of the presence of *cis–trans* isomers. The substance exhibits a very strong blue fluorescence in ultraviolet light.

Anal. Calcd. for $C_{20}H_{16}$: C, 93.71; H, 6.29. Found: C, 93.62; H, 6.49.

A dipicrate was obtained from alcohol and crystallized as very dark red needles, m. p. 141.5–143°, dec.

Anal. Calcd. for $C_{20}H_{16}\cdot 2C_6H_3O_7N_3$: N, 11.76. Found: N, 11.61.

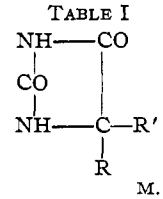
CONVERSE MEMORIAL LABORATORY
HARVARD UNIVERSITY
CAMBRIDGE, MASSACHUSETTS RECEIVED MARCH 27, 1940

Some New 5,5-Disubstituted Hydantoins

BY DAVID MARSH AND C. L. LAZZELL

It appears desirable to record data obtained on some six new 5,5-disubstituted hydantoins which have been prepared in this Laboratory following Bucherer's[1] method incidental to some other investigations. These substances were all recrystallized from 50% alcohol and were dried for five days at 85°. Except for the di-(*p*-dimethylaminophenyl) analog, which was yellow and soluble in benzene, they were all white crystalline solids, readily soluble in such organic solvents as acetone and 95% alcohol, but only moderately soluble in water.

TABLE I



—R	—R′	M. p. °C. (cor.)	Yield, %	Molecular weight Calcd.	Molecular weight Found	% Nitrogen Calcd.	% Nitrogen Found
Methyl	Cyclohexyl	204–205	48	199.31	200	14.1	14.1
Methyl	Styryl	217 d.	12	216.26	214	13.07	13.1
p-Dimethylaminophenyl	*p*-Dimethylaminophenyl	136–137	3	338.50	344	16.63	16.6
Methyl	2-Methylpropenyl	209–210	18	168.26	168	16.73	16.8
Methyl	*p*-Aminophenyl	100–101	36	205.33	202	20.57	21.0
Methyl	2-Methyl-2-hydroxypropyl	180–181	10	186.27	188	15.12	15.0

The yields obtained were rather low, but since it was only desired to obtain a pure sample of each hydantoin, no effort was made to improve them.

(1) Bucherer and Lieb, *J. prakt. Chem.*, [2] **141**, 5 (1934).

DEPARTMENT OF CHEMISTRY
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The Addition of Hydrogen Bromide to Methyl Methacrylate

BY CHARLES C. PRICE AND EUGENE C. COYNER

It has been found that methyl methacrylate adds hydrogen bromide to form methyl β-bromoisobutyrate exclusively. Only the β-bromo ester was produced even in pentane solution with peroxide catalysis, the conditions most favorable for reversing the mode of addition of hydrogen bromide to a double bond.[1]

This is in agreement with similar experiments with acrylic and crotonic acids and ethyl crotonate reported by Walling, Kharasch and Mayo and by Grimshaw, Guy and Smith[2] since the initiation of this investigation.

Since only the boiling points of the two possible addition products have been recorded, the two isomeric methyl bromoisobutyrates have been carefully characterized.

Methyl β-Bromoisobutyrate.—When redistilled methyl methacrylate[3] (10 g.) in hexane or carbon tetrachloride solution (50–100 cc.) was treated with hydrogen bromide at 0 or 25° in the presence of 1% of hydroquinone, benzoyl peroxide or "Lucidol"[4] or while exposed to direct sunlight in a quartz flask, nearly quantitative yields of methyl β-bromoisobutyrate were obtained; b. p. 67° (17 mm.),[5] $n^{20}D$ 1.4551; d^{20}_4 1.426; $M^{20}D$ (calcd.) 34.71; $M^{20}D$ (found) 34.47.

Anal. Calcd. for $C_5H_9O_2Br$: Br, 44.15. Found[6]: Br, 44.38.

No other product could be detected; even the first few drops of distillate had properties in agreement with those above. When methanol was used as a solvent no addition occurred at room temperature.

The hydrogen bromide was generated by dropping bromine into tetralin; it was bubbled through tetralin to free it from bromine vapor.

Methyl α-Bromoisobutyrate.—For comparison, the α-bromo ester was prepared by the Hell–Volhard–Zelinsky method. Bromine (102.5 g.) was added to 29.5 g. of

(1) Walling, Kharasch and Mayo, THIS JOURNAL, **61**, 1711 (1939).
(2) Walling, Kharasch and Mayo, *ibid.*, **61**, 2693 (1939); Grimshaw, Guy and Smith, *J. Chem. Soc.*, 68 (1940).
(3) E. I. du Pont de Nemours and Company, Wilmington, Delaware.
(4) Lucidol Corporation, Buffalo, New York.
(5) Vocke (*Z. physiol. Chem.*, **191**, 83 (1930)) reported the boiling point as 65–67° (12 mm.).
(6) Method described by Rauscher, *Ind. Eng. Chem., Anal. Ed.*, **9**, 296 (1937).

isobutyric acid and 5 g. of red phosphorus at 70–80°. The excess bromine was removed by evaporation under diminished pressure and the residue cooled in ice while 20 cc. of methanol was added. On fractional distillation, 14.4 g. (25%) of methyl α-bromoisobutyrate was obtained; b. p. 52° (19 mm.),[7] $n^{20}D$ 1.4410; d^{20}_4 1.331; $M^{20}D$ (calcd.), 34.71; $M^{20}D$ (found), 35.01.

Anal. Calcd. for $C_5H_9O_2Br$: Br, 44.15. Found[6]: Br, 43.14.

The physical properties of this ester changed appreciably on standing for a few hours since hydrogen bromide is evolved with extreme ease. This accounts for the low bromine content of the product. The physical properties recorded above were observed immediately after distillation.

(7) Wheeler and Barnes, *Am. Chem. J.*, **24**, 79 (1900).

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The Identity of Obaculactone, Evodin and Dictamnolactone with Limonin[1]

BY MILTON S. SCHECHTER AND H. L. HALLER

Several investigators[2,3] have isolated from the extractives of the bark of the amur cork tree (*Phellodendron amurense* Rupr.) a colorless, crystalline, optically active compound, which melts with decomposition at 292–293° and possesses the properties of a dilactone. The compound was named "obaculactone" by Fujita and Wada,[2] who were the first to describe it. On the basis of combustion analyses and molecular weight determinations they assigned the formula $C_{15}H_{16}O_6$ to obaculactone, but subsequent studies have shown this formula to be in error. The molecular formula $C_{26}H_{30}O_8$ is now generally accepted as correctly representing the composition of the compound.

In 1934 Fujita, Kaku and Kutani[4] showed that obaculactone is identical with evodin and with dictamnolactone. Evodin was first isolated by Keimatsu[5] in 1902 from the benzene extractives of the fruit of *Evodia rutaecarpa* Hook. f. and Thoms., and subsequently by several investigators from the fruits of other species of *Evodia*. Dictamnolactone was first described by Thoms and his co-workers[6] who obtained it from the extractives of white dittany (*Dictamnus albus* L.). The latter workers surmised that evodin and dictamnolactone were identical but were unable to make a direct comparison. The identity of the three compounds was established[4] by mixture melting point determinations and specific rotations in neutral and alkaline solution. In acetone all three compounds are levorotatory; $[\alpha]_D$ about −123°. In ethanolic potassium hydroxide solution they are dextrorotatory; $[\alpha]_D$ about +30°.

None of the early formulas assigned to the lactone were correct. In 1933 Chen and Chen[7] proposed the formula $C_{26}H_{30}O_8$. Mayeda[8] confirmed this and suggested that some of the previous difficulties in the determination of the molecular formula may have been due to the fact that the lactone crystallizes from acetic acid with one mole of acetic acid of crystallization. The lactone melts with decomposition, and melting points ranging from 280 to 293° have been reported for obaculactone, evodin and dictamnolactone by the several investigators.

A recent communication by Higby[9] describes the isolation of limonin from the pulp and seeds of the Valencia orange. This colorless, crystalline compound was first obtained by Bernay[10] in 1841 from the seeds of several varieties of citrus. Limonin has been shown to be an optically active dilactone, and combustion analyses and molecular weight determinations indicate it to possess the formula $C_{26}H_{30}O_8$. Koller and Czerny[11] have reported that limonin melts with decomposition at 280° (uncor.), whereas Higby found 292° (cor.). Citrolimonin, which is considered by Feist and Schulte,[12] by Koller and Czerny, and by Higby as being identical with limonin, is reported to melt with decomposition at 304° (Kofler micro melting point apparatus) by the first-mentioned workers.

In the course of our studies on the insecticidal properties of the fruit of the amur cork tree, the results of which will be reported elsewhere, obaculactone has been obtained from the ether and the acetone extracts of the fruit. The compound, when recrystallized by solution in acetone followed by the addition of ethanol, melted with decomposition at 299–300° (cor.).[13] When recrystallized from glacial acetic acid, it melted with decomposition at 297–298° (cor.). An aqueous

(1) Not subject to copyright.
(2) Fujita and Wada, *J. Pharm. Soc. Japan*, **51**, 506 (1931), (in German 52).
(3) Kaku, Cho and Orita, *ibid.*, **52**, 593 (1932), (in German 73).
(4) Fujita, Kaku and Kutani, *ibid.*, **55**, 67 (1935).
(5) Keimatsu, *ibid.*, No. **248**, 979 (1902).
(6) Thoms, *Ber. deut. pharm. Ges.*, **33**, 68 (1923).
(7) Chen and Chen, *J. Am. Pharm. Assoc.*, **22**, 716 (1933).
(8) Mayeda, *J. Pharm. Soc. Japan*, **55**, 90 (1935).
(9) Higby, THIS JOURNAL, **60**, 3013 (1938).
(10) Bernay, *Ann.*, **40**, 317 (1841).
(11) Koller and Czerny, *Monatsh.*, **67**, 248 (1936); **70**, 26 (1937).
(12) Feist and Schulte, *Ber.*, **69**, 1322 (1936).
(13) All the melting point determinations reported were made in open melting point capillaries, using a total immersion thermometer calibrated by the National Bureau of Standards, Washington, D. C.