88, 36871-45-1; 89, 36871-46-2; 90, 36871-47-3; 2-(3-hexenyl)-DHO, 36872-13-6; 2-(3-hexenyl)-THO, 3687-14-7; 2-(5-bromopentyl)-4,4,6-trimethyl-5,6-dihydro-1,3-oxazine, 36871-48-4; 2-(5-chloropentyl)-4,4,6-trimethyl-5,6-dihydro-1,3-oxazine, 36871-49-5; 2-(4-cyano-1-phenylbutyl)-4,4,6-trimethyl-5,6-dihydro-1,3-oxazine, 36871-50-8.

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Reactions of α,β-Dibromo Oximes and Related Compounds with Nitrosyl Chloride[1]

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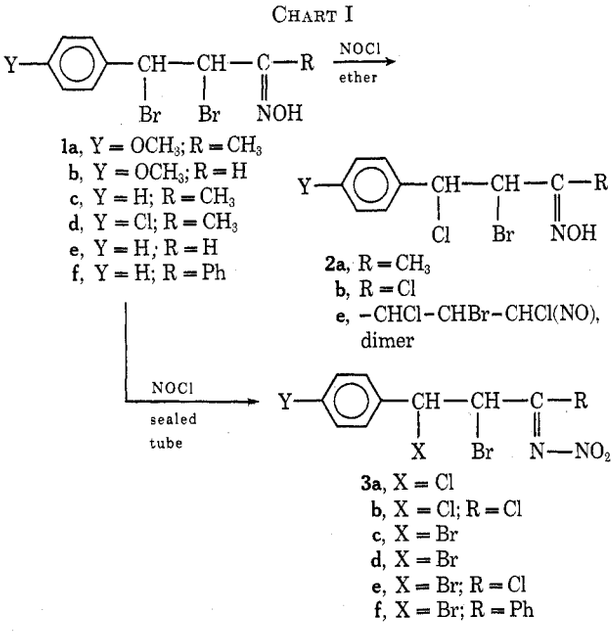
The reaction of nitrosyl chloride with α,β-dibromo oximes to give chloronitrimines consists of separate reactions even though the two reactions may occur in the same molecule. Replacement of bromine by chlorine is an SN1 reaction on the more activated secondary or on a tertiary bromine. Oxidation of the oximino function to a nitrimine occurs later in time and under more strenuous conditions in some cases, for example, in 1,2-dibromo-1-*p*-methoxyphenyl-3-butanone oxime. In other examples, the oxidation occurs without halogen displacement. In carvone oxime derivatives the replacement and oxidation occur in separated parts of the molecule.

Nitrosyl chloride[2] is known to react with aldoximes to give chloronitroso compounds, RCHClNO, or hydroxamic chlorides, ArCCl=NOH, or with ketoximes to give *gem*-chloronitroso compounds.[3] In an extension of the reaction to a series of α,β-dibromo ketoximes it was found that two reactions occurred: replacement of the α-bromine atom by chlorine and oxidation of the ketoxime to a nitrimine.[4] The reactions are not coupled; the present work shows that the replacement reaction is of SN1 character and that the oxidation is an independent reaction.

For example, 1,2-dibromo-1-*p*-methoxyphenyl-3-butanone oxime (**1a**) reacts with a slight excess of nitrosyl chloride in ether at 25° to replace the β-bromine with chlorine in 90% yield, without oxidizing the oxime, to give **2a** (Chart I). Longer treatment of **2a** with excess nitrosyl chloride or a sealed tube reaction gave the oxidized product **3a** in 46% yield. Direct treatment of **1a** with nitrosyl chloride in a sealed tube gave **3a** only. Apparently the *p*-methoxy group activates the benzylic position so that an SN1 type replacement occurs (see below).

The substituted dihydrocinnamaldoxime **1b** behaved similarly except that normal oxidation of the aldehydic hydrogen gave the hydroxamic chloride **2b**, which in turn was oxidized to the nitrimino chloride **3b**. In cases **1c–f** where the benzylic bromine was not activated by substitution on the aromatic ring, the oxidation reaction occurred without accompanying substitution with one exception. In the reaction of **1e** with nitrosyl chloride in ether, the 83% yield of α,β-dibromodihydrocinnamoyl hydroxamic chloride, a normal oxidation of the Rheinboldt type, was accompanied by a 12% yield of **2e**. However, in the sealed tube reaction a 94% yield of **3e** was obtained. Evidently under the more strenuous conditions of the sealed tube, oxidation of the aldoxime to nitrimino chloride was faster than substitution and the oxidation product was too unreactive for subsequent substitution. In ether the substitution and aldehydic oxidation reactions compete without the accompanying oxime oxidation.

CHART I



In the reaction of **1f**, the 70% yield of **3f** was accompanied by a 26% yield of 1-chloro-1-nitro-1,3-diphenylpropene (**5f**), suggesting that **4f** is an intermediate which is oxidized to **4g**. It was found recently[5] that aliphatic chloronitroso compounds are oxidized to chloronitro compounds by nitrosyl chloride, whereas after isomerization to the isomeric oximes, the oxidation produces only nitrimines, the main product in this case also. Loss of bromine to give the final product, **5f**, was not expected; none of the compounds **3c–e** behaved in that way even though these anticipated unsaturated compounds would be stabilized by more extensive conjugation than **5f**.

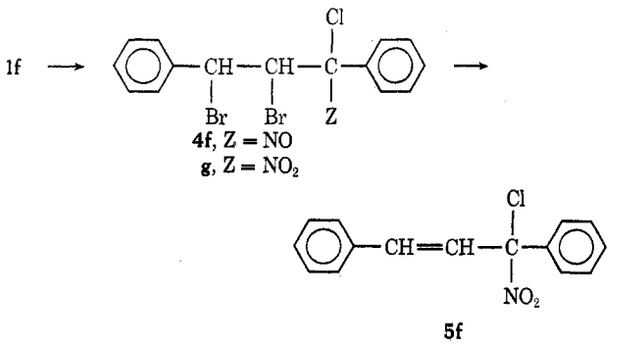
(1) Presented in part at the 163rd National Meeting of the American Chemical Society, Boston, Mass., April 14, 1972.

(2) P. P. Kadzyauskas and N. S. Zefirov, *Russ. Chem. Rev.*, **37**, 543 (1968); L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis," Wiley, New York, N. Y., 1967, pp 748–755; L. J. Beckham, W. A. Fessler, and M. A. Kise, *Chem. Rev.*, **48**, 319 (1951).

(3) H. Rheinboldt, M. Dewald, F. Jansen, and O. Schmitz-Dumont, *Justus Liebigs Ann. Chem.*, **451**, 161 (1927); H. Rheinboldt and M. Dewald, *ibid.*, **455**, 300 (1927).

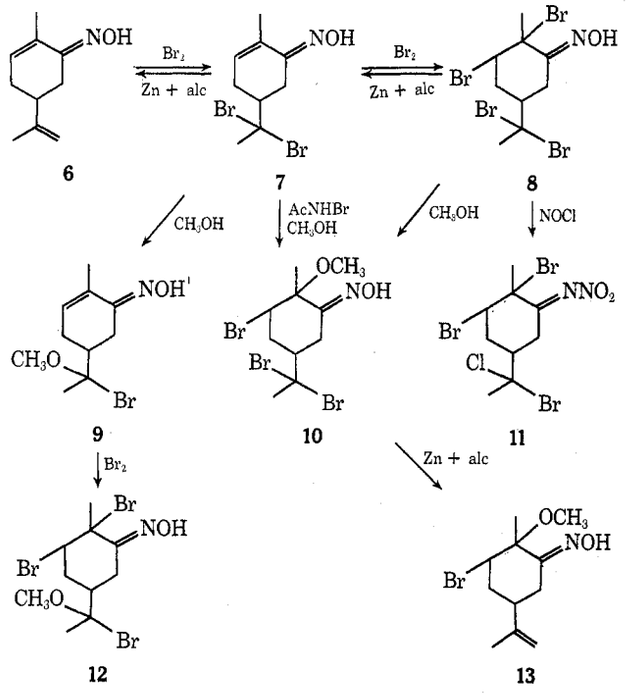
(4) C.-Y. Shiue, K. P. Park, and L. B. Clapp, *J. Org. Chem.*, **35**, 2063 (1970).

(5) C.-Y. Shiue and L. B. Clapp, *ibid.*, **36**, 1169 (1971).



Carvone oxime (6, Chart II) contains a system in which the isolated double bond $\Delta^{8,9}$ is more reactive

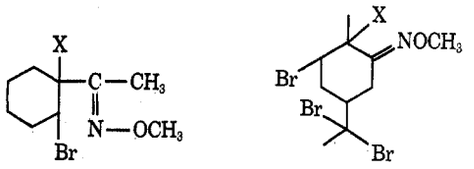
CHART II



than the conjugated double bond.[6] Addition of bromine first gives the dibromo oxime **7** and then the tetrabromo oxime **8**. The last bromines added are the first removed by zinc dust in alcohol or sodium iodide in acetone to regenerate **7**. Methanol reacts with compound **8** to give the expected 1,4-elimination–addition[7,8] product **10**, whose structure was determined by removal of 1 mol of bromine to give **13**. However, nitrosyl chloride acting on the tetrabromo compound **8** replaced the bromine at C-8 rather than at C-1 to give **11**. The tertiary bromine at C-8 is also reactive to methanol, since **7** was converted to **9** but bromine addition to **9** gave the tribromo compound **12**, an isomer of **10**. This corroborated the structure of **10**.

Independence of the replacement reaction was further demonstrated by carrying out reactions of *O*-methyl oximes where the oxidation is impossible. In compounds **14** and **16**, the tertiary bromine at C-1 was replaced by chlorine in 81 and 92% yields, respectively, to give **15** and **17** (Chart III).

CHART III



14, X = Br
15, X = Cl
16, X = Br
17, X = Cl

Since the displacement reaction appeared to be of the SN1 type, the reaction of nitrosyl chloride with various reactive alkyl bromides was carried out, with the results shown in Table I. The results indicate better yields in polar solvents, but the yields may be more a function of the change in polarity induced by the strongly polar nitrosyl chloride itself, which in turn is a function of the solubility of nitrosyl chloride in the particular solvent. Phenacyl bromide, a compound known to be very reactive toward SN2 reagents, did not react with nitrosyl chloride in any solvent shown in Table I, and *p*-nitrobenzyl bromide, containing a negatively substituted benzyl group, also did not react at all. The table shows, however, that normal SN1 substrates gave good yields of alkyl chlorides.

TABLE I
PERCENTAGE OF ALKYL CHLORIDE BY NOCl DISPLACEMENT IN VARIOUS SOLVENTS

Substrate	CCl_4	SO_2[a]	$PhNO_2$	CH_3NO_2	Liquid NOCl
t-C_4H_9Br	15	100	100	100	100
$PhCH_2Br$	0	40	100	35	25
$PhCHBrCH_3$	61	100	50[b]	40[c]	75

[a] In liquid sulfur dioxide at −6°. Others at 25°, including nitrosyl chloride in a sealed tube. [b] Accompanied by 50% oxidation to acetophenone. [c] Accompanied by 60% oxidation to acetophenone.

To pinpoint the reaction still further as an SN1 type, optically active α-bromoethylbenzene was treated with nitrosyl chloride in carbon tetrachloride and samples were removed at intervals. From this experiment it was found that the rate of replacement of bromine by chlorine was equal to the rate of racemization of the substrate. This result is considered to be diagnostic for an SN1 reaction. After 2 hr the replacement had reached 100% and the optical rotation was zero. These results are given in Table II.

TABLE II
ROTATION *vs.* CHLORIDE REPLACEMENT IN OPTICALLY ACTIVE α-BROMOETHYLBENZENE

Time, hr	Rotation $\alpha^{27}D$	Optical purity, %	Per cent Cl replacement—Calcd from rotation	Per cent Cl replacement—Calcd from nmr
0	−139.3	82	0	0
1	−72.2	42.4	51.5	50
2	−11.3	6.5	92	95
0	0.0	0	100	100

Although we have not found an example of direct nucleophilic displacement of bromine by chlorine, hints that it should be possible do appear in the literature.

(6) J. L. Simonsen and L. N. Owen, "The Terpenes," 2nd ed, Cambridge University Press, New York, N. Y., 1947, pp 394–408.
(7) A. Dornow and H. D. Jordan, *Chem. Ber.*, **94**, 67, 76 (1961); W. Pritzkow, H. Schaefer, P. Pabst, A. Ebenroth, and J. Beger, *J. Prakt. Chem.*, [4], **29**, 123 (1965); G. Collin, W. Pritzkow, H. Huebner, W. Rolle, and M. Wahren, *Tetrahedron Lett.*, 3493 (1966).
(8) W. Pritzkow, *Z. Chem.*, **10**, 330 (1970), a review.

Winstein and others[9] suggested that the order of nucleophilicity in SN2 reactions of halides in acetone is actually $Cl^- > Br^- > I^-$ when the halides are dissociated. Weaver and Hutchison[10] verified the correctness of this order in a displacement reaction run in dimethylformamide.

An SN1 mechanism has been invoked by Carlin and Larson[11] to explain a halogen interchange in a Fischer indole synthesis from acetophenone 2,6-dibromophenylhydrazone where one bromine was cinè-substituted by chlorine at C-5 of the indole when zinc chloride was the inducing agent. The authors picture one aromatic bromine changing to an allylic bromine during an intermediate stage in the reaction, which is followed by an allylic rearrangement. The corresponding 2,6-dichlorophenylhydrazone rearranged in the presence of zinc bromide to yield an indole cinè-substituted by bromine at C-5. In the present work, the reactivities of the halides might well be comparable.

Of course the replacement of bromine by chlorine is not the direction of reaction that would normally be sought, since bromine is more expensive than chlorine. Out of curiosity, in addition to the results in Table I, we found that *tert*-butyl bromide is converted to *tert*-butyl chloride at room temperature in 24 hr by other chlorinating agents: iodine monochloride to the extent of 100% in nitromethane, 60% in nitrobenzene, 0% in carbon tetrachloride; by thionyl chloride 30% in nitromethane; and by phosphorus pentachloride 60% in nitromethane. Benzyl bromide is converted to benzyl chloride in 25% yield by phosphorus pentachloride in refluxing nitromethane and by thionyl chloride to the extent of 14% in the same solvent.

The replacement reaction may well find use where it is desirable to have two halogens present (chlorine and bromine) of markedly different reactivity toward a given reagent.

Experimental Section

Properties and identifying spectral data are given for new compounds in Table III. The ir spectra were taken with KBr pellets. The nmr spectra were taken in deuteriochloroform or deuterioacetone with TMS as an internal standard. Satisfactory analyses were obtained on all compounds except **1b**, **1c**, **3b**, **7**, and 9. Intermediates **4f** and **4g** were not isolated. Compounds **1f**,[12] 6,[13] and **8**[14] had been previously reported.

The α,β-dibromo oximes (1) were prepared by adding bromine to the unsaturated oximes.[4] Oxime synthesis from the dibromo ketones was not practical, since the dibromo oximes lost hydrogen bromide spontaneously. The β-chloro oximes (2) were prepared by treating compounds 1 with nitrosyl chloride in ether, a procedure used to make α-chloronitrimines in previous work. The nitrosyl chloride (97% minimum purity, J. T. Baker) was purified by passing the gas through a series of three tubes. The tubes were connected to each other and the cylinder of nitrosyl chloride by Tygon tubing. The tubes contained, in order, sodium nitrite, moist potassium chloride (2.4% water), and calcium chloride to remove hydrogen chloride, nitrogen dioxide, and water, respectively.[15]

α,β-Dibromodihydrocinnamoyl Nitriminochloride (3e).—More strenuous conditions were needed to prepare the series of compounds **3** than were needed for **2a**, **b**, and **e**.

TABLE III

Compd	Yield, %	Mp, °C	Ir, cm^{-1} C=N[a]	Nmr, δ
1a	45	137–138	1610	7.20 (q, 4), 5.62 (s, 1), 5.45 (s, 1), 3.88 (s, 3), 2.22 (s, 3)
1b	94	71	1610	7.25 (q, 4), 5.25 (m, 2), 3.86 (s, 3)
1c	48	161–162	1625	7.43 (s, 5), 5.22 (s, 2), 2.12 (s, 3)
1d	55	160	1640	7.38 (s, 4), 5.18 (d, 2), 2.12 (s, 3)
1e	40	145	1625	7.24 (s, 5), 7.10 (s, 1), 5.10 (m, 2)
1f	37	165[b]	1630	7.30 (m, 10), 5.30 (s, 2)
2a	90	158	1610	7.30 (q, 4), 5.64 (s, 1), 5.38 (s, 1), 3.90 (s, 3), 2.20 (s, 3)
2b	98	155–157	1610	7.30 (q, 4), 5.25 (d, 2), 3.88 (s, 3)
2e	12	127–129	*c*	
3a	46	131–132	1620[d]	7.40 (q, 4), 5.65 (q, 2), 3.92 (s, 3), 2.52 (s, 3)
3b	86	Oil	1610	7.35 (q, 4), 5.27 (d, 2), 3.91 (s, 3)
3c	75	151	1635	7.43 (s, 5), 5.28 (d, 2), 2.33 (s, 3)
3d	54	135–136	1640	7.40 (s, 4), 5.20 (d, 2), 2.32 (s, 3)
3e	94	137–138	1615	7.25 (s, 5), 5.15 (s, 2)
3f	70	91–92	1630	7.40 (m, 10), 5.34 (d, 2)
5f	26	70–72	*e*	7.25 (m, 12)
6	63	66–67[f]	1640	6.0 (br, 1), 4.8 (br, 2), 1.87 (s, 3), 1.77 (s, 3)
7	71	104–106 dec	1650	6.13 (br, 1), 3.91 (s, 2), 2.18 (s, 3), 1.91 (s, 3)
8	30	127.5–129[g]	1650	4.7 (br, 1), 3.9 (s, 2), 2.17 (s, 3), 1.97 (s, 3)
9	60	113–114	1650	6.03 (br, 1), 3.91 (s, 2), 3.20 (s, 3), 1.93 (s, 3), 1.51 (s, 3)
10	50	135	1645	4.37 (br, 1), 3.95 (br, 2), 3.18 (s, 3), 1.93 (s, 3), 1.51 (s, 3)
11	20	89.0–90.5	1640[h]	4.58 (br, 1), 3.85 (s, 2), 2.00 (s, 3), 1.90 (s, 3)
12	64	119–120	1645	4.31 (t, 1), 3.89 (d, 2), 3.19 (s, 3), 1.75 (s, 3), 1.50 (s, 3)
13	87	85–86	1650	4.80 (d, 2), 4.31 (t, 1), 3.19 (s, 3), 1.75 (s, 3), 1.50 (s, 3)
14	35	36–38	1620	4.74 (br, 1), 3.87 (s, 3), 1.97 (s, 3)
15	81	31–32	1620	4.60 (br, 1), 3.89 (s, 3), 1.96 (s, 3)
16	19	109–111	1620	4.60 (m, 1), 3.83 (s, 3), 3.80 (br, 2), 2.08 (s, 3), 1.97 (s, 3)
17	92	128–129	1620	4.42 (br, 1), 3.82 (s, 3), 3.80 (br, 2), 1.90 (s, 6)

[a] All C=N absorptions medium. [b] K. von Auwers and M. Seyfried, *Justus Liebigs Ann. Chem.*, **484**, 178 (1930), mp 156°. [c] N–O, 1570, 1440 cm^{-1}, s: 83% of 2,3-dibromo-3-phenylpropanoyl chloride, mp 174°, obtained in the same reaction. [d] NO_2, 1570–1600 cm^{-1} in **3a–f**. [e] NO_2, 1540, 1340 cm^{-1}, s. [f] R. H. Reitsema, *J. Org. Chem.*, **23**, 2038 (1958), mp 66–69°. [g] Reference 3, mp 126–127°. [h] NO_2, 1590, 1320 cm^{-1}, s.

α,β-Dibromodihydrocinnamaldehyde oxime (**1e**) (0.4 g, 1.3 mmol) was sealed in glass in a Dry Ice bath with excess liquid nitrosyl chloride. The mixture was allowed to stand for 24 hr at

(9) S. Winstein, L. G. Savedoff, S. Smith, I. D. R. Stevens, and J. S. Gall, *Tetrahedron Lett.*, No. 9, 24 (1960).
(10) W. M. Weaver and J. D. Hutchison, *J. Amer. Chem. Soc.*, **86**, 261 (1964).
(11) R. B. Carlin and G. W. Larson, *ibid.*, **79**, 934 (1957).
(12) A. H. Blatt, *ibid.*, **53**, 1133 (1931).
(13) H. Goldschmidt, *Chem. Ber.*, **17**, 1577 (1884).
(14) E. Deussen, *J. Prakt. Chem.*, **90**, 318 (1914).
(15) P. L. Walker, Ph.D. Thesis, University of Alabama, 1970.

room temperature. Upon opening the tube and allowing nitrosyl chloride to boil away, a yellow oil was isolated which crystallized on standing to give 0.35 g (94%) of α,β-dibromodihydrocinnamoyl nitriminochloride. Recrystallization from carbon tetrachloride–chloroform gave the analytical sample, mp 125–127°.

Compounds **3a–d** were prepared in like manner.

1-Chloro-1-nitro-1,3-diphenylpropene (5f).—Excess nitrosyl chloride in 25 ml of ether acting on 0.50 g (1.4 mmol) of benzalacetophenone oxime dibromide (**1f**) gave a mixture of two oily products which were separated on a silica gel column. Elution with 60:40 hexane–carbon tetrachloride gave 0.29 g (70%) of nitrimine **3f** (Table III). Change of eluent to 50:50 chloroform–carbon tetrachloride gave a yellow oil (0.4 g) which lost bromine on standing. After 2 days standing, the oil crystallized to give 0.10 g (26%) of 1-chloro-1-nitro-1,3-diphenylpropene, mp 70–72°.

8,9-Dibromo-8,9-dihydrocarvone Oxime (7).—Carvone oxime[13] (2.65 g, 0.016 mol) in 25 ml of carbon tetrachloride was treated with 2.65 g (0.016 mol) of bromine in 20 ml of carbon tetrachloride dropwise. After stirring for 1 hr the solvent was removed on a rotary evaporator and the remaining solid (3.64 g, 71%) was recrystallized from a pentane–chloroform mixture, mp 104–106° dec. The product did not give a satisfactory analysis but gave satisfactory spectral data (Table III).

Compound **7** was also obtained in 87% yield from 1,6,8,9-tetrabromotetrahydrocarvone oxime[14] (**8**) by warming for 10 min with an equivalent amount of sodium iodide in acetone. A comparable yield of **7** was obtained with zinc dust in refluxing ethanol (see **13** below).

9-Bromo-8-methoxy-8,9-dihydrocarvone Oxime (9).—A solution of 0.52 g (1.9 mmol) of 8,9-dibromo-8,9-dihydrocarvone oxime (**7**) in 30 ml of absolute methanol was allowed to stand at room temperature for 25 hr and then was poured onto 200 g of ice. After standing overnight in a refrigerator the crystals were collected, dried, and recrystallized from pentane–chloroform to give 0.31 g (60%) of 9-bromo-8-methoxy-8,9-dihydrocarvone oxime, mp 113–114°.

6,8,9-Tribromo-1-methoxytetrahydrocarvone Oxime (10).—Compound **10** was prepared by treating tetrabromotetrahydrocarvone oxime[14] (**8**) with methanol as just described for **9**. The structure was confirmed by synthesis from **7** by the method of Winstein and Henderson[16] with *N*-bromoacetamide in methanol. Comparison of ir and nmr spectra showed the two samples to be identical.

8-Chloro-1,6,9-tribromotetrahydrocarvone Nitrimine (11).—Into a solution of 1.8 g (3.7 mmol) of 1,6,8,9-tetrabromotetrahydrocarvone oxime[14] in 40 ml of chloroform at room temperature, a slow stream of nitrosyl chloride was bubbled. After a yellow color was attained, the gas stream was stopped and the solution was stirred overnight. One gram of anhydrous sodium carbonate was added to the solution and the mixture was stirred for an additional 1 hr. The solution was decanted from the solid and the chloroform was removed on a rotating evaporator. The remaining green oil solidified in the refrigerator and was recrystallized twice from pentane–carbon tetrachloride to give 350 mg (20%) of white 8-chloro-1,6,9-tribromotetrahydrocarvone nitrimine (**11**), mp 89–90.5°.

The position of the chlorine at C-8 was corroborated by conversion to 8-chloro-9-bromo-8,9-dihydrocarvone in 40% yield by treatment with zinc dust in refluxing ethanol as described above: ir (CCl_4) 1660 (s, C=C–C=O), 625 (CCl), 570 cm^{-1} (CBr); nmr ($CDCl_3$) δ 6.80 (br, 1), 3.85 (s, 2), 1.89 (s, 3), 1.78 (s, 3). The absorption frequency at 570 cm^{-1} was also found in 8,9-dibromo-8,9-dihydrocarvone, synthesized by adding 1 mol of bromine to carvone, but the band at 625 cm^{-1} was missing.

8-Methoxyl-1,6,9-tribromotetrahydrocarvone Oxime (12).—Addition of bromine to compound **9** in the same manner as described here for other unsaturated oximes gave 8-methoxy-1,6,9-tribromotetrahydrocarvone oxime in 64% yield, mp 119–120°.

1-Methoxy-6-bromo-1,6-dihydrocarvone Oxime (13).—The structure of compound **10** was also verified by treating 1 g (2.3 mmol) of **10** with 0.15 g (2.3 g-atoms) of zinc dust in 30 ml of refluxing absolute ethanol for 1 hr. The clear oil obtained after evaporating the solvent crystallized upon standing for 5 days. Recrystallization from hexane gave 0.75 g (87%) of 1-methoxy-6-bromo-1,6-dihydrocarvone oxime, mp 85–86°.

Methyl 1,2-Dibromo-1-cyclohexyl *O*-Methylketoxime (14).—Methyl 1-cyclohexenyl ketone[4] was converted to the corresponding *O*-methylketoxime by the method described in the next section in 48% yield, bp 60–62° (1.5 mm). This method was more convenient than that of Müller,[17] even though the yield in the latter case using diazomethane on the oxime was 75%. Compound **14** was prepared by addition of bromine (*vide supra*) in 35% yield after recrystallization from hexane, mp 36–38°.

Compound **15**, methyl 1-chloro-2-bromo-1-cyclohexyl *O*-methylketoxime, was obtained from **14** by treatment with nitrosyl chloride in a sealed tube at 55° for 3 days, much more strenuous conditions than were needed for any other replacement reaction reported here. By putting the brown oily product obtained by this method on a silica gel column and eluting with hexane an 81% yield of **15** was obtained, mp 31–32°.

1,6,8,9-Tetrabromotetrahydrocarvone *O*-Methyloxime (16).—Carvone (4.8 g, 32 mmol) was treated with 2.6 g (32 mmol) of *O*-methylhydroxylamine hydrochloride[18] in 40 ml of ethanol. To this solution 3.2 g (32 mmol) of triethylamine in 10 ml of ethanol was added dropwise and then the mixture was refluxed for 4 hr, cooled, and poured onto ice. The organic layer was extracted with ether and the solvent was evaporated to give 2.6 g (80%) of a yellow oil, identified as carvone *O*-methyloxime[19] by ir and nmr spectra, but not isolated: ir (neat) 3070 (s, CH), 2950 (br), 1670 cm^{-1} (m, C=N); nmr (CCl_4) δ 5.75 (br, 1), 4.62 (s, 2), 3.72 (s, 3), 1.70 (s, 6).

To 0.4 g (2.3 mmol) of carvone *O*-methyloxime in 15 ml of carbon tetrachloride was added 0.74 g (4.6 mmol) of bromine in 10 ml of the same solvent. After a short time the solvent was removed on a rotary evaporator, leaving a red oil which crystallized on cooling. Recrystallization from hexane gave 0.15 g (19%) of a white solid, mp 109–111°, 1,6,8,9-tetrabromotetrahydrocarvone *O*-methyloxime.

Reaction of Optically Active α-Bromoethylbenzene with Nitrosyl Chloride.—(−)-α-Bromoethylbenzene[20] (0.5 g, 2.7 mmol) was dissolved in 25 ml of carbon tetrachloride and an excess of nitrosyl chloride was slowly bubbled into the solution. After the solution was stirred at 25° for 1 hr, an aliquot was taken from the reaction mixture and an nmr spectrum and the optical rotation were taken immediately. More nitrosyl chloride was bubbled through the remaining solution and aliquots were removed at the times given in Table II. The treatment finally ended in 100% conversion of the bromide to the racemic chloride. The percentages of chloride and bromide were determined by measuring the integrated areas of the chemical shifts of the respective protons in the –CHCl and –CHBr groups. The optical purity values given in Table II are based on a calculated rotation of −170° for the pure bromo compound.[20]

Since the percentage replacement from nmr measurements is accurate to ±5%, the conclusion is that the rate of replacement of bromine by chlorine from nitrosyl chloride is equal to the rate of racemization within experimental error.

The percentage yields of alkyl chlorides in Table I were also determined from the corresponding areas of peaks from chemical shifts in nmr spectra of the reaction mixtures.

Registry No.—**1a**, 36914-18-8; **1b**, 36914-19-9; **1c**, 36914-20-2; **1d**, 36914-21-3; **1e**, 36914-22-4; **1f**, 36914-23-5; **2a**, 36914-24-6; **2b**, 36914-25-7; **2e**, 36914-42-8; **3a**, 36914-26-8; **3b**, 36914-27-9; **3c**, 36914-28-0; **3d**, 36914-29-1; **3e**, 36914-30-4; **3f**, 36914-31-5; **5f**, 36914-32-6; **7**, 36914-33-7; **9**, 36914-34-8; **10**, 36914-35-9; **11**, 36914-36-0; **12**, 36914-37-1; **13**, 36914-38-2; **14**, 36914-39-3; **15**, 36914-40-6; **16**, 36914-41-7; **17**, 36895-16-6; α-bromoethylbenzene, 585-71-7; nitrosyl chloride, 2696-92-6.

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