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Preparation and Properties of Some Alkyl-1,2-Cyclohexanedione Dioximes[2]

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INTRODUCTION

It has been known for some time that certain alicyclic *vic*-dioximes possessed properties making them useful as analytical reagents for nickel and palladium.[4–9] In connection with a recent search[10] for more desirable alicyclic *vic*-dioximes it became advisable to synthesize a series of alkyl-1,2-cyclohexanedione dioximes (alkylnioximes).

Some alkyl-1,2-cyclohexanedione dioximes have been previously prepared by several investigators,[11–15] but the yields have been small, the intermediates expensive, or the details of the procedure not reported. The present paper is concerned with the preparation and properties of the following alkyl-1,2-cyclohexanedione dioximes: 4-methyl-, 4-isopropyl-, 4-*tert*-amyl-, 4-(1,1,3,3-tetramethylbutyl)-, 3-methyl-, 3-ethyl-, and 3,6-dimethyl-1,2-cyclohexanedione dioxime. Alkylphenols were hydrogenated at high pressure over a Raney nickel catalyst[16–20] to the corresponding alkylcyclohexanols which, in turn, were oxidized, in good yields, to the expected alkylcyclohexanones by an acid-dichromate mixture.[21] These alkylcyclohexanones were then oxidized with selenium dioxide[22,23] to the corresponding alkyl-1,2-cyclohexanediones which were then oximated to alkyl-1,2-cyclohexanedione dioximes with aqueous hydroxylamine.[22] The properties of these alkyl-1,2-cyclohexanedione dioximes are discussed and related to their structures.

PREPARATION OF THE *vic*-DIOXIMES

Materials and apparatus. 4-tert-Amylcyclohexanol was obtained from Sharples Chemical Company, Wyandotte, Michigan. *4-Isopropylcyclohexanol* was secured from the Dow Chemical Company, Midland, Michigan. The Rohm and Haas Company, Philadelphia, Pennsylvania, supplied the *4-(1,1,3,3-tetramethylbutyl)phenol.* The other phenols, cyclohexanols, and cyclohexanones were obtained from Distillation Products Industries, Rochester, New York. The Raney nickel catalyst was obtained as a nickel-aluminum alloy from Central Scientific Company, Chicago, Illinois, and was activated by boiling with sodium hydroxide as directed by the manufacturer. Selenium dioxide was obtained from the American Metals Company, Limited, New York City, New York, and was used without further purification. All of the other chemicals employed in the preparation were C.P. grade or their equivalent.

A Paar, Series 4000, High Pressure Hydrogenation Apparatus manufactured by the Paar Instrument Company, Moline, Illinois, was used for the hydrogenations. This is a rocking type hydrogenator with a 1000-milliliter bomb.

Alkylcyclohexanols. The alkylphenol was purified by fractional distillation through a 50-cm. Vigreux column under reduced pressure. One mole of the purified alkylphenol together with 2 g. of the Raney nickel catalyst was suspended in 150 ml. of ethanol and placed in the bomb. Hydrogen was introduced to a pressure of 1800 p.s.i. and the bomb was heated to 150°. When the pressure of the bomb had fallen to that calculated for complete hydrogenation (1 to 4 hours), the bomb was cooled and opened and the contents were filtered to remove the catalyst. The filtrate was fractionated through a 50-cm. Vigreux column and the alkylcyclohexanol was collected. The yields and properties are given in Table I.

Alkylcyclohexanones. The alkylcyclohexanols, obtained either commercially or synthesized as directed above, were purified by distillation. The acid-dichromate method of Nickels and Heintzelman[21] was used to oxidize the alkylcyclohexanols to the corresponding alkylcyclohexanones. In this method 100 ml. of conc'd sulfuric acid was added to a vigorously stirred mixture of one mole of the alkylcyclohexanol and 1 liter of water. The vigorous stirring was con-

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(1) The experiments were performed in the Ames Laboratory of the Atomic Energy Commission.

(2) No. XVIII in a series on "Chemistry of the *vic*-Dioximes." Previous paper in this series is No. XVII, *Anal. Chem.*, **28**, 79 (1956).

(3) Abstracted from a dissertation submitted by Donald T. Hooker to the Graduate Faculty of Iowa State College in partial fulfillment of the requirements for the degree of Doctor of Philosophy, 1955. Present address: Proctor & Gamble Co., Cincinnati 17, Ohio.

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TABLE I

PROPERTIES AND YIELDS OF ALICYCLIC INTERMEDIATES

Intermediate	B.p. range, °C.	Mm.	M.p., °C.	n_D^{20}	Yield, %	References
2-Methylcyclohexanol	163–165	758	—	1.4638	91	17, 26–34
3-Ethylcyclohexanol	185–190	751	—	1.4650	92	20, 35
2,5-Dimethylcyclohexanol	64–65	12	—	1.4580	94	20, 36–42
4-Octylcyclohexanol[a]	115–123	4	—	1.4635	80	43, 44
2-Methylcyclohexanone	162–165	754	—	1.4494	85	26–28, 31, 45–50
3-Ethylcyclohexanone	75–77	12	—	1.4430	82	35, 51–55
2,5-Dimethylcyclohexanone	176–179	755	—	1.4447	82	36, 39, 41, 51, 54, 56–58
4-Isopropylcyclohexanone	84–86	10	—	1.4562	81	50, 58–63
4-*tert*-Amylcyclohexanone	110–113	12	96	—	84	50
4-Octylcyclohexanone[a]	91–95	1	102	—	85	44
3-Methyl-1,2-cyclohexanedione	80–85	12	62	—	20	12, 14, 64–65
4-Methyl-1,2-cyclohexanedione	90–95	16	35	—	34	14, 15
3-Ethyl-1,2-cyclohexanedione	90–95	6	71	—	19	None
3,6-Dimethyl-1,2-cyclohexanedione	85–90	6	—	1.5002	2	None
4-Isopropyl-1,2-cyclohexanedione	77–84	1	65–70	—	29	None
4-*tert*-Amyl-1,2-cyclohexanedione	111–118	4	75–80	—	38	None
4-Octyl-1,2-cyclohexanedione[a]	137–143	1	90–95	—	40	None

[a] Octyl is 1,1,3,3-tetramethylbutyl.

tinued while one liter of an aqueous 10% solution of potassium dichromate was added at such a rate as to keep the temperature of the oxidation mixture between 55° and 60°. An ice-bath was used to control the temperature. After addition of the potassium dichromate was complete, the solution was stirred for another hour and allowed to cool. The aqueous layer was separated from the lighter organic phase and extracted with three 100-ml. portions of diethyl ether. The ether and organic phases were combined and washed with three 50-ml. portions of a 20% aqueous solution of potassium hydroxide, followed by two 50-ml. portions of water saturated with sodium sulfate. The ether phase was dried with sodium sulfate and fractionated to recover the ketone. Properties and yields of the ketones are listed in Table I.

Alkyl-1,2-cyclohexanediones. The alkylcyclohexanones, obtained either from commercial sources or prepared as described above, were oxidized with alcoholic selenium dioxide to yield the corresponding alkyl-1,2-cyclohexanediones. The method reported by Riley, *et al.* as modified by Hach, Banks, and Diehl[22] was employed. One mole of the alkylcyclohexanone was dissolved in 300 ml. of ethanol and placed in a one-liter flask equipped with a stirrer, reflux condenser, and dropping-funnel. One mole of selenium dioxide was dissolved in 200 ml. of 95% ethanol and the solution was added dropwise to the stirred solution of the alkylcyclohexanone. Heat was supplied by means of a steam-

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TABLE II

PROPERTIES OF *vic*-DIOXIMES

vic-Dioxime	Yield, %	Analyses				M.p., °C.	Molecular Weight	Molar Solubility, M × 10^4	References
		Calc'd C	Calc'd H	Found C	Found H				
2,3-Butanedionedioxime						240	116	34	
Nioxime[a]						188	142	58	
3-Methylnioxime	60	53.83	7.74	53.99	7.52	164–165	156	256	12–14
4-Methylnioxime	70	53.83	7.74	53.79	7.50	181–182	156	218	11, 14, 15
3,6-Dimethylnioxime	52	56.44	8.11	56.44	8.29	160–161	170	474	None
3-Ethylnioxime	65	56.44	8.11	56.80	8.23	179–180	170	144	None
4-Isopropylnioxime	72	59.31	8.85	59.19	8.73	184–185	184	41	None
4-*tert*-Amylnioxime	80	62.23	9.49	62.55	9.51	202–204	212	1.1	None
4-Octylnioxime[b]	70	66.11	10.30	66.37	9.96	199–201	254	0.004	None

[a] Nioxime is 1,2-cyclohexanedione dioxime. For convenience the alkyl-1,2-cyclohexanedione dioximes reported in Table II are listed as derivatives of nioxime. [b] 4-Octylnioxime is 4-(1,1,3,3-tetramethylbutyl)-1,2-cyclohexanedione dioxime.

bath until the oxidation started and then the temperature was maintained above 70° by the rate of addition of the selenium dioxide. An excess of unreacted selenium dioxide in the presence of the alkylcyclohexanone is to be avoided since a violent reaction may take place under this condition. When the addition of the selenium dioxide was completed, the mixture was stirred and refluxed on a steam-bath for six hours. The reaction mixture was stirred for an additional six hours at room temperature, after which time the precipitated selenium metal was filtered off and the dark-colored filtrate was fractionated through a 50-cm. Vigreux column under reduced pressure. In the case of the higher-boiling alkyl-1,2-cyclohexanediones, some selenium appeared in the distillate and was removed by stirring with freshly precipitated silver metal as described by Fieser and Ourisson.[25] The once-fractionated alkyl-1,2-cyclohexanedione was then distilled a second time. Hot water was used in the condenser to prevent clogging by solidification of the alkyl-1,2-cyclohexanedione. The yields and properties are given in Table I.

Alkyl-1,2-cyclohexanedione dioximes. The alkyl-1,2-cyclohexanediones were oximated by treatment with aqueous hydroxylamine as described by Hach, Banks, and Diehl.[22] In the case of the higher molecular weight alkyl-1,2-cyclohexanediones, up to 50 per cent ethanol was added to the oximation solution in order to increase the solubility of the alkyl-*vic*-diones. The alkyl-1,2-cyclohexanedione dioximes were recrystallized from ethanol-water mixtures. The yields and properties of the dioximes are listed in Table II.

DISCUSSION

Most of the reactions proceeded as expected with good yields. The selenium dioxide oxidations were the most difficult reactions to carry out and resulted in some unexpected products. The 4-alkylcyclohexanones yielded the expected products. However, 2-methylcyclohexanone gave 3-methyl-1,2-cyclohexanedione as the major product rather than 3-methyl-3-cyclohexene-1,2-dione as previously reported by Godchot and Cauquil.[15] This was determined by quantitative hydrogenation of the methylalicyclic-1,2-dione. Only two moles of hydrogen were absorbed per mole of the methylalicyclic-1,2-dione, thus indicating that the product was 3-methyl-1,2-cyclohexanedione. In addition, the carbon and hydrogen analysis of the resulting *vic*-dioxime corresponded to a saturated aliphatic ring.

Similarly the 3-ethylcyclohexanone might have been expected to yield 3-ethyl-3-cyclohexene-1,2-dione,[15] but again quantitative hydrogenation indicated a saturated aliphatic ring. A dibasic acid was isolated as a product of the periodate oxidation of the ethylalicyclic-1,2-dione which had an equivalent weight of 87, melted at 48°, and gave a *p*-phenylphenacyl derivative melting at 118°. This acid was characterized as *alpha*-ethyladipic acid.[66] Therefore, the product was 3-ethyl-1,2-cyclohexanedione. The elemental analysis of the corresponding *vic*-dioxime also indicated a saturated aliphatic ring.

It must be noted, however, that the yields of the 3-alkyl-1,2-cyclohexanediones were less than the corresponding yields of the 4-alkyl-1,2-cyclohexanediones. These reduced yields could be due to the formation of some unsaturated *vic*-dione which was not isolated. The very low yield of the 3,6-dimethyl-1,2-cyclohexanedione was due to major formation of a lower-boiling, yellow liquid which was identified as 3,6-dimethyl-1,2-benzoquinone. The formation of this quinone was not surprising since the work of Godchot and Cauquil[15] indicated that dehydrogenation might occur when 2- and 3-alkylcyclohexanones are oxidized with selenium dioxide.

PROPERTIES OF THE *vic*-DIOXIMES

Materials and apparatus. The alkyl-1,2-cyclohexanedione dioximes were recrystallized from water or water-ethanol mixtures at least three times, followed by a recrystallization from petroleum ether-benzene mixture.

All chemicals used were of reagent-grade or equivalent purity.

The absorption spectra taken with varying wavelength were all obtained with a Cary recording spectrophotometer, Model 12. The absorption measurements made at constant wavelength were obtained with a Beckman Model DU spectrophotometer. A Beckman, Model G, *p*H meter was used for all of the *p*H measurements.

Decomposition ranges. All of the alkyl-1,2-cyclohexanedione dioximes reported here are white, crystalline solids

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(66) Brown, Rose, and Simonsen, *J. Chem. Soc.*, 101 (1944).

which melt with decomposition. The decomposition ranges are given in Table II.

Solubilities. Saturated aqueous solutions of the alkyl-1,2-cyclohexanedione dioximes were prepared by shaking suspensions of excess *vic*-dioxime in 75 ml. of water for one week. One set of solubility determinations was made on solutions saturated at 25° and then shaken at 25°, while another set was made on solutions saturated at 90° and then shaken at 25°. The excess *vic*-dioxime was filtered off and an aliquot of the aqueous solution was treated with an aqueous solution containing nickel(II) ions. The weight of the bis-(alkyl-1,2-cyclohexanedione dioximato-*N,N'*) nickel(II) was determined[10] and the solubility was calculated. For the more insoluble alkyl-1,2-cyclohexanedione dioximes the bis(*vic*-dioximato-*N,N'*)nickel(II) complex was not weighed, but was determined quantitatively by a spectrophotometric method which will be described in a later report. The solubilities are listed in Table II.

Absorption spectra. The ultraviolet and visible absorption spectra of the alkyl-1,2-cyclohexanedione dioximes reported here were scanned on a Cary recording spectrophotometer. The spectra were all quite similar to that previously reported for 1,2-cyclohexanedione dioxime.[67] Only one absorption maxima was observed for each alkyl-*vic*-dioxime and this peak was, in each case, located at 232 mμ. The molar absorptivity,[68] ϵ, at 232 mμ varied from 7800 to 7900, the higher molecular weight compounds having the slightly higher value.

DISCUSSION

A comparison of the physical properties of the *vic*-dioximes offers significant information. The crystal structure of 2,3-butanedione dioxime has been determined by single crystal methods by Merritt and Lanterman.[69] The crystal was found to be composed of chains of essentially planar, centrosymmetric 2,3-butanedione dioxime molecules joined together by a network of hydrogen bonds. Such a structure is consistent with the high melting point (240°) and the low aqueous solubility (0.0034 *molar*) for such a low molecular weight, 116, compound as 2,3-butanedione dioxime.

It is interesting to note that the higher molecular weight, 156 to 254, alkyl-1,2-cyclohexanedione dioximes consistently melt at a significantly lower temperature (160 to 205°) than do straight chain aliphatic *vic*-dioximes such as 2,3-butanedione dioxime. This is not unexpected, however, since the alicyclic ring would greatly restrict the rotation about the carbon-carbon bond between the adjacent oxime groups and thus seriously interfere with the formation of hydrogen-bonded chains.

3-Methyl-1,2-cyclohexanedione dioxime melts 17° below 4-methyl-1,2-cyclohexanedione dioxime and 23° below the parent compound, 1,2-cyclohexanedione dioxime. This indicates that substitution in the 3-position is more effective than substitution in the 4-position in hindering intermolecular hydrogen bond formation. The fact that 3,6-dimethyl-1,2-cyclohexanedione dioxime melts at the same temperature as 3-methyl-1,2-cyclohexanedione dioxime while 3-ethyl-1,2-cyclohexanedione dioxime melts 15° higher, is further evidence that substitution in the positions adjacent to the oxime groups is quite effective in hindering intermolecular hydrogen bond formation.

The aqueous solubilities of the *vic*-dioximes likewise indicate that both rotation about the carbon-carbon bond between the adjacent oxime groups and substitution in the 3-position of the alicyclic ring markedly affect the constitutive properties of the crystalline state of these compounds. It has been previously reported[7] that the molar solubility of 1,2-cyclohexanedione dioxime in water is 17 times that of 2,3-butanedione dioxime. The greatly increased solubility of 1,2-cyclohexanedione dioxime over the lower molecular weight 2,3-butanedione dioxime again strongly indicates decreased intermolecular hydrogen bonding in the former case as a result of restricted rotation of the oxime groups by the alicyclic ring.

3-Methyl-1,2-cyclohexanedione dioxime is about 18% more soluble than 4-methyl-1,2-cyclohexanedione dioxime, while 3,6-dimethyl-1,2-cyclohexanedione dioxime is more than twice as soluble. Again, the effect of substitution in positions adjacent to the oxime groups is quite apparent. Increasing the size of the substituent group in the 4-position simply results in the expected decrease in solubility because of increased molecular weight.

It appears from both the melting point and the solubility data that substitution in the 4-position offers little interference to crystal formation.

The fact that the absorption spectra of all the alkyl-1,2-cyclohexanedione dioximes were almost identical indicates that in aqueous solution the substituents on the ring have very little effect on the dioxime groups.

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