fusion of β-D-glucose pentaacetate and phosphorus pentachloride yields 3,4,6-tri-*O*-acetyl-2-*O*-trichloroacetyl-β-D-glucopyranosyl chloride, from which 3,4,6-tri-*O*-acetyl-β-D-glucopyranosyl chloride can be obtained. Wolfrom, Pittet, and Gillam[7] reported the synthesis of β-isomaltose octaacetate using stable 3,4,6-tri-*O*-acetyl-2-*O*-nitro-β-D-glucopyranosyl chloride as the glycosyl halide component of a modified Koenigs-Knorr reaction. This β-D-glucosyl chloride could not be anomerized[7] without concomitant cleavage of the 2-*O*-nitro group, thus illustrating the deactivating power of the 2-*O*-nitro moiety.

It was of interest to attempt the synthesis of a β-D-glucosyl bromide with a nonparticipating group substituted on C-2. Low temperature nitration of 3,4,6-tri-*O*-acetyl-α-D-glucopyranosyl chloride[8] yielded a sirupy product which resisted all efforts at crystallization. Elemental analysis and specific rotation indicated that this sirup was 3,4,6-tri-*O*-acetyl-2-*O*-nitro-α-D-glucopyranosyl chloride. Attempted conversion of this substance to the corresponding β-D-glucopyranosyl bromide using the conditions cited by Schlubach[4] yielded only recovered starting material. The nitrate group evidently deactivates the chloride to such an extent that halogen exchange would not occur, under the conditions used, with an "active" silver bromide prepared according to Schlubach.

Acetylation of 3,4,6-tri-*O*-acetyl-2-*O*-nitro-α-D-glucopyranosyl chloride with mercuric acetate and acetic acid[9] yielded crystalline 1,3,4,6-tetra-*O*-acetyl-2-*O*-nitro-β-D-glucopyranose and acetylation of 3,4,6-tri-*O*-acetyl-2-*O*-nitro-β-D-glucopyranosyl chloride[7] in the same manner yielded crystalline 1,3,4,6-tetra-*O*-acetyl-2-*O*-nitro-α-D-glucopyranose.

Experimental

3,4,6-Tri-*O*-acetyl-2-*O*-nitro-α-D-glucopyranosyl Chloride.—A mixture of 45 ml. of glacial acetic acid and 75 ml. of acetic anhydride was cooled to −20° (solid carbon dioxide–acetone), and 60 ml. of absolute nitric acid was added portionwise while maintaining the temperature below 0°. The solution was then cooled to −40° and 9.6 g. of 3,4,6-tri-*O*-acetyl-α-D-glucopyranosyl chloride[8] was added portionwise, with vigorous stirring, while maintaining the temperature between −36 and −42°. The mixture was allowed to warm to 0°, with stirring, and the clear solution was poured into 2 kg. of ice with stirring. The ice was allowed to melt over a 2- to 3-hr. period, and the solid material was separated by filtration. The amorphous product was dissolved in 250 ml. of ethylene dichloride, washed with aqueous sodium hydrogen carbonate, dried over calcium chloride, filtered, and the solvent removed under reduced pressure; yield, 7.47 g. of clear yellow sirup, $[\alpha]^{20}\mathrm{D}$ +125° (*c* 1.18, chloroform).

Anal. Calcd. for $C_{12}H_{16}ClNO_{10}$: N, 3.79. Found: N, 4.15.

Attempted Synthesis of 3,4,6-Tri-*O*-acetyl-2-*O*-nitro-β-D-glucopyranosyl Bromide.—A solution of 3,4,6-tri-*O*-acetyl-2-*O*-nitro-α-D-glucopyranosyl chloride (5 g.) in 50 ml. of ether (dried according to Schlubach[4]) was refluxed, with stirring, for 5 hr. with 11 g. of "active" silver bromide (the silver bromide from 10 g. of silver nitrate according to Schlubach). The mixture was filtered and the residue washed with the same ether. The solvent was concentrated to a small volume under reduced pressure at low bath temperature. No crystalline material was obtained from this solution. Only sirupy starting material was recovered, 3.88 g., $[\alpha]^{18}\mathrm{D}$ +130° (*c* 2.0, chloroform).

1,3,4,6-Tetra-*O*-acetyl-2-*O*-nitro-β-D-glucopyranose.—The previously described, sirupy 3,4,6-tri-*O*-acetyl-2-*O*-nitro-α-D-glucopyranosyl chloride (2.5 g.) was dissolved in 20 ml. of glacial acetic acid containing 3.0 g. of mercuric acetate and maintained at room temperature for 1 hr. with occasional shaking. The mixture was diluted with 75 ml. of chloroform, washed thrice with water, the chloroform layer dried over anhydrous calcium chloride, filtered, and the solvent removed under reduced pressure. The resulting sirup was crystallized from ether–petroleum ether and recrystallized from hot ethanol; yield, 178 mg. (after three recrystallizations), m.p. 120–121°, $[\alpha]^{20}\mathrm{D}$ +21° (*c* 2, chloroform); X-ray powder diffraction pattern[10]: 9.94 s (2), 7.56 s (1), 5.59 s (3), 5.40 vw, 4.87 m, 4.29 vw, 4.06 m, 3.88 w, 3.55 w, 3.25 w, 3.04 vw, 2.72 vw.

Anal. Calcd. for $C_{14}H_{19}NO_{12}$: C, 42.75; H, 4.83; N, 3.56. Found: C, 42.79; H, 4.95; N, 3.65.

1,3,4,6-Tetra-*O*-acetyl-2-*O*-nitro-α-D-glucopyranose.—3,4,6-Tri-*O*-acetyl-2-*O*-nitro-β-D-glucopyranosyl chloride[7] (2.5 g.) was treated with mercuric acetate as described before; yield, 1.43 g. (after three recrystallizations from ethanol), m.p. 92–93°, $[\alpha]^{22}\mathrm{D}$ +107° (*c* 2, chloroform); X-ray powder diffraction pattern[10]: 8.31 s (2), 7.23 m, 6.68 w, 5.63 m, 5.05 vw, 4.68 vs (1), 4.24 m, 4.04 m, 3.91 w, 3.74 s (3), 3.54 w, 3.43 w, 3.24 w, 3.03 vw, 2.89 w, 2.72 vw, 2.51 vw, 2.27 vw, 2.18 w, 2.03 vw, 1.89 vw, 1.85 vw.

Anal. Calcd. for $C_{14}H_{19}NO_{12}$: C, 42.75; H, 4.83; N, 3.56. Found: C, 42.97; H, 5.13; N, 3.80.

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[10] Interplanar spacing, Å., $\mathrm{CuK}\alpha$ radiation. Relative intensities, estimated visually: s, strong; m, medium; w, weak; v, very. Strongest lines numbered, 1 strongest.

Oxidative Dimerization of Benzimidazole

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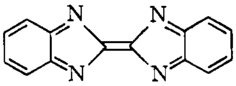
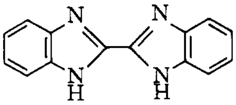
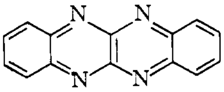
Benzimidazole (I) has been converted into $\Delta^{2,2'}$-biisobenzimidazolylidene (II), a nitrogen analog of the unknown 2,2′-biisoindene,[1,2] a dibenzofulvalene. Oxidation of I by potassium permanganate[3] or potassium dichromate[4] is known to produce imidazole-4,5-dicarboxylic acid. Prolonged oxidation of I by lead dioxide in refluxing benzene produces II, if azeotropic drying is carried out simultaneously. This reaction is slow and inefficient and the same product can be prepared more efficiently by oxidation of 2,2′-bibenzimidazole (III) under the same conditions. In this case the reaction is complete in twenty-four hours.



II



III



IV

In contrast to the fulvalenes,[5] which it resembles in its planarity and molecular structure, II is stable to heat.

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It sublimes with decomposition above 200°. It is unaffected by cold dilute alkali, but it is destroyed by hot alkali or cold dilute mineral acid. From the products of reaction with mineral acid, III can be isolated in small yield. II does not form a maleic anhydride adduct.

Structure II is indicated by the satisfactory elemental analyses and molecular weight and by absorption and p.m.r. spectroscopy. Because of the symmetry of the molecule the infrared spectrum of II is simple. In chloroform it consists of five sharp peaks assignable as follows[6]: 3050 cm.$^{-1}$ (C—H, aromatic or *cis*-vinyl), 1516 cm.$^{-1}$, 1455 cm.$^{-1}$, 1395 cm.$^{-1}$ (C—C or C—N), 1100 cm.$^{-1}$ (C—H in-plane deformation). In a potassium bromide mull three additional peaks at 768 cm.$^{-1}$, 760 cm.$^{-1}$ (very intense), and 728 cm.$^{-1}$ are observed which can be assigned to C—H out-of-plane deformation. The N—H region shows no absorption.

The p.m.r. spectrum[7] of II in deuteriochloroform (80 mg./ml.) shows only a symmetrical multiplet centered at 1.72 τ. This multiplet is of the A_2B_2 type[8] and is consistent with a structure having two pairs of equivalent protons on either end of the molecule. A very similar spectrum has been observed for naphthalene[9] which has a similar arrangement of protons.

The possibility exists that the product from oxidation of I or III is quinoxalino[2,3-*b*]quinoxaline (IV), which would be expected to have a similar infrared and p.m.r. spectrum to that described for II. However comparison of the absorption spectrum of IV in the visible and ultraviolet[10] with that of II shows that II and IV are not the same. Although both compounds are red, II in carbon tetrachloride shows an intense maximum at 409 mμ with subsidiary maxima at 386 mμ, 397 mμ, and 462 mμ, while IV shows strong maxima at 395 mμ, 410 mμ, 420 mμ and, in contrast to II, strong absorption even at 600 mμ. Furthermore reduction of II to III was carried out in good yield with hydrazine and Raney nickel.

Gieseman[11] has presented evidence that isomerization of 1-tritylimidazoles to 2-tritylimidazoles proceeds by rearrangement of a 1-radical to a 2-radical after dissociation of the trityl group from the molecule. By analogy to this it is tentatively proposed that II is produced by initial formation of a 1-benzimidazolyl radical that isomerizes to a 2-benzimidazolyl radical by a 1,2-shift. Dimerization to III followed by oxidation produces a diradical that isomerizes to II. Formation of 1,1′-bibenzimidazole is a possibility, though attempts to prepare it by treatment of silver benzimidazole with iodine in dry benzene at room temperature gave only III in poor yield. This indicates that dimerization is slow compared to the 1,2-shift.

Experimental[12]

2,2′-Bibenzimidazole (III).—This was prepared as described[13] except that diglyme was substituted for ethylene glycol. Recrystallization from aqueous diethylene glycol gave a yellow powder, m.p. >350°.

III was also prepared as follows: a solution of 5.4 g. (0.05 mole) of *o*-phenylenediamine and 3.0 g. (0.025 mole) of dithiooxamide in 150 ml. of ethanol was refluxed until the red color disappeared. The mixture was diluted to 300 ml. with water and the precipitate was crystallized from aqueous diethylene glycol to give 5.0 g. (91%) of III, m.p. >350°. $\lambda_{\max}^{\mathrm{EtOH}}$ (log ϵ): 240 mμ (4.28), 251 mμ (4.18), 316 mμ (4.42), 325 mμ (4.51), 342 mμ (4.43), 380 mμ (3.28), 400 mμ (3.41), 421 mμ (3.45), 448 mμ (3.15). The product was identical to that from the previous preparation as shown by comparison of the infrared spectra (potassium bromide).

Anal. Calcd. for $C_{14}H_{10}N_4$: N, 23.92. Found: N, 23.80.

$\Delta^{2,2'}$-Biisobenzimidazolylidene (II). **A.**—A mixture of 3.2 g. (0.025 mole) of I and 10 g. of lead dioxide[14] in 100 ml. of benzene was refluxed for 240 hr.; water produced was removed continuously by azeotropic drying. The mixture was filtered while hot and cooled. Unchanged I that crystallized was removed by filtration. The filtrate was concentrated to 25 ml., cooled, and filtered again. This filtrate was shaken with a 2% aqueous solution of silver nitrate adjusted to pH 9 with ammonia. The mixture was filtered and benzene layer of filtrate dried (magnesium sulfate) and evaporated to dryness *in vacuo*. The red residue was crystallized twice from carbon tetrachloride to give 0.26 g. (8.5%) of crimson needles, which decompose above 200° with sublimation to a green solid. The infrared spectrum (chloroform) of the crimson needles was superimposable on that of the product obtained subsequently.

B.—A suspension of 15 g. of lead dioxide[14] and 2.0 g. (0.0085 mole) of III in 100 ml. of benzene was refluxed for 24 hr.; the water produced was removed continuously by azeotropic distillation. The mixture was filtered hot and the filtrate and benzene washings of the residue were combined and concentrated to 10 ml. Cooling overnight resulted in the separation of 1.3 g. (65%) of crimson needles which decomposed above 200° with sublimation to a green solid. $\nu_{\max}^{\mathrm{CHCl_3}}$: 3050 cm.$^{-1}$, 1516 cm.$^{-1}$, 1455 cm.$^{-1}$, 1395 cm.$^{-1}$, 1100 cm.$^{-1}$ (all sharp). $\lambda_{\max}^{\mathrm{EtOH}}$ (log ϵ): 262 mμ (4.93). $\lambda_{\max}^{\mathrm{CCl_4}}$ (log ϵ): 386 mμ (4.33), 399 mμ (4.30) shoulder, 409 mμ (4.66), 435 mμ (3.83), 462 mμ (3.53).

Anal. Calcd. for $C_{14}H_8N_4$: C, 72.40; H, 3.45; N, 24.15; mol. wt., 232. Found: C, 72.51; H, 3.73; N, 23.92; mol. wt., 227, 239 (cryoscopic in benzene).

Reduction of II to III.—A solution of 0.36 g. (0.00155 mole) of II in 50 ml. of ethanol was treated with a few drops of hydrazine hydrate and 0.19 g. of Raney nickel. The mixture was stored at 40° overnight, heated to reflux, and filtered hot. The filtrate was diluted with 50 ml. of water and III separated as a yellow powde, 0.28 g. (78%). The infrared spectrum (potassium bromide) of this material was superimposable on that of the authentic material.

Reaction of Silver Benzimidazole with Iodine.—A stirred suspension of 5.0 g. (0.022 mole) of silver benzimidazole[15] in 150 ml. of dry benzene at room temperature was treated with a solution of 2.53 g. (0.02 mole) of iodine in 50 ml. of dry benzene, which was added dropwise with stirring. Care was taken to exclude atmospheric moisture. Decolorization was slow. When the addition was complete the mixture was stirred for 2 hr. longer and filtered. On evaporation the filtrate gave 0.16 g. of I, m.p. 168–170°. The residue was washed with ethanol and then extracted in a Soxhlet with ethylene glycol for 4 hr. Dilution of the extract with water gave III, 0.65 g. (27%), as a yellow powder. Its infrared spectrum (potassium bromide) was superimposable on that of the authentic material.

Acknowledgment.—Thanks are due to Dr. J. L. Kice of Oregon State University for the p.m.r. spectrum and to the Research Committee of Hobart and William Smith Colleges for a grant-in-aid.

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