TABLE I

ANALYSES AND MELTING POINTS OF THE *p*-BROMOANILIDES OF SOLID FATTY ACIDS

| *p*-Bromo-anilide | Analyses, % Carbon Calcd. | Carbon Found | Hydrogen Calcd. | Hydrogen Found | Bromine Calcd. | Bromine Found | Melting point in °C. Lit.[c] | Melting point in °C. Found |
|---|---|---|---|---|---|---|---|---|
| Capric | 58.92 | 59.03[a] | 7.37 | 7.54[a] | 24.6 | 24.7[b] | 102 | 101.9 |
| Lauric | 61.02 | 61.02 | 7.94 | 7.93 | 22.6 | 22.5 | 104 | 106.7 |
| Myristic | 62.81 | 62.94 | 8.41 | 8.26 | 20.9 | 21.2 | 107 | 110.2 |
| Palmitic | 64.38 | 64.33 | 8.81 | 8.74 | 19.5 | 19.2 | 110(114)[d] | 113.2 |
| Stearic | 65.72 | 65.63[a] | 9.16 | 9.38[a] | 18.3 | 18.4[b] | 114 | 115.2 |

[a] Analyses by W. T. Haskins, National Institute of Health; all others by C. J. Rodden, National Bureau of Standards. [b] Pregl method. Other bromine analyses by Zacherl and Krainick method. [c] Robertson's values[1a] except *d*. [d] Acree and LaForge (*J. Org. Chem.*, **2**, 308 (1937)). A sample of their material showed a melting point of 113.1° when determined by the writer by means of the Francis and Collins method.

the literature values has an opposite convexity. Hence it has seemed wise to publish our results.

The reagent quality acids were first recrystallized from concentrated sulfuric acid[2] until no further discoloration of the solvent occurred, and they were then repeatedly recrystallized interchangeably from acetone, benzene, and glacial acetic acid until no further change in melting point occurred. The acids were converted into their acid chlorides with thionyl chloride.

The *p*-bromoaniline was prepared (a) by the reduction of *p*-nitrobromobenzene (m. p. 126.3°), (b) by hydrolysis of *p*-bromoacetanilide (m. p. 168.6°) according to Vecchiotti,[3] and (c) by recrystallization of a commercial product from chloroform and then from aqueous alcohol to remove colored matter[4] and tribromoaniline, respectively. The three preparations of *p*-bromoaniline thus obtained had melting points between 63.5 and 64.0°, and gave products with palmitic acid which had identical melting points.

The chlorides were treated with a benzene solution of *p*-bromoaniline according to the procedure of Kuehn and McElvain,[5] with the single modification of first crystallizing the product directly from the benzene solution instead of evaporating the benzene. In the case of the long chain acids, this affords a more rapid purification.

The melting points were determined with a partial-immersion thermometer (calibrated at this Bureau) by the improved capillary-tube method of Francis and Collins.[6] This procedure, which maintains an extremely slow rate of temperature rise at the melting point, gives values that are somewhat lower than those usually obtained by capillary-tube methods (see footnote *d* of table). The results are, however, in better agreement with those obtained by equilibrium measurements on larger amounts of material.

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[2] F. Francis, F. J. E. Collins and S. H. Piper, *Proc. Roy. Soc. London*, **A158**, 706 (1937).

[3] L. Vecchiotti, *Gazz. chim. ital.*, **58**, 231 (1928).

[4] W. M. D. Bryant, THIS JOURNAL, **60**, 2748 (1938).

[5] M. Kuehn and S. M. McElvain, *ibid.*, **53**, 1173 (1931).

[6] F. Francis and F. J. E. Collins, *J. Chem. Soc.*, 137 (1936).

## The Separation of Hydroxy from Non-hydroxy Fat Acids by Means of a Dibasic Acid Anhydride[1]

BY FLOYD E. KURTZ[2] AND P. S. SCHAFFER[2]

The methods used for separating hydroxy from non-hydroxy fat acids have been based for the most part on differences in physical properties of the acids or of the derivatives formed with the carboxyl group. When the fat acid mixture contains acids in which these differences are small, it becomes difficult to secure a separation by such methods. This is particularly true if one of the similar acids is present as a minor constituent while the other is present in a high concentration.

In the method proposed here, the mixed esters are heated with a dibasic acid anhydride, the reaction mixture is dissolved in petroleum ether, and the derivative formed with the hydroxy esters is extracted with alkali. Since this method consists in the separation of an alcoholic from a non-alcoholic compound rather than upon the separation of two acids, its efficiency is not affected by a similarity in the physical properties of the acids.

Of the most readily available dibasic acid anhydrides, phthalic anhydride was considered unsuitable because of the difficulty of freeing the recovered fat acids from phthalic acid. Maleic anhydride was thoroughly investigated. It formed derivatives with methyl ricinoleate and with 12-hydroxymethylstearate which could be extracted readily from petroleum ether solutions, less readily from ether solutions, by means of dilute potassium hydroxide. Since ricinoleic acid and 12-hydroxystearic acid represent two hydroxy acids with quite different physical properties, it is considered likely that similar results could be ob-

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[1] The part relating to maleic anhydride was presented before the Division of Biological Chemistry at the 97th meeting of the American Chemical Society, April 3-7, 1939, at Baltimore, Maryland. (Not subject to copyright.)

[2] Division of Dairy Research Laboratories, Bureau of Dairy Industry, U. S. Department of Agriculture.

TABLE I

SEPARATION OF RICINOLEIC ACID FROM A NON-HYDROXY ACID

| Experimental conditions | | | | | Ricinoleic acid, % | | |
|---|---|---|---|---|---|---|---|
| | | | | | Concn. in | In hydroxy acid fraction | |
| Heated with | | Equiv. | Time, hr. | Temp., °C. | starting mat. | 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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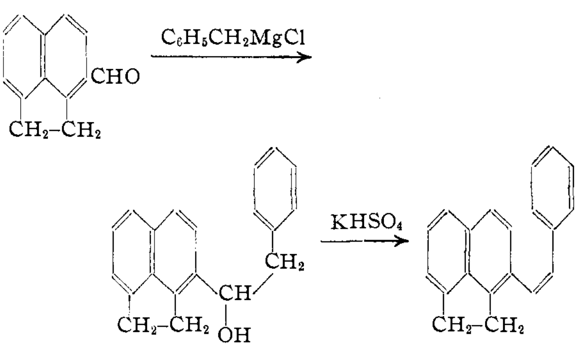
## 1-(β-Styryl)-acenaphthene

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.