other natural products by ion exchange chromatography is a decomposition product of a larger molecule.

TABLE I

PAPER CHROMATOGRAPHY OF FRACTION E

Solvent systems: 1–8, 11 isobutyric/NH_4OH/H_2O 66/1/33; 9, 10 ethanol/NH_4OH/H_2O (8:1:1); 12, 13 ethanol/NH_4OH (95:5); AMP = adenylic acid, ADP = adenosine diphosphate, ATP = adenosine triphosphate, R-P = ribose-phosphate.

		R_f		
		Ultra-violet	Ninhydrin	Phos-phate
1	5′-AMP	0.47		
2	E_1	.05		
	E_2	.15	0.15	
	E_3	.40		
3	5′-ATP	.18		
4	5′-ADP	.23		
5	E_4	.44		0.17
6	5′-RP			.17
7	E_4 (formic hydrolysis)	.84	.23	
		.52		
8	Adenine	.83		
	Hypoxanthine	.51		
	Aspartic		.24	
9	Fumaric	.21	.21	
10	E_4 (formic hydrolysis)	.21	.21	
11	E_2 (10 min., .001 *N* HCl, 100°)	.17	.13	
12	Glutamic		.02	
	Serine		.14	
13	Peptide (hydrolysed)		.02	.14

TABLE II

ANALYSIS OF COMPOUND I

Adenine succinic acid was determined by absorption at 266 mμ using E 16.9 × 10^3 at *p*H 1.0, ribose by the orcinol method, labile phosphorus by 7 min. hydrolysis in 1 *N* acid, total phosphorus by $HClO_4$ digestion, the color in both cases was developed by the Gomori method. Vicinal glycol was estimated spectrophotometrically.[8] Sulfate was determined colorimetrically after conversion to H_2S,[9] which then reacted with *p*-phenylenediamine to form Lauth's violet.[10]

	Moles
Adeninesuccinic acid	1.00
Ribose	1.12
Labile-P	0.00
Total P	1.05
Sulfate	1.37
cis Glycol	1.27

When I was subjected to mild acid hydrolysis (0.01 *N* HCl, 100°, 10 min.) and chromatographed in several systems, a single ninhydrin position spot was obtained which gave glutamic acid and serine in equal concentrations following hydrolysis in 6*N* HCl for 12 hours at 120°. It has not yet been established whether I contains a dipeptide or polypeptide of glutamic acid and serine. Fraction E from another liver preparation contained glycine so this portion of the molecule is probably a variable. The manner of linkage of the peptide to the nucleotide and the sequence of the amino acid residues in the peptide chain are under further investigation.

(9) C. L. Luke, *Anal. Chem.*, **21**, 1369 (1949).
(10) D. S. C. Polson and J. D. H. Strickland, *Anal. Chim. Acta*, **6**, 452 (1952).

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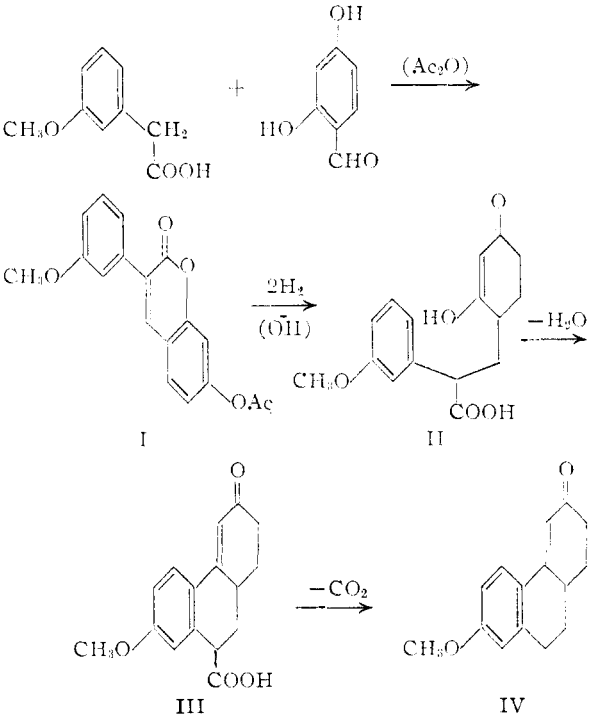
RECEIVED JANUARY 21, 1957

SYNTHESIS OF 1,2,3,9,10,10a-HEXAHYDRO-3-keto-PHENANTHRENES FROM 3-ARYL-7-ACETOXYCOUMARINS

Sir:

To the growing collection of methods for elaborating polycyclic compounds we now add a new sequence of reactions leading to some important hydrophenanthrene ketones.



Features contributing to the success of this method are (1) improved Perkin condensation of methoxyphenylacetic acids with β-resorcylaldehyde and other phenolic carbonyl compounds, (2) novel and very efficient hydrogenation and *in situ* hydrolysis of resulting coumarins, such as I, incorporating a resorcinol unit, in the presence of *palladium* and dilute alkali, to dihydroresorcinols such as II, and (3) cyclization of II with polyphosphoric acid. Dehydration of II to III evidently depends for its success upon factors similar to those at work in related reactions[1,2] involving attack of cyclic 1,3-keto-enols upon the aromatic ring, and in this case may involve intermediate enol lactone formation.

Compound I, m.p. 145–146° (Found: C, 69.5; H, 4.54; $\lambda_{max}^{chf.}$ 5.67 and 5.80 μ), was prepared in 66% yield by condensation of 2,4-dihydroxybenzaldehyde and 3-methoxyphenylacetic acid, using

(1) A. J. Birch and H. Smith, *J. Chem. Soc.*, 1882 (1951).
(2) G. N. Walker, THIS JOURNAL, **78**, 2340, 3201 (1956).

acetic anhydride and three equivalents of potassium acetate. Hydrogenation of I in the presence of 10% palladium–charcoal and 3.1 equivalents of sodium hydroxide (1% aqueous solution) at 80° resulted in absorption of two moles of hydrogen and gave, after acidification, 92% of II, m.p. 146–147° (Found: C, 66.03; H, 6.31; $\lambda_{max}^{chf.}$ 5.78 and 5.85 μ). Unlike I, compound II gave positive tests with ferric chloride and 2,4-dinitrophenylhydrazine. Treatment of II with polyphosphoric acid at 100° for an hour gave 95% of a mixture of two isomers of III, separated by fractional crystallization (methanol) into colorless crystals, m.p. 183–186° (resolidified, remelted 207–211° dec.) (Found: C, 70.8; H, 5.99; $\lambda_{max}^{chf.}$ 5.86 and 6.02–6.07 μ), and yellow, chloroform-insoluble crystals, m.p. 218–219° dec. (Found: C, 70.4; H, 5.89). Esterification of either isomer of III with methanol (sulfuric acid) gave the same methyl ester, m.p. 119–121° (Found: C, 71.3; H, 6.33; $\lambda_{max}^{chf.}$ 5 80 and 6.02–6.07 μ; λ_{max}^{EtOH} 242 and 326 mμ with log ϵ 4.05 and 4.39, respectively). The red *2,4-dinitrophenylhydrazone* of this ketoester had m.p. 246–247° dec. (Found: C, 59.3; H, 4.82). Decarboxylation of III (quinoline) gave ketone IV, m.p. 114–115.5°[3] ($\lambda_{max}^{chf.}$ 6.02–6.07 μ; λ_{max}^{EtOH} 241 and 328 mμ, with log ϵ 4.02 and 4.40, respectively), further identified as the *2,4-dinitrophenylhydrazone*, deep red crystals, m.p. 219–220° dec. (Found: C, 61.6; H, 5.13). Aromatization and decarboxylation of III (palladium–charcoal in *p*-cymene) followed by acetylation gave 2-methoxy-6-acetoxyphenanthrene, m.p. 114–115° (Found: C, 76.57; H, 5.53); λ_{max}^{EtOH} 221, 255, 278, 291, 319, 334 and 350 mμ (log ϵ 4.38, 4.84, 4.27, 4.17, 2.76, 2.91 and 2.83, respectively).[4] Aromatization and decarboxylation of the sodium borohydride reduction product from III gave 2-methoxyphenanthrene,[5] m.p. 93–95°, λ_{max}^{EtOH} 221, 229, 254, 277, 289, 319, 334 and 350 mμ (log ϵ 4.36, 4.24, 4.89, 4.27, 4.19, 2.85, 3.02 and 3.00, respectively); *picrate*, m.p. 122–123°.

The same series of reactions, starting with homoveratric acid instead of 3-methoxyphenylacetic acid, gave a mixture of isomers of 1,2,3,9,10,10a-hexahydro-3-keto-6,7-dimethoxy-9-carboxyphenanthrene. The higher-melting isomer of this compound has m.p. 229–231° dec. (Found: C, 67.43; H, 5.97; λ_{max}^{EtOH} 226, 242 and 341 mμ, with log ϵ 4.02, 4.06 and 4.30, respectively); the lower-melting isomer has not yet been obtained completely pure. The *2,4-dinitrophenylhydrazone* of the corresponding ethyl ester has m.p. 245–246° dec. (Found: C, 58.93; H, 5.28).

The concepts involved in this work eventually may prove to be applicable in preparation, reduction, and homocyclization of compounds other than coumarins (I), and future studies are aimed at finding such related processes. Aside from the fact that the work outlined above represents a long-sought, fundamental development in the chemistry of hydrophenanthrenes, the synthesis, which now makes III and similar ketoacids readily available, very likely will provide some new compounds of potential pharmacological interest.

(3) G. T. Tatevosyan, P. A. Zagorets and A. G. Vardanyan, *J. Gen. Chem., U.S.S.R.*, **23**, 979 (1953) report m.p. 114–115° and 219–220° for this ketone and its 2,4-dinitrophenylhydrazone, respectively, prepared by a more circuitous method (*cf. Chem. Abstracts*, **48**, 7593 (1954), **49**, 4604 (1955)).

(4) See R. A. Friedel and M. Orchin, "Ultraviolet Spectra of Aromatic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1951, curve 373.

(5) R. Pschorr and C. Seydel, *Ber.*, **34**, 3998 (1902).

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RECEIVED FEBRUARY 28, 1957

BOOK REVIEWS

Elements of X-Ray Diffraction. By B. D. CULLITY, Associate Professor of Metallurgy, University of Notre Dame. Addison-Wesley Publishing Company, Inc., Reading, Massachusetts. 1956. xiv + 514 pp. 16 × 23.5 cm. Price, $10.00.

Elements of X-Ray Diffraction is published as one in a series of reference books primarily designed for metallurgists. The treatment is introductory, intended for the reader who has had little or no previous experience with the theory or application of X-rays to structure problems. Problems of particular concern in the study of metals and alloys are emphasized. The book does not attempt to provide adequate background for the complete elucidation of the structures of complex crystals. It primarily presents the apparatus and theory of methods for study of crystalline powders and of the Laue method. It is written in terms of Bragg's law; reciprocal lattice theory is described only briefly in an appendix. Space group theory is also only briefly mentioned as the subject of crystal structure is approached through the concept of the point lattice.

Although the scope of the book is limited, it is written lucidly and will be found valuable as an introductory text by chemists as well as metallurgists. The author discusses basic concepts in considerable detail. Introductory chapters on properties of X-rays and the geometry of crystals are followed by a discussion of the positions of the diffracted beams and of the intensity–structure factor problem. Methods for determining structures from powder data are described and examples given. A chapter on diffractometer measurements, giving a description of instruments currently available for the measurement of the intensity of diffracted beams, is included.

Effects associated with crystal size, imperfections, twinning, solid solutions, order–disorder phenomenon, and problems of phase diagram determination, particularly as they occur in metal–metal alloy systems, are discussed.