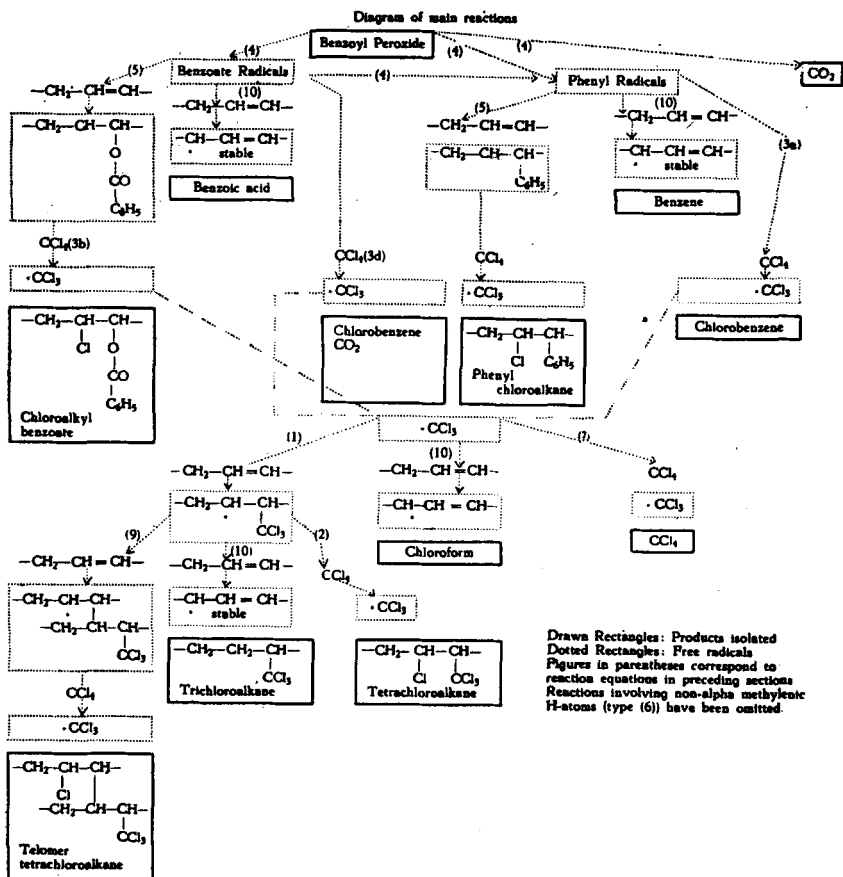
Scheme of reactions occurring in the CCl_4 addition ¹⁾

| | | | |
|--|--|---|--|
| <p>(A) <i>Initiation</i> (Benzoyl peroxide and benzoyl radicals)</p> | <p>Chlorine abstraction from CCl_4: ($\cdot\text{X} = \text{CCl}_3^2$, phenyl, secondary, (3c), (3d) alkyl, possibly benzoate) $\xrightarrow{(3a)}$ $\xrightarrow{(3d)}$</p> <p>Addition to the double bond ($\cdot\text{X} = \text{benzoate, phenyl}$) $\xrightarrow{(5)}$</p> <p>Hydrogen abstraction at non-alpha methylenic groups ($\cdot\text{X} = \text{all active radicals}$) $\xrightarrow{(6)}$</p> | <p>($\cdot\text{CCl}_3$) (XCl)</p> <p>Phenyl or benzoate substituted sec. alkyl radical</p> <p>olefinic secondary radical</p> <p>XH + alkyl radical</p> | <p>$\cdot\text{CCl}_3$</p> <p>+ CCl_4 (3b) $\xrightarrow{\quad}$ { phenylchloroalkane chloroalkyl } + $\cdot\text{CCl}_3$ benzoate</p> <p>+ CCl_4 (3c) $\xrightarrow{\quad}$ chloro olefin (other than the 1, 2 or 3 isomers) + $\cdot\text{CCl}_3$</p> |
| <p>(B) <i>Propagation</i></p> | <p>• X</p> <p>Addition to the double bond ($\cdot\text{X} = \text{CCl}_3, \text{trichloroalkyl}$) $\xrightarrow{(1), (9)}$</p> | <p>trichloroalkyl trichloro-dialkyl</p> | <p>+ CCl_4 (2) $\xrightarrow{\quad}$ Tetrachloroalkane } + $\cdot\text{CCl}_3$ Telomer</p> |
| <p>(C) <i>Termination</i></p> | <p>• X</p> <p>Hydrogen abstraction at alpha methylenic groups ($\cdot\text{X} = \text{all active radicals}$) $\xrightarrow{(10)}$</p> | <p>XH + allyl-type radicals $\xrightarrow{\quad}$</p> | <p>dimers and/or other products (8a) (8b) (8c)</p> |
| <p>(D) <i>Retardation</i></p> | <p>• X</p> <p>Hydrogen abstraction at alpha methylenic groups of the retarder, or at other groups containing loosely bound H-atoms ($\cdot\text{X} = \text{all active radicals}$) $\xrightarrow{(10) 2)}$</p> <p>Addition to the retarder ($\cdot\text{X} = \text{all active radicals}$) $\xrightarrow{\text{e.g. (11)}}$</p> | <p>XH + (allyl)-type (radical) $\xrightarrow{\quad}$ (benzyl)-type (radical) $\xrightarrow{\quad}$ stable radicals $\xrightarrow{\quad}$</p> | <p>dimers and/or other products</p> <p>?</p> |

¹⁾ • X represents an active free radical. Figures in parentheses apply to the reaction equations given in sections A, B, C, D.

²⁾ Similar to (10), with a retarder instead of an olefin.

³⁾ This "regeneration" reaction seems plausible, though no direct supporting evidence is available. (Cf. W. A. Waters in "The Chemistry of free Radicals, Oxford 1948, p. 19, 256).



E. Reactions occurring in the addition process.

The conclusions reached in sections A, B, C and D are schematically represented on the two preceding pages.

F. General remarks and conclusions.

Admittedly, not all products presumably formed on the basis of the general schemes given in section E were detected in all cases, some being identified only in experiments with cyclohexene and others with propene. However, the analogous behaviour of cyclohexene, cetene, heptene-1 and propene seems beyond reasonable doubt, differences being of a quantitative rather than of a qualitative nature. (Cf. Section A-3). Thus, on the basis of competitive addition ex-

periments with bromotrichloromethane, *Kharasch* and *Friedlander*¹²⁾ found cyclohexene to add on trichloromethyl radicals about four times more slowly than octene-1.

The picture derived from the combined results shows a satisfactory consistency. It does not contain free radical reactions involving the expulsion of free atoms (e.g. (7)), which should form the free radical counterpart of the ionic type Walden inversions. Whereas the occurrence of inversion has been definitely disproved by *Brown* and his coworkers¹³⁾ for the special case of the chlorination of optically active amylochloride, such reactions would seem to be per se plausible.

Furthermore, no indications were obtained that one or more of the proposed steps should be reversible. If this were correct, all trichloroalkyl radicals formed in step (1) should eventually lead to tetrachloroalkanes (and a small amount of trichloroalkanes formed in reactions (10)). This assumption has formed the basis of an investigation on the overall kinetics to be published later on.

Experimental part.

(With the collaboration of Miss *B. Meurs* and *S. Belgraver*).

I. Starting materials.

Analytical grade carbon tetrachloride was used (*Albright & Wilson*); chloroform could not be isolated even after careful fractionation of a 2 litre sample of CCl_4 through a 15 plate column. Benzoyl peroxide was recrystallized by dissolving in chloroform and precipitating with methanol; peroxide content 97.5%. Olefins were distilled over sodium before use.

II. Procedures.

a) Addition reactions.

All experiments were carried out with the exclusion of atmospheric oxygen, either by passing a slow stream of pure nitrogen through the reaction vessel or by periodically adding a small piece of dry ice. The experiments with propene were carried out in a stainless steel autoclave of 25 litres capacity. In the experiments with 3,3-dimethylbutene-1, sealed tubes were used. All other experiments were made in three-necked round-bottomed flasks. Working up was done by distillation, splitting up the product into three or four cuts which were then repeatedly fractionated in a 15 plate Oldershaw column.

b) Determinations of benzoyl peroxide in solutions.

Aliquot samples (1–5 ml) were taken by pipette, dissolved in 50 ml of acetone containing 2 ml of 30% aqueous KI solution and titrated after three minutes' standing in stoppered flasks. Depending on the amount of peroxide expected, either 0.02 or

¹³⁾ *H. C. Brown* et al., *J. Am. Chem. Soc.* **62**, 3435 (1940).

Preparation and properties of olefins used.

| Olefin | b p. (°C/mm Hg) | n_D^{20} | Ozonometrical titration ¹⁷⁾ (double bonds per molecule) | Preparation |
|---------------------------------|--------------------|------------|---|---------------------|
| 3,3-Dimethyl butene-1 | 41.2 | 1.3765 | 1.00 | — ¹⁴⁾ |
| Cyclohexene | 83.4 | 1.4468 | 1.01 | Standard procedures |
| n-Heptene-1 | 93.5—8 | 1.4000 | 0.99 | " " |
| n-Heptene-3 | 96.0 | 1.4050 | 1.00 | " " |
| 2,2,5,5-Tetramethyl hexene-3 | 122.0—122.3 | 1.4116 | 0.99 | — ¹⁵⁾ |
| Allylbenzene | 156 | 1.5136 | 0.95 *) | — ¹⁶⁾ |
| 2-Methyl undecene-1 | 101/15 | 1.4360 | 1.02 | — ^{**)} |
| Cerene | 208/103 | 1.4412 | 0.99 | Standard procedures |

*) This olefin contained a small amount of bromobenzene.

***) Prepared by reacting methallylchloride with n-octyl magnesiumbromide in ether.

0.1 N thiosulphate was employed. No interference by carbon tetrachloride, olefins or addition products was observed; repeatability was quite satisfactory.

c) *Identification of simple compounds.*

Benzene was determined by ultraviolet absorption analysis *) of fractions boiling below 85° C. *Chloroform* was isolated by fractionation and identified by its boiling point (61° C), refractive index ($n_D^{20} = 1.4465$) and positive carbyl amine test. *Benzoic acid* was isolated by extraction of reaction products with sodium bicarbonate solution and identified by titration (eq. weight 122), melting point and mixed melting point 121° C. *Benzoic esters* were determined by saponification with excess potassium hydroxide in ethanol and isolation of the acid; the identification of chlorocyclohexylbenzoate will be described in a separate section on special or new compounds. (IV). The carbon tetrachloride addition products were isolated by rectification; their structures were not determined in view of the structural proofs given for the n-1,1,1,3-tetrachloroalkanes by *Kharasch* and his coworkers²⁾ The other compounds were isolated and identified as described in section IV. *Hexachloroethane* was never found, except with 3,3-dimethylbutene-1. (III d).

d) *Determinations of olefinic unsaturation.*

These were made by ozonometric titrations¹⁷⁾; in the case of the determination of telomerisation (Section B-2) the bromine addition method of *McIlhiney*¹⁸⁾ was employed.

¹⁴⁾ L. Schmerling et al., J. Am. Chem. Soc. 62, 2446 (1940).

¹⁵⁾ F. L. Howard et al., J. Res. Natl. Bur. Stand. 38, 365 (1947).

¹⁶⁾ H. Bredereck, as quoted in C. Weygand's „Organic Preparations”, Interscience, New York 1945, p. 356.

¹⁷⁾ H. Boer and E. C. Kooyman, Anal. Chim. Acta 1951, in press.

*) Our thanks are due to Dr. J. Beintema of this Laboratory for carrying out these analyses.

¹⁸⁾ P. C. McIlhiney, J. Am. Chem. Soc. 16, 275 (1894); 21, 1084 (1899); 24, 1103 (1902).

e) *Determination of carbon tetrachloride bound to cetene* (Cf. Sections B and D).

25 ml of cetene (87 millimoles), 25 ml of carbon tetrachloride (259 millimoles) and varying amounts of peroxide were heated in an oil bath at a temperature of $91\frac{1}{2} \pm \frac{1}{2}^{\circ}$ C. The remaining peroxide was then determined by titration (II b) and the solution was evaporated at reduced pressure below 75° C in order to avoid further decomposition of the peroxide. The last traces of carbon tetrachloride were then removed by gradually increasing the temperature to $115\text{--}120^{\circ}$ C and lowering the pressure to 0.1 mm Hg. The residual weight then indicates the sum of cetene intake, carbon tetrachloride bound to olefin and non-volatile peroxide decomposition products. A small correction was applied to account for volatile peroxide decomposition products, based on the results obtained with heptene-1. Thus, besides the remaining peroxide, 50% of the peroxide decomposed had to be subtracted. Duplicate experiments seldom showed deviations of more than 50 mg, indicating this method to be satisfactory. Cetene appeared to remain completely behind, as was established in a series of control experiments with cetene and carbon tetrachloride alone.

In the experiments with retarders, the latter were chosen either sufficiently volatile to be quantitatively removed by distillation or to remain behind. The amounts of carbon tetrachloride bound were then compared with those obtained in the absence of retarders on the basis of otherwise identical conditions of peroxide intake and decomposition.

III. *Addition experiments.*a) *With cyclohexene.*

1760 g of carbon tetrachloride (11.4 moles), 246 g of cyclohexene (3.03 moles) and 36 g (0.145 moles) of benzoyl peroxide were refluxed for forty hours, the temperature remaining between 78 and 80° C. Carbon dioxide (2.43 g, 55 millimoles or 19% based on peroxide) was absorbed in a sodium hydroxide trap connected to the top of the condenser. The peroxide had nearly completely decomposed, titration of a sample indicating the presence of only 100 mg. Olefinic unsaturation had decreased from 3.03 moles to 2.34 moles, indicating that about 0.69 moles of olefin had been converted.

The reaction product (2011 g, losses 27 g, or 1.4%) was split up into three fractions A, B and C (Cf. Section II, a):

| | |
|---|-------------|
| Intake | 2011 g |
| Fraction A (b.p. below 85° C) | 1820 g |
| Fraction B (85° C— 85° C/100 mm Hg) | 5 g |
| Fraction C (above 85° C/100 mm Hg) | 159 g |
| Total | 1984 g |
| Losses | 37 g (1.9%) |

A contained chloroform (35 g, 96% based on peroxide), benzene (2.1 g or 8% on peroxide) and unreacted carbon tetrachloride and cyclohexene. The refractionation of the other fractions gave a number of cuts, which were combined according to similarity in refractive indices when boiling within the same range.

Total intake 144 g after removal of benzoic acid with sodium bicarbonate solution

C_1 : b.p. 71—80° C/100 mm Hg, $n_D^{20} = 1.4950$ (7 g, mixture of chlorobenzene and 3-chlorocyclohexene, 10 and 11 % based on peroxide, respectively);

C_2 : 115—135° C/30 mm Hg, $n_D^{20} = 1.5110$ (17.8 g, mainly 3,3'-dicyclohexenyl, 60 % based on peroxide);

C_3 : 148—150° C/30 mm Hg, $n_D^{20} = 1.5251$ (60.3 g 1-chloro-2-trichloromethyl cyclohexane, 89 % based on peroxide);

C_4 : 135—161° C/5 mm Hg, $n_D^{20} = 1.5356$ (38 g, 1-chlorocyclohexyl-2-benzoate, 55 % based on peroxide).

Residue 8 g, containing 2.2 g of benzoic acid present as benzoates (6 %). Total output 123.1 g plus 8 g residue. Losses 13 g, which were partly present as intermediate fractions. Converted olefin accounted for: $(0.03 + 0.17 + 0.26 + 0.16 = 0.62$ moles, or 90 %).

Fractions C_1/C_4 were redistilled and identified as indicated in Section IV. The percentages recorded in tables I and II of the theoretical part apply to the above fractions without corrections for losses.

b) *With n-heptene-1.*

1839 g of carbon tetrachloride (12 moles), 392 g of heptene (4 moles) and 20.0 g of benzoyl peroxide (0.081 moles) were refluxed for five hours, after which the peroxide had completely decomposed. The products were worked up as described for cyclohexene. The tetrachlorooctane fraction contained a forerun (10 g, b.p. 120—129° C/19 mm Hg which showed a lower chlorine content as compared with the main fraction, viz. 50.8 % instead of 56.3 %; trichlorooctane requires 49.0 % Cl. Attempts at hydrolyzing this product — by means of 85 % sulphuric acid — to caprylic acid failed. The acid(s) formed still contained some chlorine. As a result of the large quantity of tetrachlorooctane present and the high boiling points of all products, no benzoic esters could be isolated in a pure form. The residue remaining after distillation of tetrachlorooctane was therefore saponified in order to isolate benzoic acid.

The tetrachlorooctane was obtained in 79 % yield based on heptene (793 g). $n_D^{20} = 1.4772$; b.p. 130° C/19 mm Hg; chlorine content 56.2 %; tetrachlorooctane requires 56.3 % Cl.

c) *With propene* *).

These experiments were carried out and evaluated in the same way as described for the other two olefins. From 4 litres of carbon tetrachloride (41 moles), 2½ kg of a propene/propane mixture (17 moles of propene, 45 moles of propane) and 100 g of benzoyl peroxide (0.40 moles), 1850 g of tetrachlorobutane were obtained (55 % on propene intake). By-products isolated: isopropyl chloride, chloroform, benzene, chlorobenzene, benzoic acid, 1,1,1-trichloro-n-butane, 1-phenyl-2-chloropropane 1,1,1,5-tetrachloro-3-methyl-hexane and unidentified benzoic esters (Cf. Section IV).

d) *Experiments with 3,3-dimethylbutene-1.*

1) Addition of carbon tetrachloride under the influence of traces of peroxide. 25 ml of carbon tetrachloride (about 259 millimoles) and 10 ml of the hexene

*) This experiment is also described in a forthcoming paper on pyrolysis products of tetrachlorobutane by one of the present authors (E. C. K.).

(78 millimoles) were heated in a sealed tube placed in a steam bath for three hours. 15 mg of benzoyl peroxide was used as the initiator (0.06 millimoles). After working up by distillation, the addition product (1,1,1,3-tetrachloro-4,4-dimethyl pentane) was obtained as a colourless liquid of camphorlike odour: 7.8 g (42%), b.p. $105^{\circ}/20$ mm Hg, $n_D^{20} = 1.4834$, $d_4^{20} = 1.265$. MR_D from these data: 53.96, calculated from Eisenlohr's tables: 53.99. 42 millimoles of olefin were recovered.

Calculated for $C_6H_{12} \cdot CCl_4$ (238): C 35.2%; H 5.05%; Cl 59.7%.

Found: C 35.1%; H 5.0%; Cl 59.1%.

In a similar experiment with 24 mg of peroxide (0.1 millimole, or 0.13% molar based on the olefin), the yield amounted to 80% of theory (14.8 g). In the latter experiment, a small amount (a few mg) of crystals were observed sublimating into the condenser after unreacted olefin and carbon tetrachloride had been removed. These melted at 181° C in a closed capillary; no depression of this melting point was observed with an authentic sample of *hexachloroethane*.

2) Competitive additions of dimethylbutene and cetene.

30 ml of carbon tetrachloride (312 millimoles), 5 ml of dimethylbutene (39 millimoles) and 15 ml of cetene (52 millimoles) were reacted with 252 mg of benzoyl peroxide (1.0 millimoles). After heating in a steam-bath for five hours, the mixture was worked up by distillation. No peroxide could be detected. 11 millimoles of dimethylbutene were recovered, whereas only 2 millimoles of cetene remained after the removal of carbon tetrachloride. Therefore, the cetene was converted nearly quantitatively, whereas about 72% of the dimethylbutene was converted. In a similar experiment with 150 mg of peroxide these figures were 60% and 35% respectively.

3) Retardation of the addition to dimethylbutene by allylbenzene. 25 ml of CCl_4 (259 millimoles), 10 ml of dimethylbutene (78 millimoles) and 0.8 ml of allylbenzene (6.1 millimoles) were reacted with 250 mg of benzoyl peroxide (1.01 millimoles) at 100° C for four hours. Although 250 mg of benzoyl peroxide decomposed, as much as 31 millimoles of olefin had not reacted; distillation revealed that at least 25 millimoles of this was 3,3-dimethylbutene-1. In an experiment with twice the amount of allylbenzene (1.6 ml or 12.2 millimoles), the amount of unreacted dimethylbutene amounted to 50 millimoles.

e) *With allylbenzene.*

200 ml of carbon tetrachloride (2.8 moles), 50 ml allylbenzene (353 millimoles based on ozonometric titration) and 2.0 g of benzoyl peroxide (8.2 millimoles) were refluxed for five hours; the peroxide had then completely decomposed. After removal of unreacted CCl_4 and allylbenzene, the residue amounted to only 16 g; 35 g (300 millimoles) of allylbenzene were recovered. Upon distillation at 0.3 mm Hg, 12 g of allylbenzene-carbon tetrachloride addition product were obtained, b.p. $99-101^{\circ}$ C. Yield 12% of theory, or about $5\frac{1}{2}$ millimoles per millimole of peroxide decomposed. The addition product showed an n_D^{20} of 1.5478 and a d_4^{20} of 1.3290. Chlorine content 50.8%. $C_{10}H_{10}Cl_4$ requires 52.1% of Cl. No attempts were made to establish the structure of the product; probably, it is 1,1,1,3-tetrachloro-4-phenylbutane. Similar experiments with a lower peroxide/allylbenzene ratio gave even smaller yields of the same addition product.

IV. Identifications of special products.

a) *Products formed from cyclohexene* (Cf. IIIa, fractions C_1 , C_2 , C_3 and C_4).

3-Chlorocyclohexene (fraction C_1) appeared to be present in the chlorobenzene

fraction (b.p. 130—140° C). Upon redistillation, a compound boiling at 139—141° C was obtained, which contained 0.85 double bond equivalents per 100 mg (calc. for chlorocyclohexene 0.86). The chlorine content amounted to 30.4% (calc. 30.2%); $n_D^{20} = 1.4880$.

Upon oxidation with potassium permanganate in acetic acid, an acid was obtained which analyzed correctly for a chloroadipic acid:

Calculated for $C_6H_8O_4Cl$ (180.5): C 39.9%; H 5.0%; Cl 19.7%.
 Found: eq.wt. 90: C 40.0%; H 5.1%; Cl 19.6%.

The melting point of this acid was 99° C, it was readily soluble in water and in alcohol. As the two chloroadipic acids were unknown in the literature, a sample of the 1-isomer was prepared from 3-chlorocyclohexene as described for the unknown chlorocyclohexene: 2-chloroadipic acid was made by nitric acid oxidation of 4-chlorocyclohexanol. The melting points of the isomers amounted to 99° C and 153—154° C, respectively. No depression was observed when taking a mixed melting point of the unknown chloroadipic acid with the 1-chloro compound (99—100°), whereas a marked depression was found with the 2-isomer (95—136°). These facts form conclusive evidence that the chlorocyclohexene formed in our experiments with cyclohexene was the 3-isomer.

1-Chloroadipic acid: 3-Chlorocyclohexene was made by treating cyclohexadiene-1,3 with hydrogen chloride¹⁹). Boiling point 84° C/100 mm, $n_D^{20} = 1.4886$.

2 g (17 millimoles) of the halide were dissolved in 20 ml of glacial acetic acid and treated with 5 g (32 millimoles) of $KMnO_4$ at 10° C for two hours. After evaporation of the excess acetic acid, the residue was shaken with water and then treated with sulphur dioxide in order to dissolve the manganese dioxide. A semi-solid product was obtained after extracting the aqueous solution with ether and evaporating the solvent; it was recrystallized from a small amount of chloroform. Yield 0.8 g (27%). The acid appeared to be readily soluble both in water and in alcohol. M.p. 101° C. Chlorine content 19.6%, eq.wt. 90.

2-Chloroadipic acid: 4-Chlorocyclohexanol was made from 1,4-cyclohexanediol and HCl as indicated by Owen and Robins²⁰). The oxidation of the chlorocyclohexanol was carried out with nitric acid, following the directions of Ellis²¹) for the preparation of adipic acid from cyclohexanol. Yield 42% of theory. Found: C 40.1%; H 5.0%; Cl 19.6%; equivalent weight 90.

2-Chloroadipic acid melts at 153—154° C; it is much less soluble in water and in other solvents than the 1-isomer. A sample of 2-chloroadipic acid prepared by permanganate oxidation of 4-chlorocyclohexene, made by dehydrating 4-chlorocyclohexanol with potassium hydrosulphate, showed the same melting point as that prepared by oxidation of 4-chlorocyclohexanol with nitric acid.

Surprisingly, both 3-chlorocyclohexene and 4-chlorocyclohexene yielded succinic acid when oxidizing their ozonides with hydrogen peroxide (m.p. and mixed m.p. 186; equivalent weight 59). The same acid was also obtained by oxidation of the ozonide formed from fraction C_1 .

Dicyclohexenyl (fraction C_2) boiled at 120—125° C/21 mm Hg; according to ozonometrical titration it contained 0.96 double bond equivalents per 100 g.

¹⁹) F. Hoffmann and P. Damm, Mitt. Kohlenf. Inst. Breslau, 2, 127 (1925) C. 1926, I, 2342.

²⁰) L. N. Owen and P. A. Robins, J. Chem. Soc. 1949, 320.

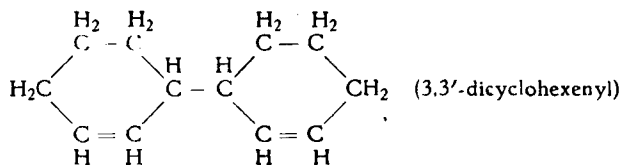
²¹) The directions were followed which are given by Ellis (Org. Synth., Coll. Vol. I., p. 18) for the nitric acid oxidation of cyclohexanol to adipic acid.

whereas dicyclohexenyl requires 1.23. A small amount of halogen compounds was also present. The mixture was therefore converted into tetrabromo-dicyclohexyl by means of the calculated amount of bromine in carbon tetrachloride. After evaporation of the solvent, the product was recrystallized from ethanol to give white crystals of m.p. 155—156° C. *Farmer* and *Michael* (l.c.) give m.p. 158—159° C.

Calculated for $C_{12}H_{18}Br_4$ (482): C 29.9 %; H 3.75 %; Br 66.35 %.

Found: C 30.1 %; H 3.9 %; Br 65.5 %.

No depression of the melting point was caused when mixing this sample with an authentic sample *) of 2,3,2',3'-tetrabromodicyclohexyl: 156—157° C. This was prepared by reacting 3-bromocyclohexene with magnesium in ether according to *Hoffmann* and *Damm* ¹⁹). The 3,3'-dicyclohexenyl thus formed boiled at 110° C/12 mm Hg $n_D^{20} = 1.5100$ (The German authors gave 103° C at 8 mm Hg). The compound analyzed 2.00 double bonds per molecule. The 3-bromocyclohexene was prepared according to *Ziegler* ²²) by bromination of cyclohexene with N-bromosuccinimide. From the above, the structure of the dicyclohexenyl isolated is concluded to be:



1-Chloro-2-trichloromethylcyclohexane (fraction C_3): This compound boiled at 149° C/30 mm Hg; $n_D^{20} = 1.5241$, $d_4^{20} = 1.395$, $MR_D = 51.91$; from *Eisenlohr's* values: 51.79.

Calculated for $C_7H_{10}Cl_4$ (236): C 35.6 %; H 4.2 %; Cl 60.2 %.

Found: C 36.0 %; H 4.2 %; Cl 59.7 %.

2-Chlorocyclohexyl benzoate (fraction C_4) boiled at 130—135° C/0.3 mm Hg; $n_D^{20} = 1.5356$. It has not been reported in the literature.

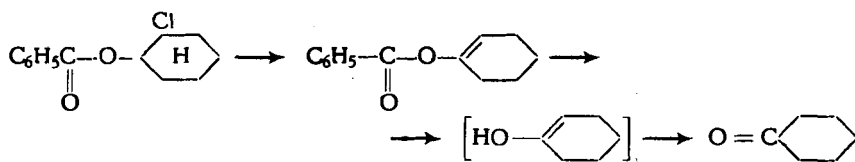
Calculated for $C_{13}H_{15}O_2Cl$ (238½): C 65.4 %; H 6.3 %; Cl 14.9 %.

Found: C 65.9 %; H 6.6 %; Cl 14.9 %.

Saponification with alcoholic potassium hydroxide yielded hydrogen chloride, benzoic acid and cyclohexanone. The latter was identified in the form of its 2,4-dinitrophenyl hydrazone, m.p. and mixed m.p. with an authentic sample 156—157° C. From 2.1 g of the ester, 0.99 g of benzoic acid were obtained (47 % required 51.2 %). These data prove that the compound is a chlorocyclohexyl benzoate having the two functional groups either at the same or at adjacent carbon atoms of the cyclohexane ring. As cyclohexene had formed the starting material, the latter structure is the only plausible possibility. The formation of cyclohexanone from the benzoate may proceed by way of the enol benzoate of cyclohexanone:

*) We are indebted to Dr. *H. Boer* of this Laboratory for preparing this sample.

²²) *K. Ziegler* et al. *Ann.* **551**, 80 (1942).



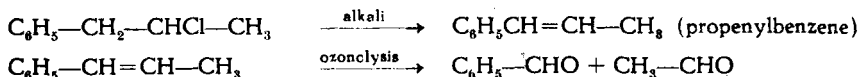
The enol form of cyclohexanone is stated by *Grignard and Blanchon*²³) to rearrange rapidly to the ketone; it could not be isolated as such. An alternative interpretation would be the intermediate formation of cyclohexene oxide (via the chlorohydrin) which then rearranges to cyclohexanone.

b) *Products formed from propene* (cf. IIIc).

Isopropyl chloride boiled at 34.5–36° C; $n_D^{20} = 1.3797$, Lit.: 35° C, $n_D^{20} = 1.3792$. It did not react with bromine water, but gave a strongly positive Beilstein test for halogen. Because of these data and of the characteristic odour, no further identification was considered necessary.

1,1,1-Trichloro-n-butane was detected in the chlorobenzene fraction, b.p. 129–131° C. Assuming only a single contaminant, the chlorine content, refractive index and density of this fraction indicated the presence of an aliphatic polychloro compound. Hydrolysis with sulphuric acid (85%) yielded *n*-butyric acid, b.p. 164° C, equivalent weight 88; m.p. *p*-bromophenacyl ester 63° C. The latter m.p. was not depressed by admixing an authentic sample of the ester. Pure chlorobenzene was simultaneously formed. On the basis of the chlorine content of the original product (38.6%, chlorobenzene requires 31.6%, trichlorobutane 71.4% Cl) the amount of trichlorobutane should be about 20% by weight, or 15% molar calculated on chlorobenzene. 1,1,1-Trichlorobutane is the only halide capable of giving *n*-butyric acid upon hydrolysis, *n*-butyrylchloride being excluded because of its low boiling point (102° C), low chlorine content (33.3%) and ready hydrolysis upon shaking with water.

1-Phenyl-2-chloropropane. Boiling point 92–93° C/19 mm Hg; $n_D^{20} = 1.5134$. Chlorine content 26.0%, required 23.0%. Treatment with alkali in ethanol gave propenylbenzene, b.p. 174–177° C; this compound contained 0.96 double bonds per molecule and showed an n_D^{20} of 1.5473 (propenylbenzene is reported to have a b.p. 175° C and n_D^{20} of 1.5492). Ozonolysis of the olefin gave benzaldehyde and acetaldehyde, which were identified in the form of the corresponding 2,4-dinitrophenylhydrazones. These could be readily separated by chromatographical absorption, using silicic acid as the absorbent and a pentane-ether mixture as the eluent. Melting points and mixed m.p. with authentic samples 238–239 and 239–240, 158–160 and 160–161° C, respectively. These data indicate the phenylchloropropane to be either the 1,2 or the 1,1-derivative; the latter is very unlikely because propene had been the starting material. The following equations are representing the formation of benzaldehyde and acetaldehyde from 1-phenyl-2-chloropropane:



²³) *V. Grignard and H. Blanchon, C.A. 24, 1342 (1930).*

1-Phenyl-2-chloropropané has not been described in the literature; as the chlorine content of the fraction which was converted into propenylbenzene was some 3% high, our sample was not quite pure.

1,1,1,5-Tetrachloro-3-methylhexane. Boiling point 123° C/23 mm Hg. Camphorlike odour. $n_D^{20} = 1.4829$; $d_4^{20} = 1.2534$. MR_{11} from these data: 54.21; from Eisenlohr's values: 53.99.

Calculated for $C_8H_{12}CCl_4$ (238): C 35.3%; H 5.05%; Cl 59.7%.

Found: C 35.5%; H 5.0%; Cl 59.6%.

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