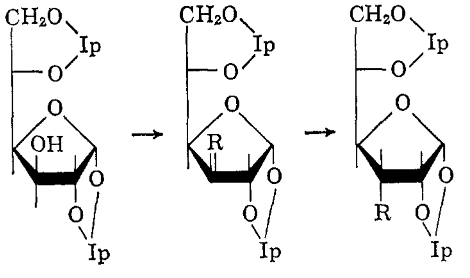
hr., using a mixture of dimethyl sulfoxide and phosphorus pentoxide (0.6 mmole), gave 1,2:5,6-di-O-isopropylidene-α-D-*ribo*-3-hexulofuranose (VI) in 65% yield; m.p. 108–112°, $[\alpha]^{28}D$ +40.0° (*c* 2.0, $CHCl_3$). This was recrystallized three times from ligroin; monohydrate, m.p. 118–119°, $[\alpha]^{28}D$ +110° (*c* 1.0, $CHCl_3$) (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, H_2O)[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, $CHCl_3$). 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, $CHCl_3$). 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, $CHCl_3$). All the physical constants of IX were in good agreement with those reported.[14]

Scheme II



V　　VI, R=O　VIII, R=NH_2
　　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).

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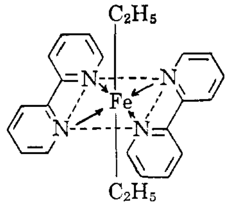
Butadiene Polymerization Catalysts. Diethylbis(dipyridyl)iron and Diethyldipyridylnickel

Sir:

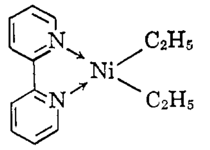
Cyclooligomerization of butadiene with nickel complex catalysts has been extensively studied by Wilke and his co-workers, and various zerovalent complexes relevant to the catalysis have been prepared.[1]

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%.



I



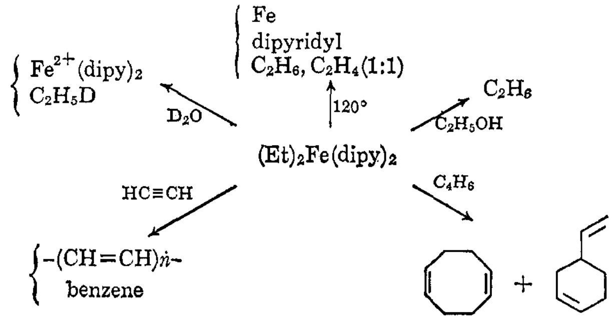
II

Anal. Calcd. for $C_{24}H_{26}N_4Fe$ (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 $C_{14}H_{18}N_2Ni$ (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 CH_2 and CH_3 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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[1] G. Wilke, *Angew. Chem.*, **75**, 10 (1963).

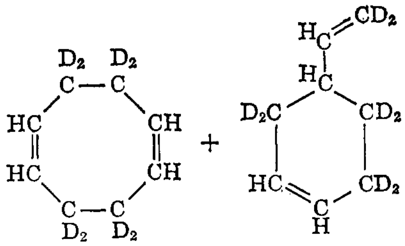
[2] A. Misono, Y. Uchida, and M. Hidai, Japan Chemical Society annual meeting, Tokyo, April 1964; to be published in *Bull. Chem. Soc. Japan.*

action with deuterium oxide gave C_2H_5D as a main gas product (confirmed by infrared and mass spectroscopy). Alcoholysis gave only ethane. The visible spectra of hydrolysis and alcoholysis products were identical with that of ferrous dipyridyl chloride.

The nickel complex has similar chemical properties with the iron complex, but the gaseous pyrolysis products contained a considerable amount of *n*-butane in addition to ethylene and ethane.

Oligomerization of butadiene was carried out at 50° in the presence of the catalytic amount of the dipyridyl complexes in benzene solution. Butadiene was converted with the iron complex in up to 95% yield to cycloocta-1,5-diene and 4-vinylcyclohexene in the ratio of 3:1. Ethylene was evolved, accompanied by ethane. Dimerization of butadiene-1,1,4,4-d_4 gave cyclooctadiene-3,3,4,4,7,7,8,8-d_8 and 4-vinyl-β,β-d_2-cyclohexene-3,3,5,5,6,6-d_6.

$D_2C{=}CH{-}CH{=}CD_2 \rightarrow$



Cyclooligomerization of butadiene with the nickel complex gave cyclododecatriene in the yield of 30% with small amounts of cyclooctadiene and vinylcyclohexene. Acetylene was converted with the complexes to benzene and a black polymer with conjugated double bonds.

The detailed discussion of the mechanism of polymerization will be reported later.

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A Novel Photochemical Cycloaddition Reaction of Benzene

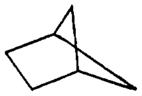
Sir:

Earlier reports on the photochemical addition reactions of benzene have invariably led to products in which the benzene has been found to add in its Kékulé structure.[1] We wish to report an instance in which the benzene molecule seems to have undergone addition in a Dewar structure. There is reason to believe that this reaction is by no means an isolated example and that the photochemical dimerization of benzene also follows a similar pathway.[2]

Photolysis of benzene solutions (20% by volume) of cyclobutene at 2537 Å. at room temperature gave a 50% yield (based on cyclobutene) of a product[3] (b.p. 24° (1.5 mm.)) which could readily be separated by distillation at reduced pressure from the unreacted materials and any polymer that may be present. The material had an empirical formula of C_5H_6 (*Anal.*[4] C, 90.98; H, 9.16. C_5H_6 requires C, 90.84; H, 9.16) and a molecular weight (mass spectrometry) of 132, so that it corresponded to a 1:1 adduct of benzene and cyclobutene. The n.m.r. spectrum[5] showed two olefinic protons at τ 4.25 (singlet) and a complex absorption at τ 6.4–8.9 which accounted for all of the remaining protons. The absence of absorptions which could be attributed to cyclopropyl rings was noticeable in both the n.m.r. and infrared spectra. The compound absorbed exactly 1 mole of hydrogen when reduced with hydrogen gas at 10 cm. in the presence of Adams catalyst. The liquid product had the molecular formula $C_{10}H_{14}$ (*Anal.* Calcd. for $C_{10}H_{14}$: C, 89.49; H, 10.51. Found: C, 89.54; H, 10.75. Molecular weight by mass spectrometry: 134; $n^{24}\mathrm{D}$ 1.5051) and showed no absorption due to olefinic protons in its n.m.r. spectrum. Hydrogenation of the $C_{10}H_{12}$ product at 1 atm. in the presence of Adams catalyst led to the absorption of 2 moles of hydrogen to give a solid product (m.p. 71°), mol. wt. 136, which also showed no unsaturation in its n.m.r. spectrum.

It is obvious that both the 1:1 adduct and the $C_{10}H_{14}$ product must be tetracyclic and, further, should be made up of rings larger than three carbons. The thermal decomposition of the adduct in the vapor phase in a quartz cell in a degassed system proceeded rapidly at 200° and yielded benzene and butadiene, as identified by their ultraviolet spectra. Cyclobutene itself decomposes rapidly under identical conditions at *ca.* 150,[6] while bicyclo[2.2.0]hexane (I) decomposes around 170°,[7] and bicyclo[2.1.1]hexane (II) decomposes at *ca.* 345°.[8] At 200°, it is unlikely that hydrogen migrations and rearrangements of the carbon skeleton take place during pyrolysis. These results suggest that the structure of the adduct can be best represented by III,[9] and it follows that the $C_{10}H_{14}$ product is probably IV.


I


II


III


IV

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(1) H. J. F. Angus and D. Bryce-Smith, *J. Chem. Soc.*, 4791 (1960); G. O. Schenck and R. Steinmetz, *Tetrahedron Letters*, **21**, 1 (1960).

(2) This is probably the origin of the yellow polymer that is the major product of the irradiation of liquid benzene at 2537 Å.

(3) It was advantageous not to carry the reaction to completion, but terminate it when the solution turned intensely yellow, recover the unreacted cyclobutene and benzene, and reirrradiate the fresh solution.

(4) Microanalysis by Midwest Microlab, Inc., Indianapolis, Ind.

(5) The authors wish to thank Drs. E. B. Whipple and D. A. Arnold of the Union Carbide Research Institute, Tarrytown, N. Y., for the n.m.r spectra. These spectra were obtained in carbon tetrachloride with $(CH_3)_4Si$ as internal reference.

(6) W. Cooper and W. D. Walters, *J. Am. Chem. Soc.*, **80**, 4220 (1958).

(7) C. Steel, R. Zand, P. Hurwitz, and S. G. Cohen, *ibid.*, **86**, 679 (1964).

(8) R. Srinivasan and A. A. Levi, **85**, 3363 (1963).

(9) The infrared spectrum of III as a pure liquid had a weak absorption at 1600 cm.$^{-1}$ which could be attributed to the double bond located in a cyclobutane ring. This absorption was absent in the infrared spectrum of IV. The olefinic protons in cyclobutene appear as a singlet at τ 4.05 (S. Borcic and J. D. Roberts, *ibid.*, **87**, 1054 (1965)).