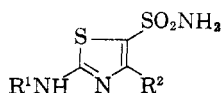


TABLE I

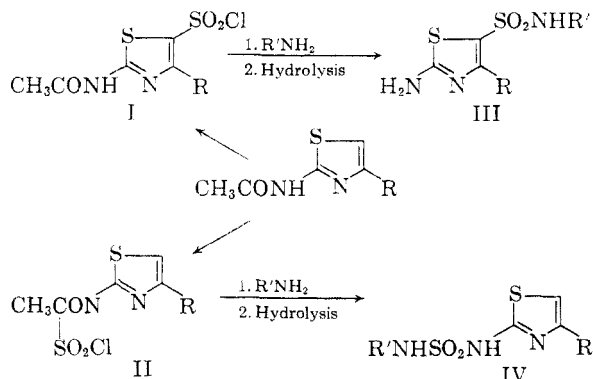


R ¹	R ²	M.P. ° uncorr.	Formula	Analysis ^c						
				Calcd.			Found			Yield, %
				C, %	H, %	N, %	C, %	H, %	N, %	
<i>p</i> -HO ₂ CC ₆ H ₄ SO ₂	H	297-298	C ₁₀ H ₉ N ₃ O ₆ S ₃	33.05	2.50	11.56	32.60	2.70	11.42	50 ^a
<i>p</i> -HO ₂ CC ₆ H ₄ SO ₂	CH ₃	298-300	C ₁₁ H ₁₁ N ₃ O ₆ S ₃	35.00	2.94	11.14	35.09	3.22	11.06	19 ^a
C ₆ H ₅ SO ₂	CH ₃	201-203	C ₁₀ H ₁₁ N ₃ O ₄ S ₃	36.03	3.33	12.61	36.27	3.49	12.60	54 ^a
<i>p</i> -NCC ₆ H ₄ CO	CH ₃	260-262	C ₁₂ H ₁₀ N ₃ O ₃ S ₂	44.70	3.13	17.38	44.89	3.08	17.36	76 ^a
C ₆ H ₅ -CH=CHCO	CH ₃	244-245	C ₁₃ H ₁₂ N ₃ O ₃ S ₂	48.27	4.05	12.98	48.34	4.07	12.96	52 ^a
C ₆ H ₅ -CH=CHSO ₂	CH ₃	239-240	C ₁₅ H ₂₁ N ₃ O ₃ S ₃ ^b	43.05	4.82	10.04	43.51	4.90	10.07	24 ^a
C ₃ H ₇ CO	CH ₃	166-167	C ₈ H ₁₃ N ₃ O ₃ S ₂	36.49	4.98	15.96	36.36	4.83	15.95	33
CH ₃ CO	C ₆ H ₅ ^d	301-303	C ₁₁ H ₁₁ N ₃ O ₃ S ₂	44.43	3.73	14.13	44.94	3.90	13.6	30
H	C ₆ H ₅ ^d	271 dec.	C ₉ H ₉ N ₃ O ₂ S ₂	42.34	3.55	16.46	42.95	3.85	16.17	72

^a From the amine and the appropriate acid chloride. ^b Solvated with isopropanol. ^c We are indebted to Mr. K. B. Streeter and his associates for the microanalyses. ^d Cf. ref. 8.

of the sulfonyl chlorides with ammonia or amines would, in one case, lead to a 2-thiazolylsulfamide (IV), and in the other to a 2-aminothiazole-5-sulfonamide (III). As 2-aminothiazoles can be diazotized and coupled with α -naphthylidimethylamine to give characteristic dyes,⁷ III would be expected to undergo this reaction but IV would not.

The work of the previous investigators was repeated in our laboratories and the products subjected to the diazo test. Acid hydrolysis of the acetyl derivatives in all instances (R = H, CH₃ or C₆H₅) yielded products that gave a diazo color; therefore, these products must have the 5-sulfonamide structure III and not the sulfamide structure IV.



In addition to the compounds prepared by Backer *et al.*, the 4-phenyl derivative (R = C₆H₅) was also prepared and found to possess structure III; this compound has been reported by Bas and Rout.⁸ Several sulfonyl and acyl derivatives of the aminosulfonamides (III) were prepared through reaction with the appropriate sulfonyl or acyl chloride. The formation of these derivatives under the conditions employed also supports structure III. These compounds are recorded in Table I.

(7) J. M. Sprague, A. H. Land, and C. Ziegler, *J. Am. Chem. Soc.*, **68**, 2155 (1946).

(8) B. Bas and M. K. Rout, *J. Indian Chem. Soc.*, **32**, 663 (1955).

EXPERIMENTAL

Sulfonyl chlorides. The method of Backer *et al.*⁴ was used, except that prolonged heating of the chlorosulfonic acid solutions was found unnecessary. Heating longer than 2 hr. on the steam bath did not increase the yield of product.

Sulfonamides. Crude, moist sulfonyl chloride was added to a large excess of liquid ammonia according to the method of Roblin and Clapp.⁹ Hydrolysis to the 2-aminothiazole-5-sulfonamides was carried out in acidic medium by the method of Backer.⁴ The diazotization and coupling test was carried out as previously described.⁷

Derivatives. Of the compounds listed in Table I, most were prepared by the reaction of a 2-aminothiazole-5-sulfonamide with the appropriate acyl chloride or sulfonyl chloride in pyridine solution.

2-Methylamino-4-methylthiazole, prepared by the method of Burtles *et al.*,¹⁰ was acetylated with acetic anhydride. Subsequent treatment with chlorosulfonic acid gave a crude sulfonyl chloride. This was treated with liquid ammonia to give a low yield (<1%) of 2-acetylthiazole-5-sulfonamide, m.p. 204-206°.

Anal. Calcd. for C₇H₁₁N₃O₂S₂: C, 33.72; H, 4.45; N, 16.86. Found: C, 34.20; H, 4.80; N, 16.84.

MERCK SHARP AND DOHME
RESEARCH LABORATORIES
WEST POINT, PA.

(9) R. O. Roblin, Jr., and J. W. Clapp, *J. Am. Chem. Soc.* **72**, 4890 (1950).

(10) R. Burtles, F. L. Pyman, and J. Roylance, *J. Chem. Soc.*, 589 (1925).

Potential Anticancer Agents.¹ XXXV.
Nonredox Analogs of Riboflavin. II.
Synthesis of 3,4-Dihydro-4,4,6,7-tetramethyl-1-(1-D-ribityl)carboystil

ELMER J. REIST, HARLAN P. HAMLOW, IRENE G. JUNGA,
R. M. SILVERSTEIN, AND B. R. BAKER

Received February 8, 1960

A recent program in these laboratories devoted to the synthesis of antagonists of riboflavin, such as

X, as potential anticancer agents² involved the synthesis of 3,4-dihydro-4,4,6,7-tetramethyl-1-(1-D-ribityl)carbostyryl (VI) as a key intermediate. One of the more attractive synthetic sequences of VI involves the alkylation of 3,4-dihydro-4,4,6,7-tetramethylcarbostyryl (V) with 2,3,4,5-tetra-*O*-acetyl-1-D-(*p*-tolylsulfonyl)ribitol (III). Model studies showed that alkylation of the carbostyryl (V) with butyl bromide or butyl tosylate to give the *N*-butyl derivative (IV) proceeded in satisfactory yield.

The synthesis of the 1-tosylate (III) was accomplished in two steps from 2,3,4,5-tetra-*O*-acetyl-D-ribose (I).³ Hydrogenation of tetraacetyl-D-ribose (I) with Raney nickel in ethyl acetate-acetic acid⁴ gave a 76% yield of crude 2,3,4,5-tetra-*O*-acetyl-D-ribitol (II) which could be crystallized in low yield from benzene-Skellysolve B.⁶ A more satisfactory procedure consisted of a direct tosylation of the crude tetraacetyl-D-ribitol (II) to give the crystalline 1-tosylate (III) in 39% over-all yield from I.

Several attempts to condense the sodium salt of the carbostyryl (V),² prepared from sodium hydride, with the tosylate (III) in *N,N*-dimethylformamide at 100° were unsuccessful. With a three-hour reaction time, a mixture of tosylate (III) and carbostyryl (V) was recovered. Use of a twenty-four hour reaction time brought decomposition of the tosylate (III), recovery of carbostyryl (V), and no evidence for the ribityl carbostyryl tetraacetate (VII).

An alternative method for the synthesis of the ribitylcarbostyryl (VI) commenced with *N*-(1-D-ribityl)-3,4-xylylidine (VIII). Since various attempts to accomplish a selective *N*-acylation or *O*-acylation of the ribitylxylylidine (VIII) resulted in mixtures of *O*- and *N*-acylated derivatives of VIII, the preparation of the di-*O*-isopropylidene derivative (XII) was investigated; the latter could then presumably be acylated with 3-methylcrotonyl chloride to IX without the complications of *O*-acylation.

(1) This work was carried out under the auspices of the Cancer Chemotherapy National Service Center, National Cancer Institute, National Institutes of Health, Public Health Service, Contract No. SA-43-ph-1892. The opinions expressed in this paper are those of the authors and are not necessarily those of the Cancer Chemotherapy National Service Center.

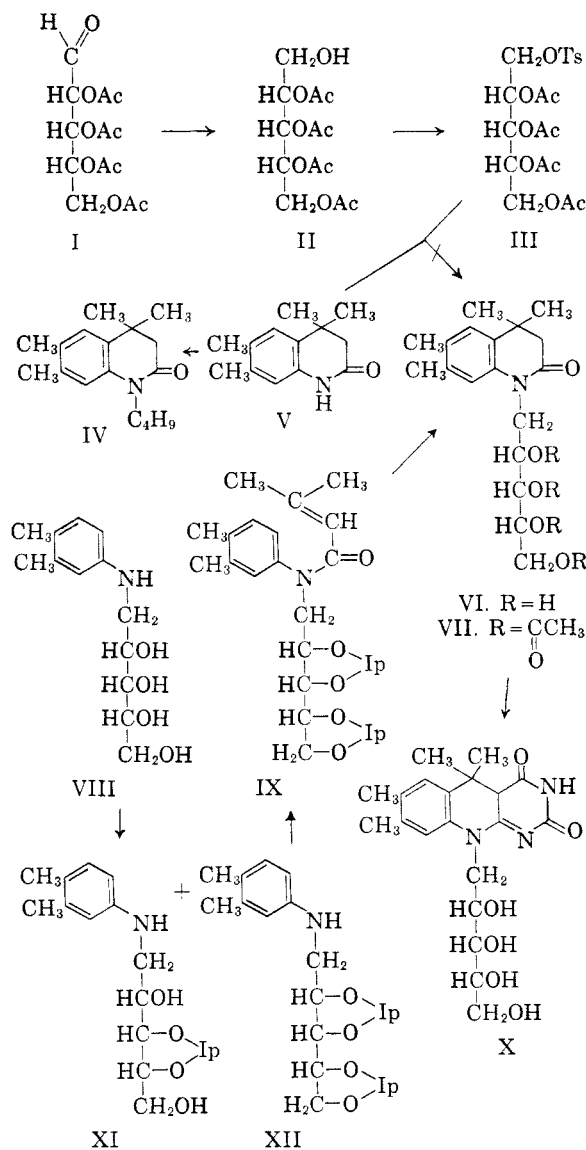
(2) For the preceding paper in this series, cf. E. J. Reist, H. P. Hamlow, I. G. Junga, R. M. Silverstein, and B. R. Baker, *J. Org. Chem.*, **25**, 1368 (1960).

(3) H. Zinner, *Ber.*, **83**, 418 (1950).

(4) Hydrogenation of I with Raney nickel in dioxane has been described by Fox.⁵ Substitution of ethyl acetate-acetic acid as a solvent gives a smoother reaction and avoids possible *O*-acetyl migration caused by the alkaline catalyst.

(5) H. H. Fox, *J. Org. Chem.*, **13**, 580 (1948).

(6) Skellysolve B and Skellysolve C are petroleum hydrocarbon fractions with boiling ranges of 62–70° and 88–99°, respectively. They are supplied by the Special Products Division, Phillips Petroleum Co., Bartlesville, Okla.



Treatment of *N*-(1-D-ribityl)-3,4-xylylidine (VIII) with acetone in the presence of alkanesulfonic acid and copper sulfate for three hours gave a crude product which proved to be a mixture of the expected diacetone derivative (XII) and a monoacetone derivative (XI).⁷ The monoacetone derivative (XI) could be crystallized in 12% yield. This crystalline material was converted to an *N,O,O*-triacetate in quantitative yield. The triacetate showed *O*-acetate and *N*-acetate absorption of approximately equal intensity in the infrared, indicating that the carbonyl of the *N*-acetyl has twice the extinction coefficient of the carbonyl of the *O*-acetyl.

(7) The assignment of the 3,4-position for the monoacetone derivative is based on the observation that extended treatment of the ribitylxylylidine (VIII) under acetonating conditions failed to drive the reaction any further to completion and the same amount of monoacetone derivative relative to diacetone derivative was obtained. Any 2,3- and/or 4,5-monoacetone derivative would be expected to yield eventually the diacetone derivative (XII).

In a second acetonation reaction, the crude acetonation mixture was distilled to separate the products XI and XII from other by-products. Acetylation of an aliquot of the distillate, followed by infrared examination of the resulting acetate mixture, showed that mono- and diacetone compounds were present in approximately equal amounts, each in 30–35% yield. The pure diacetone derivative was obtained by distillation through a small Vigreux column.

Based on the above information, a more satisfactory technique was developed for the separation of the mono- and diacetone derivatives (XI and XII, respectively), utilizing a solvent partition system of hexane-methanol-water (7:7:2). The hexane layer contained virtually pure diacetone derivative in 37% yield while the aqueous layer contained all the monoacetone derivative essentially free of diacetone derivative. This separation was particularly useful for large-scale separations, since distillation caused considerable decomposition.

Reaction of the diacetone derivative (XII) with 3-methylcrotonyl chloride gave *N*-(2,3,4,5-di-*O*-isopropylidene-1-*D*-ribityl)-3-methyl-3',4'-crotonoxylidide (IX) in quantitative yield as a gum. Cyclization of this amide (IX) with anhydrous aluminum chloride in Skellysolve C⁶ gave an aluminum chloride complex of the diacetone derivative of the carbostyryl (VI). In order to break this complex, it was necessary to use warm, strong acid. Since this acid treatment caused partial deacetonation, the remainder of the acetone blocking groups were removed by refluxing the crude product in methanolic hydrochloric acid. Crystallization from 50% ethanol gave a 20% yield of 3,4-dihydro-4,4,6,7-tetramethyl-1-(1-*D*-ribityl)-carbostyryl (VI). That this compound was the desired carbostyryl (VI) and not the uncyclized 3-methylcrotonoxylidide was clearly demonstrated by its infrared spectrum. The product had no band at 6.13 μ characteristic of the double bond in the acyl group of IX. Good evidence for ring closure to a carbostyryl (VI) was evidenced by the presence of an N—C band at 7.06 μ which has been present in all the model 1-alkyl-3,4-dihydrocarbostyryls,² but absent in their open-chain anilide precursors, including IX.

EXPERIMENTAL⁸

1-Butyl-3,4-dihydro-4,4,6,7-tetramethylcarbostyryl (IV). A mixture of 9.0 g. (0.04 mole) of 3,4-dihydro-4,4,6,7-tetramethylcarbostyryl (V)² and 1.2 g. (0.05 mole) of sodium hydride in 75 ml. of benzene was heated under reflux with

(8) Melting points were taken on a Fisher-Johns apparatus and are uncorrected. Paper chromatograms were run by the descending technique on Whatman No. 1 paper and the spots were located by visual examination under ultraviolet light. The solvent systems used were *n*-butyl alcohol-methyl ethyl ketone-water (5:3:2) (solvent A) and 5% aqueous disodium phosphate (solvent B).

stirring for 23 hr. The benzene was removed *in vacuo* and the solid sodium salt suspended in 125 ml. of *N,N*-dimethylformamide. The mixture was heated at 100 \pm 2° with stirring while a solution of 6.5 g. (0.05 mole) of butyl bromide in 10 ml. of *N,N*-dimethylformamide was added dropwise over about 10 min. The suspension cleared as the mixture was heated with stirring for 80 min. The solvent was removed under reduced pressure and the viscous residue extracted with 100 ml. of benzene. The extract was washed with 100 ml. of water, dried over magnesium sulfate, and concentrated *in vacuo*. The residual product (10.4 g., 91%) was recrystallized from 50 ml. of Skellysolve B⁶ with the use of Norit; yield 7.1 g. (62%) of colorless crystals, m.p. 62.5–63.5°; $\lambda_{\text{max}}^{\text{KBr}}(\mu)$ 6.04 (amide C=O), 11.36 (1,2,4,5-tetra-substituted benzene), no NH in 3.0 region.

Anal. Calcd. for C₁₇H₂₃NO: C, 78.7; H, 9.72; N, 5.40. Found: C, 78.4; H, 9.52; N, 5.65.

Similar yields were obtained using *n*-butyl tosylate.

2,3,4,5-Tetra-O-acetyl-D-ribitol (II). A solution of 6.0 g. (0.02 mole) of 2,3,4,5-tetra-*O*-acetyl-*D*-ribose (I)⁸ in 25 ml. of ethyl acetate was treated with 2.2 g. of Norit, heated to boiling, and filtered. The filtrate was treated with 25 ml. of ethyl acetate and 10 ml. of glacial acetic acid. Raney nickel (W-5, 2 g.) was added and the mixture hydrogenated overnight under a pressure of 41 lb. The catalyst was removed by filtration and washed with 25 ml. of ethyl acetate. The filtrate was neutralized with saturated sodium bicarbonate solution. The sodium bicarbonate solution was separated and washed with three 25-ml. portions of methylene chloride. The combined organic solutions were concentrated *in vacuo*. The residue weighed 4.8 g. (80%). The crude product was dissolved in 30 ml. of benzene-Skellysolve B⁶ (3:2), treated with Norit, heated to boiling, and filtered. The solvents were removed *in vacuo* and 4.57 g. (76%) of a viscous oil was obtained which was suitable for the preparation of the 1-tosylate (III); $\lambda_{\text{max}}^{\text{film}}(\mu)$ 2.87 (OH), 3.37 (CH), 5.47 (acetate C=O), 8.17, 9.50 (C—O—C).

In a similar run using dioxane as the solvent for the hydrogenation,⁸ recrystallization from Skellysolve C⁶ gave a 4% yield of colorless needles, m.p. 56–58°, along with a 15% yield of oil which crystallized on standing; $\lambda_{\text{max}}^{\text{KBr}}(\mu)$ 2.90 (OH), 5.70 (acetate C=O), 8.20 (ester C—O—C).

Anal. Calcd. for C₁₃H₂₀O₉: C, 48.8; H, 6.30. Found: C, 49.3; H, 6.61.

Fox⁹ reported a melting point of 55–57°.

2,3,4,5-Tetra-O-acetyl-1-D-(p-tolylsulfonyl)ribitol (III). A solution of 4.57 g. (0.014 mole) of the crude 2,3,4,5-tetra-*O*-acetyl-1-*D*-ribitol (II) in 25 ml. of pyridine was cooled in an ice bath with stirring while 3.3 g. (0.02 mole) of *p*-tolylsulfonyl chloride was added in portions. The temperature was kept below 5°. The solution was stirred and cooled in an ice bath for 1.5 hr. protected from moisture, and allowed to warm to room temperature overnight. The brown solution was poured into 300 ml. of ice water. The oil which formed soon solidified to a white solid and was collected on a filter and dried; yield 4.32 g. (63%), m.p. 98–101°. The crude product was recrystallized from 25 ml. of ethanol with the use of Norit; yield 3.44 g. (50%) of white crystals, m.p. 103–104°. This compound had an infrared spectrum identical with that of the analytical sample prepared in a pilot run.

The analytical sample had m.p. 104–105°; $\lambda_{\text{max}}^{\text{KBr}}(\mu)$ 5.75 (acetate C=O), 8.14 (ester C—O—C), 7.38, 8.42, 8.54 (sulfonate).

Anal. Calcd. for C₂₀H₂₆O₁₁S: C, 50.6; H, 5.52; S, 6.75. Found: C, 50.8; H, 5.67; S, 7.15.

N-(3,4-*O*-Isopropylidene-1-*D*-ribityl)-3,4-xylylidine (XI) and *N*-(2,3,4,5-di-*O*-isopropylidene-1-*D*-ribityl)-3,4-xylylidine (XII). A mixture of 12.0 g. (0.047 mole) of *N*-(1-*D*-ribityl)-3,4-xylylidine (VIII) and 10 g. of anhydrous cupric sulfate in 150 ml. of acetone was cooled to 2–3° in an ice-salt bath, then a solution of 11.5 ml. of ethanesulfonic acid in 20 ml. of acetone was added dropwise with stirring. After the addition was complete, the mixture was stirred with continued cooling for 4 hr., then left at room temperature overnight.

The reaction mixture was filtered and the filter cake was washed with 20 ml. of acetone. The combined filtrate and washings were poured into 400 ml. of cold 10% aqueous sodium carbonate. The resulting basic mixture was extracted with 300 ml. of methylene chloride. The methylene chloride layer was evaporated to dryness *in vacuo* to give a sirupy mixture of mono- and diacetone derivatives (XI and XII). The crude mixture was partitioned in the solvent system hexane-methanol-water (7:7:2) (336 ml.) to give 5.8 g. (32%) of crude monoacetone derivative (XI) in the methanol-water layer and 5.4 g. (32%) of crude diacetone derivative (XII) in the hexane layer which was satisfactory for the Friedel-Crafts cyclization.

Trituration of the crude monoacetone derivative (XI) with cold hexane caused the sirup to crystallize. Recrystallization from 50 ml. of hexane and 3 ml. of absolute ethanol gave 2.85 g. of a white crystalline material, m.p. 101–102°, the infrared spectrum of which was essentially identical with that of the analytical sample. No effort was made to obtain a second crop.

The analytical sample, prepared from a similar run, melted at 103–104° after two recrystallizations from Skellysolve B⁶-ethanol and had $\lambda_{\max}^{\text{KBr}(\mu)}$ 2.94 (NH, OH), 7.24 (CH₃), 9.50 (C—O—C), 12.34 (1,3,4-trisubstituted benzene).

Anal. Calcd. for C₁₆H₂₆NO₄: C, 65.1; H, 8.53; N, 4.74. Found: C, 65.0; H, 8.72; N, 4.39.

To 0.2 g. (0.61 mmole) of crystalline *N*-(3,4-*O*-isopropylidene-1-*D*-ribose)-3,4-xylylidine (XI) was added a solution of 1 ml. of pyridine and 1 ml. of acetic anhydride. The solution was allowed to stand for 2 days protected from moisture and then was poured into 100 ml. of ice water. The oil which separated was extracted with 50 ml. of methylene chloride. The extract was washed with 50 ml. of 5% sodium bicarbonate solution and 50 ml. of water, and dried over magnesium sulfate. The solution was concentrated *in vacuo*; yield, 0.35 g. of *N,O*-triacetyl derivative of XI as a tan, viscous oil which did not crystallize; $\lambda_{\max}^{\text{film}(\mu)}$ 5.74 (acetate C=O), 6.01 (amide C=O), 8.15 and 9.35 (acetate C—O—C). The relative intensities of the amide and acetate carbonyl absorption were almost equal.

A small portion of the crude diacetone derivative (XII) was acetylated in the manner described above for the monoacetone derivative (XI). The infrared spectrum of the *O*-diacetate showed an *O*-acetate/*N*-acetate intensity ratio of 1:17 in the C=O region, indicating less than 5% contamination by the monoacetone derivative.

An analytical sample of the diacetone derivative (XII) was obtained by distillation of the crude material after one partition treatment, b.p. 135–140° (0.025 mm.); $\lambda_{\max}^{\text{film}(\mu)}$ 2.96 (NH), 7.31 (CH₃), 9.31 (C—O—C).

Anal. Calcd. for C₁₈H₂₈NO₄: C, 68.0; H, 8.71; N, 4.18. Found: C, 67.9; H, 8.83; N, 4.64.

A small portion of the distilled product was acetylated, using acetic anhydride and pyridine. The infrared spectrum showed only a trace amount of *O*-acetate compared to *N*-acetate.

3,4-Dihydro-4,4,6,7-tetramethyl-1-(1-D-ribose)carbostyryl (VI). To a stirred solution of 5.3 g. (1.6 mmoles) of *N*-(2,3:4,5-di-*O*-isopropylidene-1-*D*-ribose)-3,4-xylylidine (XII) in 13 ml. of dry pyridine was added dropwise 2.3 g. (1.9 mmoles) of 3-methylcrotonyl chloride with ice cooling. The addition time was 5 min. A precipitate formed and the resulting mixture was stirred with ice cooling for 2 hr. and then stirred at 30° for 18 hr. protected from moisture. The volatile materials were removed *in vacuo* and the residue dissolved in 50 ml. of methylene chloride. The methylene chloride solution was washed with 50 ml. of saturated sodium bicarbonate solution and concentrated *in vacuo*. The residue was dissolved in a small amount of toluene and then concentrated *in vacuo*. This procedure was repeated several times. The last traces of solvents were removed *in vacuo* at 60° at 0.1 mm. to yield 7.0 g. (theory 6.7 g.) of crude *N*-(2,3:4,5-di-*O*-isopropylidene-1-*D*-ribose)-3-methyl-3',4'-crotonoxylylidene (IX); $\lambda_{\max}^{\text{film}(\mu)}$ 6.05 (amide C=O), 6.13

(shoulder, >C=C<), 7.30 (CH₃), 9.37 (C—O—C), no ester C=O in the 5.8 region.

The crude IX (7.0 g., 1.6 mmoles) was dissolved in 80 ml. of Skellysolve C⁶ and treated with 8.0 g. (0.060 mole) of powdered, anhydrous aluminum chloride. The mixture was stirred under reflux on the steam bath for 2 hr. The resulting mixture was decomposed with ice and the Skellysolve C decanted from the gummy residue. The residue was suspended in 125 ml. of chloroform and heated to boiling with 100 ml. of 6*N* hydrochloric acid. The mixture was cooled, shaken vigorously, and the chloroform layer separated. The aqueous layer was extracted with 25 ml. of chloroform. The combined chloroform solutions were washed with 3*N* hydrochloric acid, dried over magnesium sulfate, and concentrated *in vacuo*; weight 6.5 g. The infrared spectrum of this material showed that not all of the isopropylidene groups had been removed. The residue was dissolved in 150 ml. of methanol, treated with 6 ml. of 6*N* hydrochloric acid; the solution was heated under reflux on the steam bath for 1 hr. and then concentrated *in vacuo*. The residue (5.72 g.) was dissolved in 110 ml. of hot 50% aqueous ethanol, treated with Norit, filtered, and chilled. The crystals were collected and dried *in vacuo*; yield 0.35 g., m.p. 69–71°. The filtrate was concentrated and a second crop of 0.75 g., m.p. 60–70°, was obtained; total yield 1.10 g. (20.4%). Recrystallization of the first crop from aqueous alcohol with use of Norit gave white crystals that softened at 85°, partially melted at about 100°, then melted at 115–200°; $\lambda_{\max}^{\text{KBr}(\mu)}$ 2.95 (OH), 6.05 (lactam C=O), 8.92, 9.59 (C—O—), 11.37 (1,2,4,5-tetrasubstituted benzene), no C=C at 6.13.

Anal. Calcd. for C₁₈H₂₇NO₅: C, 64.1; H, 8.07; N, 4.15. Found: C, 64.5; H, 8.16; N, 4.01.

The filtrate from the second crop was concentrated to obtain a third crop; however, only an oil separated. The infrared spectrum of this oil was similar to that of the product.

Paper Chromatography	R _f in Solvent System A	R _f in Solvent System B
Analytical sample	0.87	0.00
Second crop	0.86	0.00
Oil	0.88	0.58
		0.71
Mother liquor	0.00	0.00
	0.85	

The oil contained little or no product. The mother liquor may have had additional product.

Acknowledgment. The authors wish to thank Dr. Peter Lim for interpretation of the infrared absorption spectra and his staff for the paper chromatography. The authors are also indebted to Mr. O. P. Crews, Jr., and his staff for large-scale preparation of certain intermediates.

DEPARTMENT OF BIOLOGICAL SCIENCES
STANFORD RESEARCH INSTITUTE
MENLO PARK, CALIF.

Action of Hydroxylamine, Hydrazine Hydrate, and Phenylhydrazine on 2-Acetoaceto-1-naphthol

ABD ELMAGED AMIN SAMMOUR

Received November 25, 1959

Recently Schönberg, Fateen, and Sammour¹ have reported the reaction of I with hydroxylamine