

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's¹ 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.

isobutyrate 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

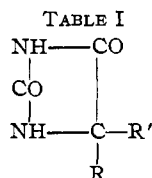
This is in agreement with similar experiments with acrylic and crotonic acids and ethyl crotonate reported by Walling, Kharasch and Mayo and by Grimshaw, Guy and Smith² since the initiation of this investigation.

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

Methyl β -Bromoisobutyrate.—When redistilled methyl methacrylate³ (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_D^{20} 1.4551; d_4^{20} 1.426; M^{20}_D (calcd.) 34.71; M^{20}_D (found) 34.47.

Anal. Calcd. for $C_5H_9O_2Br$: Br, 44.15. Found⁶: Br, 44.38.

No other product could be detected; even the first few drops of distillate had properties in agreement with those



—R	—R'	M. p. °C. (cor.)	Yield, %	Molecular weight Calcd.	weight Found	% Nitrogen Calcd.	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
<i>p</i> -Dimethylaminophenyl	<i>p</i> -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	<i>p</i> -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
WEST VIRGINIA UNIVERSITY
MORGANTOWN, WEST VIRGINIA

RECEIVED FEBRUARY 5, 1940

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 -bromo-

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).