Pyrolysis of Ethyl N-Carbethoxy-N-nitrosoalanate (VIb).—Nitrosocarbamate VIb (2.12 g., 9.72 mmoles) was heated for 8 hr. at 125–135° (50–100 mm.) in the same apparatus used in the pyrolysis of the nitrosocarbamate VIa. The yield of yellow ethyl α-diazopropionate (VIIb) (n^{18}D 1.4489, lit.[16] n^{18}D 1.4472) was 0.89 g. (6.9 mmoles, 71%); the infrared spectrum was consistent with the structure assigned. Treatment with 3,5-dinitrobenzoic acid yielded the ester IXb, m.p. 74.5–76°. An infrared spectrum of the dark residue (0.45 g., 2.4 mmoles, 25%) was identical with the spectrum of carbamate Vb; distillation of the brown residue gave the carbamate Vb (n^{14}D 1.4397). Pyrolyses in the presence of solid sodium carbonate led to essentially the same results. For optimum yields in the pyrolyses, temperatures between 115 and 140° and pressures between 50 and 150 mm. should be used.

Reaction of Ethyl Diazoacetate (VIIa) with 3,5-Dinitrobenzoic Acid.—Ethyl diazoacetate (0.101 g., 0.89 mmole) was mixed with 0.188 g. (0.89 mmole) of 3,5-dinitrobenzoic acid and the stirred mixture was kept at 0°. After 1 day, 10 ml. of ether was added and the mixture was stirred at 25–30° for 1 day. Ether was added to a total volume of 50 ml. and the solution was washed with cold sodium bicarbonate solution and water, and then dried. When the ether was evaporated *in vacuo*, 0.249 g. (0.84 mmole, 94%) of light yellow crystals was obtained, m.p. 59–60°. The infrared spectrum of this ester (IXa) was identical with the spectrum of ester prepared from ethyl chloroacetate (*vide infra*).

Reaction of Ethyl α-Diazopropionate (VIIb) with 3,5-Dinitrobenzoic Acid.—Compound VIIb (0.50 g., 3.9 mmoles) and 3,5-dinitrobenzoic acid (0.83 g., 3.9 mmoles) were dissolved in 25 ml. of dry dioxane and the solution was kept at 25–30° for 2 days. The volatiles were evaporated *in vacuo* to give 0.17 g. (0.54 mmole 14%) of ester IXb, m.p. 74.5–76°. The infrared spectrum was identical with that of a sample of the ester prepared from ethyl lactate (*vide infra*).

Carbethoxymethyl 3,5-Dinitrobenzoate (IXa).—Sodium 3,5-dinitrobenzoate (2.8 g., 12 mmoles) was dissolved in 50 ml. of 50% aqueous ethanol. After 1.2 g. (9.8 mmoles) of ethyl chloroacetate and 1.5 g. (10 mmoles) of sodium iodide were added, the mixture was heated on the steam bath for 4 hr. Most of the solvent was removed *in vacuo*, after which the residue was extracted with ether. The ether was removed to give 1.4 g. (4.7 mmoles, 48%) of yellow crystalline ester, m.p. 48–51°. After three recrystallizations from methylene chloride–hexane, 0.13 g. (0.44 mmole) of very light yellow needles of ester IXa was isolated, m.p. 59–60°.

Anal. Calcd. for $C_{11}H_{10}N_2O_8$: C, 44.30; H, 3.38; N, 9.40. Found: C, 44.36; H, 3.65; N, 9.46.

1-Carbethoxyethyl 3,5-Dinitrobenzoate (IXb).—Ethyl lactate (3.5 g., 0.030 mole) and 4.0 g. (0.020 mole) of 3,5-dinitrobenzoyl chloride were added to 25 ml. of dry pyridine. The reaction was allowed to proceed with stirring at room temperature for 2 hr. after which the pyridine was removed *in vacuo* to give a highly viscous residue. This residue was dissolved in methylene chloride and washed successively with dilute hydrochloric acid, sodium bicarbonate solution, and water. The solution was then dried and evaporated to a yellow-brown solid (4.1 g., 0.013 mole, 65%; m.p. 66–70°) which was fractionally crystallized from methylene chloride–hexane at 0°. White needles of ester IXb were obtained, m.p. 75–76° (0.80 g., 2.6 mmoles, 13.0%).

Anal. Calcd. for $C_{12}H_{12}N_2O_8$: C, 46.16; H, 3.38; N, 8.97. Found: C, 46.02; H, 3.66; N, 8.95.

An attempt to prepare ester IXb from excess ethyl lactate and 3,5-dinitrobenzoyl chloride in the absence of pyridine at 70° yielded mainly ethyl 3,5-dinitrobenzoate.

Ethyl N-(3,5-Dinitrobenzoyl)glycinate.—This compound (light yellow needles from methylene chloride–hexane, m.p. 152–154°) was prepared in 56% yield from ethyl glycinate hydrochloride and 3,5-dinitrobenzoyl chloride in dry pyridine (4-hr. reaction time).

Anal. Calcd. for $C_{11}H_{11}N_3O_7$: C, 44.45; eq. H, 3.73; eq. N, 14.13. Found: C, 44.51; H, 3.71; N, 13.97.

Ethyl N-(3,5-Dinitrobenzoyl)-N-nitrosoglycinate (Xc).—This compound was prepared in 73% yield by the nitrogen tetroxide nitrosation of the corresponding amide (see above) in methylene chloride.[14] Recrystallization from ether–hexane mixtures yielded light yellow crystals of Xc, m.p. 68–70° (followed by gas evolution at 78°). This compound was unstable, and samples showed signs of decomposition (NO_2) after several days.

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Anal. Calcd. for $C_{11}H_{10}N_4O_8$: C, 40.50; H, 3.10; N, 17.17. Found: C, 40.42; H, 3.04; N, 16.28.

Pyrolysis of this compound at 75° (100 mμ) yielded principally the parent amide. Recrystallization of the product yielded pure amide, m.p. 151–154°.

The Nitrosoacetamide and Benzamide of Ethyl Alanate.[13]—These compounds were prepared by the nitrogen tetroxide nitrosation of the acetyl and benzoyl derivatives of methyl alanate. Pyrolyses at 50–90° (100–200 mm.) yielded a mixture of ethyl diazopropionate and the carboxylic acids; the acid could be removed with dilute solutions of sodium carbonate.

Ethyl Diazoacetate (VIIa).—In addition to the pyrolytic methods outlined above, this compound can be prepared in 50–75% yields by the dropwise addition of ethyl N-nitroso-N-acetylglycinate to an excess of tetraethylenepentamine under high vacuum. The mixture is stirred vigorously and the product collected in a cooled receiver; about 4–8 hr. are required for the reaction.

Acknowledgment.—This work was supported by a grant from the National Institutes of Health (CY 3554). Analyses were performed by Joe Walter, The Johns Hopkins University, and the Galbraith Laboratories, Knoxville, Tennessee.

Action of Nitrous Acid on Osazone Acetates. A New Synthesis of Osotriazoles

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Received January 31, 1964

Osazones are known[1] to react with nitrous acid to give first the aldosulose ("osone") 1-hydrazone (II) and then with excess reagent to yield the aldosulose (IV) in yields up to 65%. We have now carried out this reaction with the tetra-*O*-acetylphenylosazones from D-galactose, D-glucose, and L-sorbose, but, instead of the expected aldosulose tetraacetates, we obtained the corresponding phenylosotriazole tetraacetates in about 80% yields. The D-galactose derivative crystallized from the crude reaction mixture and the D-glucose and L-sorbose derivatives were identified by deacetylation to the free osotriazoles. The different course followed by the reaction with osazone acetates seems to be due to the absence in the molecule of free hydroxyl groups which allow the formation of cyclic modifications. Osazone acetates have been shown[2] to possess acyclic bis(hydrazone) structures (V), whereas the unacetylated derivatives may form in solution some of the cyclic hydrazino hydrazone forms (I). If we now assume that nitrous acid reacts more rapidly with the labile and highly reactive hydrazino group,[3] than with a true hydrazone residue, we would expect the unacetylated osazones to undergo a series of cyclizations and eliminations of hydrazino groups leading first to the aldosulose hydrazone (II) and finally to the aldosulose (IV). Scission of the hydrazino groups is probably achieved through the intermediate

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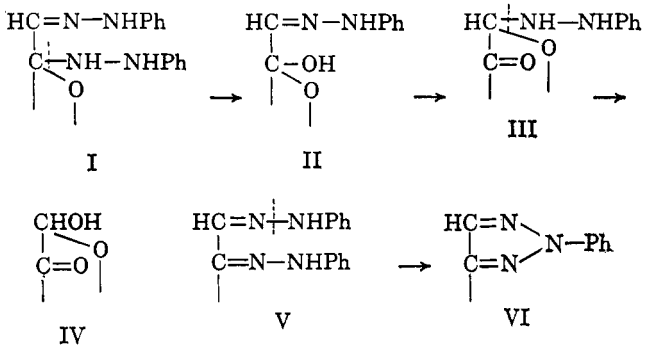
(3) H. S. Isbell, *Ann. Rev. Biochem.*, **12**, 205 (1943); F. Weygand, *Ber.*, **73**, 1284 (1940).

formation of *N*-nitroso compounds on the β-hydrazino nitrogen followed by hydrolytic splitting of the C–N bond. In the case of acetylated osazones which have only hydrazone groups, nitrous acid would be expected to attack the α-nitrogen of the phenylhydrazone residue and cause the hydrolytic scission of the N–N bond and closure of the triazole ring.



The high yields of osotriazole obtained with osazone acetates render this reaction of value for preparative purpose.

Experimental[4]

D-*lyxo*-**Hexose Phenylosotriazole Tetraacetate.**—A suspension of D-*lyxo*-hexose phenylosazone tetraacetate[2] (5.3 g.) in a mixture of ethanol (40 ml.), water (20 ml.), and concentrated hydrochloric acid (2.4 ml.) was treated, with stirring, at 50–55° with a solution of sodium nitrite (1.4 g.) in water (10 ml.) during the course of 30 min. The now clear reddish brown solution was treated with 1.5 g. of sodium acetate trihydrate in water (50 ml.) and extracted with chloroform. The chloroform layer which contained the osotriazole tetraacetate was washed successively with dilute hydrochloric acid, aqueous sodium hydrogen carbonate, and water. The residue obtained after solvent removal from the dried extract crystallized from methanol–ether in needles, m.p. 106° undepressed with authentic D-*lyxo*-hexose phenylosotriazole tetraacetate,[5] yield 3.5 g.

Anal. Calcd. for $C_{20}H_{23}N_3O_8$: C, 55.42; H, 5.35; N, 9.70; CH_3CO, 39.73. Found: C, 55.27; H, 5.00; N, 9.54; CH_3CO, 39.57.

Deacetylation.—The acetate (3 g.) in methanol (50 ml.) was treated with concentrated aqueous ammonia (20 ml.) and the mixture kept overnight at room temperature. On evaporation and distillation of the residue under reduced pressure at 190–200° (0.05 mm.), D-*lyxo*-hexose phenylosotriazole was obtained in needles, m.p. 111–112° undepressed on admixture with an authentic specimen.[5] Both products had identical infrared spectra.

Anal. Calcd. for $C_{12}H_{15}N_3O_4$: C, 54.33; H, 5.70; N, 15.84. Found: C, 54.20; H, 5.94; N, 15.94.

D-*arabino*-**Hexose Phenylosotriazole.**—D-*arabino*-Hexose phenylosazone tetraacetate[6] (5.3 g.) was treated with nitrous acid in exactly the same manner as the D-*lyxo*-hexose derivative and the residue, after evaporation of the chloroform, was subjected directly to deacetylation with ammonia in aqueous methanol. D-*arabino*-Hexose phenylosotriazole was obtained by evaporation and crystallization from water or ethanol in needles, m.p. 196° undepressed on admixture with an authentic specimen,[7] yield 2 g. Both products had identical infrared spectra.

Anal. Found: C, 54.29: H, 5.79; N, 15.96.

L-*xylo*-**Hexose Phenylosotriazole.**—Amorphous L-*xylo*-hexose phenylosazone tetraacetate (about 5 g.), obtained by the action of acetic anhydride and pyridine on the osazone and carefully washed with water, was treated in exactly the same manner as the D-*arabino*-hexose derivative, yielding finally L-*xylo*-hexose phenylosotriazole. This crystallized from water in needles, m.p. 159° undepressed on admixture with an authentic specimen,[5] yield 2 g. Both products gave identical infrared spectra.

Anal. Found: C, 54.82; H, 6.03; N, 16.02.

Acknowledgment.—Support is acknowledged of Grant No. CY-3232(C6) (The Ohio State University Research Foundation Project 759F) from the Department of Health, Education, and Welfare, U. S. Public Health Service, National Institutes of Health, Bethesda, Maryland. H. El K. is indebted to the Educational and Cultural Exchange Program for a Fulbright Grant.

(4) Microanalyses were by W. N. Rond, The Ohio State University; infrared spectra were measured with a Perkin-Elmer Infracord spectrophotometer.

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Benzoylation of Sugar Phenylhydrazones

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Received February 24, 1964

Acyclic sugar hydrazones when acetylated with pyridine and acetic anhydride yield *O*-acetylated derivatives[2] which can be converted to tetraacetoxy-1-phenylazo-1-hexene.[3] The more drastic reaction with boiling acetic anhydride[4] yields derivatives having acetyl groups attached to the nitrogen as well as to the oxygen which no longer undergoes this conversion. To study the behavior of sugar hydrazones toward benzoylation, the phenyl hydrazones of D-mannose, D-arabinose, and L-rhamnose were treated with benzoyl chloride in pyridine, and the structure of their crystalline benzoates investigated. D-Mannose phenylhydrazone yielded a hexabenzoate (I) which showed in the infrared spectrum a C=N band at 1610, an ester band at 1725, and an amide band at 1660 cm.$^{-1}$, denoting the presence of *O*- and *N*-benzoyl groups in an acyclic hydrazone. This was confirmed by trans-hydrazonation; the hexabenzoate was treated with *p*-nitrophenylhydrazine, which replaced the *N*-benzoyl phenylazo residue yielding a *p*-nitrophenylhydrazone pentabenzoate (II). This showed the C=N band at 1605 and the ester band at 1730 but not the amide absorption at 1660 cm.$^{-1}$, denoting that all five benzoyl groups were linked to oxygen. The presence of five *O*-benzoyl groups on a hexose aryl hydrazone excludes the possibility of cyclic structures, which would have yielded a benzoate having fewer *O*-benzoyl groups. Accordingly the hexabenzoate (I) was formulated as *N*-benzoylpenta-*O*-benzoyl-*aldehydo*-D-mannose phenylhydrazone (I), and the transhydrazonation product as penta-*O*-benzoyl-*aldehydo*-D-mannose *p*-nitrophenylhydrazone (II). Similarly, D-arabinose and L-rhamnose phenylhydrazones yielded pentabenzoates which showed the C=N bands at 1605 and 1610, the ester bands at 1725 and 1730, and the amide bands at 1670 and 1680 cm.$^{-1}$, respectively, denoting that, like the mannose

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