method (as above) at 95°; yield 87%; crystallized from acetone as truncated rhombohedra; m. p. 142° (corr.).

Anal. Calcd. for $C_{22}H_{13}O_2Br$: Br, 43.59. Found: Br, 43.55.

Reduction of 1 g. with zinc dust in 15 cc. of glacial acetic acid (refluxed for two minutes) gave 0.7 g. (84%) of di-(bromophenyl)-phenylfuran. Both di-(bromobenzoyl)-phenylethane and di-(bromophenyl)-phenylbromofuran are stable under these conditions in the presence of added zinc bromide in the amount that is formed during a reduction. The residues from this reduction were examined carefully and none of the difficultly soluble and easily crystallized di-(bromobenzoyl)-phenylethane was isolated.

Summary

The triphenyl saturated and unsaturated 1,4-diketones and furans react with phosphorus pentahalides giving halogenated furans; phosphorus pentabromide also brominates the α- (but not the β-) phenyl groups of the furans.

The nitric–acetic acid oxidation of triarylfurans leads to the formation of some new *cis* unsaturated 1,4-diketones which have been studied. Some reductions are described.

UNIVERSITY, VIRGINIA RECEIVED AUGUST 11, 1934

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

The Vapor Pressure of Certain Ketones

BY M. GLENN MAYBERRY[1] AND JOHN G. ASTON

Several ketones of the methyl, isopropyl and the first two members of the cyclohexyl series have been prepared in rather large quantities for other work. Since it was thus possible to obtain pure samples, it was decided to determine the vapor pressures of these ketones, acetone being the only ketone whose vapor pressure curve has been studied.

Experimental

Preparation and Purification of the Ketones.—Methyl ethyl ketone was purified by drying over sodium sulfate and fractionating through an insulated column 46 × 1.5 cm. packed with glass rings.[2] The fraction boiling 78–78.2° was again dried over sodium sulfate and redistilled. For the vapor pressure determination, a 15-cc. portion was collected from the middle of a 100-cc. fraction boiling 78.1° at 728 mm.

Methyl isopropyl ketone was prepared from tertiary amyl alcohol and bromine.[3] The other ketones of the methyl series were prepared through the acetoacetic ester synthesis.[4] These ketones were distilled through a column 25 × 0.8 cm. packed with glass helices.[5]

The ketones of the isopropyl and cyclohexyl series were prepared from the corresponding alcohols by the oxidation method of Faworsky.[6] These ketones were distilled through a column 76 × 1.5 cm.[2]. The diisopropyl ketone was furnished by T. S. Oakwood of this Laboratory.

The boiling point ranges of the ketones used were as follows: methyl ethyl ketone, 78.1° (728 mm.); methyl isopropyl ketone, 92.5–92.8° (727 mm.); methyl propyl ketone, 100.8–101° (726 mm.); methyl isobutyl ketone, 113.4–114° (727 mm.); methyl butyl ketone, 124.5–124.8° (727 mm.); ethyl isopropyl ketone, 112.5–113.2° (734.4 mm.); diisopropyl ketone, 123–124.5° (740 mm.); propyl isopropyl ketone, 132–132.6° (725 mm.); isobutyl isopropyl ketone, 142.5–143.2° (728 mm.); butyl isopropyl ketone, 154.2–154.4° (736 mm.); methyl cyclohexyl ketone, 61.2–61.5° (11 mm.); ethyl cyclohexyl ketone, 75.2–75.7 (11 mm.).

Vapor Pressure Measurements.—The vapor pressures of the ketones of the isopropyl and cyclohexyl series were determined by comparing their boiling points with those of water at the same pressure, using two Cottrell boiling point units in the way described by Woodburn and Whitmore of this Laboratory.[7] The corresponding pressures were then obtained from a table of vapor pressures for water.[8]

The vapor pressures of diisopropyl ketone and the ketones of the methyl series were determined directly by the method of Ramsay and Young.[9] The liquid whose vapor pressure was to be measured was placed in a Cottrell boiling point apparatus which was connected directly to a U-type manometer, the inside diameter of which was 1 cm. The pressure at which the liquid boiled was determined by comparison of the mercury levels with a meter stick, using a cathetometer accurate to 0.05 mm. The cathetometer was placed in such a position that both arms of the manometer and the meter stick were in focus at the same setting of the cathetometer telescope. The meter stick was calibrated to 0.05 mm. by comparison with a standard meter (Bureau of Standards). The system was usually evacuated by means of a water pump (in some cases an oil pump was used) and a capillary air leak used to adjust the pressure. A 5-liter flask was also placed in the system to maintain constant pressure, as the system was entirely closed off from the pump and air leak, before a reading was taken. It was thus possible to get readings with the pressure varying less than 0.1 mm.

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[1] Submitted in partial fulfilment of the requirements for the Ph.D. degree.

[2] Whitmore and Lux, THIS JOURNAL, **54**, 3448 (1932).

[3] "Organic Syntheses," 1933, Vol. XIII, p. 68.

[4] "Organic Syntheses," 1927, Vol. VII, p. 36.

[5] Wilson, Parker and Laughlin, THIS JOURNAL, **55**, 2795 (1933).

[6] Faworsky, *J. prakt. Chem.*, **88**, 641 (1913).

[7] Woodburn and Whitmore, not yet published.

[8] Landolt-Börnstein-Roth-Scheel, "Physikalisch-chemische Tabellen," 1923, Julius Springer, Berlin, p. 1317.

[9] Ramsay and Young, *J. Chem. Soc.*, **47**, 42 (1885).

A mercury thermometer, 60 cm. in length and calibrated to 0.2° intervals, was used to measure the boiling points. It had been calibrated to 0.01° by the Bureau of Standards. Readings were recorded only when the thermometer was bathed in vapor above the mark representing the boiling point of the liquid, thus eliminating the necessity of a stem correction.

The observed vapor pressures in mm. can be represented adequately by the formula $\log_{10} p = A/T + B$, the values of $-A$ and B, together with the average deviation, being given in Table I.

Ketone	$-A$	B	Average deviation of p, %
Methyl ethyl ketone	1760.5	7.8746	1.06
Methyl isopropyl ketone	1830.9	7.8717	1.35
Methyl propyl ketone	1870.4	7.8642	1.27
Methyl isobutyl ketone	2009.5	8.0590	1.13
Methyl butyl ketone	2117.2	8.1852	0.80
Ethyl isopropyl ketone	1989.7	8.0277	1.95
Diisopropyl ketone	2021.4	7.9752	1.54
Propyl isopropyl ketone	2159.5	8.1930	0.87
Isopropyl isobutyl ketone	2221.9	8.1873	1.95
Isopropyl butyl ketone	2271.9	8.1827	0.86
Methyl cyclohexyl ketone	2418.7	8.2238	1.17
Ethyl cyclohexyl ketone	2512.5	8.2379	0.86

The boiling points of all the ketones were determined at several different pressures. These were all plotted against the boiling point of methyl isopropyl ketone at the same pressure. The points thus obtained for each ketone were found to lie on a straight line. When these lines were extended, it was found that they intersected at −440, −440, showing that the rule of Dühring[10] for predicting the vapor pressure curves from the boiling point at one pressure is applicable. Calculations of Trouton's constant show that the ketones are slightly associated, values of $\Delta H/T$ ranging from 22.7–24.

Summary

1. The vapor pressures of twelve ketones of the methyl, isopropyl and cyclohexyl series have been measured.

2. Dühring's rule applies to the ketones of the methyl, isopropyl and cyclohexyl series using methyl isopropyl ketone as standard.

[10] White, *Ind. Eng. Chem.*, **22**, 230 (1930).

STATE COLLEGE, PA.

RECEIVED AUGUST 13, 1934

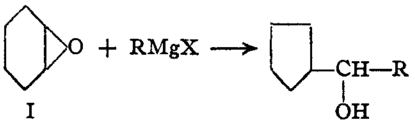
[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

The Reaction of Dimethylmagnesium and of Diethylmagnesium with Cyclohexene Oxide

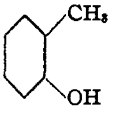
BY PAUL D. BARTLETT AND C. MANLY BERRY

The reaction of ethylene oxide with Grignard reagents is a useful way of preparing alcohols containing the group $—CH_2CH_2OH$,[1] but with substituted ethylene oxides the reaction is often attended by rearrangements.[2] In the alicyclic series this has given rise to some confusion. Thus, Godchot and Bédos[3] originally reported that the single substance (phenylurethan, m. p. 71°) which they obtained from the action of methylmagnesium iodide on cyclohexene oxide (I) was the *cis*-2-methylcyclohexanol (II). A later careful study of the reduction products of *o*-cresol led to the characterization of two isomeric 2-methylcyclohexanols,[4] both different from the product of Godchot and Bédos.

An explanation was provided in the work of Godchot and Cauquil[5] and Vavon and Mitchovitch[6] who showed that the reaction of Grignard reagents with oxides or chlorohydrins of the cycloheptane and cyclohexane series led to ring contraction



The supposed *cis*-2-methylcyclohexanol of Godchot and Bédos was accordingly methylcyclopentylcarbinol (III), which has been prepared in other ways and has the properties of this alcohol.



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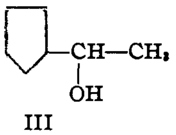
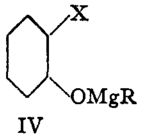
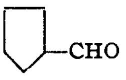


III



IV



V

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[1] "Organic Syntheses," John Wiley & Sons, Inc., New York, 1932, Coll. Vol. I, p. 299.

[2] For a number of examples, see Schlenk in Houben-Weyl, "Methoden der organischen Chemie," Georg Thieme, Leipzig, 1924, 2d. ed., Vol. IV, p. 781.

[3] Godchot and Bédos, *Bull. soc. chim.*, **37**, 1451 (1925).

[4] Gough, Hunter and Kenyon, *J. Chem. Soc.*, 2052 (1926).

[5] Godchot and Cauquil, *Compt. rend.*, **186**, 375, 955 (1928).

[6] Vavon and Mitchovitch, *ibid.*, **186**, 702 (1928).