oxygen-containing solvents. This work has now been continued, particularly to study the effect of high proton concentrations in the chlorination reaction. For this purpose 1-hexyne was chlorinated as an emulsion in concentrated hydrochloric acid, 30%[4] sulfuric acid and 30%[4] phosphoric acid and as a solution in methanol previously saturated with hydrogen chloride. The various experiments gave complex mixtures of hexyne chlorides as shown in Table I. Fortunately the individual substances boil sufficiently far apart to permit their separation by fractional distillation through an efficient column.

TABLE I

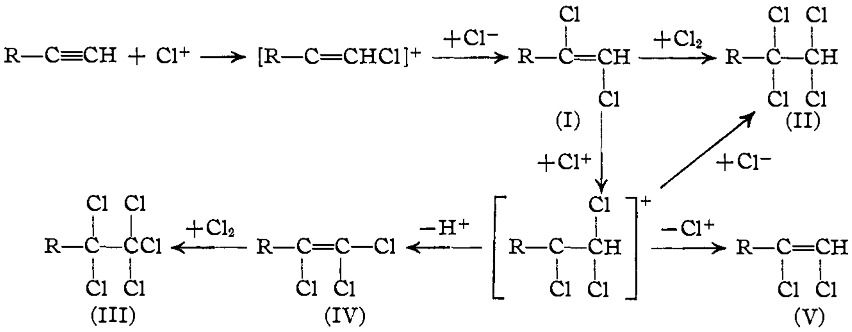
WEIGHTS OF REAGENTS AND PRODUCTS IN THE CHLORINATION OF ONE MOLE OF 1-HEXYNE AT 40–50°

Reagents			Products, R is n-C_4H_9				
Solvent	Vol., ml.	Cl_2, g.	$R\overset{Cl}{C}=\overset{Cl}{C}H$	$R\overset{Cl}{C}=\underset{Cl}{C}H$	$R\overset{Cl}{C}=\overset{Cl}{C}Cl$	$R\underset{Cl}{\overset{Cl}{C}}-\underset{Cl}{\overset{Cl}{C}}H$	$R\underset{Cl}{\overset{Cl}{C}}-\underset{Cl}{\overset{Cl}{C}}Cl$
35% HCl-H_2O	300	176	23	26	25	11	14
30% H_2SO_4-H_2O	300	150	25	25	30	8	14
30% H_3PO_4-H_2O	300	115	24	30	36	10	17
22% HCl-MeOH	400	122	45	16	65	18	6

It is noteworthy that *cis*-1,2-dichloro-1-hexene (V) was obtained in each case as well as the anticipated *trans* isomer (I) and that oxygen-containing compounds were not isolated. In methanol[2] and in water,[3] to which acid has not been added, the *trans* dichloride is obtained as well as oxygen-containing products.

The trichloride (IV) listed in Table I previously was formulated[3] as 1,2,2-trichlorohexane. It appears now that this compound actually is 1,1,2-trichloro-1-hexene and is the precursor of the pentachloride (III). Attempts[5] to prepare 1,2,2-trichlorohexane from 1-hexyne have failed. Neither *cis*- nor *trans*-1,2-dichloro-1-hexene could be made to add hydrogen chloride.

Chlorination of 2-chloro-1-hexene in carbon tetrachloride also failed to give the anticipated trichlorohexane, but yielded rather *cis*-1,2-dichloro-1-hexene (V) and 1,1,2,2-tetrachlorohexane (II). The following mechanism explains satisfactorily the various products obtained in the present investigation.



The experimental procedure and analyses and physical constants for the products have been cited previously[3] and need not be repeated. However, the product having b. p. 90–93° at 10 mm.; $n^{25}D$ 1.4760; d^{25} 1.225 now is reported as 1,1,2-trichloro-1-hexene rather than as 1,2,2-trichlorohexane.

CHEMICAL LABORATORY
UNIVERSITY OF NOTRE DAME
NOTRE DAME, INDIANA

RECEIVED NOVEMBER 20, 1939

---

[4] Concentration by volume.

[5] Unpublished work, Chas. Welsh and G. F. Hennion.

Remarks on "A New Method for the Cleavage of Unsaturated Fatty Acids"

BY DONALD PRICE AND RICHARD GRIFFITH

Under the above title Chi-yi Hsing and Kou-jen Chang [THIS JOURNAL, **61**, 3589 (1939)] report the application of Criegee's[1] lead tetraacetate oxidation to polyhydroxy fatty acids, which are readily obtained from the corresponding unsaturated acids by oxidation with alkaline permanganate. They describe in detail the oxidation of 9,10-dihydroxyoctadecanoic acid, the cleavage products of which were found to be pelargonic aldehyde and the hemialdehyde of azelaic acid.

These authors seem to have overlooked the fact that Criegee's method previously was applied to the same as well as other acids by Nunn and Smedley-MacLean, *Biochem. J.*, **29**, 2742 (1935),

---

[1] Criegee, *Ber.*, **64**, 260 (1931); *Ann.*, **481**, 263 (1930); **507**, 159 (1933).

with the identical results obtained by them. It was also applied similarly by Raudnitz, Schindler and Petru, *Ber.*, **68**, 1675 (1935), to the determination of the structure of aleuritic acid. More recently Mr. Daniel Swern of the Bureau of Agricultural Chemistry and Engineering, U. S. Department of Agriculture read a paper at the Boston meeting of the American Chemical Society on Sept. 12, 1939, entitled, "Action of Lead Tetraacetate upon Hydroxylated Oils, Fats, Fatty Acids, and Related Compounds."

RESEARCH LABORATORY
NATIONAL OIL PRODUCTS COMPANY
HARRISON, N. J.
RECEIVED DECEMBER 30, 1939

Hydrogen Fluoride as a Condensing Agent. IX.[1] Reactions of Di- and Triisobutylene with Phenol

BY J. H. SIMONS AND S. ARCHER

In connection with other work, it became necessary to determine whether or not highly branched aliphatic olefins would react with aromatic compounds to give normal or cleaved products. It is known that in the presence of large amounts of sulfuric acid, diisobutylene reacts with phenol to give cleaved products, but with small quantities of the acid the uncleaved product is obtained.[2] The same olefin reacts with toluene in liquid hydrogen fluoride to give mono and di-*t*-butyltoluene.[3]

We have found that under conditions similar to those employed by Calcott and co-workers, di- and triisobutylene both react to give *p*-*t*-butylphenol as the only monoalkylated phenol. However, by employing milder conditions it was possible to effect condensation without cleavage in the case of diisobutylene. By using a small amount of 70% hydrofluoric acid at 0°, *p*-*t*-octylphenol was isolated unaccompanied by any cleavage products. Under the same conditions dodecylphenol was not isolated when the twelve-carbon olefin was employed, although even this might be accomplished under even milder conditions.

The triisobutylene used was the so-called "lower isomer," which consists chiefly of dineopentylethylene and methylneopentyl-*t*-butylethylene. The diisobutylene was the usual commercial product, dried and redistilled, the fraction boiling at 100–103° being used.

Experimental

Phenol and Diisobutylene

A. Large Quantities of Hydrogen Fluoride.—To 121 g. of hydrogen fluoride contained in a copper flask, was added a solution of 94 g. of phenol in 300 cc. of carbon tetrachloride. One mole of the olefin was dropped in with constant stirring, the reaction being kept at 0°. After twenty-four hours the reaction was stopped and then treated in the usual way. Distillation gave 88 g. of *t*-butylphenol, m. p. 97–98.5°, 14 g. of a fraction boiling at 165–185° (28 mm.), and a residue of 41 g. The higher boiling fraction did not solidify even after standing for some weeks.

B. Small Quantities of Hydrogen Fluoride.—A mixture of 20 g. of 70% hydrofluoric acid, 56 g. of the olefin, and 47 g. of phenol was kept at 0° for forty-eight hours. After the usual treatment, distillation gave 35 g. of *p*-*t*-octylphenol, m. p. 82–83°, and recovered phenol. When mixed with an authentic specimen there was no depression in melting point.

Phenol and Triisobutylene

A. Large Quantities of Hydrogen Fluoride.—One mole of phenol was dissolved in 300 cc. of carbon tetrachloride and added to 122 g. of hydrogen fluoride maintained at 0°. To this mixture one mole of the olefin was added slowly. After being stirred for twenty-four hours, the reaction was stopped. Removal of the solvent left a residue of 206 g. of which 64 g. boiled at 152–160° (38 mm.) and melted at 96–97°. This was *t*-butylphenol. The remainder of the material boiled over a wide range and probably consisted of the polybutylphenols.

B. Small Quantities of Hydrogen Fluoride.—Equimolar quantities of the olefin and the phenol were mixed and added to 20 g. of 70% hydrogen fluoride. After sixty hours the usual procedure was followed and the product treated with Claisen solution.[4] The latter, when examined, did not give any compound that corresponded to a dodecylphenol. When 33 g. of anhydrous hydrogen fluoride was used with 105 g. of phenol and 174 g. of the olefin, for a reaction time of fourteen hours, 52 g. of *t*-butylphenol and considerable residual phenolic material were obtained.

---

(1) For previous paper of this series, see THIS JOURNAL, **61**, 1821 (1939).

(2) Ipatieff, Pines and Friedman, *ibid.*, **60**, 2495 (1938).

(3) Calcott, Tinker and Weinmayr, *ibid.*, **61**, 1010 (1939).

(4) Claisen, Eisleb and Kremers, *Ann.*, **418**, 96 (1919).

DEPARTMENT OF CHEMISTRY
THE PENNSYLVANIA STATE COLLEGE
STATE COLLEGE, PENNSYLVANIA
RECEIVED DECEMBER 1, 1939

Activity Coefficients in Concentrated Aqueous Solutions of Strong Electrolytes Described by Means of a Formula Containing the Mean Ionic Diameter as Single Parameter. II. Corrected Formulation

BY PIERRE VAN RYSSELBERGHE AND SYLVAN EISENBERG

In a previous paper of the same title[1] a formula with a single parameter was set up which provided

---

(1) P. Van Rysselberghe and S. Eisenberg, THIS JOURNAL, **61**, 3030 (1939).