

*Anal.* Calcd. for  $C_{22}H_{35}O_2$ : C, 78.98; H, 11.45. Found: C, 78.85; H, 11.25.

**3 $\beta$ -Methoxy-17 $\alpha$ -methyl-5 $\alpha$ -androst-17 $\beta$ -ol (VII).**—To a solution of 3 $\beta$ -methoxy-17 $\alpha$ -methyl-5-en-17 $\beta$ -ol<sup>15</sup> (1.0 g.) in 95% ethanol (35 ml.) was added 5% palladium-on-carbon (0.1 g.). The mixture was hydrogenated at atmospheric pressure and room temperature.<sup>14</sup> Hydrogen uptake was complete after 3 hr. and the catalyst was removed by filtration and washed with ethanol. The solvent was removed from the filtrate and

(15) M. N. Huffman and J. W. Sadler, *J. Org. Chem.*, **18**, 924 (1953).

the residue crystallized from 95% ethanol. This gave VII (0.8 g.), m.p. 178–179°, and a second crop (0.15 g.), m.p. 176–178°. Recrystallization from methanol–water afforded an analytical sample, m.p. 180–181°,  $[\alpha]_D^{25} -16.5^\circ$ .

*Anal.* Calcd. for  $C_{21}H_{30}O_2$ : C, 78.69; H, 11.32. Found: C, 78.71; H, 11.35.

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## New Compounds

### Synthesis of the Three Isomeric 7-Pyridylbenz(a)anthracenes

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In view of the suspected causal relationship between certain polynuclear compounds related to benz(a)anthracene found in some polluted air and lung cancer,<sup>2</sup> we decided to prepare the three isomeric 7-pyridylbenz(a)anthracenes and have them screened for possible carcinogenic activity. The synthetic route to these compounds involves extensions to useful cyclodehydration reactions previously recorded.<sup>3,4</sup>

#### Experimental<sup>5</sup>

**2-(1-Naphthylmethyl)phenyl 4-Pyridyl Ketone.**—A Grignard reagent was prepared in dry ether from 1.6 g. (0.068 mole) of magnesium and 20 g. (0.068 mole) of 2-(1-naphthylmethyl)-bromobenzene.<sup>6</sup> When the reaction was complete, a solution of 7.0 g. (0.068 mole) of 4-cyanopyridine<sup>7</sup> in dry ether was added dropwise and the mixture was then heated under reflux overnight. It was then cooled, decomposed with dilute hydrochloric acid, stirred, and heated under reflux for 4 hr. The aqueous layer was separated, made basic with sodium hydroxide, and extracted with an acetone–ether mixture. The organic portions were combined, dried over anhydrous magnesium sulfate, and concentrated. The residue was distilled; yield, 13.5 g. (62%), b.p. 246–254° (3 mm.). The viscous oil crystallized on standing and was recrystallized twice from ethanol, m.p. 107–108°.

*Anal.* Calcd. for  $C_{23}H_{17}NO$ : C, 85.45; H, 5.30; N, 4.33. Found: C, 85.12; H, 5.28; N, 4.29.

The 3- and 2-pyridyl isomers were prepared in a similar manner. The 3-isomer, b.p. 248–255° (3 mm.) was obtained in 48% yield as a viscous red oil. The analytical sample was taken from a redistilled portion, b.p. 237–239° (0.5 mm.).

*Anal.* Calcd. for  $C_{23}H_{17}NO$ : C, 85.45; H, 5.30; N, 4.33. Found: C, 85.82; H, 5.28; N, 3.90.

The 2-isomer, b.p. 250–253° (2 mm.) was obtained in 40% yield as a viscous red oil. The analytical sample was taken from a redistilled portion, b.p. 225–226° (0.5 mm.).

*Anal.* Calcd. for  $C_{23}H_{17}NO$ : C, 85.45; H, 5.30; N, 4.33. Found: C, 85.59; H, 5.38; N, 4.37.

**7-(4-Pyridyl)benz(a)anthracene.**—A mixture of 1 g. (0.0031 mole) of 2-(1-naphthylmethyl)phenyl 4-pyridyl ketone and 7 g. of dihydrogen phenyl phosphate was heated at 190° for 5 hr.

(1) This investigation was supported by a research grant (AP-88) from the Division of Air Pollution, Bureau of State Service, Public Health Service.

(2) E. L. Wynder, F. R. Lemon, and I. J. Bross, *Cancer*, **12**, 1016 (1959).

(3) C. K. Bradsher, *J. Am. Chem. Soc.*, **62**, 486 (1940).

(4) F. A. Vingiello, E. Kramer, S.-G. Quo, and J. Sheridan, *J. Org. Chem.*, **26**, 2669 (1961).

(5) All melting points were taken on a Fisher-Johns melting point block and are corrected; all the analyses were carried out by Geller Laboratories Bardonia, New York, except those marked with an asterisk which were carried out by Galbraith Laboratories, Knoxville, Tennessee.

(6) A Grignard reaction between 2-bromobenzaldehyde and 1-naphthylmagnesium bromide gave a mixture which was reduced to 2-(1-naphthylmethyl)bromobenzene. For details see P. Polss, Ph.D. dissertation, Virginia Polytechnic Institute, Blacksburg, Va., 1962.

(7) D. G. Leis and Br. C. Curran, *J. Am. Chem. Soc.*, **67**, 79 (1945).

The mixture was cooled and made alkaline with sodium hydroxide solution. The precipitate which resulted was collected and dried; 0.9 g. (96%), m.p. 243–244°. The material was recrystallized from ethanol giving light tan plates; m.p. 245–246°.

*Anal.* Calcd. for  $C_{23}H_{15}N$ : C, 90.46; H, 4.95; N, 4.59. Found\*: C, 90.29; H, 4.92; N, 4.47.

The same product was obtained in 87% yield using a previously described standard acid mixture.<sup>8</sup>

The 3-pyridyl isomer, m.p. 221–222°, was obtained in 69% yield (45% by standard acid mixtures<sup>8</sup>). It was recrystallized from ethanol and formed white plates, m.p. 222–223°.

*Anal.* Calcd. for  $C_{23}H_{15}N$ : C, 90.46; H, 4.95; N, 4.59. Found\*: C, 90.24; H, 4.86; N, 4.57.

*Anal.* Calcd. for  $C_{23}H_{15}N$ : C, 90.46; H, 4.95; N, 4.59.

The 2-isomer, m.p. 151–152°, was obtained in 45% (80%<sup>8</sup>) yield. It was recrystallized from ethanol as white plates, m.p. 152.5–153.5°.

*Anal.* Calcd. for  $C_{23}H_{15}N$ : C, 90.46; H, 4.95; N, 4.59. Found\*: C, 90.18; H, 4.99; N, 5.64.

(8) F. A. Vingiello and J. G. Van Oot, *ibid.*, **73**, 5070 (1951).

### $\alpha$ -Alkyloximinocarboxamides for Biological Testing

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The title compounds, not previously reported, were prepared according to the procedure outlined by Woolley and co-workers.<sup>1</sup> At present the compounds are being screened for biological activity.

Amide	% Amide based on acid	M.p., °C.	% Nitrogen <sup>a</sup>	
			Calcd.	Found
$\alpha$ -Benzyloximino- butyramide	70.4	59–61	13.59	13.80
$\alpha$ -Benzyloximino- $\beta$ - phenylpropionamide	37 <sup>b</sup>	86–88	10.44	10.47
$\alpha$ -Benzyloximino- propionamide	86.7	91–94	14.58	14.72
$\alpha$ -Methyloximino- propionamide	35.1	68–71	24.13	23.82
$\alpha$ -Benzyloximino- phenylacetamide	80.4	100–102	11.02	11.00

<sup>a</sup> Nitrogen analyses were obtained from the Coleman Nitrogen Analyzer. <sup>b</sup> Prepared from  $\alpha$ -benzyloximino- $\beta$ -phenylpropionyl chloride and aqueous ammonia. Acids were prepared from substituted malonic esters by established procedures.<sup>2,3</sup>

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(1) D. W. Woolley, J. W. B. Hershey, and H. A. Jodlowski, *J. Org. Chem.*, **28**, 2012 (1963).

(2) J. Martin and W. H. Hartung, *ibid.*, **19**, 338 (1954).

(3) W. E. Weaver and W. H. Hartung, *ibid.*, **15**, 741 (1950).