TABLE I

SEPARATION OF RICINOLEIC ACID FROM A NON-HYDROXY ACID

Experimental conditions					Ricinoleic acid, %		
Heated with		Equiv.	Time, hr.	Temp., °C.	Concn. in starting mat.	In hydroxy acid fraction Concn. sepd.	Orig. recov.
Maleic anhydride		6	18	120	5	47	63
		6	18	120	10	86	70
		1.5	6	100	50	95	84
Succinic anhydride with solvent	AmOAc	10	18	120	10	68	70
	Dioxane	10	18	120	10	73	47
	Pyridine	10	7	130	10	93	78
	Pyridine	10	18	130	10	92	86

tained with a large variety of hydroxy fat acids. Maleic anhydride is sufficiently soluble in esters, so that the reaction mixture can be made homogeneous by the addition of only a small proportion of dioxane and often without any solvent. Pyridine is not suitable as a solvent because of the formation of large amounts of a tarry precipitate. A disadvantage in the use of maleic anhydride was found in an unexpected side reaction which takes place to a certain extent between methyl oleate and maleic anhydride to form a saturated compound. Succinic anhydride does not have this disadvantage but because of its lower solubility in the higher esters a solvent is necessary. With dioxane low yields are obtained. With pyridine better yields are obtained, but on prolonged heating considerable quantities (though much less than with maleic anhydride and pyridine) of a tarry precipitate are formed. It is recommended that when the separation involves only saturated acids, maleic anhydride be used, and that when unsaturated acids are present, succinic anhydride be used.

Table I summarizes the results of some typical experiments. It is obvious from the data that, in most cases, more than one application of the separation would be necessary to secure the one type of acid free from the other. In the case of the castor oil acids, which contain about 85% of hydroxy acids, it was found that by two applications of the separation the hydroxy acids were obtained practically free from non-hydroxy acids.

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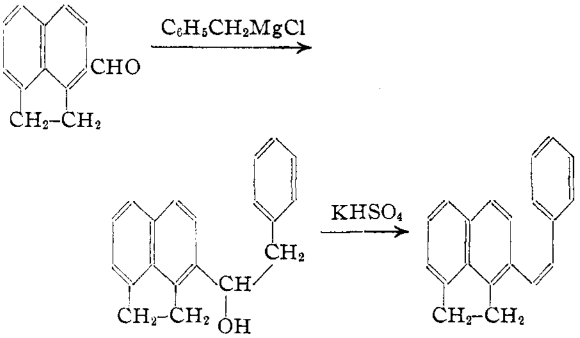
1-(β-Styryl)-acenaphthene

BY E. B. HERSHBERG[1] AND LLOYD M. JOSHEL[2]

The hydrocarbon mentioned in the title seemed of interest because in the *cis* form it constitutes an "opened" model of the carcinogenic cholanthrene from which it differs merely by the absence of one linkage connecting the benzenoid rings. The substance was synthesized by condensing 1-acenaphthaldehyde[3] with benzylmagnesium chloride and dehydrating the resulting carbinol. The hydrocarbon is crystalline and shows fluorescence in ultraviolet light.



Experimental Part[4]

1-Acenaphthylbenzylcarbinol.—A solution of 3.7 g. of 1-acenaphthaldehyde in benzene was added to the Grignard reagent from 3.5 cc. of benzyl chloride and 0.8 g. of magnesium in ether and after refluxing for one and one-half hours the mixture was decomposed with ammonium chloride and the solvents removed with steam. The product was taken up in ether and after washing and drying was obtained from ether–ligroin as needles, m. p. 107–109.5°, sufficiently pure for the next step; yield 4.9 g. (88%). A sample recrystallized for analysis from ether–ligroin (Norit) formed colorless needles, m. p. 109–110°.

Anal. Calcd. for $C_{20}H_{18}O$: C, 87.55; H, 6.61. Found: C, 87.62; H, 6.82.

1-(β-Styryl)-acenaphthene.—A mixture of 1.5 g. of the carbinol and about 0.1 g. of fused potassium bisulfate was heated at 200° until the evolution of water had ceased (ten minutes) and the product was then vacuum distilled and crystallized from absolute alcohol. The yield of twice crystallized hydrocarbon, m. p. 91.5–93°, was 1.0 g. (71%), but further recrystallizations were required to give material of the constant m. p. 93.2–94.0° (0.6 g.), possibly because

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(1) Research Fellow on grants from the National Cancer Institute and the Eli Lilly Company.

(2) Fellow of the Finney-Howell Research Foundation.

(3) Fieser and Hershberg, THIS JOURNAL, **62**, 49 (1940).

(4) All melting points are corrected. Microanalyses by Lyon Southworth.

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.

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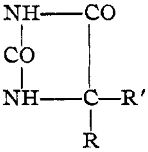
Some New 5,5-Disubstituted Hydantoins

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		% Nitrogen	
				Calcd.	Found	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
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
WEST VIRGINIA UNIVERSITY
MORGANTOWN, WEST VIRGINIA
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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

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[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).