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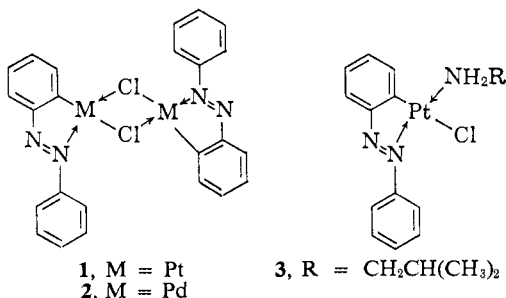
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Formation of Covalent Bonds from Platinum or Palladium to Carbon by Direct Substitution

Sir:

An unusual reaction has been found between aromatic azo compounds and potassium tetrachloroplatinate(II) or palladium(II) dichloride.

Azobenzene and potassium tetrachloroplatinate(II) were dissolved in a mixture of dioxane and water and allowed to stand at room temperature for 2 weeks. A dark maroon material was isolated by evaporating the mixture to dryness and by extracting the residue with benzene. About 48% yield of a compound believed to have structure **1** was obtained.¹ Compound **1** does not melt before decomposition, which occurs at about 270°. The palladium analog **2** melts at 279–281° dec.



The infrared spectrum (KBr pellet) of the platinum compound (**1**) reveals major absorptions at 3050, 1580, 1450, 1360, 1320, 1305, 765, 720, and 695 cm.⁻¹; ultraviolet spectrum (m μ (ϵ)): $\lambda_{\text{max}}^{\text{EtOH}}$ 257 (34,400) 350 (19,700), 373 (sh), 390 (sh), 440 (6320), and 535 (3870).

Compound **1** did not liberate azobenzene upon treatment with an excess of potassium cyanide, triphenylphosphine, or amines. Rather, new complexes were produced. For example, isobutylamine in benzene transformed compound **1** to a material assigned structure **3** (m.p. 162–164°). The ultraviolet spectrum of compound **3** and its infrared spectrum between 1300 and 1600 cm.⁻¹ are similar to those of complex **1**.

The azobenzene–platinum chloride complex (**1**) underwent decomposition upon treatment with lithium aluminum hydride in tetrahydrofuran to yield hydrazobenzene (90%).

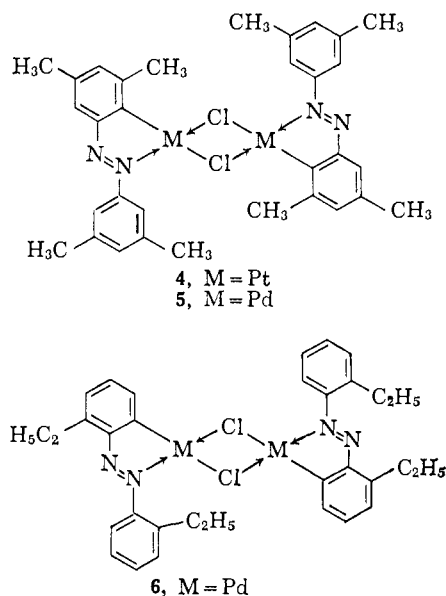
The presence of a bond between the metal atom and an *ortho* carbon atom of the azobenzene molecule was established as follows. Complex **1** was treated with lithium aluminum deuteride. After decomposition of the reaction mixture with water, the resulting hydrazobenzene was oxidized with air or mercuric oxide to azobenzene for convenience of analysis. Mass spectrometric analysis of azobenzene from two decompositions showed the following deuterium content: (A) 23% d₀, 75% d₁, 2% d₂ species; (B) 24% d₀, 74% d₁, 2%

(1) Satisfactory microanalytical data have been obtained for each of the compounds described.

d₂ species. When the reduction of compound **1** was modified by using deuterium oxide to hydrolyze the reaction mixture, the azobenzene was found to contain 4% d₀, 93% d₁, and 3% d₂ species.

Azobenzene-2-d₁, azobenzene-3-d₁, and azobenzene-4-d₁ were synthesized by standard reaction sequences.^{2,3} The nuclear magnetic resonance spectra of these deuterated azobenzenes differed slightly from each other and the spectrum of the material obtained from compound **1** was identical with the spectrum of azobenzene-2-d₁.

Compounds **4** (decomposition at 295°) and **5** (m.p. 270–275° dec.) were prepared and decomposed with lithium aluminum deuteride to yield 3,5,3',5'-tetramethylazobenzene after work-up with deuterium oxide and oxidation of the product with mercuric oxide. The platinum complex **4** afforded an azo compound in 89% yield which was found by mass spectrometry to contain 8% d₀ and 91% d₁ species. The tetramethyl-



azobenzene obtained in like manner from compound **5** contained 5% d₀ and 94% d₁ species. Both samples of tetramethylazobenzene showed nuclear magnetic resonance absorption for the protons *ortho* to the nitrogen atoms as a singlet at 7.45 p.p.m. (below tetramethylsilane), while the protons *para* to the nitrogen atoms absorbed at 7.0 p.p.m. The ratio of the areas of the absorptions was *ortho/para* = 3:2 for both samples, indicating that deuterium had been substituted in place of the metal atom in the *ortho* position of the tetramethylazobenzene.

The reaction of palladium(II) dichloride with azobenzene and its derivatives has been found to be more rapid than the reaction of platinum salts. For instance, compound **6** (m.p. 210–215°), derived from 2,2'-diethylazobenzene, was formed in 95% yield after 2 hr. at room temperature in methanol.

The structures proposed for the platinum- and palladium-azobenzene compounds are similar to the structure proposed for the product of reaction of dicyclopentadienylnickel and azobenzene,⁴ except that the authors represent coordinate bonding to nickel as

(2) T. Prosser and E. Eliel, *J. Am. Chem. Soc.*, **79**, 2544 (1957).

(3) H. Anspion, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 711.

(4) J. Kleiman and M. Dubeck, *J. Am. Chem. Soc.*, **85**, 1544 (1963).

occurring through the π -electrons of the nitrogen-nitrogen double bond.

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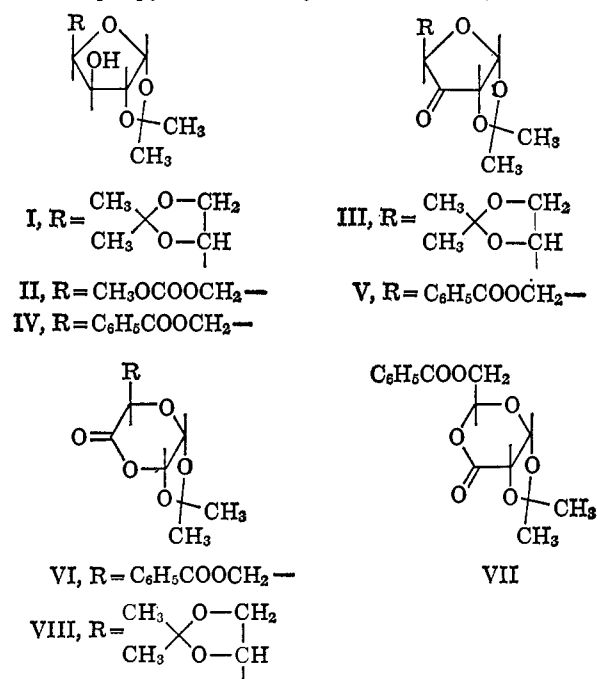
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An Oxygen Insertion Reaction of Osuloses

Sir:

As a starting point for further synthetic work we were interested in preparing a suitably constituted 3-ketofuranose. To this end, both 1,2:5,6-di-*O*-isopropylidene- α -D-glucufuranose (I) and 5-carbomethoxy-1,2-*O*-isopropylidene- α -D-xylofuranose (II) were sub-



jected to several oxidizing conditions in an attempt to convert the free 3-hydroxyl to a keto function. However, none of the oxidizing agents, which included chromium trioxide in pyridine, acetone, and acetic acid, aluminum isopropoxide in acetone, potassium permanganate in acetone, and lead tetraacetate in benzene, gave a useful amount of the desired product. Either complex mixtures or unreacted starting materials were obtained. During the course of this work a new method for oxidizing hindered hydroxyl groups in carbohydrate derivatives using ruthenium tetroxide¹ was reported,² whereby 1,2:5,6-di-*O*-isopropylidene- α -D-glucufuranose was converted into 1,2:5,6-di-*O*-isopropylidene- α -D-ribo-3-hexulofuranose (III). Another group recently reported³ that an oxidation of 5-*O*-benzoyl-1,2-*O*-isopropylidene- α -D-xylofuranose (IV) with chromium trioxide in *t*-butyl alcohol gave 5-*O*-benzoyl-1,2-*O*-isopropylidene- α -D-erythro-3-pentulofuranose (V). We have applied the ruthenium tetroxide procedure to the oxidation of IV [$\lambda_{\text{max}}^{\text{Nujol}}$ 2.8 (hydroxyl)

(1) Prepared from ruthenium dioxide obtained from Englehard Industries, Newark, N. J. For other oxidations using ruthenium tetroxide see L. M. Berkowitz and P. N. Rylander, *J. Am. Chem. Soc.*, **80**, 6682 (1958).

(2) P. J. Beynon, P. M. Collins, and W. G. Overend, *Proc. Chem. Soc.*, 342 (1964).

(3) K. Oka and H. Wada, *Yakagaku Zasshi*, **83**, 890 (1963); *Chem. Abstr.*, **60**, 1825 (1964).

and 5.82 μ (benzoate); τ^{CDCl_3} 4.03 (C-1 proton, doublet; $J_{1,2} = 3.5$ c.p.s.), 5.42 (C-2 proton, doublet; $J_{2,1} = 3.5$ c.p.s.), and 5.44 \pm 0.42 p.p.m. (C-3, 4, 5 protons, multiplet)] and have also isolated V [$\lambda_{\text{max}}^{\text{Nujol}}$ 5.62 (cyclic ketone) and 5.77 μ (benzoate); $\lambda_{\text{max}}^{\text{CHCl}_3}$ 5.62 (cyclic ketone) and 5.81 μ (benzoate); τ^{CDCl_3} 3.87 (C-1 proton, doublet; $J_{1,2} = 4.5$ c.p.s.) and 5.44 \pm 0.28 p.p.m. (C-2, 4, 5 protons, multiplet)]. The course of reaction was followed by t.l.c. (silica; CHCl_3 -EtOAc, 4:1) and it was noted that, as the oxidation proceeded in the presence of excess ruthenium tetroxide, an increasing amount of an unexpected product was being formed. After 24 hr. this product, now the major product, was isolated and its elemental analysis and infrared and n.m.r. spectra indicated that it was the product of oxygen insertion, 1,2-*O*-isopropylidene-6-*O*-benzoyl-3-oxa- α -D-erythro-4-hexulopyranose (VI) [m.p. 111–112°; $[\alpha]_D +81^\circ$ (*c* 1.03, CHCl_3); $\lambda_{\text{max}}^{\text{Nujol}}$ 5.70 (lactone) and 5.80 μ (benzoate); τ^{CDCl_3} 4.08 (C-1 proton, doublet; $J_{1,2} = 3.8$ c.p.s.), 4.32 (C-2 proton doublet; $J_{2,1} = 3.8$ c.p.s.), and 5.23 \pm 0.19 p.p.m. (C-5, 6 protons, multiplet)]. That the inserted oxygen is in the 3-position as in VI and not in the 4-position as in the isomeric VII is indicated by n.m.r. spectra. The position of the C-5 proton resonance in VI is essentially unchanged compared to that of the C-4 proton in V, whereas the C-2 proton resonance of VI shows a large downfield chemical shift compared to that of the C-2 proton in V.

Overend's² oxidation of 1,2:5,6-di-*O*-isopropylidene- α -D-glucufuranose (I) [τ^{CDCl_3} 4.07 (C-1 proton, doublet; $J_{1,2} = 3.8$ c.p.s.), 5.48 (C-2 proton, doublet; $J_{2,1} = 3.8$ c.p.s.), and 5.81 \pm 0.26 p.p.m. (C-3, 4, 5, 6 protons, multiplet)] with ruthenium tetroxide was repeated. After a few hours the product III, as reported² previously, was produced, while after 48 hr. the product of oxygen insertion, 1,2:6,7-di-*O*-isopropylidene-3-oxa- α -D-ribo-4-heptulopyranose (VIII) [m.p. 62–64°; $[\alpha]_D +86^\circ$ (*c* 0.5, CHCl_3); $\lambda_{\text{max}}^{\text{Nujol}}$ 5.68 μ (lactone); τ^{CDCl_3} 4.12 (C-1 proton, doublet; $J_{1,2} = 3.7$ c.p.s.), 4.29 (C-2 proton, doublet; $J_{2,1} = 3.7$ c.p.s.), and 5.64 \pm 0.34 p.p.m. (C-5, 6, 7 protons, multiplet)] was obtained.

The products VI and VIII⁴ represent a new class of carbohydrate derivatives, and the oxygen insertion reaction is a new reaction⁵ of ruthenium tetroxide.

(4) All compounds reported have given satisfactory elemental microanalyses.

(5) H. Nakata, *Tetrahedron*, **19**, 1959 (1963), has reported the conversion of β -cholestanol into 4-oxo-A-homo-5 α -cholestan-3-one in acetic acid solution containing excess lead tetraacetate and catalytic amounts of ruthenium tetroxide. It seems likely that in this case, as Nakata suggested, the oxygen insertion results from a Baeyer-Villiger reaction involving peracetic acid.

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A Total Synthesis of *dl*- Δ^1 -Tetrahydrocannabinol, the Active Constituent of Hashish¹

Sir:

We wish to report that we have completed the first total synthesis² of *dl*-cannabidiol³ (Ia) and *dl*- Δ^1 -3,4-

(1) Hashish. VI. For Part V see H. Budzikiewicz, R. T. Aplin, D. A. Lightner, C. Djerassi, R. Mechoulam, and Y. Gaoni, *Tetrahedron*, in press.