Synthesis of 1-Decene-1,10-dicarboxylic Acid.—Undecylenic acid methyl ester (b. p. 119–120°, 10 mm.) prepared from Eastman Kodak Co. undecylenic acid was ozonized according to the procedure of Noller and Adams[7] in acetic acid solution and the half aldehyde of methyl sebacate (b. p. 124–125° (4 mm.)) obtained in 40% yield. Thirteen grams of this product was mixed with 15 g. of malonic acid and 15 g. of dry pyridine and heated under reflux for four hours. A vigorous evolution of carbon dioxide was observed in the early stages of the reaction. The resulting clear solution was acidified, poured into water and extracted with ether. After removal of the pyridine by extraction with dilute hydrochloric acid, the ether was evaporated and the crude product hydrolyzed directly by heating under reflux with 3 normal sodium hydroxide for two hours. Upon acidification the 1-decene-1,10-dicarboxylic acid precipitated and was recrystallized from alcohol or acetone, m. p. 165–166°. This product showed no depression of melting point when mixed with the naturally occurring material and was identical with the latter in crystalline form and physiological activity.

Anal. Calcd. for $C_{12}H_{20}O_4$: C, 63.05; H, 8.80. Found: C, 62.98; H, 8.85.

The S-benzyl thiuronium salt of traumatic acid was prepared according to the method of Donleavy.[11]

Anal. Calcd. for $C_{28}H_{40}O_4N_4S_2$: C, 59.96; H, 7.79; N, 9.99. Found: C, 59.78; H, 7.49; N, 9.90.

An oxidation of the synthetic product with permanganate in hot water solution gave sebacic acid, identified by melting point (133°) and mixed melting point.

Summary

The crystalline substance isolated from string bean pods and capable of inducing renewed cell division and cell extension activity in the parenchymatous cells of the bean pod mesocarp is shown to be 1-decene-1,10-dicarboxylic acid. Synthetic 1-decene-1,10-dicarboxylic acid was prepared and shown to be identical with the natural product both in physical properties and in physiological activity. It is proposed that the name "traumatic acid" be used in referring to this substance.

Traumatic acid is also shown to be capable of inducing wound periderm formation in washed disks of potato tuber and to function thus as a wound hormone of the potato. Traumatic acid is also capable of partially replacing the juice of the tomato fruit in reversibly inhibiting the germination of tomato seeds.

PASADENA, CALIF. RECEIVED AUGUST 10, 1939

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[11] J. J. Donleavy, THIS JOURNAL, **58**, 1004 (1936).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The System *n*-Butylmagnesium Bromide–Magnesium Bromide–Ethyl Ether

BY W. E. DOERING AND C. R. NOLLER

The system magnesium bromide–ethyl ether has been investigated by Menschutkin[1] who found that the solubility of the dietherate varied from 1.08% at −8° to 5.80% at 22°. At 22.8° the dietherate melted under ether to give two liquid phases. The composition of the upper layer changed from 6.8% dietherate at 30° to 10.2% at 90° while that of the lower layer changed from 69.8% at 30° to 68.6% at 90°.

During the course of another investigation[2] it was found that quantities of magnesium bromide greatly in excess of its solubility in ether could be added to Grignard solutions without the separation of two phases and in connection with studies on the composition and constitution of Grignard reagents it became desirable to determine quantitatively the effect of Grignard reagents on the solubility of magnesium halides. Table I and Fig. 1 summarize our results on the system *n*-butylmagnesium bromide–magnesium bromide–ethyl ether. Since the molecules of both the Grignard reagent and the magnesium bromide are present in all probability as the dietherates at ordinary temperatures when an excess of ether is present, the numerical values have been calculated on this basis. It is realized of course that the system is more complicated than indicated because of the equilibrium between *n*-butylmagnesium bromide, di-*n*-butylmagnesium and magnesium bromide. Since it is not possible at the present time to determine accurately the position of this equilibrium,[3] all of the active Grignard reagent has been calculated as being in the form of *n*-butylmagnesium bromide.

It can be seen that the presence of *n*-butylmagnesium bromide greatly modifies the solubility of magnesium bromide dietherate. Whereas magnesium bromide dietherate and ether form homogeneous solutions at 25° only when the con-

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[1] Menschutkin, *Z. anorg. Chem.*, **49**, 34, 207 (1906).

[2] Probert, Master's Thesis, Stanford University, 1933.

[3] Noller and White, THIS JOURNAL, **59**, 1354 (1937).

TABLE I

COMPOSITION IN WEIGHT PERCENTAGE OF UPPER AND LOWER LAYERS FOR VARIOUS MIXTURES OF *n*-BUTYLMAGNESIUM BROMIDE DIETHERATE, MAGNESIUM BROMIDE DIETHERATE AND DIETHYL ETHER AT 25°

Point[a]	Layer	$C_4H_9MgBr\cdot 2C_4H_{10}O$	$MgBr_2\cdot 2C_4H_{10}O$	Ether (by diff.)
a	Lower[b]	0.2	72.5	27.3
b	Lower	2.3	73.3	24.4
c	Lower	6.1	70.4	23.5
c′	Upper	.8	5.5	93.7
d	Lower	8.4	67.7	23.9
d′	Upper	1.4	5.8	92.8
e	Lower	13.9	60.7	25.4
e′	Upper	2.9	5.9	91.2
f	Lower	16.1	57.9	26.0
f′	Upper	3.6	5.8	90.6
g	Lower	23.1	39.2	37.7
g′	Upper	10.3	10.9	78.8
h	Lower	22.3	31.4	46.3
h′	Upper	14.4	15.3	70.3

[a] Primed and unprimed letters denote compositions in equilibrium with each other. [b] This is an analysis of the liquid magnesium bromide dietherate saturated with ether. A small amount of basic magnesium was present which was calculated as if it were *n*-butylmagnesium bromide but this readily can be ignored.

centration of the dietherate is greater than 73% or less than 5.5%, if the total concentration of *n*-butylmagnesium bromide dietherate is greater than approximately 23% the ratio of the magnesium bromide dietherate to the ether may be any value without the separation into two phases. It is also of interest that when separation into two phases does occur the concentration of the *n*-butylmagnesium bromide dietherate is always greater in the lower layer than in the upper layer. These two results indicate that the mutual solubility of the two dietherates is greater than their solubility in ether.

Experimental

The liquid magnesium bromide dietherate was prepared by the addition of bromine in slight excess over the calculated amount to pure magnesium turnings[4] under absolute ether. The solutions always darkened somewhat as the reaction progressed. The heavy liquid layer was transferred under nitrogen to a graduated reservoir which was fitted so that the liquid could be transferred to the reaction tubes by pressure. A 2 *N* solution of *n*-butylmagnesium bromide was prepared by the usual procedure and stored in the same way as the magnesium bromide solution.

The reaction vessels were cylindrical tubes of approximately 80 cc. capacity and 3 cm. in diameter fitted with necks and stoppers made from 10/30 standard taper "No-Lub" ground joints. The stoppers and necks had hooks so that they could be held firmly together by means of rubber bands. The hooks on the necks also permitted the tubes to be suspended above the pan of an analytical balance. Even the "No-Lub" joints permitted the passage of ether by capillarity but this could be prevented by putting a thin line of vaseline around the outermost edge of the stopper. This sealed the air in the ground joint so that the ether did not pass more than a third of the way through the stopper.

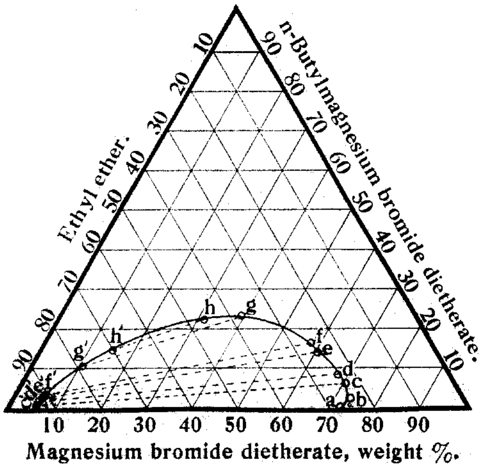

Fig. 1.—System *n*-butylmagnesium bromide–magnesium bromide–ethyl ether.

Varying amounts of the magnesium bromide dietherate, Grignard solution and absolute ether were added to the flasks under nitrogen and the mixtures shaken for one-half hour at 25 ± 1°. The tubes were then weighed accurately to one centigram and samples of both upper and lower layers rapidly removed by long wash-out pipets, the tubes being reweighed after each withdrawal. The samples were analyzed for Grignard reagent by titration with standard sulfuric acid and for bromine by the Mohr procedure. From these data the weight of *n*-butylmagnesium bromide dietherate and of magnesium bromide dietherate could be calculated and the ether determined by difference. At least duplicate determinations were made of each analysis and the results averaged. The agreement between duplicate determinations was in all cases better than 2%, except in point g′ where the variation was of the order of 5%.

Summary

A study of the system *n*-butylmagnesium bromide–magnesium bromide–ether shows that *n*-butylmagnesium bromide dietherate greatly modifies the solubility of magnesium bromide dietherate in ether and that the mutual solubility of the two dietherates is greater than their solubility in ether.

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[4] Aluminum Company of America, No. 651 ingot.