determined for three representative hydroxy compounds.

3. The role of hydroperoxides and their decomposition products in autoxidation has been further investigated.

PITTSBURGH, PENNSYLVANIA RECEIVED AUGUST 9, 1948

[CONTRIBUTION FROM THE NAVAL RESEARCH LABORATORY]

Pyrolysis and Chlorinolysis of Some Perchlorinated Unsaturated Hydrocarbons[1]

BY J. A. KRYNITSKY AND H. W. CARHART

In earlier work,[2] it was shown that the pyrolysis of octachlorocyclopentene yields hexachlorocyclopentadiene, chlorine and small amounts of hexachlorobenzene. It has been reported[3] that both hexachloroethane and octachloropropane give carbon tetrachloride and tetrachloroethylene on thermal decomposition. Carbon tetrachloride and tetrachloroethylene have been reported[4] as being highly stable.

Prins[6,7] has shown that one mole of chlorine adds rapidly and quantitatively in sunlight to tetrachloroethylene, hexachloropropene and hexachlorocyclopentadiene without causing rupture of the carbon chain. On the other hand, hexachloroethane,[3] hexachloro-1,3-butadiene,[5] octachloro-1,3-pentadiene,[7,8] and octachlorocyclopentene,[2,8,9,10] have been reported either to resist the action of chlorine or, under drastic conditions, to be cleaved by it.

In the present work, tetrachloroethylene, hexachloropropene, hexachloro-1,3-butadiene and octachloro-1,3-pentadiene were subjected both to vapor phase pyrolysis and to the action of chlorine at temperatures up to 500°. In addition, hexachloropropene and octachloro-1,3-pentadiene were exposed to prolonged heating in the liquid state at their reflux temperatures and to chlorination under similar conditions. Small samples of two isomeric C_6Cl_8 compounds having melting points of 43–44° and 182–183° were also decomposed at 500°, and a sample of hexachloro-1,3-butadiene was treated with chlorine in bright sunlight for an extended period of time.

Results and Discussion

Pyrolyses.—Both tetrachloroethylene and hexachloro-1,3-butadiene were found to be quite thermostable as no pyrolysis products were found on heating at 500°.

Hexachloropropene was recovered unchanged after a six-hour reflux (210–213° pot temperature). Vapor phase pyrolysis became appreciable at temperatures over 400° and yielded carbon tetrachloride, tetrachloroethylene and hexachloroethane as the major products. The amounts of these products obtained are summarized in Table I. In addition to these, a minor quantity of hexachlorobenzene was isolated from the 490–500° pyrolysis but not at the lower temperatures. A compound, C_6Cl_8 (m. p. 43–44°), was also obtained from the products of pyrolysis at 450–460° and 490–500°. It is believed that this compound is the same as the C_6Cl_8 (m. p. 45°) prepared by Prins[11] to which he assigns the structure 1-(trichloromethyl)-pentachloro-2,4-cyclopentadiene. In the pyrolysis of hexachloropropene, carbonization was insignificant and very little, if any, chlorine was evolved. In contrast to hexachloropropene, prolonged refluxing decomposed octachloro-1,3-pentadiene completely. The principal products of the reflux and vapor phase pyrolyses were carbon tetrachloride, hexachloro-1,3-butadiene and hexachlorocyclopentadiene. The amounts of these compounds and hexachlorobenzene found are given in Table II. Small amounts of hexachloroethane were obtained from the vapor phase but not from the reflux pyrolyses. Traces of tetrachloroethylene were found in all but the 400–410° pyrolyses. Two other compounds, octachlorocyclopentene and C_6Cl_8 (m. p. 182–183°) were isolated from the products of the reflux pyrolysis. The latter compound was shown to be identical with a C_6Cl_8 compound prepared by Prins[6] to which he assigns the probable structure 1-(dichloromethylene)-hexachloro-2-cyclo-

TABLE I

PRINCIPAL PYROLYSIS PRODUCTS OF HEXACHLOROPROPENE

Temp., °C.	Moles product/mole starting material			
	CCl_4	C_2Cl_4	C_2Cl_6	C_3Cl_6 (recovered)
Reflux[a]	0	0	0	*ca.* 1
400–410	Trace	0.03	0.01	0.94
450–460	0.04	.28	.12	.57
490–500	.11	.67	.21	Trace
490–500	.14	.70	.24	Trace

[a] Refluxed six hours. Pot temperature, 210–213°.

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(1) The opinions contained in this paper are the authors' and are not to be construed as official or reflecting the views of the Department of the Navy.

(2) Krynitsky and Bost, THIS JOURNAL, **69**, 1918 (1947).

(3) McBee, Hass, *et al.*, *Ind. Eng. Chem.*, **33**, 176 (1941).

(4) Hurd, "The Pyrolysis of Carbon Compounds," Reinhold Publishing Corp., New York, N. Y., 1929, p. 132. It is also stated that hexachloro-1,3-butadiene is quite thermostable; however, Fruhwirth[5] has shown that the compound previously thought to have been hexachloro-1,3-butadiene was in all probability octachlorocyclopentene.

(5) O. Fruhwirth, *Ber.*, **74B**, 1700 (1941).

(6) H. J. Prins, *J. prakt. Chem.*, **89**, 414 (1914).

(7) H. J. Prins, *Rec. trav. chim.*, **65**, 455 (1946).

(8) Bost and Krynitsky, THIS JOURNAL, **70**, 1027 (1948).

(9) McBee, Hass and Pierson, *Ind. Eng. Chem.*, **33**, 181 (1941).

(10) McBee, Hass and Bordenca, *ibid.*, **35**, 317 (1943).

(11) H. J. Prins, *Rec. trav. chim.*, **65**, 184 (1946).

TABLE II

PRINCIPAL PYROLYSIS PRODUCTS OF OCTACHLORO-1,3-PENTADIENE

Temp., °C.	Moles product/mole starting material CCl₄	C₄Cl₆	C₅Cl₆	C₆Cl₆	C₅Cl₈ (recov.)
Reflux[a]	0.32	0.55	0.08	0.22[b]	0
400-410	.01	.03	.04	0	0.86
450-460	.22	.36	.30	.02	.25
490-500	.37	.42	.39	.08	0

[a] Refluxed five hours. Pot temperature, 261-279°. [b] Combined C_6Cl_8 and C_6Cl_6. Calcd. as C_6Cl_7.

pentene.[11] In the pyrolyses of octachloro-1,3-pentadiene, small amounts of chlorine were evolved; however, carbonization was insignificant.

When small samples of the two C_6Cl_8 isomers (m. p. 43-44° and 182-183°) were heated at 500°, hexachlorobenzene and chlorine were found to be the major products. However, the pyrolysis of the 43-44° compound was not as complete as that of the 182-183° isomer.

TABLE III

CHLORINOLYSIS PRODUCTS OF TETRACHLOROETHYLENE

Temp., °C.	Moles product/mole starting material C₂Cl₆	C₂Cl₄ (recovered)
350-360	Trace	0.99
400-410	0.01	.96
490-500	.06	.91

TABLE IV

CHLORINOLYSIS PRODUCTS OF HEXACHLOROPROPENE

Temp., °C.	Moles product/mole starting material CCl₄	C₂Cl₄	C₂Cl₆	C₃Cl₆ (recovered)
Reflux[a]	0.32	0.44	0	0.50
300-310	.08	.09	0	.88
350-360	.62	.69	0.02	.26
400-410	.92	.96	.04	0
490-500	.90	.90	.12	0

[a] Refluxed seven hours. Pot temperature, 207-211°.

TABLE V

PRINCIPAL CHLORINOLYSIS PRODUCTS OF OCTACHLORO-1,3-PENTADIENE

Temp., °C.	Moles product/mole starting material CCl₄	C₄Cl₆	*Cycl.* C₅Cl₆	*Cycl.* C₅Cl₈	C₅Cl₈ (recov.)
Reflux[a]	[b]	0.61	Trace	0.18	0
350-360	0.13	.14	0.05	[c]	.79[d]
400-410	.56	.59	.20	[c]	.16[d]
490-500	.60	.62	.27	0.04	0

[a] Refluxed seven hours [b] 0.48 found. An additional undetermined amount lost during recovery. [c] Undetermined. [d] Contains unknown amount of octachlorocyclopentene

Chlorinolyses.—Tetrachloroethylene was found to be stable toward chlorinolysis at temperatures up to 500° as no carbon tetrachloride was found. However, as shown in Table III, addition of chlorine did occur to a limited extent.

Hexachloro-1,3-butadiene was found to be inert to chlorination in the dark since no reaction products were found even at 500°. On the other hand, prolonged exposure to chlorine in bright sunlight at 10-20° cleaved this compound to hexachloroethane.

As may be seen in Table IV, the principal products of both the reflux and vapor phase chlorinolyses of hexachloropropene were found to be carbon tetrachloride and tetrachloroethylene. The vapor phase reaction became appreciable at temperatures above 300° and was complete at 400-410°. Small amounts of hexachloroethane were also found at the higher temperatures. In addition to the compounds mentioned, the reflux chlorinolysis produced a small amount of higher boiling material which was not identified.

Both reflux and vapor phase chlorinolyses of octachloro-1,3-pentadiene yielded carbon tetrachloride and hexachloro-1,3-butadiene as the major products. Lesser amounts of hexachlorocyclopentadiene and octachlorocyclopentene were also isolated from these reactions. The amounts of products obtained are summarized in Table V. In addition to these compounds, small quantities of tetrachloroethylene were found in all but the 350-360° reaction. Small amounts of hexachlorobenzene were also isolated from the reflux and 490-500° chlorinolyses.

In all reactions involving chlorine, carbonization was insignificant. The vapor phase chlorinolyses of both hexachloropropene and octachloro-1,3-pentadiene were observed to be exothermic. It is noteworthy that the chlorinolysis of these compounds is essentially complete at 400-410°. This is in contrast to their simple pyrolysis where decomposition is only slight at this temperature. There is insufficient evidence to substantiate complete mechanisms for these reactions; however, the results indicate that they probably proceed through free radical chain reactions involving several steps.

It was observed that hexachlorocyclopentadiene has a strong tendency to supercool. By using a Dry Ice-bath, however, two different crystalline forms may be obtained. One of these melts at 10-10.8° and the other at −0.8 to −0.2°. The lower melting form is converted to the higher melting form by sudden strong cooling (liquid air) or by seeding with a small crystal of the latter. In view of this and the fact that the higher melting form is the one more frequently obtained on freezing, it is indicated that it is the more stable form. Samples of both crystalline forms have remained unchanged when kept for several months at a temperature a few degrees below their melting points.

Experimental

Materials.—Hexachloropropene (b.p. 140-142° at 100 mm.) and octachloro-1,3-pentadiene (b.p. 139-140° at 10 mm.) were prepared through condensation and dehydrohalogenation reactions from chloroform, tetrachloroethylene and trichloroethylene as described by Prins.[6,7,12] Hexachloro-1,3-butadiene (b.p. 142-144° at 100 mm.) was obtained from the pyrolysis and chlorinolysis products

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[12] H. J. Prins, *ibid.*, **51**, 1065 (1932).

of octachloro-1,3-pentadiene. The two C_6Cl_8 compounds (m. p. 43–44° and 182–183°) were obtained from the pyrolysis products of hexachloropropene and octachloro-1,3-pentadiene.

Vapor Phase Pyrolyses.—In general, the vapor phase pyrolyses of tetrachloroethylene, hexachloropropene, hexachloro-1,3-butadiene and octachloro-1,3-pentadiene were carried out at 400, 450 and 500° by passing approximately 200 g. of compound through a 20-mm. Pyrex tube heated over a 30-cm. zone. The rate was adjusted so that the passage was between 70 and 120 g. per hour. This resulted in contact times which varied from twelve to fifteen seconds for the first three compounds and sixteen to twenty-four seconds for the last. All pyrolyses involving hexachloropropene and octachloro-1,3-pentadiene were carried out in the dark to prevent photocatalytic action of chlorine should it be formed. When evolution of chlorine was detected, it was removed from the warmed products by air aspiration in the dark using suitable traps for retaining volatile components. The pyrolysis of hexachloropropene at 500° will serve to illustrate the method used.

Two hundred grams of hexachloropropene was passed dropwise, in the dark, over a period of two hours through the tube set at a slight incline and electrically heated to 490–500°. The product which was collected in an ice-cooled receiver weighed 199 g., was red in color and contained some solid material. During the pyrolysis, tests of the exit vapors with potassium iodide paper showed that very little, if any, chlorine was evolved. Fractionation of the product through a 17 mm. × 60 cm. helix-packed column gave the following principal fractions: (1) 14 g. b.p. 77–78°, (2) 6 g. b.p. 78–120°, (3) 90 g. b.p. 120–122°, (4) 44 g. (solid) b.p. 123–130° (100 mm.), (5) 5 g. b.p. 130–150° (100 mm.), and (6) 17 g. b.p. 164–165° (20 mm.).

Fraction 1 was carbon tetrachloride and fraction 3 was tetrachloroethylene. Refractive index measurements showed fraction 2 to be composed of approximately 3 g. each of carbon tetrachloride and tetrachloroethylene. Fraction 4 was hexachloroethane which was collected as a solid in the still head. An additional 2 g. of hexachloroethane was obtained by cooling the intermediate fraction 5. Fraction 6 solidified on standing to a reddish-orange solid melting at 36–40°. Two recrystallizations from ethanol yielded 10 g. of a white compound melting at 43–44°, which was not changed by further treatment. Analyses showed this compound to be C_6Cl_8. *Anal.* Calcd. for C_6Cl_8: Cl, 79.74; mol. wt., 355.8. Found: Cl 79.7, 79.4; mol. wt., 354.

Ten grams of hexachlorobenzene was isolated from the fractionation residue by crystallization using carbon tetrachloride and ethanol.

Reflux Pyrolysis.—Octachloro-1,3-pentadiene (152 g.) was placed in a still pot fitted to a 17 mm. × 60 cm. helix-packed column connected to an ice-cooled receiver. The column jacket was maintained at 200–215° by an external heater. The material was heated for five hours in the dark at the end of which time reaction seemed to be complete. During this period, the pot temperature varied between 261 and 279° and a slight amount of chlorine was detected in the exit vapors. The free chlorine was removed from the warmed distillate (in the dark) by aspirating dry air through it until the effluent air gave a negative test for chlorine. A reflux condenser and efficient ice-cooled trap was used to prevent loss of volatile materials. The product obtained was combined with the residue in the still pot. Fractionation yielded the following principal fractions: (1) 22 g. b.p. 77–78°, (2) 1 g. b.p. 58–65° (100 mm.), (3) 58 g. b.p. 141–145° (100 mm.), (4) 8 g. b.p. 145–160° (100 mm.), (5) 7 g. b.p. 117–121° (20 mm.), (6) 12 g. b.p. 157–163° (20 mm.), and (7) 28 g. residue.

Fraction 1 was carbon tetrachloride. Fraction 2 was shown to be chiefly tetrachloroethylene by chlorination to hexachloroethane. On refractionation of fraction 3, the main bulk distilled at 143.0–143.1° (100 mm.). This was identified as hexachloro-1,3-butadiene through its physical constants which are in good agreement with those previously reported[5] and by analyses: b.p. 213° (775 mm.), 123° (50 mm.), 101° (20 mm.); m.p. −20 to −19°; n^{20}_{D} 1.5558, n^{25}_{D} 1.5535; d^{20}_{4} 1.6804. *Anal.* Calcd. for C_4Cl_6; Cl, 81.58; mol. wt., 260.8; *MR*, 48.94.[13] Found: Cl, 81.3, 81.6; mol. wt., 262; *MR*, 49.87.

Fraction 5 was identified as hexachlorocyclopentadiene by comparison with a known sample. Purified hexachlorocyclopentadiene has the following properties in addition to those given previously:[2,7,14] b.p. 163.6–163.8° (100 mm.), m.p. 10–10.8° and −0.8 to −0.2°, n^{20}_{D} 1.5647.

Refractive index measurements of fraction 4 showed it to be composed of approximately 5 g. hexachloro-1,3-butadiene and 3 g. hexachlorocyclopentadiene. On crystallizing fraction 6 from ethanol and carbon tetrachloride, there was obtained 3 g. of a compound m. p. 182–183° and 7 g. of octachlorocyclopentene. The 182–183° compound was shown to be identical to the C_6Cl_8 compound obtained by the action of copper on hexachloropropene, by a mixed melting point and by hydrolysis to a diketone[6] which melted at 226–228° (sealed tube).

Fractional crystallization of the 28 g. of residue from ethanol–carbon tetrachloride yielded several grams each of the C_6Cl_8 compound and hexachlorobenzene.

Pyrolyses of C_6Cl_8 Compounds at 500°.—Four grams of the 43–44° isomer was melted over four to five minutes into the heated zone (8 mm. × 30 cm.) of a Pyrex tube set at a slight incline. During this time, the exit vapors gave a strong test for chlorine. The pyrolysis product was a solid which when worked up with ethanol–carbon tetrachloride yielded approximately 1 g. of hexachlorobenzene. In addition, approximately 1.5 g. of C_6Cl_8 was recovered.

In a like fashion, 4 g. of the 182–183° isomer evolved chlorine and yielded approximately 2 g. of hexachlorobenzene and a very small amount of liquid which was not identified. None of the original C_6Cl_8 could be recovered.

Photochlorinolysis of Hexachloro-1,3-butadiene.—A 12.7-g. sample of hexachloro-1,3-butadiene was placed in a Pyrex test-tube fitted with a gas bubbler tube. The system was exposed to direct sunlight and chlorine was admitted in a slow stream. During this time, the ambient temperature varied from 10 to 20°. The reaction was stopped after a total of sixteen hours as the material had become semisolid. After removal of the unreacted chlorine by air aspiration through the warmed mixture, the sample showed a gain in weight of 6.3 g. The solid reaction product was identified as hexachloroethane.

Vapor Phase Chlorinolyses.—In general the vapor phase chlorinolyses of tetrachloroethylene, hexachloropropene, hexachloro-1,3-butadiene and octachloro-1,3-pentadiene were carried out in the dark at various temperatures up to 500° by passing approximately 200 g. of compound through a 20-mm. Pyrex tube heated over a 30 cm. zone. An ice-cooled receiver was used for collection of the products. Chlorine gas was admitted at a rate such that a bubbler at the end of the system indicated that an excess was always present. The rate of compound addition was between 70 and 120 g. per hour. Unreacted chlorine was removed from the warmed products (in the dark) by air aspiration using suitable traps to retain volatile components. The methods used for separation and identification of the products were the same as those given earlier.

Reflux Chlorinolyses.—The reflux chlorinolyses of hexachloropropene and octachloro-1,3-pentadiene were carried out in a manner similar to the reflux pyrolysis of the latter compound except that an excess of chlorine was maintained in the system by bubbling the gas into the liquid. The products were analyzed by methods already described.

Summary

1. Tetrachloroethylene and hexachloro-1,3-

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(13) Does not include value for exaltation due to conjugation.

(14) The melting point in ref. 2 was listed erroneously as −10 to −9° rather than 9–10°.

butadiene were found to be stable at a temperature of 500°.

2. The pyrolysis of hexachloropropene yielded principally carbon tetrachloride, tetrachloroethylene, and hexachloroethane. Smaller amounts of hexachlorobenzene and a compound C_6Cl_8 (m. p. 43–44°) were obtained under some conditions.

3. The pyrolysis of octachloro-1,3-pentadiene yielded principally carbon tetrachloride, hexachloro-1,3-butadiene and hexachlorocyclopentadiene. Smaller amounts of tetrachloroethylene, hexachloroethane, octachlorocyclopentene, hexachlorobenzene and a compound C_6Cl_8 (m. p. 182–183°) were obtained under some conditions.

4. The pyrolysis of two C_6Cl_8 compounds (m. p. 43–44° and 182–183°) yielded chiefly hexachlorobenzene and chlorine.

5. Hexachloro-1,3-butadiene yielded hexachloroethane slowly on chlorinolysis in sunlight at 10–20°. In the dark, it was found to resist the action of chlorine at a temperature of 500°.

6. Tetrachloroethylene was found to be stable to thermal chlorinolysis at temperatures up to 500°; however, small amounts of hexachloroethane were produced by addition of the halogen.

7. Thermal chlorinolysis of hexachloropropene yielded principally carbon tetrachloride and tetrachloroethylene and smaller amounts of hexachloroethane.

8. Thermal chlorinolysis of octachloro-1,3-pentadiene yielded carbon tetrachloride and hexachloro-1,3-butadiene as the principal products and lesser amounts of hexachlorocyclopentadiene and octachlorocyclopentene. Small amounts of tetrachloroethylene and hexachlorobenzene were also obtained under some conditions.

WASHINGTON, D. C. RECEIVED AUGUST 19, 1948

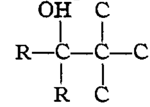
[CONTRIBUTION FROM THE WHITMORE LABORATORY OF THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

Hydrocarbons. IX.[1] 2,2,4-Trimethylheptane, 2,2,4-Trimethyloctane, 2,2,4,6-Tetramethylheptane and 2,2,4,5,5-Pentamethylhexane

BY GEORGE W. MOERSCH[2] AND FRANK C. WHITMORE[3]

In a continuation of previous work the present paper reports the syntheses of a decane and three undecanes containing the neopentyl system, and the determination of several of their physical constants.

With some exceptions, the hydrocarbons were prepared by catalytic hydrogenation of the olefins resulting from dehydration of the tertiary alcohols, 2,2,4-trimethyl-4-heptanol, 2,2,4-trimethyl-4-octanol, 2,2,4,6-tetramethyl-4-heptanol, and 2,2,3,5,5-pentamethyl-3-hexanol. In the case of 2,2,3,5,5-pentamethylhexane, the alcohol was prepared by two different methods and the olefins were also obtained by a Kolbe electrolysis of Butlerow's beta acid, methyl-*t*-butylneopentylacetic acid.

The reactions involved in these syntheses are not of the type usually accompanied by rearrangement[4] except for the dehydration of 2,2,3,5,5-pentamethyl-3-heptanol.[5] Structures similar to the latter,  $R—\underset{R}{\overset{OH}{C}}—\underset{C}{\overset{C}{C}}—C$, always rearrange to a small degree, about 5% under the conditions employed here,[4] and it is therefore reasonable to assume that the 2,2,3,5,5-pentamethylheptane contains some 2,3,3,5,5-pentamethylheptane. This contamination from a closely related isomer could not be expected to affect appreciably the physical properties of the compound. This was substantiated when the electrolysis of Butlerow's beta acid gave material that checked the product made by dehydration of the alcohol.

The decane, 2,2,4-trimethylheptane, is mentioned in the literature[6] in connection with the investigation of impurities in isoöctane. From still residues there was isolated a material of b. p. 151.97° at 760 mm., d^{20} 0.7349, n^{20}_{D} 1.41278. It was suggested that this compound was either 2,2,4- or 2,2,5-trimethylheptane. The physical properties of the 2,2,4-trimethylheptane reported in this paper are not in agreement with the values found for the above material.

Experimental

Distillations were made through columns of the adiabatic, total reflux, variable take-off type, packed with (A) one-eighth inch glass helices, packed section 1.7 × 67 cm., 11 theoretical plates, (B) three thirty-second inch stainless steel helices, 1.0 × 100 cm., 25 theoretical plates, and (C) one-sixteenth inch stainless steel helices, 1.0 × 100 cm., 65 theoretical plates.

2,2,4-Trimethylheptane.—A typical preparation of methyl neopentyl ketone is given.[7] Sodium dichromate

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[1] For previous papers of this series see: Whitmore, Marker and Plambeck, THIS JOURNAL, **63**, 1626 (1941); Whitmore and Southgate, *ibid.*, **60**, 2571 (1938); Whitmore and Orem, *ibid.*, 2573; Whitmore, Fleming, Rank and Larson, *ibid.*, **56**, 749 (1934); Whitmore and Laughlin, *ibid.*, **55**, 5056 (1933); Whitmore and Fleming, *ibid.*, 3803; Whitmore, Stehman and Herndon, *ibid.*, 3807; Laughlin and Whitmore, *ibid.*, 2607.

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[3] Deceased.

[4] Unpublished work, this Laboratory.

[5] Whitmore and Laughlin, THIS JOURNAL, **54**, 4011 (1932).

[6] Brooks, Cleaton and Carter, *J. Research Natl. Bur. Standards*, **19**, 319 (1937).

[7] The authors are indebted to Dr. Sutherland for preparation of the methyl neopentyl ketone: L. H. Sutherland, Ph.D. Thesis, Penn State, 1942.