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Annotated Bibliography of 1,2-Cycloheptanedionedioxime

by

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## Annotated Bibliography of 1,2-Cycloheptanenedionedioxime

Charles V. Banks and Howard B. Nicholas

## Introduction

This annotated bibliography concerning the preparation, reactions and uses of 1,2-cycloheptanenedionedioxime has been prepared as a reference for analytical research and control chemists.

Much work has been done on the uses and application of the numerous vic-dioximes, other than 1,2-cycloheptanenedione-dioxime. However, comparatively little has been done on this reagent. It is hoped that this bibliography will stimulate further research on the analytical applications of this reagent.

The references are listed in chronological order and each is numbered consecutively. This bibliography begins with the work of Godchot and Cauquil and ends with listings of most of the works published in 1955.

1936

1. Godshot, M., and Cauquil, G., "The Action of Selenium Dioxide on Some Cyclanones," Compt. rend., 202, 326-328, 444 (1936) C. A., 30, 2931 (1936).

Cycloheptanone oxidized in alcohol with selenium dioxide gives 1,2-cycloheptanenedione, b.p. 107-109° at 17 mm.; diphenylhydrazone, m.p. 135°; dioxime, m.p. 181-182°.

1949

2. Vander Haar, W., Voter, R. C., and Banks, C. V., "Synthesis of 1,2-Cycloheptanenedionedioxime," (Iowa State College, Ames), J. Org. Chem., 14, 836-838 (1949) C. A., 44, 5320 (1950).

To three moles of cycloheptone refluxing in 700 ml. of absolute alcohol, were added three moles of selenium dioxide dissolved in 500 ml. of

absolute alcohol and 1600 ml. of 95% ethyl alcohol. The refluxing continued for six hours and the mixture was left to stand for 18 hours, filtered and fractionated, giving 340 g. of 1,2-cycloheptanenedione  $b_{17}^{107-109}$ . The selenium can be recovered for reuse. 1,2-Cycloheptanenedione (0.5 mole) in 400 ml. of methyl alcohol was added slowly at 0°C to a well stirred mixture of 2 moles hydroxylammonium chloride in 250 ml. water, 2 moles of sodium hydroxide in 150 ml. water, and 200 ml. methyl alcohol, stirring continued for 24 hours. The crystals are filtered and additional crops obtained from the filtrate.

On concentration in vacuo, tarry bubbles sometimes form. These are extracted with a suitable petroleum ether (range 75-120°) such as Skelly solve D. From the aqueous phase one recovers additional dioxime by cooling to 0°C. The crystalline product was recrystallized from water, yielding 36 g. (46%), m.p. 179-180. Recrystallization from benzene (useful for small amounts only) yields the anhydrous dioxime, m.p. 182°.

This compound has gained wide use among analysts for the determination of nickel and palladium.

1950

3. Longo, R. E., "Semimicro Determination of Nickel with Heptoxime (1,2-Cycloheptanenedionedioxime)," (Univ. Nacl. litoral, Santa Fe, Arg.) Anales Soc. Cient. Argentina, 154, No. 3, 87-94, (1950) C. A., 47, 2083 (1953) 7.

In the light of the work of Voter and Banks, the effect of various ions on the accuracy of the method was studied. The method is applicable to 0.1 mg. nickel. For 2-10 mg. the error was less than 1% even in the presence of a large quantity of acetate, tartrate, or citrate. Cations of the third group do not interfere, except cobalt(II), if their concentration is less than five times that of nickel(II). Precipitation of aluminum(III), iron(III), or chromium(III) is prevented by addition of tartrate and of titanium by citrate.

4. Longo, R. E., "Cycloheptanedioxime in the Microdetermination of Nickel," (Rosario, Arg.), Pubs. Inst. Invest Microquim., Univ. nacl litoral, 14, 127-32 (1950) C. A., 46, 5484 (1952).

Since the molecular weight of cycloheptanedioxime is greater than that of dimethylglyoxime (2,3-dibutanedionedioxime) it should permit greater accuracy in the microgravimetric determination of nickel(II). Longo studied the precipitation of nickel(II) from a solution of the chloride alone, and in the presence of manganese, zinc and cobalt, respectively, with satisfactory results. The solution contained 0.5 g. of the reagent in 100 ml. water. To precipitate the nickel, adjust the solution to pH 4 by adding 10% ammonium acetate solution. Heat to approximately 70° and slowly add 2.3 ml. of the vic-dioxime reagent while stirring. Digest the mixture at 80° for 10 minutes and let stand in a cool place for one hour. Filter and wash the precipitate with cold water, dry at 120° for one hour and weigh.

5. Voter, R. C., and Banks, C. V., "Water-Soluble 1,2-Dioximes as Analytical Reagents" (Iowa State College, Ames), Anal. Chem., 21, 1320-1323 (1949) C. A., 44, 2404 (1950).

Of six supposedly water soluble 1,2-dioximes tested, only 1,2-cyclohexanedionedioxime (I) and 1,2-cycloheptanedionedioxime (II) are sufficiently soluble to replace dimethylglyoxime in analysis. (II) gives a yellow precipitate with nickel(II) and precipitation is complete at pH 2.7 or higher. Nickel(II) can be determined in solutions containing acetate, nitrate and thiocyanate anions and in the presence of aluminum, antimony, arsenic, beryllium, bismuth, cadmium, chromium, cobalt, copper, iron, lead, magnesium, manganese, molybdenum, titanium, vanadium and zinc. To determine nickel in steel, dissolve the sample in a suitable mineral acid, decompose carbides with nitric acid, add perchloric and evaporate to fumes. After gentle boiling for 15 minutes, cool, add 50 ml. of water, boil and filter off silicon dioxide (or silica). Wash with 1% hydrochloric acid and then water. Add an excess of 33% acid

solution and 20% ammonium acetate solution if lead is present. Add 10% sodium sulfite solution, add ammonium hydroxide to pH 3.5. Heat to 50°, add 20 ml. of 50% ammonium thiocyanate solution and an excess of saturated solution of (II). Filter, wash, dry and weigh. The precipitate contains 15.9% nickel.

1951

6. Ferguson, R. C., Voter, R. C., and Banks, C. V., "1,2-Cycloheptanedionedioxime as a Gravimetric Reagent for Nickel," (Iowa State College, Ames), Mikrochemie ver Mikrochim Acta, 38, 11-14 (1951) C. A., 45, 6529 (1951) 7.

This reagent is given the trivial name, "Heptoxime," and with it nickel(II) can be precipitated quantitatively at a pH of 2.7 or more, as a yellow nickel compound  $\text{Ni}(\text{C}_7\text{H}_{11}\text{N}_2\text{O}_2)_2$ . It can be weighed after drying at 110-120°. In determining 0.05 - 0.10 mg. of nickel, the greatest error in six determinations was 8% of nickel. With 30 mg. of steel, the results were accurate.

7. Ferguson, R. C. and Banks, C. V., "Spectrophotometric Determination of Nickel with 1,2-Cycloheptanedione-dioxime," (Iowa State College, Ames), Anal. Chem., 23, 1486-1487 (1951) C. A., 46, 854 (1952) 7.

A further study of the 1,2-cycloheptanedione-dioxime (Heptoxime) reaction with Ni(II) provides a more sensitive method than either nioxime or 2,3-butanedionedioxime (dimethylglyoxime). Absorption spectra of nickel(II)-heptoxime solutions are given for the range 330-650  $\text{m}_{\mu}$ .

8. Voter, R. C., Banks, C. V., Fassel, V. A., and Kehres, P. W., "Nature of the Hydrogen Bond in 1,2(vic-dioxime- $\text{N},\text{N}'$ )-Nickel(II) Compounds," (Iowa State College, Ames), Anal. Chem., 23, 1730-1735 (1951) C. A., 46, 2909 (1952) 7.

The absorption spectra of 1,2-cyclohexanedione-dioxime, 1,2-cycloheptanedionedioxime, and 2,3-butanedionedioxime in Nujol and perfluorokerosene were studied in the range 2 to 7  $\mu$  by the

use of the mull technique. Absorption maxima attributed to O - H vibration frequencies were observed at 2.98, 3.11 and 3.13, respectively, for each of the above.

The O - D absorption maxima in 1,2-cyclohexanedionedioxime, 1,2-cyclopentanedionedioxime and 2,3-butanedionedioxime were observed at 3.99, 4.18 and 4.19, respectively.

The absorption spectra of 1,2-bis(1,2-cyclohexanedionedioxime-N,N')nickel(II), 1,2-bis(1,2-cycloheptanedionedioxime-N,N')nickel(II) and 1,2-bis(2,3-butanedionedioxime-N,N')nickel(II) and the respective deuterio compounds did not exhibit absorption maximum for the O - H or O - D vibration frequencies in the region in which they normally occur; this fact indicates a radical change in the identity of the O - H and O - D groups.

Weak absorption maxima were observed at various points as well as points of strong absorption maximum which occurred in both the Nujol and perfluorokerosene mulls of the nickel derivatives.

The above evidence plus the lack of reactivity of the O - H hydrogens suggested an O - H - O structure unlike that observed in normal bonding. The similarity of the O - H - O bond of the complex nickel compounds to the F - H - F bonds of potassium bifluoride is discussed.

9. Nakazawa, K., and Matsuura, S., "Synthesis of Dihydroresorcinol and Ethyl Dihydroresorcinol by Cyclization," (Gifu Coll. Pharmacy), J. Pharm Soc. Japan, 71, 805-806 (1951) C. A., 46, 8025 (1952)

By refluxing 2.3 g. sodium in 40 ml. xylene and 0.5 ml. absolute alcohol, with dropwise addition of 7.9 g. 4-acetylethylbutyrate in 40 ml. xylene for one hour on an oil bath (140-150°), cooling, adding ethyl alcohol to take up the unreacted sodium, then adding 30 ml. of water, transferring to a separatory funnel, removing the xylene layer, acidifying the aqueous layer, extracting with ether six times and recrystallizing from benzene, giving 2 g. (35.7%) dihydroresorcinol needles, m.p. 103°; vic-dioxime needles, m.p. 154°. 4-Acetylethylbutyrate (9.5 g.)

in 25 ml. xylene, 2.3 g. sodium in 50 ml. xylene and 0.5 ml. absolute alcohol as above gave 3.5 g. (50%) 6-ethyl-1,5-cyclohexanedione, prisms, m.p. 177°; vic-dioxime granules, m.p. 222°.

1954

10. Gillis, J., Hoste, J., and van Moffaert, Y., "Spectrophotometric Determination of Nickel with Heptoxime," (University Ghent, Belg.), Chim. Anal., 36, 43-47 (1954) [C. A., 48, 4361 (1954)].

Treatment of nickel(II) solution with cycloheptanedionedioxime (heptoxime) followed by extraction with chloroform gives an orange-colored solution which can be measured at 337 m $\mu$  at a concentration of about 1-10  $\text{mg}$  per ml. Two detailed procedures are given for carrying out the test.

11. Triebs, W., and Mdlhstaedt, M., "The Mannich Bases of Cycloheptanone and the 1-Methylene-2-cycloheptanone," (Univ. Leipzig, Germany), Chem. Ber., 87, 407-411 (1954), [C. A., 49, 3928 (1955)].

Because 1-methylene-2-cyclohexanone dimerizes so readily that the monomer cannot be isolated, the behavior of other isocyclic ortho-methylene ketones is studied. Heating 112 g. of cycloheptanone (I), 75 g. 40% formaldehyde and 81 g. dimethyl ammonium chloride with stirring on a water bath in a carbon dioxide atmosphere and distilling off the water formed, and the unchanged (I) leaves 1-(dimethylaminomethyl)-2-cycloheptanone hydrochloride (II), m.p. 127°, from which, with 110 g. sodium carbonate, 47% (II),  $b_{2.5}^{18}$  105-107,  $N_D^{18}$  1.4750 is obtained.

Heating 21 g. of (II) at 10 mm. slowly to 180° yields 30% 1-methylene-2-cycloheptanone (III)  $b_{2.5}^{18}$  1.4786. (III) is also obtained in 70% yield when 17 g. of 1-(piperidinomethyl)-2-cycloheptanone hydrochloride is heated at 160-180° / 1 mm., leaving 20-25% dimeric (III) as a residue.

12. Ramirez, F., and Bellet, R. J., "The Osazones of 1,2-Cyclobutanedione and other Alicyclic  $\alpha$ -Diketones", (Columbia University), J. Am. Chem. Soc., 76, 491-493 (1954), [C. A., 49, 1599 (1955)].

The 2,4-dinitrophenylosazones (I) of 1,2-cyclobutanedione (II), 1,2-cyclopentanedione (III), 1,2-cyclohexanedione (IV), and 3,3-dimethyl-1,2-cyclohexanedione (V) have been prepared from the corresponding  $\alpha$ -halo ketones and their ultraviolet absorption spectra in chloroform compared to that of diacetyl. The alicyclic (I) exhibited 3 absorption maxima in the ultraviolet (352, about 400, and about 450  $\mu\text{m}$ ) while the (I) of diacetyl exhibited only two (about 400 and about 450  $\mu\text{m}$ ). The similarity between the spectra of the alicyclic (I) in the ultraviolet and infrared suggests that the structure of the presumably highly strained (I) of (II) does not differ significantly from those of the less strained alicyclic (I).

Various methods and data are given for the preparation of (I) of (II), (III), and (IV).

13. Dauben, H. J., Ringold, H. J., Wade, R. H., Pearson, D. L., and Anderson, A. G., "Cycloheptanone," (University of Washington), Organic Synthesis, 34, 19-24 (1954), C. A., 49, 5331 (1955) 7.

The addition of a mixture of 2.5 moles cyclohexanone and 3.25 moles methyl nitrate is made during 3.5 hours to the solution of 2.5 moles sodium ethylate in 1.2 liters ethyl alcohol at 42-48°. After standing 16 hours the mixture is cooled and filtered. An addition of sodium salt to 2.9 moles dilute acetic acid and ether externally gives a crude oily substance of 1-hydroxy-1-nitromethyl-1-cyclohexane. Hydrogenation was done in 450 ml. acetic acid with W-4 Raney nickel at 40-45 psi. below 35°; the mixture is diluted with 2.3 liters of ice water. To the oily layer was added 4.2 moles of aqueous sodium nitrate, dropwise, during a one hour period at a temperature of -5°. Upon standing at room temperature over night, the excess was neutralized with sodium bicarbonate and steam distilled. Ether extraction of the distillate gives 40-42% cycloheptanone.

14. de Boer, T. J., and Backer, H. J., "Cycloheptanone,"  
(De Rijks-Univ., Groningen, Neth.), Organic  
Synthesis, 34, 24-26 (1954), C. A., 49, 5331  
(1955) 7.

The addition of 15 grams of potassium hydroxide in 50 ml. 50% ethyl alcohol is made during 2 hours to the mixture of 0.5 mole cyclohexanone, 0.58 mole (p-tolylsulfonyl) methyl nitrosoamide, 150 ml. ethyl alcohol and 10 ml. water at 10-20°. After stirring for 30 minutes 50 ml. of 2 N hydrochloric acid is added. To this mixture is added 100 g. of sodium bisulfite in 200 ml. water. The entire batch is now shaken at room temperature with the exclusion of air for 10 hours. Treatment of the precipitated addition compound with a solution (125 g. sodium carbonate in 150 ml. water) and ether extraction gives 33-36% cycloheptanone.

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