

is not suitable for micro-amounts since the least detectable amount is *ca.* 50 μg for all investigated derivatives except for MeImAA for which *ca.* 100 μg is necessary. In contrast, only 1.0–10.0 μg quantities produce colored spots on regular cellulose paper.

Using the above technique, quantitative analysis of ^{14}C -histamine metabolites from embryonating chicken eggs is being investigated. Metabolic radioactive products are chromatographed by the described procedure with known compounds as markers, and the developed spots cut out and their radioactivity measured with a liquid scintillating spectrometer¹⁰.

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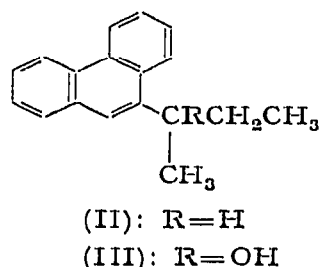
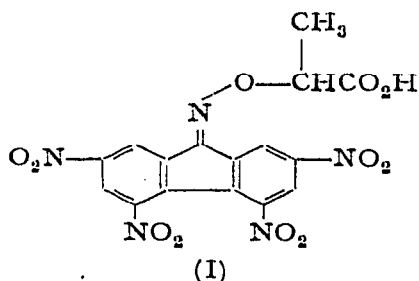
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Optical resolution of 9-sec.-butylphenanthrene by molecular complexation chromatography

KLEMM AND REED¹ described the use of columns of silicic acid impregnated with the optically active molecular complexing agent (+)- or (–)- α -(2,4,5,7-tetranitro-9-fluorenylideneaminooxy)-propionic acid (I) for optical resolution of an ether and of an ester containing one center of asymmetry (on carbon) for each compound. In addition the method was used for optical resolution of a hydrocarbon wherein optical activity



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results from serious restriction to rotation around a pivotal bond of the biphenyl type. We now report the successful extension of the method to the partial optical resolution of 9-*sec.*-butylphenanthrene (II), a hydrocarbon containing a single center of asymmetry and expected to have a small specific rotation. The alkylarene II was selected for investigation because it contains the simplest alkyl group (devoid of isotopic labelling) possessing asymmetry when attached to an aryl moiety and because maximum overlap² of the angular fluorene and phenanthrene nuclei during molecular complexation should bring the centers of asymmetry in I and II into spatial proximity for maximal interaction.

Experimental

Synthesis of II. Methyl ethyl 9-phenanthryl carbinol (III, 47.1 g, m.p. 102–104°, 94 % yield from 9-bromophenanthrene³) was dehydrated by distillation at 0.3 mm pressure. Treatment of the crude distillate with an equimolar amount of anhydrous picric acid in absolute ethanol gave 58 g (67 % yield from III) of yellow 9-(2-butanyl)-phenanthrene picrate, m.p. 101–103°. *Anal.* Calcd. for C₁₈H₁₆·C₆H₃N₃O₇: neut. equiv. 461.4. Found⁴: neut. equiv. 464. Chromatographic dissociation of the picrate using benzene and Alcoa F-20 alumina and distillation of the effluent gave slightly yellow 9-(2-butanyl)-phenanthrene, 96 % recovery, b.p. 137–142° (0.3 mm); infrared absorption bands at 905 cm⁻¹ (strong, terminal methylene) and 825 cm⁻¹ (medium, trisubstituted ethylene?); showing positive test with aqueous permanganate. *Anal.* Calcd. for C₁₈H₁₆: C, 93.06; H, 6.94. Found* (for sample of b.p. 140–141°): C, 92.74; H, 7.24.

Agitation of a mixture of 11.6 g of the preceding alkenylphenanthrene, 2 g of 5 % Pd-BaSO₄, and 75 ml of glacial acetic acid in hydrogen gas at 4 atm pressure for 5 h followed by removal of the catalyst and distillation gave 8.2 g (71 %) of II, a faintly yellow liquid, b.p. 150–155° (0.3 mm); showing negative test with aqueous permanganate. *Anal.* Calcd. for C₁₈H₁₈: C, 92.26; H, 7.74. Found* (for sample of b.p. 151–152°): C, 92.38; H, 7.51.

II-picrate was obtained as yellow crystals from ethanol, m.p. 97–98.5°. *Anal.* Calcd. for C₁₈H₁₈·C₆H₃N₃O₇: neut. equiv. 463.4. Found⁴: neut. equiv. 464.

Optical resolution. In a manner similar to that previously reported¹ a glass burette (1.5 cm in diameter) with a non-lubricated stopcock was packed (dry and without suction) with successive layers of glass wool, 2 cm of plain silicic acid, 50 cm of a mixture of 13 g of Johns-Manville Celite (anal. grade) and 27 g of silicic acid impregnated with (–)-I (8.9 % by wt.), and 2 cm of purified sand. The column was wrapped in aluminum foil. "Pure grade" cyclohexane (99 mole % minimum) was used as prewash for the column and as eluent for the 0.58 g of racemic II used. As soon as the red color of the molecular complex had reached the bottom of the column, fractions of 200 drops each were collected in tared test tubes at the average rate of 1 fraction per 26 h. Fractions were evaporated to constant weight in a stream of nitrogen, quantitatively diluted to 5 ml (the volume of the 1 dm polarimetric cell) with cyclohexane, and measured for optical rotation at 365 mμ and 24° by means of a Perkin-Elmer model 141 polarimeter (accuracy of ±0.002°). Only fractions 2–5 (of 11 total) showed significant rotations as follows (in order of appearance): 0.11 g, α = +0.008°, [α] = +0.36°; 0.17, +0.005°, +0.15°; 0.06, –0.005°, –0.42°; 0.05,

* Elemental analyses by Micro-Tech Laboratories, Skokie, Ill.

-0.007° , -0.70° . No significant rotations were found at wavelengths longer than 500 $m\mu$.

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Book Reviews

Thin-layer Chromatography, by JAMES M. BOBBIT, Reinhold Publishing Corporation, New York, 1963, xi + 208 pages, price \$ 8.50.

This book gives a very detailed and complete account of the principles and techniques of thin-layer chromatography in the first 123 pages. Then follows a chapter on "specific applications of thin-layer chromatography" which consists of fifty odd pages of tables listing the compound type, the adsorbent, the developer, visualisation, "comments" and the reference number. In introducing the chapter the author states that specific R_F values are not given because of their notorious inconstancy. This remark would certainly be criticised by some authors. But even where R_F values are not reproducible it would help the reader to see exactly which compounds were separated and what differences in R_F values were obtained. These tables are thus only a very inadequate guide to the literature. The reference list contains 460 references, many as recent as 1963, and there is an adequate subject index.

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