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

Hexamethylethane

BY FRANK C. WHITMORE, C. J. STEHMAN AND JOHN M. HERNDON

Since hexamethylethane contains two neo carbon atoms it is of particular interest in the field of intramolecular rearrangements.[1] Because the literature contains no satisfactory method for the preparation of this substance, an extended study has been conducted on this subject and the present paper contains two satisfactory methods for its preparation. The study of the halogenation products of hexamethylethane is in progress in this Laboratory.

Experimental

The summary of the methods tried in the work on the preparation of hexamethylethane follows.

		Yield of hexamethylethane, %
1	Ether solution of *tert*-butylmagnesium bromide added to *tert*-butyl chloride	4
2	Ether solution of *tert*-butylmagnesium bromide added to a paraffin oil solution of *tert*-butyl chloride	0
3	Ether solution of *tert*-butylmagnesium chloride added to an ether solution of tetramethylethylene dibromide	0
4	Ether solution of *tert*-butylmagnesium chloride added to a cooled, well-stirred suspension of silver bromide in dry ether	18–19
5	*Tert*-butyl chloride added to sodium pellets in ether	0
6	*Tert*-butyl chloride added to a xylene solution of *tert*-butylmagnesium chloride heated to 50°	0
7	Mercuric chloride added to an ether solution of *tert*-butylmagnesium chloride and *tert*-butyl chloride	0
8	Cupric chloride added to an ether solution of *tert*-butylmagnesium chloride	0
9	Ether solution of pentamethylethyl chloride added to an ether solution of methylmagnesium chloride	3
10	Xylene solution of pentamethylethyl bromide added to a xylene solution of methylmagnesium chloride, heated to 60°	10
11	Xylene solution of pentamethylethyl bromide added to a xylene solution of zinc dimethyl	50

In addition, hexamethylethane as a by-product in reactions involving an ether solution of *tert*-butylmagnesium chloride has been obtained with the following reagents in ether solution: (1) allyl bromide, 8%; (2) acetaldehyde, 7%; (3) *n*-butyraldehyde, 5%; (4) isobutyraldehyde, 4%.

Experimental

Preparation of Hexamethylethane

A. By Reaction of Pentamethylethyl Bromide with Dimethylzinc.—Pentamethylethyl alcohol[2] was prepared in 25% yield from *tert*-butylmagnesium chloride and puri-

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(1) Whitmore and co-workers, THIS JOURNAL, **54**, 3274, 3431, 3435, 3714 (1932).

(2) Edgar, Calingaert and Marker, *ibid.*, **51**, 1483 (1929).

fied acetone. The corresponding bromide[3] was prepared in 85% yield by the reaction of hydrogen bromide with pentamethylethyl alcohol in cold ether solution.

Dimethylzinc was prepared by the method of Noller[4] and distilled at atmospheric pressure.

Eight grams (0.084 mole) of dimethylzinc in 50 cc. of xylene was placed in a 500-cc. 3-necked round-bottomed flask fitted with a 100-cc. dropping funnel, a mechanical stirrer, reflux condenser and a thermometer well. The flask was surrounded by a water-bath. Twenty-eight grams (0.16 mole) of pentamethylethyl bromide in 56 cc. of dry xylene was added from the dropping funnel during three hours to the well-stirred solution of dimethylzinc in xylene kept at 32°. This temperature was maintained almost entirely by the heat of the reaction. A few minutes after all of the bromide had been added the reaction was complete as evidenced by a fall in temperature. The mixture was then heated to 43° for fifteen minutes, after which a mixture of 70 cc. of water and 15 cc. of concentrated hydrochloric acid was added in ten minutes from the dropping funnel to decompose any excess dimethylzinc.

The xylene and water layers were separated and the xylene layer dried over 20 g. of anhydrous potassium carbonate for twenty-four hours. A rapid distillation was then made through a 70 × 1.1 cm. indented column[5] equipped with a heating unit on the side arm. The following fractions were collected at 740 mm.: 1, b. p. 75–85°, 2.8 g., $n^{20°}_D$ 1.4067; 2, b. p. 85–98°, 1.2 g., $n^{20°}_D$ 1.4112; 3, 98–119°, 11.3 g. (solid at room temperature); 4, 119–130°, 4 g., partly solid. The residue of xylene was 80 g. Fractions 2 and 3 combined and cooled in ice–salt mixture gave 9.0 g., 50% yield of hexamethylethane, m. p. 101°. A lowering of the melting point resulted when this material was mixed with a sample of the solid alcohol hydrate and with a sample of pentamethylethyl bromide.

B. By Reaction of Tert-butylmagnesium Chloride with Silver Bromide.—This type of reaction has been run previously and the silver bromide used in this experiment was prepared accordingly.[6]

This preparation of *tert*-butylmagnesium chloride was recently described.[7]

In a 2-liter round-bottomed flask, fitted with a mechanical stirrer, dropping funnel, reflux condenser arranged for the collection of gases, surrounded by an ice–salt bath, was placed 93.9 g. (0.5 mole) of silver bromide and 200 cc. of dry ether. Vigorous stirring was started and an ether solution (volume 190–200 cc.) of 0.5 mole of *tert*-butylmagnesium chloride was slowly added from the dropping funnel. After the first few cc. of the Grignard solution was added the black precipitate of silver could be seen and the ether began to reflux. The remainder of the Grignard reagent was then added at such a rate that a gentle refluxing was maintained. When the reaction was complete, all of the Grignard reagent added and the ether no longer refluxed, the reaction mixture was poured on 1.5 kg. of cracked ice contained in a 3-liter flask. As soon as the reaction mixture was added to the ice the 3-liter flask was securely stoppered until the separation of the phases was complete. The ether layer was removed and kept in a closed container during the extraction of the aqueous portion with 200 cc. of ether. The combined ether portions were dried over 20 g. of anhydrous potassium carbonate. After the careful removal of the ether through a 90 × 2.2 cm. glass-packed column[8] the remaining oil was quickly transferred and distilled through a 68 × 1.1 cm. indented column. The forerun was collected as one fraction 2.0 g. up to 92° when the hexamethylethane began to solidify in the head of the column. The flask was then cooled and the hexamethylethane solidi-

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[3] Henry, *Bull. Acad. Roy. Belg.*, 352 (1906); *Chem. Zentr.*, II, 748 (1906).

[4] Noller, THIS JOURNAL, **51**, 594 (1929).

[5] Whitmore and Church, *ibid.*, **54**, 3711 (1932).

[6] Gardner and Borgstrom, *ibid.*, **51**, 3377 (1929).

[7] Whitmore and Badertscher, *ibid.*, **55**, 1561 (1933).

[8] Whitmore and Lux, *ibid.*, **54**, 3451 (1932).

fied at room temperature; yield 5.5 g., 19.4%. The yields in 1.0 and 2.0 mole runs were 18 and 13%, respectively.

Summary

1. Practical methods have been developed for making hexamethylethane.

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Some Aspects of the Tschugaeff Reaction for Dehydrating Alcohols[1]

BY FRANK C. WHITMORE AND C. T. SIMPSON[2]

Tschugaeff was the first to suggest the dehydration of alcohols by decomposition of their xanthates.[3] His original paper dealt with the preparation of menthene from menthol, and gave two possible alternative reactions for the decomposition of the xanthate upon heating

$$C_nH_{2n-1}OCS_2R \xrightarrow{\text{Heat}} C_nH_{2n-2} + COS + RSH \qquad (1)$$

$$C_nH_{2n-1}OCS_2R \xrightarrow{\text{Heat}} C_nH_{2n-2} + CS_2 + ROH \qquad (2)$$

It has since been found that (1) is the reaction. The yield is best when R is methyl.

By the same method Tschugaeff[4] also prepared thujene from thujyl alcohol, limonene from carvone, cholesterylene from cholesterylin, and bornylene from borneol. Others have extended the application of the method. Gandurin[5] prepared guajene from guajol. Kurssanoff[6] dehydrated benzhydrol to give tetraphenylethylene and phenylcyclohexylcarbinol to give benzylidene cyclohexane.

In the aliphatic series Fomin and Sochanski[7] prepared tertiary-butylethylene from pinacolyl alcohol. More recently Stevens[8] dehydrated *dextro*-2-methyl-3-ethoxybutanol-2 to secure *dextro*-3-ethoxy-2-methylbutene-1.

In all these preparations the general method was the same. Sodium or potassium (preferably the latter) reacted with the alcohol in a solvent such as xylene. Carbon disulfide was added to form the xanthate of the metal,

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(1) Presented before the Organic Division, American Chemical Society, March 28, 1933.

(2) Submitted in partial fulfilment of the requirements for the M.S. degree.

(3) Tschugaeff, *Ber.*, **32**, 3332 (1899).

(4) Tschugaeff, *ibid.*, **33**, 3118, 735 (1900); **34**, 2276 (1901); **37**, 1481 (1904); **42**, 4631 (1909); **45**, 1293 (1912); *Ann.*, **375**, 288 (1910); **388**, 280 (1912).

(5) Gandurin, *Ber.*, **41**, 4362 (1908).

(6) Kurssanoff, *Chem. Centr.*, I, 997 (1921); *Ber.*, **64**, 2297 (1931).

(7) Fomin and Sochanski, *ibid.*, **46**, 246 (1913).

(8) Stevens, THIS JOURNAL, **54**, 3736 (1932).