The values calculated in this way from the vapor pressure measurements, as well as those found in the normal distillation of gasoline according to the A. S. T. M. method and for benzenes by the method of Krämer–Spilker, are given in Table I and are shown in Fig. 5.

Comparison shows that the differences in specific gravity of the components of a mixture make possible a direct calculation from the vapor pressure measurements of the temperature in the A. S. T. M. method corresponding to the numerical volume percentages of the distillate, with an accuracy sufficient for technical purposes.

Summary

A method has been described for ascertaining the behavior of small quantities of material during distillation. In this method temperatures are measured in a tension eudiometer at 20 mm. From these measurements it is possible to calculate the behavior of a substance in a regular A. S. T. M. distillation or in one carried out by the Krämer–Spilker method. The mean molecular weight of the distillate fractions may be determined simultaneously in the tension eudiometer, which is a further valuable attribute in the characterization of liquid mixtures.

PRAGUE, CZECHOSLOVAKIA

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF WASHINGTON]

PREPARATION OF CERTAIN REDUCTION PRODUCTS OF BENZOIN

BY DONALD A. BALLARD AND WILLIAM M. DEHN

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Theoretically benzoin can yield thirteen reduction products; all of these except the optically active phenylbenzylcarbinols are known. Isostilbene has not been prepared by the reduction of benzoin; we have prepared didesyl and isodidesyl by reduction of benzoin. All of the other compounds have been prepared from benzoin; however, most of them have usually been prepared either from one another or from other compounds.

Since benzoin is easily and cheaply prepared,[1] it seemed desirable to prepare from it certain of these reduction products. Superior yields and simple methods of preparation of stilbene, desoxybenzoin and β-desoxybenzoinpinacone were developed.

Stilbene.[2]—In a one-liter beaker or large evaporating dish are placed in order, 50 g. of mercuric chloride, 500 cc. of water and 200 g. of zinc dust, the last having been freed

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[1] "Organic Syntheses," John Wiley and Sons, Inc., New York, 1921, Vol. I, p. 33.

[2] Hitherto stilbene has best been prepared by the Grignard reaction, involving the intermediate formation of benzylmagnesium bromide, phenylbenzylcarbinol and the acetate of the carbinol [Hell, *Ber.*, **37**, 453 (1904)]. The above-described method gives 50% yields in two to three hours by one operation. Variations of conditions and materials gave no larger yields, because, perhaps, only the *d*- or the *l*-form of benzoin is reduced.

from lumps by sifting through a thirty-mesh screen. The mixture is stirred until all the mercuric chloride dissolves. The zinc is then allowed to settle, supernatant liquid is decanted and the solid is washed with water. The amalgamated zinc dust is placed in a 2–3 liter battery jar equipped with a mechanical stirrer and surrounded by ice; 100 g. of benzoin and 500 cc. of alcohol are added. While stirring and maintaining a temperature below 15°, 400 cc. of concentrated hydrochloric acid is added through a dropping funnel at such a rate that the addition is complete in one to two hours. Stirring is continued for another hour to ensure further reaction of the acid. The jar is filled with cold water and the contents are filtered. The precipitate is transferred to a large beaker, the stilbene is extracted with 500 cc. of hot alcohol, and the mixture is filtered through a hot water funnel to remove zinc dust. After cooling with ice the stilbene is filtered off and washed with a small quantity of alcohol, and the filtrate and washings are used for a second extraction of the zinc dust. Two extractions should remove all the stilbene, which amounts to 42–47 g. or about 50% of the theoretical.

Evaporation of the alcohol filtrate yields an oil which contains phenylbenzylcarbinol, desoxybenzoin and a small mass of tarry substance. If this oil is boiled with acetic anhydride for about one hour and distilled, the phenylbenzylcarbinol present will be converted into stilbene which can be freed from the desoxybenzoin by recrystallization from alcohol.

Desoxybenzoin.—In a 1-liter flask are placed 100 g. of powdered tin, 15 g. of mercuric chloride and 100 cc. of water. This mixture is permitted to stand with occasional shaking until the tin acquires a shiny coating of mercury. The solution is decanted and the tin is washed with water and drained. In the flask containing the tin are then placed 100 g. of benzoin, 250 cc. of alcohol and 200 cc. of concentrated hydrochloric acid. The flask is attached to a reflux condenser and the contents are boiled for sixteen hours. The flask is then removed, filled to the neck with water and cooled until the oil which has formed has solidified. The desoxybenzoin and tin are filtered off, dissolved in a small quantity of hot alcohol and filtered hot to remove the tin, which is washed with a little hot alcohol. While stirring, the filtrate and washings are cooled with ice and the precipitated desoxybenzoin is filtered and washed with a small volume of 50% alcohol. At this point, 65 g. or 70% of the theoretical amount melting at 52–58° is obtained. The remainder of the yield is obtained by evaporation of the alcohol and distillation of the oil up to 325°. This will give an additional 17 g., which can be recrystallized from alcohol, making a total yield[3] of 88%.

β-Desoxybenzoin Pinacone.—In a 500-cc. round-bottomed flask are placed 100 g. of benzoin, 47 g. of potassium iodide and 10 g. of red phosphorus. The flask is attached to a reflux condenser and the contents are heated to melting, when 26 cc. of concentrated hydrochloric acid is added gradually[4] through the top of the condenser. After the acid has been added, the contents are boiled gently for twenty hours. The flask is then filled with water and heated to boiling, after which the contents are poured into a beaker and stirred occasionally while cooling to break up the oil into small globules before it solidifies. When cold the solid is filtered off and dissolved in a small quantity of hot benzene, and filtered to separate the red phosphorus. The filtrate is transferred to a

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[3] Other methods of preparation employed zinc. See THIS JOURNAL, **51**, 2164 (1929). If benzoin is reduced by zinc and sodium hydroxide, there are obtained desoxybenzoin, isodidesyl melting at 160°, didesyl melting at 248–250° and an unknown compound characterized by fine needles and melting at 208°. When 50 g. each of benzoin zinc dust and sodium hydroxide were heated for twenty-three hours with 300 cc. of alcohol and 100 cc. of water, 5 g. of isodidesyl was obtained.

[4] The hydrochloric acid is added slowly to minimize the escape of hydriodic acid through the condenser.

large beaker and the benzene is evaporated on the water-bath, leaving a mixture of desoxybenzoin and desoxybenzoin pinacone. To this mixture 500 cc. of 80% alcohol is added and the beaker is heated on the steam-bath for one hour, while breaking up the lumps[5] that are formed. After filtering through a hot water funnel and washing with a little alcohol, 30 g. of β-desoxybenzoin pinacone melting at 160–165° is obtained. The filtrate contains desoxybenzoin which can be recovered. One recrystallization from boiling alcohol yields β-desoxybenzoin pinacone[6] melting at 172°.

Summary

Four methods of reduction of benzoin were studied and superior methods of preparation of stilbene, desoxybenzoin and β-desoxybenzoin pinacone developed.

[5] Since desoxybenzoin is very soluble in alcohol and β-desoxybenzoin pinacone so very insoluble, a good separation can be made by this method provided the lumps are broken up to allow the alcohol to penetrate.

[6] β-Desoxybenzoin pinacone was first made by Wislicenus and Blank [*Ann.*, **248**, 7 (1888)] together with the α-form and other products by the reduction of benzoin with zinc dust and acetic acid. Since then it has only been made by the prolonged action of light on an alcoholic solution of desoxybenzoin, Cohen, *Rec. trav. chim.*, **38**, 110 (1919).

SEATTLE, WASHINGTON

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, IOWA STATE COLLEGE]

ELECTRON SHARING ABILITY OF ORGANIC RADICALS. VI. ALPHA-SUBSTITUTED PYRROLINES AND PYRROLIDINES

BY D. F. STARR, HELEN BULBROOK AND R. M. HIXON

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The preceding paper by Craig and Hixon extended the studies[1] of this Laboratory on the electron sharing ability of organic radicals to the nitrogen heterocyclics. The data available have been increased in this paper by the preparation and measurement of a series of α-substituted pyrrolines and pyrrolidines.

The α-substituted pyrrolines were synthesized by the reaction of Cloke[2] as modified by Craig and Hixon.[3] In using this reaction, it was found that the yields of the pyrrolines were markedly increased by avoiding the large excess of Grignard reagent recommended by Cloke. The yields obtained by using equimolar quantities of Grignard reagent and γ-chlorobutyronitrile are reported in Table I in comparison with yields by the original procedure as used by Craig.

The α-substituted pyrrolidines were prepared by the catalytic reduction of the corresponding α-substituted pyrrolines.

[1] I, Hixon and Johns, THIS JOURNAL, **49**, 1786 (1927); II, Allison and Hixon, *ibid.*, **50**, 168 (1928); III, Johns, Peterson and Hixon, *J. Phys. Chem.*, **34**, 2218 (1930); IV, Johns and Hixon, *ibid.*, **34**, 2226 (1930); V, Craig and Hixon, THIS JOURNAL, **53**, 4367 (1931).

[2] Cloke, *ibid.*, **51**, 1174 (1929).

[3] Craig, Bulbrook and Hixon, *ibid.*, **53**, 1831 (1931).