ners: (a) by means of the Onsager–Fuoss theory of diffusion; (b) by applying the simple viscosity correction to the mobility at infinite dilution; (c) by applying the viscosity correction to the Onsager–Fuoss mobilities.

3. It is shown that the viscosity correction is at least as important as the Onsager–Fuoss interionic effects and that, with sodium chloride, the correct sign for the variation of the mobility cannot be obtained without the viscosity correction.

4. Remarks are made concerning the minima in the diffusion and activity coefficient curves and concerning the diffusion of sucrose. A modified form of the Stokes–Einstein law of diffusion is proposed.

STANFORD UNIVERSITY, CALIF.

RECEIVED FEBRUARY 16, 1938

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

Hydrogen as Carrier Gas for the Catalytic Dehydrogenation of Borneol to Camphor

BY B. E. CHRISTENSEN, E. C. GILBERT AND MAX BOCEK

In connection with another investigation it became necessary to convert borneol quantitatively into camphor. Since oxidation or dehydrogenation in the vapor phase appeared to have many advantages over other methods available, attack upon the problem was made from this aspect.

Although there are numerous references (largely patents) to the vapor phase dehydrogenation of borneol to camphor, the majority deal with the use of copper in some form as the catalyst.[1] Examination of these references, however, reveals data of highly conflicting and contradictory nature, one reporting 100% conversion,[1a] while others[1e] found only traces, and one of the latest[1i] states that reduced copper is a poor catalyst from the standpoint of yield.

In the hope of clearing some of the contradictory points and establishing conditions under which the method might be used reliably, extensive experiments have been carried out in this Laboratory with different catalysts and carrier (diluent) gases. In this paper the results obtained with reduced copper are reported.

Preliminary tests were made with many forms of this catalyst. Using a spongy form obtained by the reduction of fused cupric oxide, conversions of 96–100% were observed at 360°, confirming to some extent the work of Aloy and Brustier.[1a] Repeated tests under these conditions indicated, however, that the high catalytic efficiencies could not be maintained over any period of time and that the color of the copper gradually changed with use. This discoloration could not be restored by further reduction with hydrogen.

Since it was believed that either undesired decomposition products of borneol (due to the high concentration of borneol) or oxidation of the catalyst by traces of oxygen were responsible for the discoloration and diminishing catalytic activity, experiments were next attempted using carrier gases. Others have shown that borneol vapor diluted with benzene gave yields around 86%[1h] while another process using carbon dioxide[1d] (no data given) has been patented.

Although hydrogen is a product of the reaction and in excess logically should retard its progress, this gas would prevent oxidation of the catalyst while also serving as a diluent for the borneol vapor. Attempts made to use hydrogen as the carrier gas met with immediate success, making it possible to maintain the catalyst at high efficiency through many runs, and, under the optimum conditions, apparently minimizing side reactions, so that the product was uniformly of high quality.

Experimental

A borneol reservoir was maintained at any desired temperature by an air-bath. From this, borneol vapor was passed over the catalyst either by its own vapor pressure or by a stream of diluent or carrier gas. Approximately 2–3 g. samples of borneol were generally used. The temperature of the catalyst was controlled by an electric furnace and was measured by a thermocouple. The volume of carrier gas was measured by a calibrated flow-meter.

The catalyst in every run reported in this part of the work consisted of spongy copper prepared by the reduction of fused copper oxide with hydrogen at 200°. The volume

[1] (a) Aloy and Brustier, *Bull. soc. chim.*, **9**, 733 (1911); (b) Aloy and Brustier, *J. pharm. chim.*, **10**, 42 (1914); (c) French Patent 353,919; *C. A.*, **1**, 383 (1907); (d) British Patent 17,573, Aug. 31, 1906; *C. A.*, **1**, 2320 (1907); (e) Ikeda, *Sci. Papers Inst. Phys. Chem. Research* (*Tokyo*), **7**, 1 (1927); (f) Masumoto, *Mem. Coll. Sci. Kyoto Imp. Univ.*, **9A**, 219 (1925); (g) Japanese Patent 99,469, Feb. 9, 1933; *C. A.*, **28**, 2373 (1934); (h) Shoruigin and Makarov-Zemlyanski, *Zhur. Prikladnoi Khim.*, **4**, 68 (1931); (i) Sivov, Korotaeva and Kochneva, *J. Chem. Ind.* (*Moscow*), **3**, 52 (1933); *C. A.*, **28**, 138 (1934).

of catalyst was 23 cc., contained in a tube of 1-cm. diameter. Catalysts which lost their activity were reactivated easily by repeated oxidation by air at 500°, followed by the regular reduction at 200°. The use of a catalyst prepared by the reduction of copper nitrate on porous plate gave very poor results. (Porous plate was later found to be quite active alone, yielding liquid products.)

In all more than one hundred runs were made, and since the standard method of estimating camphor is time consuming,[2] the percentage conversion in a given run was estimated by comparing the melting point of the product with a known borneol–camphor melting point curve. Confidence was had in this procedure because repeated comparison of estimations from the melting points with those obtained by the gravimetric method gave quantitative agreement, within the limit of accuracy of either method.[2] Certainly, therefore, in those instances where a high yield is indicated by the melting point method the estimation is trustworthy. No attempt was made to identify products other than camphor which may conceivably have been present in runs carried out far from the optimum conditions.

Results

Attempts to duplicate the quantitative conversion reported by Aloy and Brustier[1a] using only borneol vapor resulted in a rapid decrease in the catalyst efficiency (about 30% per run).

Hydrogen as Carrier Gas.—The exploratory tests with hydrogen having shown excellent promise, experiments were carried out to determine the optimum conditions for its use. To study the effect of temperature, runs were made at 20° intervals. The results are shown in Table I.

TABLE I

EFFECT OF TEMPERATURE, USING HYDROGEN AS CARRIER

Temp. of borneol reservoir 135–140°. Product in all cases uniformly white and solid. Each run given a number, the missing runs being omitted from the table in the interest of brevity. Space velocity 880.

Run	Catalyst temp., °C.	M. p. product, °C.	Est. % camphor in product
1	280	187.5	65
3	320	180.0	96
11	480	180.0	96
13	520	183.5	86

It is important to note that above 420° Aloy and Brustier obtained considerable amounts of liquids identified as terpenes. With the present precedure the products are still solid at a reaction temperature of 520°, though the camphor percentage has dropped somewhat. Furthermore, life tests at 300° in the presence of hydrogen showed the same percentage conversion in the *tenth* run as in the first (95–96%). In no case did hydrogen seem to reverse the process or reduce the yield as might have been predicted.

In order to determine the effect of time of contact, runs were made under otherwise optimum conditions with various space velocities of hydrogen gas. It was observed that maximum efficiencies were maintained with space velocity as high as 2000. Above this value the efficiencies slowly diminished.

Carbon Dioxide as Carrier Gas.—Although the use of carbon dioxide is mentioned in some patents[1d] no data were found in the literature. In order to determine whether the beneficial effect of hydrogen on this reaction is specific or due merely to its action as a diluent, a series of runs was made with carbon dioxide. The effect of catalyst temperature, space velocity, and length of catalyst life were studied in over twenty runs. The effect of temperature is shown in Table II.

TABLE II

EFFECT OF TEMPERATURE USING CARBON DIOXIDE AS CARRIER

Temperature of borneol reservoir 140°. Space velocity 800.

Run	Catalyst temp., °C.	M. p. product, °C.	Est. % camphor in product
1	270	203	1
2	320	179	100
5	380	179	100
9	480	185	78

No particular significance is attached to the fact that some of the yields are apparently 100% as compared to 96% for hydrogen because of the method of estimation. The catalyst soon lost its activity, the efficiency dropping to 73% on the fourth run at 400° and to 65% on the seventh run at 340°. The use of carbon dioxide is less advantageous in other respects because it is slower and less efficient also in carrying over the borneol vapor.

Other Catalysts.—Preliminary experiments using hydrogen as a carrier gas for this reaction with other catalysts (notably reduced cobalt and nickel) have given excellent results. Although the effective temperature range is lower and narrower (200–250°) and there is more tendency to form terpenes, experiments conducted in this Laboratory have given very high yields of camphor. Cobalt seems to be superior in many respects to copper.

Published with the approval of the Monographs Publications Committee, Oregon State College, as Research Paper No. 10, School of Science, Department of Chemistry.

---

(2) U. S. Pharmacopoeia, Vol. XI, p. 353; Hampshire and Page, *Quart. J. Pharm. Pharmacology*, **7**, 558 (1934); Goldstein and Reindollar, *J. Am. Pharm. Assoc.*, **XXVI**, 887 (1937).

Summary

1. Results have been given to show that hydrogen is highly efficient as a carrier gas for the dehydrogenation of borneol vapor over reduced copper, particularly in respect to catalyst life and purity of product.

2. Optimum conditions with respect to temperature and time have been established for the reaction thus conducted.

3. Results have been given to show that carbon dioxide is in most respects inferior to hydrogen as a carrier.

4. Preliminary experiments have been reported which indicate that reduced cobalt and nickel are excellent catalysts for the dehydrogenation of borneol when used in the presence of hydrogen.

CORVALLIS, OREGON RECEIVED MARCH 30, 1938

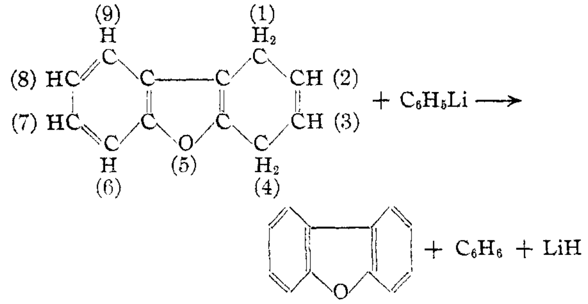
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

Dehydrogenation by Organometallic Compounds

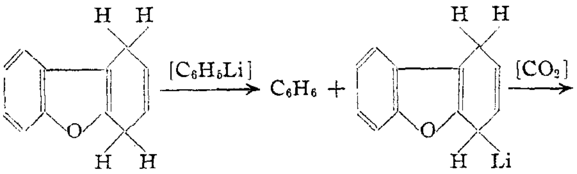
BY HENRY GILMAN AND CHESTER W. BRADLEY

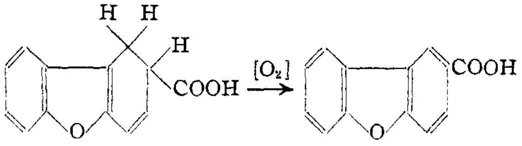
Introduction

In attempting to metalate 1,4-dihydrodibenzofuran in ether solution by means of phenyllithium, dibenzofuran instead of the expected metalation product was the chief compound isolated. The brown color produced at the inception of reaction indicated the formation of a metalation product. This color slowly disappeared on refluxing and a white precipitate, subsequently shown to be lithium hydride, formed. The isolation of dibenzofuran, lithium hydride and benzene indicated that the following transformation had taken place.



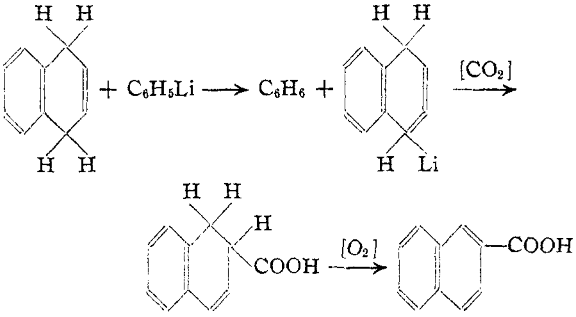
The intermediate metalation product was characterized subsequently (after allowing the reaction to proceed for a shorter time and at a lower temperature) by carbonation, to yield 1,2-dihydrodibenzofuran-2-carboxylic acid. The position of the carboxyl group was established by oxidizing the dihydro acid to the known dibenzofuran-2-carboxylic acid.





Dehydrogenation of 1,4-dihydrodibenzofuran also was effected by *n*-butyllithium and *n*-butylsodium. It was shown subsequently that the related 1,4-dihydrodibenzothiophene is dehydrogenated to dibenzothiophene by organolithium and organopotassium compounds.[1]

A related series of reactions was then observed with 1,4-dihydronaphthalene. Here, also, moderate conditions made it possible to characterize the intermediate metalation compound.



Carbonation of the intermediate organometallic compounds derived from 1,4-dihydrodibenzofuran, 1,4-dihydrodibenzothiophene and 1,4-dihydronaphthalene probably involves an allylic rearrangement. An illustration of a related rearrangement with organosodium compounds is the work of Schlenk and Bergmann.[2] These authors obtained the same acid by carbonating the organosodium compounds obtained from the

---

[1] Gilman and Jacoby, *J. Org. Chem.*, **3**, in press (1938).

[2] Schlenk and Bergmann, *Ann.*, **479**, 78 (1930).