Oxidation.—A 1-g. sample of β,β-di-(*p*-chlorophenyl)-propionic acid was oxidized by heating it for six hours with a solution of 4 g. of potassium permanganate in 80 cc. of water. The alkali-insoluble product was crystallized from alcohol; melting point, 144–145°. This is the melting point given by Dittrich[8] for *p,p'*-dichlorobenzophenone.

Summary

It has been shown that in the presence of aluminum chloride and hydrogen chloride benzene adds to halobenzalquinaldines and to chlorocinnamic acids. In all of these cases the halophenyl group is replaced by an unsubstituted phenyl group, giving a benzohydryl derivative in place of the halobenzohydryl derivative which was to be expected.

In the case of *p*-bromobenzalquinaldine it has been shown that bromobenzene is a product of the reaction.

Chlorobenzene adds to *o*- and *p*-chlorocinnamic acids in the presence of aluminum chloride to give, in both instances, β,β-di-(*p*-chlorophenyl)-propionic acid.

It has been suggested that the condensation of aromatic compounds with α,β-unsaturated carbonyl compounds and similarly constituted systems is a reversible process. An interpretation of the results, based on this assumption, has been given.

[8] Dittrich, *Ann.*, **264**, 175 (1891). See also Norris and Green, *Am. Chem. J.*, **26**, 496 (1901).

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

Preparation of Tetramethylmethane (Neopentane) and Determination of its Physical Constants[1]

BY FRANK C. WHITMORE AND GEO. H. FLEMING[2]

Tetramethylmethane has been prepared by relatively few workers and only its boiling point and freezing point have been reported. Because of the importance of the neopentyl system in rearrangements[3] the preparation and properties of the parent hydrocarbons have been studied.

This hydrocarbon has been obtained from petroleum,[4] also synthesized by the reaction of dimethylzinc with *tert*-butyl halides,[5] dimethyl sulfate with *tert*-butyl Grignard,[6] Grignards with halides,[7] and the hydrogenation of trimethylethylene in a silent electric discharge.[8] This formation is most interesting from the point of view of the current theory of rearrangements.[3]

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[1] THIS JOURNAL, **54**, 3460 (1932).

[2] Presented in partial fulfilment of the requirements for the Ph.D. degree.

[3] Whitmore and co-workers, THIS JOURNAL, **54**, 3279, 3431 (1932); **55**, 1106, 1528 (1933).

[4] Markownikoff, *Ber.*, **32**, 1449 (1899); Poni, *Ann. Sci. Univ. Jassy*, **1**, 205 (1901).

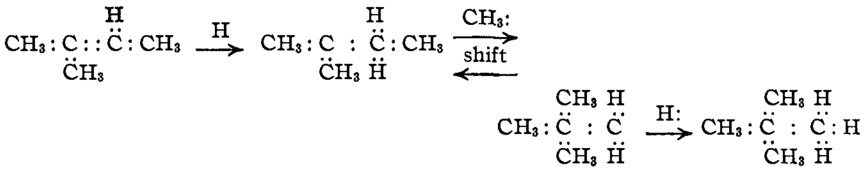
[5] Lwow, *Z. Chem.*, 520 (1870); dimethylzinc with 2,2-dichloropropane, *ibid.*, 257 (1871).

[6] Ferrario and Fagetti, *Gazz. chim. ital.*, **38**, [II], 630–634 (1908).

[7] Späth, *Monatsh.*, **34**, 1965–2014 (1913).

[8] Meneghini and Sargato, *Gazz. chim. ital.*, **62**, 621 (1932).

All the predictable products were obtained. The formation of neopentane may take place as follows



$$\mathrm{CH_3:\underset{\ddot{C}H_3}{C}::\overset{H}{\ddot{C}}:CH_3} \xrightarrow{H} \mathrm{CH_3:\underset{\ddot{C}H_3}{C}\ :\ \underset{\ddot{H}}{\overset{H}{\ddot{C}}}:CH_3} \underset{\longleftarrow}{\xrightarrow[\text{shift}]{CH_3:}} \mathrm{CH_3:\underset{\ddot{C}H_3}{\overset{CH_3}{\ddot{C}}}\ :\ \underset{\ddot{H}}{\overset{H}{\ddot{C}}}} \xrightarrow{H:} \mathrm{CH_3:\underset{\ddot{C}H_3}{\overset{CH_3}{\ddot{C}}}\ :\ \underset{\ddot{H}}{\overset{H}{\ddot{C}}}:H}$$

The fact that this involves the reverse of the ordinary rearrangement process[3] explains the small amount of neopentane found in the products. It is important to note that the fragment containing a carbon with only six electrons is formed by the *addition of a positive group* (H, in this case) instead of by the *removal of a negative group* with a complete octet of electrons.[3] This phenomenon is being intensively studied in this Laboratory.

Preparation of Neopentane

The work of Lwow was repeated using *tert*-butyl chloride and bromide as well as the iodide. The procedure consisted of adding a tetralin solution of the halide to the dimethylzinc, also in tetralin, at about 35°. The yields of neopentane were as follows: *tert*-butyl chloride, 51.2%; *tert*-butyl bromide, 46.1%; *tert*-butyl iodide, 42.0%.

Ferrario and Fagetti[6] report a 75% yield of neopentane by reaction of *tert*-butylmagnesium iodide with dimethyl sulfate in ether. This work was repeated using *tert*-butylmagnesium chloride in place of the iodide. A negligible quantity of neopentane was found. No improvement was obtained by using a higher boiling solvent (toluene).

E. Späth[7] treated methylmagnesium iodide with *tert*-butyl bromide but did not determine the yield of neopentane. This reaction was repeated and the yield found to be 18.2%. A toluene solution of the bromide was added to the Grignard reagent in ether and toluene at 40–49°.

The sodium salt of *tert*-butylacetic acid was fused with (1) soda-lime, (2) sodium hydroxide and (3) sodium methoxide, but in each case the yield of neopentane was negligible.

According to H. Fay[9] fatty acids are decomposed by uranyl nitrate in the presence of sunlight to give carbon dioxide and hydrocarbons. This reaction was tried with *tert*-butylacetic acid but even after two months' exposure only a very small quantity of gas was liberated.

Sabatier and Senderens,[10] and Mailhe[11] have found that fatty acids are decomposed by a nickel catalyst into carbon dioxide and hydrocarbons. When *tert*-butylacetic acid was decomposed in this manner at 350° it gave a 28.2% yield of neopentane. The apparatus used was of such design that the acid was distilled into a horizontal tube (30 × 1.2 cm.) containing 5.5 g. of freshly reduced nickel. By means of a reflux condenser the unchanged acid or other condensable material was returned to the flask. The gases formed by the decomposition were collected in gas-holders. It was found that starting with 10 g. of acid, only 4.1 g. was decomposed in thirteen hours.

The method finally adopted for the preparation of neopentane was the action of *tert*-butyl chloride and methylmagnesium chloride, both in toluene, at 45–50°. Consistent yields of 42–50% were obtained repeatedly.

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(9) Fay, *Am. Chem. J.*, **18**, 269 (1896).

(10) Sabatier and Senderens, *Ann. chim. phys.*, [8] **4**, 467 (1903).

(11) Mailhe, *Bull. soc. chim.*, [4] **5**, 616 (1909).

Determination of Physical Constants of Neopentane.—The neopentane, free from olefins, was fractionated through a packed column (42 × 1.2 cm.) provided with total condenser and variable take-off.[12] The jacket of the column was maintained at 9–10° and the reflux condenser at 0–3°, by circulating suitably cooled water through them. The head of the column was heavily lagged with asbestos.

The distillate from the first fractionation, which consisted of 3.6 moles, was allowed to vaporize and after being scrubbed with 85% sulfuric acid, 25% potassium hydroxide, and dried with phosphorus pentoxide, was condensed. The middle cuts (2.6 moles) were combined and fractionated, the distillate being collected in four cuts. The freezing points of these cuts were found to be approximately −30, −25, −21 and −19°, respectively.

Refractive Index.—Refractive indices of the four cuts mentioned above were determined from 0 to +6° and the following values were obtained for cut 4 for n_D: 0°, 1.3513; 2°, 1.3498; 4°, 1.3486; 6°, 1.3476.

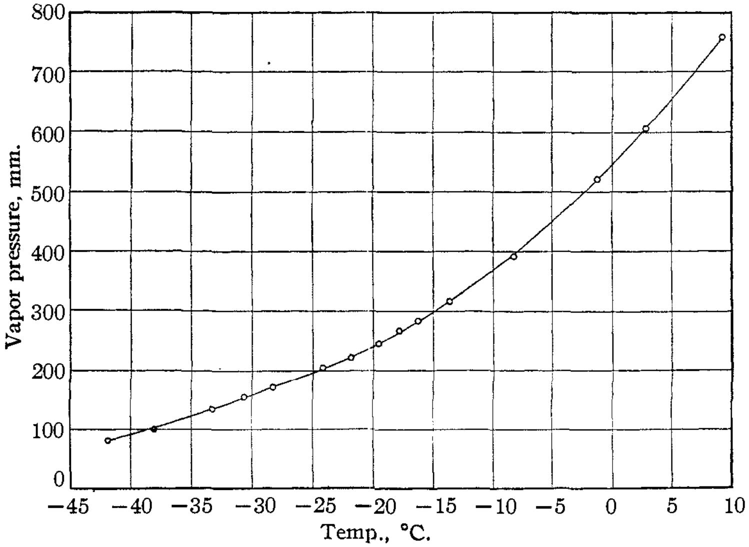

Fig. 1.

Boiling Point.—The Cottrell boiling point on cut 4 was 9.4° (760 mm.). This temperature remained constant for two-thirds of the distillation, which was started with 30 cc. of hydrocarbon.

Freezing Point.—A temperature–time curve on cut 4 indicated its freezing point to be −19.5° (corr.).

Density.—The density of cut 4 was d_0^0 0.613.

Molecular Refraction.—Calcd. for C_5H_{12}, 25.12; obs., 25.36.

Vapor Pressure *vs.* **Temperature.**—The apparatus consisted of a long-necked 10-cc. flask connected to one arm of a mercury gage which was provided with bulbs at the top of the two arms. The other arm of the gage led to a 10-gallon carboy which was connected to a vacuum pump, a mercury manometer and to the atmosphere. The temperature in the Dewar flask which surrounded the flask was maintained fairly constant by mixtures of ice and hydrochloric acid and acetone and solid carbon dioxide. The temperature in the flask was observed by means of an alcohol thermometer whose

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[12] Whitmore and Lux, This Journal, **54**, 3451 (1932).

bulb was immersed completely in the liquid. The accuracy of this apparatus was determined by measuring the vapor pressure of acetone at 0°. The value found was 71.5 mm. compared to the "I. C. T." value of 72.0 mm.

The flask and connection to the mercury gage were freed from air by boiling, and in doing so the vapor was pulled through the gage. With neopentane the system was boiled out six times, the last three readings being constant.

OBSERVED VAPOR PRESSURES AT DIFFERENT TEMPERATURES

Temperature, °C.	9.4	3.1	−1.0	−8.0	−13.4	−15.8	−17.2	−17.6
Vapor press., mm.	760.0	605.7	523.7	394.0	316.5	286.9	276.0	269.5
Temperature, °C.	−19.4	−21.7	−24.0	−28.1	−30.5	−33.1	−38.0	−42.0
Vapor press., mm.	247.0	222.0	206.1	172.1	155.6	135.1	104.6	87.1

Figure 1 shows the vapor pressure *vs.* temperature plot, and Fig. 2, the log vapor pressure *vs.* reciprocal absolute temperature.

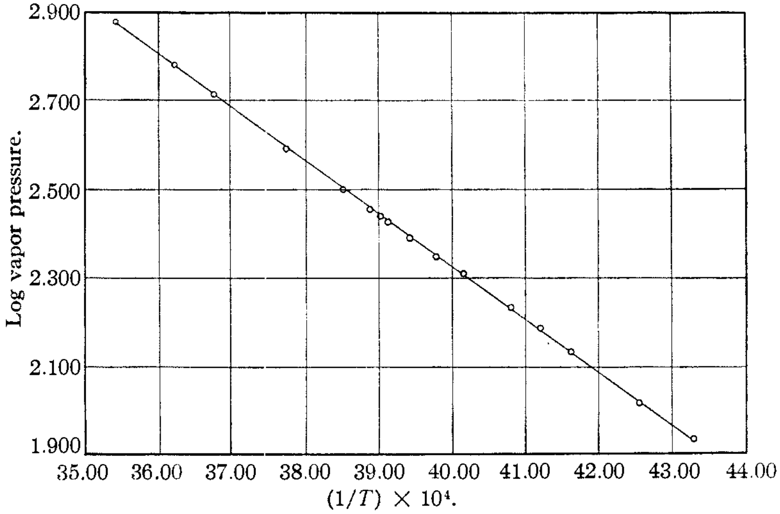

Fig. 2.

Summary

1. A practical method has been developed for making tetramethylmethane (neopentane) in quantity.

2. The physical properties of neopentane have been studied.

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