original reaction mixture, and the oil was taken into ether. The ethereal solution was washed with water until the washings were free of acid. On drying and removal of solvent, the dark red oil was distilled under reduced pressure. The fraction, distilling at 42–44° and 1 mm., was collected and weighed 9.5 gm. or 87% of theory. It was shown to be 98–100% pure benzaldehyde by its reaction with 2,4-dinitrophenylhydrazine. The hydrazone melted at 236–237°. The melting point did not change when the material was mixed with an authentic sample of the 2,4-dinitrophenylhydrazone of benzaldehyde.

*Quinaldyl chloride.* Anhydrous quinaldic acid[13] was converted to the acid chloride by treatment with an excess of thionyl chloride (Eastman White Label) after the procedure of Besthorn and Ibele.[14] Seventeen and three-tenths grams of the anhydrous acid were suspended in 140 ml. of thionyl chloride and the mixture was heated on a water bath until evolution of HCl ceased. The excess thionyl chloride was removed under reduced pressure and the bright red crystalline mass of quinaldyl chloride recrystallized from ether. Eighteen grams of long yellow needles which melted at 96–97° were obtained.

The compounds listed in Table I which follows were prepared by two different procedures, depending upon the use of aqueous or non-aqueous reaction media. These are designated as *Procedure A* and *Procedure B*, and are described below.

*Procedure A:* Ten millimoles of the amino acid, peptide, etc., were dissolved in 20 ml. of normal sodium hydroxide and cooled to 0–10°. The solution was stirred, and 10 millimoles of quinaldic acid were added over a period of about 10 minutes. The cooling bath was removed and the mixture was allowed to come to room temperature. The clear orange solution was treated with a small amount of norite and filtered. On acidification with 10 ml. of normal hydrochloric acid an oil precipitated, which usually crystallized on standing. The crystals were collected by filtration and dried in air. When the oil formed on acidification did not crystallize, it was extracted with methylene chloride and dried. On removal of solvent and scratching with a glass rod, crystals were formed. Yields were from 95–100% of theory. The material was recrystallized from the appropriate solvent. In general, the quinaldyl amino acids will crystallize from chloroform–petroleum ether, but some of them may be crystallized from alcohol water.

*Procedure B:* Ten millimoles of amine, amino acid ester, etc., were dissolved in 10 ml. of methylene chloride to which had been added 10 millimoles of triethylamine or other tertiary base.[15] The solution was cooled to 0–10° and 10 millimoles of quinaldyl chloride was added over a period of 10 minutes. After the reaction mixture was allowed to come to room temperature it was washed well with water, dried, and treated with norite. The solvent was removed under reduced pressure, and the residual oil crystallized on being scratched with a glass rod. The yields were similar to those obtained in *Procedure A* above. The quinaldyl amides usually crystallize from petroleum ether (B.P. 60–100°) or isopropyl ether. Water sometimes interferes with the crystallization.

It is of interest to note that the presence of a hydroxyl group in the amino compound does not interfere with the reaction under the conditions described above. This is exemplified in the preparation of the ethanolamine adduct.

PASADENA, CALIF.

(13) Obtained by heating several hundred grams of the hydrated material under high vacuum at 100° for 24 hr. This material, as well as quinaldyl chloride, is available commercially from Radio-Carbon Laboratories, Pasadena, California.

(14) E. Besthorn and J. Ibele, *Ber.*, **38**, 2127 (1905).

(15) When possible, it is preferable to use a 1 mole excess of the amine being acylated instead of the tertiary base.

---

[COMMUNICATION NO. 1999 FROM THE KODAK RESEARCH LABORATORIES]

# The Preparation of Alicyclic Trioximes

DONALD C. BATESKY AND NEIL S. MOON

*Received June 18, 1959*

The reaction of cyclohexanone and its 4-methyl derivative with isoamyl nitrite results in the formation of the symmetrical dioximino ketones: 1,2,3-cyclohexanetrione-1,3-dioxime and 5-methyl-1,2,3-cyclohexanetrione-1,3-dioxime, instead of the expected keto monoximes. Oximation of the keto dioximes gives the corresponding trioximes. These trioximes give color reactions with various cations.

Alicyclic *vic*-dioximes, commonly prepared by the oxidation of alicyclic ketones with selenium dioxide to $\alpha$-diketones followed by oximation,[1] and more recently by oximation of $\alpha$-bromoalicyclic ketones,[2] have found widespread use as analytical reagents for nickel and palladium.[3] 1,2-Cyclohexanedione dioxime and its 4-methyl derivative, owing to their greater solubility than dimethylglyoxime in water, are excellent substitutes for this latter reagent in analysis.

To avoid the use of the toxic and expensive selenium dioxide, another route was taken to attempt the preparation of these reagents. Murakami and Yukawa[4] have reported the preparation of 1,2-cyclohexanedione dioxime by passing ethyl nitrite gas into a mixture of cyclohexanone and hydrochloric acid to obtain 1,2-cyclohexanedione monoxime, a solid decomposing at 227° which was then treated with hydroxylamine to yield the *vic*-dioxime melting at 186–187°. This method, because of the availability and low cost of starting materials, was selected in these Laboratories to pre-

(1) D. T. Hooker and C. V. Banks, *U. S. Atomic Energy Comm., ISC-597*, 113 pp. (1955).

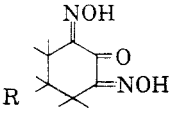
(2) R. Belcher, W. Hoyle, and T. S. West, *J. Chem. Soc.*, 2743 (1958).

(3) C. V. Banks and D. T. Hooker, *Anal. Chem.*, **28**, 79 (1956).

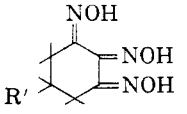
(4) M. Murakami and Y. Yukawa, *Mem. Inst. Sci. Ind. Research Osaka Univ.*, **5**, 150 (1947); *Chem. Abstr.*, **47**, 2714 (1953).

pare 1,2-cyclohexanedione dioxime and its 4-methyl derivative.

On reacting equimolecular portions of cyclohexanone or 4-methylcyclohexanone with isoamyl nitrite (used in place of ethyl nitrite because of the greater ease of handling) in the presence of hydrochloric acid, well defined crystalline compounds were obtained. This is in agreement with Murakami and Yukawa but contrary to the results reported by other authors[1,5-7] who obtained the "monoxime" as a noncrystallizable oil. Elemental and infrared analysis of these compounds showed however, that two rather than one isonitroso groups had added to the cyclohexane ring, one on each side of the carbonyl group. This reaction took place even with an insufficient amount of isoamyl nitrite for the addition of two groups and at temperatures from −15° to +20°. Thus, keto dioximes (I, II), rather than the expected keto monoximes, were formed.




I. R = H
II. R = $CH_3$




III. R′ = H
IV. R′ = $CH_3$

This may account for the stability of product formed as opposed to the low stability of the product obtained by other investigators who used different methods to obtain the keto monoxime. On treating each of the keto dioximes with hydroxylamine, the predicted trioximes (III, IV) were obtained. The trioximes exhibit good water solubility and gave, as well as did the keto dioxime intermediates, color reactions with various cations. 5-Methyl-1,2,3-cyclohexanetrione-1,3-dioxime gave color reactions with $Fe^{+2}$, $Fe^{+3}$, $Co^{+2}$, $Hg^{+2}$, and $Cu^{+2}$ ions. 1,2,3-Cyclohexanetrione trioxime and its 5-methyl derivative gave color reactions with $Fe^{+2}$, $Fe^{+3}$, $Co^{+2}$, $Cu^{+2}$, $Cr^{+3}$, $Pb^{+2}$, $Hg^{+2}$, and $Sn^{+2}$ ions, and a deep red precipitate with $Ni^{+2}$ ion. The analytical applications of these new compounds have not been exploited and are open for development.

(5) F. M. Jaeger and J. A. van Dijk, *Proc. Koninkl. Ned. Akad. Wetenschap.*, **39**, 384 (1936).

(6) T. A. Geissman and M. J. Schlatter, *J. Org. Chem.*, **11**, 771 (1946).

(7) E. G. Rauh, G. F. Smith, C. V. Banks, and H. Diehl, *J. Org. Chem.*, **10**, 199 (1945).

## EXPERIMENTAL

*5-Methyl-1,2,3-cyclohexanetrione-1,3-dioxime* (II). To a well stirred mixture of 112 g. (1 mole) of 4-methylcyclohexanone and 4 ml. (0.05 mole) of concentrated hydrochloric acid, cooled in a Dry-Ice–isopropyl alcohol bath, 117 g. (1 mole) of isoamyl nitrite was slowly added in four hr. at −5°. The product separated during the addition of a fine tan solid. Upon completion of the addition the product was filtered, washed with light petroleum ether, and recrystallized from ethanol, yielding pale yellow platelets decomposing at 202°. The yield was 59.5 g. or 70% (based on the isoamyl nitrite used).

*Anal.* Calcd. for $C_7H_{10}N_2O_3$: C, 49.5; H, 5.9; N, 16.5. Found: C, 49.4; H, 6.1; N, 16.3.

*5-Methyl-1,2,3-cyclohexanetrione trioxime* (IV). To a cooled, stirred solution of 23 g. (1 mole) of freshly cut sodium dissolved in 300 ml. of methanol was added a slurry of 69.5 g. (1 mole) of hydroxylamine hydrochloride in 200 ml. of methanol, followed by 170 g. (1 mole) of 5-methyl-1,2,3-cyclohexanetrione-1,3-dioxime. The mixture was stirred overnight at room temperature, filtered to remove the insoluble salt, and slowly concentrated to near dryness at reduced pressure and low heat. The resulting solid was recrystallized once from distilled water and finally from ethyl acetate, giving white crystals decomposing at 170°. The yield was 82 g. or 45%.

*Anal.* Calcd. for $C_7H_{11}N_3O_3$: C, 45.4; H, 6.0; N, 22.7. Found: C, 45.4; H, 6.0; N, 23.0.

*1,2,3-Cyclohexanetrione-1,3-dioxime* (I). This was prepared using the procedure just described for preparing the 5-methyl derivative. The keto dioxime is a yellow-brown solid decomposing at 197°. This material was not purified since it appeared to break down when heated in solvents. The yield was 46%.

*Anal.* Calcd. for $C_6H_8N_2O_3$: C, 46.2; H, 5.2; N, 17.9. Found: C, 46.0; H, 5.1; N, 18.0.

*1,2,3-Cyclohexanetrione trioxime* (III). This was prepared by the oximation of 1,2,3-cyclohexanetrione-1,3-dioxime with hydroxylamine. The trioxime is a white crystalline solid (from dioxane) melting at 170°, with decomposition. The yield was 25%.

*Anal.* Calcd. for $C_6H_9N_3O_3$: C, 42.1; H, 5.3; N, 24.6. Found: C, 42.2; H, 5.4; N, 24.7.

ROCHESTER, N. Y.