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Several Products on Some Organic Chemical Reactions

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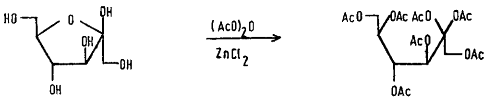
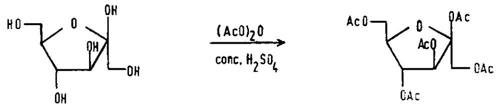
I. Acetylation of D-Fructose

It is known popularly that by the acetylation of D-fructose on the condition of acetic anhydride and zink chloride, pentaacetyl D-fructose is produced.[1] But practically from the result of the experiment, heptaacetyl D-fructose (I) was obtained because the ketone group of D-fructose was changed to acetal by this condition. Then, next to that, on the condition of acetic anhydride and conc. sulfuric acid, pentaacetyl D-fructose (II) on the data of the nmr spectrum was obtained.[2]



(I)



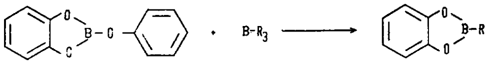
(II)

II. Synthesis of Catecholborane

It is also known that catecholborane (III) is obtained by the reaction of catechol with diborane,[3] and this compound react with double or triple bond compounds.[4]

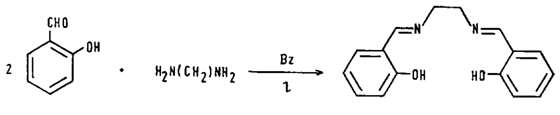
(III)

This compound also react with phenols and alcohols, then several kinds of phenoxy and alkoxy borane compounds will be derived, and these react with trialkylborane, then alkylcatecholborane will be produced.

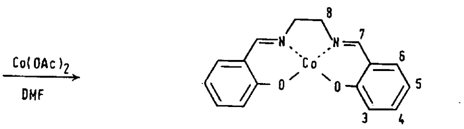


III. Synthesis of Co(salen)

The nmr spectrum of Co(salen) (V) compound could be measured in the long chemical shift range on the solution of DMSO-d_6 including tetramethylsiane as an internal standard.[5]



(IV)



(V)

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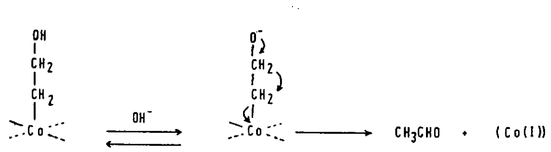
And sodium Co(salen) was known as a reversible carbon dioxide carrier, the green solution of sodium Co(salen) in tetrahydrofuran absorbed 1 m*l* of CO_2 per cobalt atom in a few minites at room temperature giving a brown solid insoluble in tetrahydrofuran.[6]

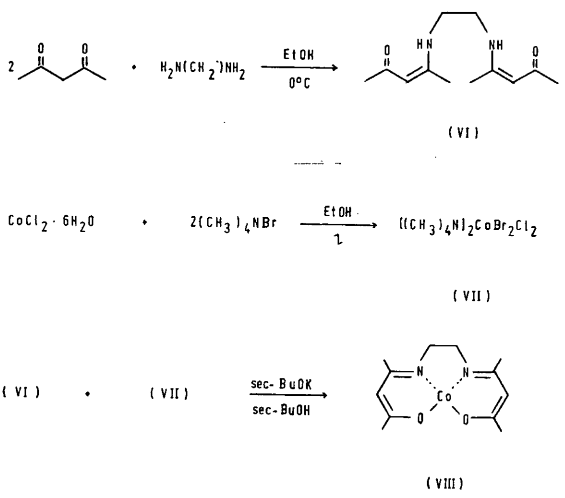
$$\mathrm{Co(salen)Na} + \mathrm{CO_2} \underset{}{\overset{\mathrm{THF}}{\rightleftharpoons}} \mathrm{Co(salen)CO_2Na}$$

It is also known that hydroxyethylcobalt compound such as Co(salen) derivatives decompose in alkaline medium yielding acetaldehyde as the initial product.[7]



IV. Synthesis of Co(acasen)

Co(acasen) (VIII) undergoes reversible oxygenation and deoxygenation in solution.



It is known that the best charactarized systems are Schiff base complexes such as Co(acasen) in dimethylformamide, pyridine and substituted pyridines, the general reaction which is reversible at room temperatures below 0°C is typified by the following :

$$\mathrm{Co(acacen)} + \mathrm{DMF} + \mathrm{O_2} \longrightarrow \mathrm{Co(acacen)(DMF)O_2}$$

The initial complex has one unparied electron and so also so the oxygen adducts.[8]

Experimental

Infrared spectra were taken by a JOEC IRA-1 spectrometer. Nuclear magnetic resonance spectra were recorded using a Hitachi R-40 90 MHz spectrometer using tetramethylsilane as an internal reference.

The elementary analysis was measured by a staff of the analytical center at University of California, Berkeley.

All chemicals used were of the highest and reagent-grade quality commercially in the U. S. and Japan

Preparation :

Heptaacetyl D-fructose(I)—One hundred grams of D-fructose was added to the solution of 1 *l* of acetic anhydride and 10 g of zink chloride in a 2 *l* of a four neck flask with a mechanical stirrer, a condenser and a thermometer connected to it and stirred for 24 hr at 0°C in an ice bath. And then it was heated at 50°C for 2 hr and cooled at room temperature, the reaction mixture was poured into ices and neutralized with sodium carbonate. The product was extracted with chloroform, washed with water several times and dried with anhydrous sodium sulfate. After filtration, the chloroform solution was concentrated with a rotary evaporator. From the result of the TLC, the product was pure, then 200 g of dark brown viscous product was obtained (Yield 73. 1%), ir(film), 3650, 3532, 2960, 1750, 1650(sh), 1440, 1380, 1220, 1150, 980, 940, 750 cm^{-1} ; nmr($CDCl_3$), δ 2. 12(q. 21 H), 3. 95—5. 58 (m. 7 H) ppm.

Pentaacetyl D-fructose(II)—twenty grams of D-fructose was added to the solution of 120 m*l* of acetic anhydride and 5 m*l* of conc. sulfuric acid in a four neck flask with a mechanical stirrer, a condenser and a thermometer connected to it. And it was stirred for 1 hr at 0°C in an ice bath. The reaction mixture was poured into ices and neutralized with sodium carbonate. The product was extracted with chloroform, washed with water several times and dried with anhydrous sodium sulfate. The chloroform solution was concentrated with a rotary evaporator. Then 3. 9 g of the dark brown viscous product was obtained (Yield 20%), it was pure from the result of the TLC; ir(film), 3500, 2900, 1740, 1420(sh), 1360, 1220, 1040, 900(sh)cm^{-1} ; nmr(CDCl$_3$), δ 2. 15(q. 15 H), 3. 85(m), 4. 30(m), 4. 96—5. 40(m), 5. 95(m) (totally 7 H) ppm.

1, 3, 2-Benzodioxaborol (*Catecholborane*) (III)—Fifteen grams of catechol was dissolved in 50 m*l* of tetrahydrofuran and cooled at 0°C with an ice bath. Then diborane gas which was generated with 5 g of sodium borotetrafluoride and 25 g of borone trifluoride in 50 m*l* of digrime was charged and stirred for 30 min in argon atmosphere. The tetrahydrofuran solution was concentrated with a rotary evaporator. The residue was distilled under vacuum. The fraction of bp. 48—58°C(30—32 mmHg) was collected(10 g, Yield 61. 2%) ; ir(film), 2620, 1440, 1330, 1115, 790, 720 cm^{-1} ; nmr(CDCl$_3$), 6. 85—7. 30(m)ppm., the nmr-spectum was the same as that of the reference.[8]

Bis(*salicylaldehyde*)*ethylenediimine*(IV)—Eight hundred grams of salicylaldehyde and 435. 74 g of ethylenediamine hydrochloride salt was dissolved in 800 m*l* of benzene and 262 g of sodium hydroxide was added to it, then it was refluxed for 6 hr in a 2 *l* of a flask with a distilling tube connected to it. After that, the benzene solution was washed with water several times and dried with anhydrous sodium sulfate. 900 m*l* of n-hexane was added to it and the solution was warmed and cooled, then 738 g of yellow plate crystalline product was obtained(Yield 84%) ; mp 59—60°C ; ir (nujol), 3400, 1620, 1580, 1420, 1380, 1300, 1260, 1230, 1220, 1160, 1120, 1050, 1030, 980, 940, 860, 780, 750 cm^{-1} ; nmr(CDCl$_3$), δ 3. 90(s. 4 H), 6. 90(m. 4 H), 7. 30 (m. 4 H), 8. 35(s. 2 H) ppm.

N, N′-Ethylenebis (*salicylideneiminato*) *cobalt* (V)—Ten grams of bis (salicylaldehyde)ethylenediimine and 9. 3 g of cobalt acetate tetrahydrate was dissolved in 80 m*l* of dimethylformamide and 1 g of anhydrous sodium sulfate was added to it. The mixture was stirred for 24 hr at room temperature in argon atmosphere, then 2 g of the dark red-brown precipitate was obtained, it was filtered and washed with diethyl ether and dried in vacuo(Yield 16. 5%) ; mp>250°C ; ir(nujol), 1620, 1600, 1550, 1530, 1450, 1350, 1330, 1290, 1200, 1190, 1130, 1120, 1080, 1040, 940, 895, 840, 740, 720 cm^{-1} ; nmr(DMSO-d$_6$), δ -16(5-H), 8(3-H), 11(4-H), 16(6-H), 20(imino-H), 66(CH$_2$) ppm, both spectra were the same as those of references.[5,10]

Bis(*acetylacetone*)*ethylenediimine* (VI) —Twenty grams of acetylacetone was dissolved in 100 m*l* of absolute ethanol in 200 m*l* of a flask and cooled at 0°C with an ice bath, and 6. 03 g of ethylenediamine was added dropwise to it and stirred over night. After concentration of it with a rotary evaporator, 15. 9 g of the pale yellow plate crystalline product was obtained after washing with diethyl ether and dried in vacuo(Yield 59. 1%) ; mp 88. 0—89. 0°C ; ir(nujol), 1540, 1480, 1350, 1250, 1060, 1000, 960, 930, 840, 748, 730 cm^{-1} ; nmr(CDCl$_3$), δ 1. 95(s. 6 H), 2. 05(s. 6 H), 3. 45(t. 4 H), 5. 00(s. 2 H) ppm.

Bis(*tetramethylammonium*)*dibromodichlorocobalt*(VII) —To 8. 8 g of cobalt chloride hexahydrate in 200 m*l* of ethanol, 14. 52 g of tetramethylammonium bromide was added, then the mixture was refluxed for 4 hr. Then the white blue precipitate was produced, it was filtered off and washed with ethanol and diethyl ether, 16. 1 g of the white blue powdery precipitate was obtained after drying in vacuo (Yield 99%) ; mp> 300°C ; ir(nujol), 2800, 1480, 1400(sh), 940, 940, 770 cm^{-1}.

N, N′-Ethylenebis(*acetylactoneiminato*)*cobalt* (VIII) —Six grams of bis(acetylacetone)ethylenediimine and 12 g of bis(tetramethylammonium)dibromodichlorocobalt were dissolved in 100 m*l* of sec-butanol including 8. 6 g of potassium sec-butoxide and stirred at room temperature for 20 hr in argon atmosphere, the color of the solution was changed yellow brown from green within 1 hr. Then the solution was concentrated with a rotary evaporator to 50 m*l* and kept cool in the refrigirator over night. 2. 03 g of the red needle crystalline product was obtained from the solution after washing with chloroform and dichloromethane (Yield 13. 5%) ; mp 126. 5—128. 0°C ; ir (nujol), 1500, 1460, 1350, 1250, 1180, 1025, 1000, 930, 770, 680 cm^{-1} ; this compound was negative to the nmr spectrum on the usual method. Anal. Calcd for $C_{12}H_{18}N_2O_2Co$; C, 51. 25 ; H, 6. 45 ; N, 9. 96. Found : C, 51. 37 ; H, 6. 41 ; N, 10. 14%.

Finally some parts of these works were taken from graduation theses of the students in my laboratory.

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数種の有機化学反応の生成物

山 口　功

(昭和55年 9 月22日受理)

D—フルクトースのペンタアセテートは次にジアゾ化により炭素を1個ふやし，過ヨウ素酸で末端炭素を切断することによりD—アピオースを得ようとする出発物質としての意味を持つ．カテコールボランは数種の誘導体に光照射し，ボロンがどの様な挙動を示すかを調べるためのものである。Co (Salen) Na は炭酸ガスのキャリアとしてのみの役割が多少とも炭酸ガスを活性化していないかという期待に基づく． Co(acacen) も酸素との付加体を生ずるが炭酸ガスとはどうであるかという興味により合成されたものである．