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Reactions of 2-Chlorocycloalkanone Oximes. I. Their Preparations and Conversion to 2-Alkoxy-, 2-Acyloxy- and 2-Alkylthiocycloalkanone Oximes[1]

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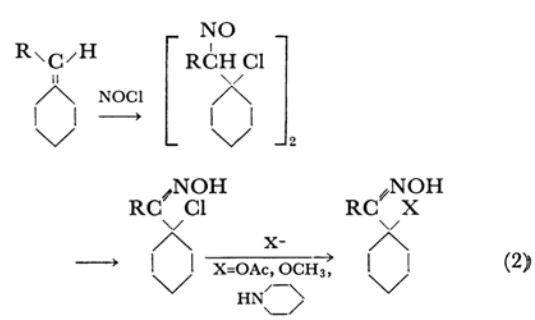
The preparation of 2-chlorocycloalkanone oximes has been investigated in detail. 2-Chlorocyclooctanone oxime is prepared in an excellent yield by the reaction of cyclooctene with nitrosyl chloride under the irradiation of light from a high-pressure mercury lamp. 2-Chlorocyclododecadienone oxime, 2-chlorocyclohexanone oxime and 3-chloronorcamphor oxime are prepared in good yields by the addition of nitrosyl chloride to *cis*, *trans*, *trans*-1, 5, 9-cyclododecatriene, cyclohexene and norbornene respectively in the presence of hydrochloric acid. Their displacement reactions with such nucleophilic reagents as sodium alkoxides, sodium ethanethiolate and sodium salts of carboxylic acids have been studied, and the syntheses of 2-alkoxy-, 2-ethylthio- and 2-acyloxycycloalkanone oximes have been successfully achieved.

The addition of nitrosyl chloride to olefins has been of considerable importance in the developement of cyclic terpene chemistry.[2,3] It has mainly played an important role in unsaturation tests of natural products by affording dimers of nitrosochlorides, which are very easily obtained in crystalline forms if the formation of bimolecular compounds is not prevented from steric hindrance (Eq. 1):

$$\rangle C{=}C\langle + NOCl \rightarrow ON\text{-}\overset{|}{C}\text{-}\overset{|}{C}\text{-}Cl \rightleftarrows (ON\text{-}C\text{-}C\text{-}Cl)_2 \qquad (1)$$

The first synthetic application of the reaction was studied by Wallach[4] and Deussen[5] on exo double bonds of cyclohexane derivatives and on a sesquiterpene, caryophyllene, as is expressed in Eqs. 2 and 3 respectively:



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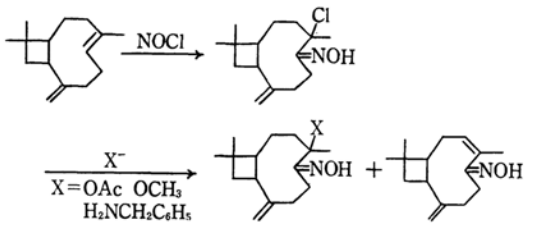
1) Presented at the 17th and 18th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1964 and Osaka, April, 1965, respectively.

2) W. A. Tilden, *J. Chem. Soc.*, **1875**, 514.

3) L. J. Beckham, W. A. Fessler and M. A. Kise, *Chem. Revs.*, **48**, 369 (1951).

4) O. Wallach, *Ann.*, **332**, 305 (1904); **360**, 26 (1908); **374**, 198 (1910); **389**, 185 (1912); **414**, 257 (1918).

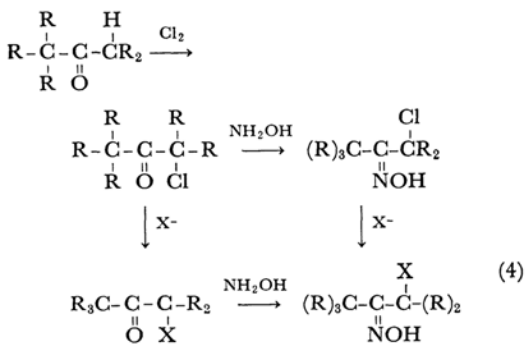
5) E. Deussen, ibid., **369**, 41 (1909).



(3)

However, these reactions were limited to trisubstituted olefins, and later investigations have shown that stable adducts nitrosochlorides can be formed only from tetra and trisubstituted olefins,[3] while disubstituted olefins have been considered to afford unstable or tarry materials.

Another way[6,7] of preparing α-chlorooximes is based on ketones, as is expressed in Eq. 4:



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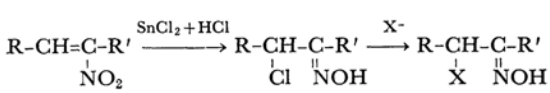
This method has been chiefly applied to steroidal ketones; it obviously requires many steps and affords by-products.

Recently, Dornow[8] reported the new method of preparing α-chlorooxime from nitroolefins expressed in Eq. 5:



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The method is limited to acyclic olefins.

In this report, we have first investigated the reactions of cyclohexene, cyclooctene, cyclododecatriene and norbornene with nitrosyl chloride, since these disubstituted olefins are now easily available as a result of the recent progress in petroleum chemistry but have not been treated with nitrosyl chloride in detail. Secondly, the successful preparation of their α-chlorooximes has enabled us to investigated their displacement reactions with nucleophilic reagents.

Results

When cyclohexene was treated with nitrosyl chloride in liquid sulfur dioxide, an isomer of bis(1-chloro-2-nitrosocyclohexane) was isolated in a 60—90% yield.[9] Another isomer of bis(1-chloro-2-nitrosocycolhexane) was obtained from the reaction in trichloroethylene.[10] These adducts were, however, found to be unsatisfactory as starting materials for displacement reactions. Therefore, the hydrochloride of 2-chlorocyclohexanone oxime, prepared from a reaction of cyclohexene and nitrosyl chloride in the presence of hydrochloric acid,[11] has been used in this research.

2-Chlorocyclooctanone oxime was obtained in an excellent yield when cyclooctene was treated with nitrosyl chloride under the irradiation of light from a high-pressure mercury lamp. The usual addition method affords 2-chlorocyclooctanone oxime in a poor yield,[12,13] and the product of the addition in the presence of hydrochloric acid is accompanied by a considerable amount of 2-chlorocyclooctanone when it is converted into the free oxime with a base.

2-Chlorocyclooctanone oxime is very stable at room temperature, while 2-chlorocyclohexanone oxime is very unstable to air and heat; the extreme instability of the latter might be the main reason why synthetic reactions for such a simple system have not yet been investigated.

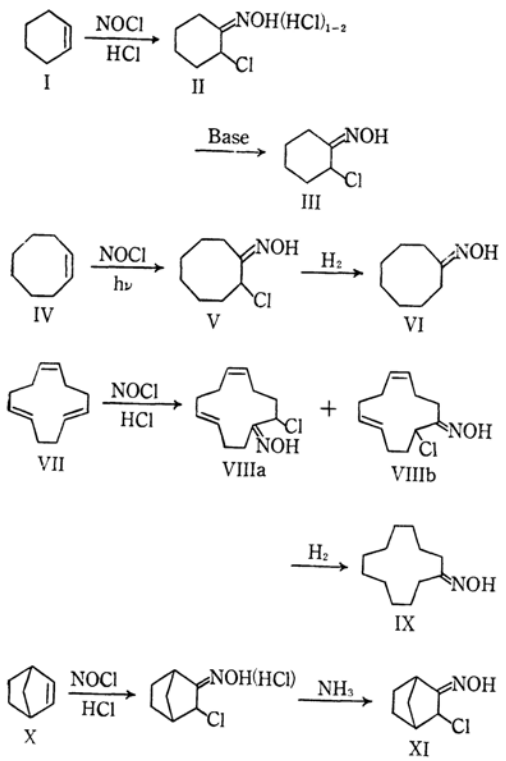
The reaction of *cis, trans, trans*-1, 5, 9-cyclododecatriene with nitrosyl chloride in the presence of hydrochloric acid afforded 2-chlorocyclododecadienone oxime in nearly quantitative yields.[14] It should be mentioned that the product is obtained in a free oxime state simply by recrystallization from such organic solvents as ligroin and ethanol. Furthermore, the double bond preferentially attacked by nitrosyl chloride was found to be one of the *trans* double bonds of *cis, trans, trans*-1, 5, 9-cyclododecatriene. This method provides the most convenient way to prepare α-chlorooxime of a 12-membered ring system, since the starting material is now easily available from the trimerization of butadiene.[15]

The addition of nitrosyl chloride to norbornene in the presence of hydrochloric acid afforded 3-chloronorcamphor oxime hydrochloride in a good yield and did not involve molecular rearrangement. Previously, Miller[16] showed that the dimeric

6) C. L. Stevens, P. Blumbergs and M. Munk, *J. Org. Chem.*, **28**, 331 (1963).
7) B. Tchoubar, *Bull. Soc. Chim. France*, **1955**, 1363.
8) A. Dornow, H. D. Jordan and A. Müller, *Chem. Ber.*, **94**, 67 (1961).
9) R. K. Allison, U. S. Pat. 2485180 (1949).
10) M. Ohno, M. Okamoto and K. Nukada, *Tetrahedron Letters*, **1965**, 4047.
11) O. von Schickh and H. Metzger, U. S. Pat. 3078306 (1963).
12) L. E. Craig, U. S. Pat. 2890248 (1959).
13) O. von Schickh and H. Metzger, German Pat. 1068708 (1959).
14) M. Ohno, M. Okamoto and N. Naruse, *Tetrahedron Letters*, **1965**, 1971.
15) G. Wilke, *Angew. Chem.*, **75**, 10 (1963).
16) J. B. Miller, *J. Org. Chem.*, **26**, 4905 (1961).

nitrosochloride of norbornene can be converted into α-chlorooxime with neither hydrochloric acid nor heat, but with urea; therefore, our method presents a simple method for the preparation of 3-chloronorcamphor oxime.

The methods of preparing 2-chlorocycloalkanone oximes are shown in the following schemes:



Displacement reactions of 2-chlorocyclooctanone and 2-chlorocyclododecadienone oximes with sodium alkoxides, sodium ethanethiolate, and sodium salts of carboxylic acids were investigated first, and then the investigation was extended to unstable 2-chlorocyclohexanone oxime.

α-Chlorooximes were treated with sodium alkoxides in the corresponding alcohol or in tetrahydrofuran at 40—60°C. Methanol, ethanol, 2-propanol, *t*-butyl alcohol and phenol were used for the displacement reactions. The best yields were generally obtained when more than two mole equivalents of sodium alkoxide were used. In each reaction, a blue color was always observed at the beginning, but it always disappeared soon, strongly suggesting the formation of nitroso compounds during the reaction. The reaction with 2-propanol and *t*-butyl alcohol afforded products only in the case of the 8-membered ring.

It has been shown that the yields of α-alkoxyoximes of the 8- and 12-membered rings are better than those of the 6-membered ring and that no appreciable amount of an unsaturated oxime was detected in these reactions, contrary to the cases of trisubstituted olefins.[4]

Treatments of α-chlorooximes with sodium ethanethiolate were carried out in tetrahydrofuran with vigorous stirring. The expected α-ethylthiooximes were obtained in good yields from the 8- and 12-membered rings, but not from the 6-membered ring. In these cases, too, a blue color was observed during the reactions.

α-Chlorooximes were treated with sodium salts of various carboxylic acids in tetrahydrofuran or acetone, affording α-acyloxyoximes in good yields.

The yields of these reactions are summarized in Table I.

Table I. Displacement reactions with RONa, EtSNa, and RCOONa

Reagent	2-Substituted-cyclohexanone oxime %	2-Substituted-cyclooctanone oxime %	2-Substituted-cyclododeca-dienone oxime %
MeONa	77	97.5	90
EtONa	55	90	88
i-PrONa	*	40—58	*
t-BuONa	*	60—80	*
PhONa	*	80	*
EtSNa	*	72	84.6
HCOONa	*	80	*
CH_3COONa	86	80	81
PhCOONa	65	72	65

* Only a tarry material was obtained; the isolation of the expected products was unsuccessful.

The mechanism of these reactions seems not to be a simple S_N2-type, but a Michael-type, addition of nucleophiles to the α, β-unsaturated nitroso compound formed during the reaction, since a freshly-prepared solution of 2-chlorocyclooctanone oxime and *n*-butyllithium in tetrahydrofuran possessed a deep blue color with maximum absorptions at 258 mμ (ε, 3300) and 645 mμ (ε, 10).

Experimental

2-Chlorocyclohexanone Oxime (III).[11]—Cyclohexene (100 g.) was placed in a 300-ml. three-necked round-bottom flask equipped with a stirrer, a gas inlet and gas outlet tubes; then at the bottom of the flask a two-way stop cock was fitted in order to remove the products. A mixed gas of nitrosyl chloride (1.3 mole equivalent) and hydrogen chloride was passed through cyclohexene, and the reaction temperature was kept at about −10°C. The oily product which was gradually formed at the bottom of the flask was removed through the stopcock. The oily product (62 g.) solidified on standing at room temperature and was confirmed to be the hydrochloride of 2-chlorocyclohexane oxime from its infrared spectrum and from its conversion into cyclohexanone oxime by catalytic reduction. Free 2-chlorocyclohexanone oxime was obtained by neutralizing the hydrochloride with aqueous ammonia, followed by extraction with ether and the removal of the solvent.

It was immediately used for displacement reactions.

2-Chlorocyclooctanone Oxime (V).—Nitrosyl chloride (13 g.) was passed through a solution of cyclooctene (10 g.) in a mixed solvent of methylene chloride (100 ml.) and methanol (15 ml.) under the irradiation of light from a high-pressure mercury lamp (200 W.) for 70 min. After the reaction, and after the solvent had been removed under reduced pressure, a colorless solid (17 g.) was obtained, along with a very small amount of an oily material. The solid material was washed with ligroin and recrystallized from methanol. It melted at 98—99°C and showed infrared absorptions at 3200 cm^{-1} for the hydroxy group and 1650 cm^{-1} for the C=N group. The NMR spectrum showed a triplet signal at τ 5.48; thus the structure proved to be 2-chlorocyclooctanone oxime.

Found: C, 54.70; H, 8.06; N, 8.07; Cl, 20.24. Calcd. for $C_8H_{14}NOCl$: C, 54.71; H, 8.05; N, 8.01; Cl, 20.21.

2-Chlorocyclododecadienone Oxime (VIIIa and VIIIb). — *cis, trans, trans*-1, 5, 9-Cyclododecatriene (200 g.) dissolved in 1 l. of trichloroethylene was placed in a 2-l. three-necked flask equipped with a stirrer and an inlet tube for nitrosyl chloride. A mixed gas of nitrosyl chloride (81 g.) and hydrogen chloride was bubbled into the solution over 3 hr, while the reaction temperature was kept below 12°C. After the addition of nitrosyl chloride, hydrogen chloride was passed through the solution for another hour. After the reaction, the solvent was removed under aspirator pressure; a pale-yellow crude product (287 g.) was thus obtained. It was crystallized from ligroin, showing a m. p. of 127—129°C.

Found: C, 63.15; H, 7.85; N, 5.85; Cl, 15.99. Calcd. for $C_{12}H_{19}NOCl$: C, 63.29; H, 7.92; N, 6.16; Cl, 15.60.

Its infrared spectrum showed absorptions at 980 cm^{-1} characteristic of a *trans* double bond and at 707 cm^{-1} characteristic of a *cis* double bond, thus showing that one of the *trans* double bonds was preferentially attacked by nitrosyl chloride. Besides the above absorptions, an absorption for the hydroxyl group was observed at 3210 $cm.^{-1}$ No skeletal change or transannular reaction was observed, since its hydrogenation with palladium charcoal afforded cyclododecanone oxime in a quantitative yield. Therefore, the product must be a mixture of 2-chloro-*cis*-5, *trans*-9-cyclododecadienone oxime (VIIIa) and 2-chloro-*trans*-5, *cis*-9-cyclododecadienone oxime (VIIIb), which were used for displacement reactions without separation.

Similar reactions using methylene chloride, chloroform, and carbon tetrachloride showed that there was no essential change in the product, which always afforded 2-chlorocyclododecadienone oxime in yields of 60—90%.

3-Chlorononorcamphor Oxime (XI).—A mixed gas of nitrosyl chloride (17.5 g.) and hydrogen chloride was introduced into a solution of norbornene (25 g.) in 120 ml. of trichloroethylene over a 2-hr. period, During the reaction, the temperature was kept at 0—5°C. The reaction mixture became green at the beginning, and then colorless precipitates were formed. After the reaction, a solid fraction (60 g.) was separated by filtration. It was treated with a 2 N ammonia solution to neutralize it and extracted with ether. The ethereal solution afforded colorless needle crystals (38 g.), m. p. 117—119°C, which were recrystallized from ethanol.

Found: C, 52.95; H, 6.21; N, 8.41; Cl, 22.36; M. W.=161.3. Calcd. for $C_7H_{10}NOCl$: C, 52.68; H, 6.32; N, 8.74; Cl, 22.22%; M. W.=159.6.

The NMR spectrum showed a signal (singlet, 1H) at 0.38τ for the hydroxyl proton and a signal (doublet J=3 c. p. s., 1H) at 5.60τ for the endo hydrogen on C-3.

2-Methoxycyclooctanone Oxime.—Sodium metal (3 g.) was dissolved in 100 ml. of methanol. 2-Chlorocyclooctanone oxime (10 g.) dissolved in 50 ml. of methanol was then added to the solution over a 1 hr. period. The reaction temperature was kept at 50—60°C. A blue color was observed immediately after chlorooxime was added, but it soon disappeared. After another hour, the solvent was removed under reduced pressure. When the residue was treated with water and then ether, the ethereal solution afforded a pale-yellow solid (9.5 g.). It was recrystallized from *n*-hexane and melted at 65—67°C. The infrared spectrum showed absorptions at 3,300 cm^{-1}(–OH), 1640 cm^{-1}(–C–N–), and 1085 cm^{-1}(–C–O–C).

Found: C, 60.14; H, 10.06; N, 7.60. Calcd. for $C_9H_{17}NO_2$. $1/2H_2O$: C, 59.97; H, 10.07; N, 7.77%.

2-Methoxycyclododecadienone Oxime. — 2-Chlorocyclododecadienone oxime (10 g.) dissolved in 100 ml. of methanol was treated with a sodium methoxide solution, prepared from 2 g. of sodium and 100 ml. of methanol, at 40—50°C for 3 hr. After the reaction, the methanol was removed under reduced pressure, and the residue was treated with water and then ether. The ethereal solution afforded a colorless, oily product. The infrared spectrum showed absorptions at 3300 cm^{-1}(–OH), 1650 cm^{-1}(>C=N–), and 1080—1090 cm^{-1}(–C–O–C). The 2, 4-dinitrophenylhydrazone showed a m. p. of 191—193°C.

Found: C, 57.97; H, 7.20; N, 14.23. Calcd. for $C_{19}H_{28}O_5N_4$: C, 58.14; H, 7.19; N, 14.28%.

2-Methoxycyclohexanone Oxime. — Crude 2-chlorocyclohexanone oxime (10 g.), freshly prepared from its hydrochloride by treatment with ammonium hydroxide, was dissolved in a methanol solution (100 ml.) of sodium methoxide prepared from 4 g. of sodium. It was then heated to 40—50°C for 2 hr. After usual treatments, a brown oily material was obtained. The chromatography on alumina using ether as an eluent afforded a pale-yellow oil (6.2 g.). An attempt to distill the oil was unsuccessful, since it decomposed readily at 80°C. Therefore, it was hydrolyzed to 2-methoxycyclohexanone, b. p. 70—72°C/12 mmHg (reported b. p. 72—73°C/14 mmHg[17]), according to the procedure of DePuy and Ponder.[18] The phenylhydrozone showed a m. p. of 92—94°C (reported m. p. 94—96°C[17]).

Found: C, 71.42; H, 8.21; N, 12.52. Calcd. for $C_{13}H_{18}ON_2$: C, 71.51; H, 8.32; N, 12.84%.

2-Ethoxycyclooctanone Oxime.—Sodium (2.6 g.) was dissolved in ethanol (50 ml.), and then 2-chlorocyclooctanone oxime (10 g.) dissolved in ethanol (50 ml.) was added to the solution. After one hour at 40—50°C, the reaction mixture was treated as usual. The

17) M. Bergmann and M. Gierth, *Ann.*, **448**, 64 (1926).
18) C. H. DePuy and B. W. Ponder, *J. Am. Chem. Soc.*, **81**, 4629 (1959).

ethereal extract was washed with water, dried, and evaporated to dryness to give 9.5 g. of a yellow solid. It was recrystallized from aqueous ethanol, giving an analytical sample, m. p. 84.5—85.5°C.

Found: C, 65.11; H, 10.34; N, 7.78; O, 17.14. Calcd. for $C_{10}H_{19}O_2N$: C, 64.83; H, 10.34; N, 7.56; O, 17.27%.

2-Ethoxycyclododecadienone Oxime.—2-Chlorocyclododecadienone oxime (20 g.) was treated with a sodium ethoxide solution prepared from sodium (4.5 g.) and ethanol (100 ml.). A pale yellow oily product (18.5 g.) was obtained after the usual work-up, described above. The 2, 4-dinitrophenylhydrazone showed a m. p. of 143—145°C.

Found: C, 59.22; H, 7.60; N, 13.80. Calcd. for $C_{20}H_{30}O_5N_4$: C, 59.09; H, 7.44; N, 13.79%.

2-Ethoxycyclohexanone Oxime. — According to procedures similar to those described above, 2-ethoxycyclohexanone oxime (8.2 g.), an oily product, was obtained from the reaction of 2-chlorocyclohexanone oxime (10 g.) with sodium ethoxide (14.1 g.). The infrared spectrum showed abosrptions at 3300 cm^{-1} (–OH), 1660 cm^{-1}(–C=N–), and 1100 cm^{-1}(–C–O–C). It was distilled under reduced pressure to give an oily material, b. p. 87—88°C/1.3 mmHg.

Found: C, 61.02; H, 9.41; N, 9.00. Calcd. for $C_8H_{15}O_2N$: C, 61.12; H, 9.62; N, 8.91%.

2-*t*-Butoxycyclooctanone Oxime.—According to procedures similar to those described above, 2-*t*-butoxycyclooctanone oxime (9.8 g.), an oily product, was obtained from the reaction of 2-chlorocyclooctanone oxime (20 g.) with sodium *t*-butoxide (7.1 g.). IR: 3300, 1645, 1100 cm^{-1} (KBr). NMR: 6.14 τ (1H, triplet). The dinitrophenylosazone showed a m. p. of 205—207°C.

Found: C, 48.24; H, 4.22; N, 22.01. Calcd. for $C_{20}H_{20}N_8O_8$: C, 48.64; H, 4.02; N, 22.39%.

2-Isopropoxycyclooctanone Oxime.—According to procedures similar to those described above, 2-isopropoxycyclooctanone oxime (6.7 g.), an oily product, was obtained from the reaction of 2-chlorocyclooctanone oxime (10 g.) with sodium isopropoxide (5.2 g.). IR: 3300, 1650, 1110 cm^{-1} (KBr). NMR: 6.18 (1H, triplet), 6.32 (1H, multiplet), 8.66 τ (6H, doublet). It formed the same osazone as has been described above.

2-Phenoxycyclooctanone Oxime.—Sodium phenoxide was prepared from sodium (4 g.) and phenol (25 g.) in tetrahydrofuran (100 ml.). To the solution was added a solution of 2-chlorocyclooctanone oxime (10 g.) in tetrahydrofuran (50 ml.) over a 30 min. period. The reaction mixture was kept at 50°C while being stirred for 2 hr. The solvent was then removed under reduced pressure. The ethereal extract was washed with water, dried, and evaporated to dryness to give 21.2 g. of a pale-yellow solid. It was recrystallized from ligroin, giving an analytical sample with a m. p. of 76—78°C.

Found: C, 72.31; H, 8.26; N, 5.88. Calcd. for $C_{14}H_{19}NO_2$: C, 72.07; H, 8.21; N, 6.00%. IR: 3250(–OH), 1650(–C=N–), 1600(–C_6H_5), 1030 (–C–O–C), 750(–O–C_6H_5)cm^{-1} (KBr).

2-Ethylthiocyclooctanone Oxime.—Sodium ethanethiolate was prepared in tetrahydrofuran from ethanethiol (30 ml.) and sodium (3.5 g.). 2-Chlorocyclooctanone oxime (20 g.) dissolved in tetrahydrofuran (50 ml.) was added to the solution over a 1 hr. period. A blue color was observed immediately after the addition, but it soon disappeared. The reaction was continued for 3 hr. with stirring. Sodium chloride was removed by filtration, and the solvent of the filtrate was removed under reduced pressure. The ethereal extract of the residue was washed with water, dried, and evaporated to dryness to give 16.5 g. of pale yellow needle crystals. They were recrystallized from ligroin, giving an analytical sample with a m. p. of 95—96.5°C.

Found: C, 59.75; H, 9.56; N, 6.67; S, 15.90. Calcd. for $C_{10}H_{19}NOS$: C, 59.66; H, 9.51; N, 6.96; S, 15.93%.

IR: 3200(–OH), 1640(–C=N–) cm^{-1} (KBr).

2-Ethylthiocyclododecadienone Oxime.—According to procedures similar to those described above, an oily product (31 g.) was obtained from the reaction of 2-chlorocyclododecadienone oxime (35 g.) and sodium ethanethoilate (20 g.) in tetrahydrofuran. This product was chromatographed on silica gel and eluted with chloroform. A homogeneous oily product (27 g.) was thus obtained, showing the presence of an ethyl group in the NMR spectrum; this was consistent with 2-ethylthiocyclododecadienone oxime.

Found: C, 66.69; H, 9.44; N, 5.93. Calcd. for $C_{14}H_{23}NOS$: C, 66.37; H, 9.15; N, 5.53%.

The Reaction of 2-Chlorocyclohexanone Oxime with Sodium Ethanethiolate. — 2-Chlorocyclohexanone oxime (6 g.) was treated with sodium ethanethiolate (a 2.13 mole equivalent) at 40—50°C for 2 hr. The reaction product was chromatographed on silica gel and eluted with chloroform, but an attempt to isolate a homogeneous fraction was unsuccessful.

2-Formyloxycyclooctanone Oxime.—Acetone (100 ml.) and sodium formate (6.8 g.) were placed in a 300 ml. three-necked round-bottom flask equipped with a stirrer, a condenser, and a separatory funnel. 2-Chlorocyclooctanone oxime (8.8 g.) dissolved in acetone (50 ml.) was added to the sodium formate solution over a 15 min. period. The reaction mixture was refluxed for 3 hr. and the precipitates were removed by filtration. The filtrate was evaporated under reduced pressure; the residue afforded a solid product (8.2 g.) when triturated with cyclohexane. It was recrystallized from cyclohexane, giving an analytical sample with a m. p. of 82—83°C.

Found: C, 58.48; H, 8.25; N, 7.54. Calcd. for $C_9H_{15}O_3N$: C, 58.36; H, 8.16; N, 7.56%.

2-Acetoxycyclooctanone Oxime.—2-Chlorocyclooctanone oxime (8.8 g.) dissolved in tetrahydrofuran (50 ml.) was added to a solution of sodium acetate (8.2 g.) in tetrahydrofuran, over a 15 min. period, using the reaction vessel which has been described in the case of the formyloxylation. It was refluxed for 2 hr. A blue color was observed during the reaction and disappeared in 30 min. After the reaction, sodium chloride was removed, and the filtrate was evaporated under reduced pressure. The residue was triturated with a small amount of cyclohexane, affording 8.0 g. of a solid. It was recrystallized from cyclohexane, giving an analytical sample with a m. p. of 92—93°C. The infrared spectrum showed the absorptions at 1740 cm^{-1} and 1210—35 cm^{-1} characteristic of the acetoxyl group.

Found: C, 60.14; H, 8.54; N, 6.95. Calcd. for $C_{10}H_{17}O_3N$: C, 60.28; H, 8.60; N, 7.03%.

2-Benzoyloxycyclooctanone Oxime. — 2-Chlorocyclooctanone oxime (8.8 g.) dissolved in acetone (70 ml.) was added to a solution of sodium benzoate (14.5 g.) in acetone (100 ml.) over a 15 min. period and heated to 50°C for 2 hr. with stirring, using the reaction vessel described in the case of the formyloxylation. After a similar treatment, a solid (9.5 g.) was obtained. It was recrystallized from cyclohexane, giving an analytical sample with a m. p. of 93—94°C. The infrared spectrum showed the absorptions at 1725 cm^{-1} and 1210 cm^{-1} characteristic of the benzoyloxy group.

Found: C, 68.97; H, 7.24; N, 5.35. Calcd. for $C_{15}H_{19}O_3N$: C, 68.94; H, 7.33; N, 5.36%.

2-Acetoxycyclododecadienone Oxime.—2-Chlorocyclododecadienone oxime (10 g.) dissolved in acetic acid (50 ml.) was added to a solution of sodium acetate (25 g.) in acetic acid (100 ml.) over a 15 min. period and then heated to 70°C for 2 hr. After the reaction, water (300 ml.) was added to the reaction mixture, and a solid (9 g.) was deposited. This solid was recrystallized from cyclohexane and shown to have a m. p. of 117—119°C. The infrared spectrum showed the absorptions at 1740 and 1230 cm^{-1} characteristic of the acetoxyl group.

Found: C, 67.07; H, 8.49; N, 5.73. Calcd. for $C_{14}H_{21}O_3N$: C, 66.90; H, 8.42; N, 5.57%.

A part of the 2-acetoxycyclododecadienone oxime (2.5 g.) was hydrogenated with 10% palladium charcoal in acetic acid, absorbing two mole equivalents of hydrogen and affording 2.3 g. of a colorless product. This product, when recrystallized from cyclohexane, showed a m. p. of 111—112°C.

The infrared spectrum showed no absorption of a double bond; thus, the structure of the hydrogenated product was consistent with that of 2-acetoxycyclododecanone oxime.

Found: C, 65.77; H, 9.77; N, 5.44. Calcd. for $C_{14}H_{25}O_3N$: C, 65.85; H, 9.87; N, 5.49%.

2-Benzoyloxylcyclododecadienone Oxime.—2-Chlorocyclododecadienone oxime (10 g.) dissolved in acetone (100 ml.) was stirred into a solution of sodium benzoate (23 g.) in acetone (100 ml.) over a 15 min. period and then refluxed for 3 hr.

The sodium chloride formed was removed by filtration immediately after the reaction, and the filtrate was evaporated to dryness to give a solid material (9.1 g.).

When this solid material was recrystallized from ethanol, it showed a m. p. of 163—164°C. The infrared spectrum showed the absorptions at 1725 and 1210 cm^{-1} of the benzoyloxy group, besides those at 980 cm^{-1} and 707 cm^{-1} for *trans* and *cis* double bonds respectively.

Found: C, 72.69; H, 7.40; N, 4.44. Calcd. for $C_{19}H_{23}O_3N$: C, 72.82; H, 7.40; N, 4.47%.

The unsaturated product (3.2 g.) was further hydrogenated in methanol with 10% palladium charcoal. Two mole equivalents of hydrogen were absorbed, and a colorless material was quantitatively obtained, with a m. p. of 125—126°C after recrystallization from ethanol.

The infrared spectrum showed no double-bond absorption.

Found: C, 71.81; H, 8.51; N, 4.34. Calcd. for $C_{19}H_{27}O_3N$: C, 71.89; H, 8.57; N, 4.41%.

2-Acetoxycyclohexanone Oxime.—2-Chlorocyclohexanone oxime hydrochloride (9.5 g.) suspended in acetone (100 ml.) was stirred into a solution of sodium acetate (24.6 g.) in acetone (100 ml.) and heated at 50°C for 2 hr. A colorless solid (7.2 g.) was obtained after treatment similar to that described above. It was recrystallized from cyclohexane, giving an analytical sample with a m. p. of 103—104°C. IR: 3200(-OH), 1725(-OCCH_3), 1660(-C=N-), 1230—1260(-OCCH_3), cm^{-1} (KBr).

Found: C, 55.99; H, 7.45; N, 8.06. Calcd. for $C_8H_{13}O_2N$: C, 56.12; H, 7.65; N, 8.15%.

2-Benzoyloxycyclohexanone Oxime.—2-Chlorocyclohexanone oxime hydrochloride (19 g.) dissolved in acetone (100 ml.) was added to a suspension of sodium benzoate (57.6 g.) and sodium carbonate (20 g.) in acetone (200 ml.) over 30 min. and then heated at 50°C for 2 hr. while being stirred. After a usual work-up, a solid (16 g.) was obtained. It showed a m. p. of 118—119°C after recrystallization from cyclohexane.

Found: C, 67.10; H, 6.50; N, 5.96. Calcd. for $C_{13}H_{15}O_3N$: C, 66.93; H, 6.48; N, 6.01%. IR: 3450 (-OH), 1705 (-OCC_6H_5), 1660(-C=N-), 1280 (-OCC_6H_5), 720(-C_6H_6) cm^{-1} (KBr).