molecule incorporates two different sites with which benzyne can react, and relative reactivity ratios can easily be obtained. This method would be somewhat simpler and more versatile than that reported previously.[8] To this end, benzyne was generated from diphenyliodonium-2-carboxylate[1d] and allowed to react with 1b and 1c. B:A values of 3 and 1, respectively, were obtained in comparison with values of 4 and 1 for benzyne generated from benzenediazonium-2-carboxylate in methylene chloride–acetone at 40°. Considering the change in solvent (diglyme) and temperature (160°), these values indicate that this method is valid. The cyano group limits the usefulness of 1b and 1c because this group interferes with Grignard intermediates and strong bases. Further work in this area with A-ring and/or B-ring substituents is in progress.

Acknowledgment. The author wishes to thank Dr. T. H. Regan for n.m.r. spectra and Mr. G. P. Happ and Mr. D. P. Maier for mass spectra.

(8) R. Huisgen and R. Knorr, *Tetrahedron Letters*, 1017 (1963).

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Oxidation of Carbohydrates with Dimethyl Sulfoxide Containing Phosphorus Pentoxide

Sir:

Recently oxidation of alcohols to ketones and aldehydes with dimethyl sulfoxide has been reported. Pfitzner and Moffatt[1] found that primary and secondary hydroxyl groups of carbohydrates and steroidal alcohols were oxidized to the corresponding aldehydes and ketones with dimethyl sulfoxide containing both dicyclohexylcarbodiimide and phosphorus compounds such as phosphoric acid or pyridinium phosphate. This procedure was applied to the synthesis of streptose by Dyer, *et al.*[2] Traynelis, *et al.*,[3] also reported the oxidation of arylcarbinols to the corresponding aldehydes with dimethyl sulfoxide.

In the course of our work[4] on the syntheses of nucleosides and polysaccharides with phosphorus pentoxide as dehydrating agent, we have observed that phosphorus pentoxide accelerated the oxidation of the various hydroxyl groups of carbohydrates and other compounds with dimethyl sulfoxide to the corresponding aldehydes, ketones, and carboxylic acids. We wish to report some results of the oxidation of carbohydrates with this reagent.

(1) K. E. Pfitzner and J. G. Moffatt, *J. Am. Chem. Soc.*, **85**, 3027 (1963).

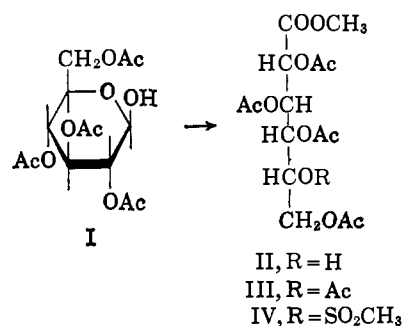(2) J. R. Dyer, W. E. McGonigal, and K. C. Rice, *ibid.*, **87**, 654 (1965).

(3) V. J. Traynelis and W. L. Hergenrother, *ibid.*, **86**, 298 (1964).

(4) Paper presented at the annual meeting of the Agricultural Chemical Society of Japan, Tokyo, April 1–4, 1965. For example, the reaction of 2,3,4,6-tetra-O-acetyl-β-D-glucopyranose with theophylline in N,N-dimethylformamide in the presence of phosphorus pentoxide produced 7-(2′,3′,4′,6′-tetra-O-acetyl-β-D-glucopyranosyl)theophylline. When dimethyl sulfoxide was used as solvent, however, no nucleoside was isolated. The polymerization of hexoses, pentoses, hexosamines, or uronic acids was observed as the result of the reaction in a mixture of dimethyl sulfoxide and phosphorus pentoxide. These results will be published elsewhere.

2,3,4,6-Tetra-O-acetyl-β-D-glucopyranose (1 mmole) (I; m.p. 134°, $[\alpha]^{28}$D +2.2° (c 1.2, CHCl₃)) was heated in anhydrous dimethyl sulfoxide containing phosphorus pentoxide (1.2 mmoles as P_4O_{10}) at 60–65° for 10–15 hr. The syrup obtained by extracting the reaction mixture with chloroform followed by concentration was dissolved in methanol, and to the solution were added ether and petroleum ether to incipient turbidity. After allowing the solution to stand in a refrigerator, methyl 2,3,4,6-tetra-O-acetyl-D-gluconate (II) crystallized; yield 20–30%, m.p. 111–112°, $[\alpha]^{28}$D +13.9° (c 1.4, CHCl₃). *Anal.* Calcd. for $C_{15}H_{22}O_{11}$: C, 47.62; H, 5.86; OCH₃, 8.21. Found: C, 47.29; H, 5.74; OCH₃, 7.9. The infrared spectrum[5] of II showed OH absorption at 3500 cm.$^{-1}$. The n.m.r. spectrum[6] showed the presence of four O-acetyl groups (δ 2.0–2.2), one O-methyl group (δ 3.75, COOCH₃), and six hydrogens (δ 3.8–4.2, 3 H; δ 5.1–5.8, 3 H). Acetylation of II gave methyl 2,3,4,5,6-penta-O-acetyl-D-gluconate (III); m.p. 123–124°, $[\alpha]^{28}$D +8.2° (c 1.1, CHCl₃). All the physical constants of III were in good agreement with those reported.[7] No OH absorption was observed in the infrared spectrum, and five acetyl CH₃ signals were observed at δ 2.0–2.2 in the n.m.r. spectrum.

Methylsulfonylation of II gave methyl 2,3,4,6-tetra-O-acetyl-5-O-(methylsulfonyl)-D-gluconate (IV); m.p. 143°, $[\alpha]^{28}$D −4.9° (c 1.33, CHCl₃), ν_{max}^{KBr} no OH absorption, 1350 and 1185 cm.$^{-1}$ (sulfonyloxy), n.m.r. δ 2.0–2.2 (O-acetyl, 4 CH₃), 3.1 (S–CH₃, 1 CH₃), 3.75 (COOCH₃, 1 CH₃), 4.2–4.4 (2 H), and 4.9–5.6 (4 H). *Anal.* Calcd. for $C_{16}H_{24}O_{13}S$: C, 43.3; H, 5.25; S, 7.00; OCH₃, 6.79. Found: C, 42.7; H, 5.28; S, 6.94; OCH₃, 6.1. On the basis of the analysis of coupling constants of six hydrogens of II, III, and IV, in addition to the evidence mentioned above, it is concluded that the hydroxyl group of II is attached to C-5 of the original carbon chain of the D-glucopyranose molecule.

Scheme I

II, R = H
III, R = Ac
IV, R = SO₂CH₃

The mechanism of formation of methyl ester in this oxidation is not yet known, although some novel reactions of dimethyl sulfoxide in connection with methylation have recently been reported.[8,9]

Oxidation of 1,2:5,6-di-O-isopropylidene-α-D-glucofuranose (1.0 mmole) (V; m.p. 108–109°, $[\alpha]^{28}$D −13.5° (c 1.0, CHCl₃)) at room temperature for 24

(5) Spectra were measured with KBr pellets.

(6) Chemical shifts were expressed as p.p.m. downfield from tetramethylsilane as internal standard and measured at 60 Mc. in CDCl₃.
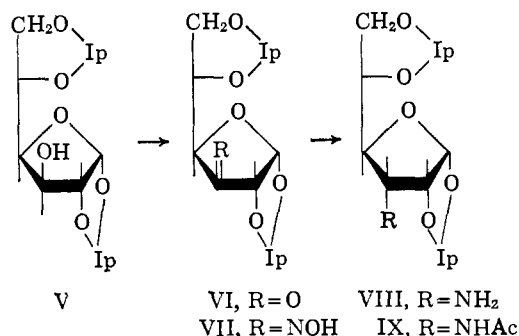
(7) G. B. Robbins and F. W. Upson, *J. Am. Chem. Soc.*, **62**, 1074 (1940).

(8) H. Metzger, H. König, and K. Seelert, *Tetrahedron Letters*, **15**, 867 (1964).

(9) D. H. Ball, E. D. M. Eades, and L. Long, Jr., *J. Am. Chem. Soc.*, **86**, 3579 (1964).

hr., using a mixture of dimethyl sulfoxide and phosphorus pentoxide (0.6 mmole), gave 1,2:5,6-di-O-isopropylidene-α-D-*ribo*-3-hexulofuranose (VI) in 65% yield; m.p. 108–112°, $[\alpha]^{28}D$ +40.0° (c 2.0, CHCl₃). This was recrystallized three times from ligroin; monohydrate, m.p. 118–119°, $[\alpha]^{28}D$ +110° (c 1.0, CHCl₃) (lit. b.p. 97° (0.01 mm.),[10] $[\alpha]D$ 107°[10]; hydrate, m.p. 109–113°,[10] $[\alpha]D$ +45°[10]; monohydrate, m.p. 108–110°,[11] $[\alpha]^{22}D$ +40.2° (c 0.5, H₂O)[11]). A strong ketone absorption was observed at 1770 cm.⁻¹ in the infrared (Nujol). The oxime (VII) was obtained from VI by the usual procedure; m.p. 103–104°, $[\alpha]^{28}D$ +187° (c 1.5, CHCl₃). All the physical constants of VII were in good agreement with those reported.[10] The reduction of VII with lithium aluminum hydride gave 3-amino-3-deoxy-1,2:5,6-di-O-isopropylidene-α-D-allofuranose (VIII); m.p. 88–90°, $[\alpha]^{28}D$ +41.3° (c 1.2, CHCl₃). All the physical constants of VIII were in good agreement with those reported.[12,13] Acetylation of VIII gave 3-acetamido-3-deoxy-1,2:5,6-di-O-isopropylidene-α-D-allofuranose (IX); m.p. 128–129°, $[\alpha]^{28}D$ +71.8° (c 0.8, CHCl₃). All the physical constants of IX were in good agreement with those reported.[14]

Scheme II

V   VI, R = O   VIII, R = NH₂
           VII, R = NOH   IX, R = NHAc

This method of oxidation is also a convenient way for preparing 3-*keto*-glucose, which is a component of some microbial disaccharides.[15]

Application of this procedure to the oxidation of other carbohydrates and the study of reaction mechanism are in progress, and the details will be reported elsewhere.

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(11) O. Theander, *Acta Chem. Scand.*, **18**, 2209 (1964).

(12) M. L. Wolfrom, F. Shafizadeh, and R. K. Armstrong, *J. Am Chem. Soc.*, **80**, 4885 (1958).

(13) K. Freudenberg, O. Burkhart, and E. Braun, *Ber.*, **59**, 714 (1926).

(14) R. U. Lemieux and P. Chu, *J. Am. Chem. Soc.*, **80**, 4745 (1958).

(15) (a) M. J. Bernaerts and J. De Ley, *Biochim. Biophys. Acta*, 30, 661 (1958); (b) M. J. Bernaerts, J. Furnelle, and J. De Ley, *ibid.*, 69, 322 (1963); (c) S. Fukui and R. M. Hochster, *J. Am. Chem. Soc.*, 85, 1697 (1963).

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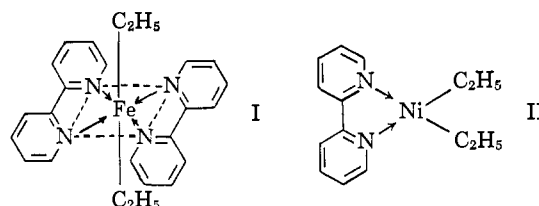### Butadiene Polymerization Catalysts. Diethylbis(dipyridyl)iron and Diethyldipyridylnickel

Sir:

Cyclooligomerization of butadiene with nickel complex catalysts has been extensively studied by Wilke and his co-workers, and various zerovalent complexes relevant to the catalysis have been prepared.[1]

One of our laboratories has reported that butadiene is converted to cyclooctadiene and vinylcyclohexene with a catalyst system prepared from iron acetylacetonate, triethylaluminum, and α,α'-dipyridyl.[2] We wish to report now on the preparation and properties of crystalline organoiron and organonickel dipyridyl complexes isolated from the catalyst systems containing iron and nickel acetylacetonates.

The complexes were prepared from Fe(acac)₃ or Ni(acac)₂, α,α'-dipyridyl, and diethylaluminum monoethoxide or triethylaluminum in ether at −20 to 0°. The crystalline precipitates separated out of the reaction mixtures were washed repeatedly with absolute ether under rigorous exclusion of air. The products are soluble in benzene, acetone, and ether and can be recrystallized from these solutions as fine needles. The analyses of the iron and nickel complexes were in agreement with the structures shown below. The yield of the iron complex based on Fe(acac)₃ was *ca.* 50%, and the nickel complex 70%.
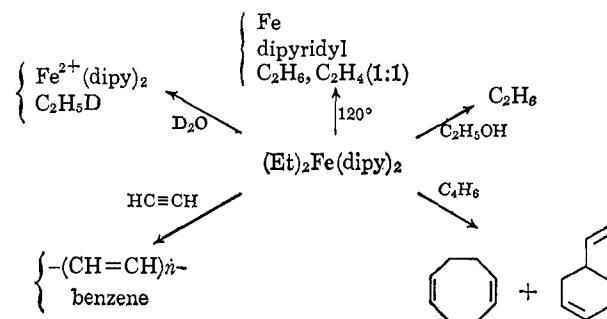

Anal. Calcd. for C₂₄H₂₆N₄Fe (I): C, 67.61; H, 6.15; N, 13.15; Fe, 13.10. Found: C, 67.93; H, 6.17; N, 12.6; Fe, 13.2. Calcd. for C₁₄H₁₈N₂Ni (II): C, 61.61; H, 6.62; N, 10.26; Ni, 21.51. Found: C, 61.28; H, 6.28; N, 10.1; Ni, 21.4.

Infrared spectra of these complexes in benzene have several absorption bands in the C–H stretching region indicating the presence of CH₂ and CH₃ groups. These bands disappear when air is introduced to the benzene solutions.

Chemical properties of the iron complex are summarized in Scheme I.

Scheme I

When the iron complex was heated at 120° in the absence of air, ethylene and ethane were evolved in a ratio of *ca.* 1:1, and a black pyrophoric residue and crystals of dipyridyl were obtained as the decomposition products. The volume of the gaseous product amounted to 1.75 moles/mole of the compound. Re-

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(2) A. Misono, Y. Uchida, and M. Hidai, Japan Chemical Society annual meeting, Tokyo, April 1964; to be published in *Bull. Chem. Soc. Japan*.