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Reaction of Nitrosyl Chloride with Norbornene and Norbornadiene

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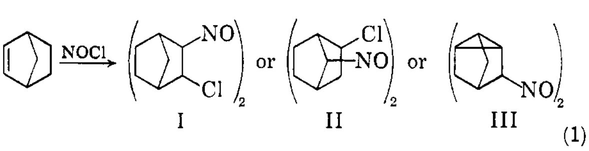
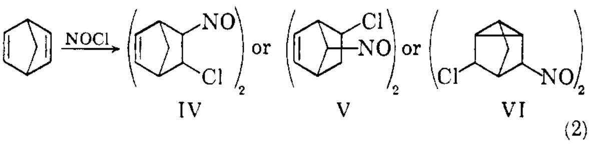
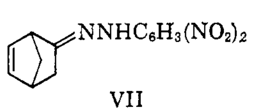
Nitrosyl chloride was shown to add to norbornene and norbornadiene without rearrangement.

Nitrosyl chloride adds to olefins in the same direction as hydrogen chloride and thus gives the products expected for the addition of NO^+Cl^-.[1] If the first step in the addition of nitrosyl chloride to norbornene and norbornadiene is the addition of NO^+, then the resulting carbonium ion might undergo rearrangement to yield the products shown in Equations 1 and 2, respectively.

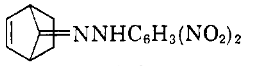




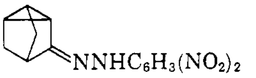
The addition of nitrosyl chloride to norbornadiene has been reported to yield IV[2] although VI has been suggested.[3] The structure of the adduct was considered proven by conversion to a 2,4-dinitrophenylhydrazone which was presumably either VII, VIII, or IX.[2] The 2,4-dinitrophenylhydrazone obtained had m.p. 134–136° and was considered different from authentic IX (m.p. 188.2–189.6°) prepared by Roberts[4] and was considered identical with authentic VII (m.p. 133–137° cited) prepared by Parham.[5] Authentic VIII has not been prepared. However, Parham in addition to reporting m.p. 133–137° further states that after repeated recrystallization the compound had m.p. 149–154°[5] and was still not pure. Roberts, however, in addition to preparing IX also reports in the same paper[4] the preparation of pure VII having m.p. 173.8–175.0°.



VII

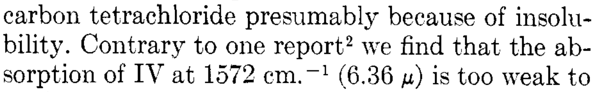


VIII



IX

Since the melting point of the 2,4-dinitrophenylhydrazone obtained from the nitrosyl chloride adduct of norbornadiene does not prove its identity, we report here our proof of structure for the nitrosyl chloride adduct of norbornene and confirmation of the published structure[2] of the norbornadiene adduct. Equation 3 indicates the scheme followed.



Compounds I and IV have nearly identical melting (decomposition) points and do not show an appreciable mixed melting point depression. They are distinguished, however, by potassium permanganate in acetone which is decolorized by IV but not by I. Neither compound decolorized bromine in carbon tetrachloride presumably because of insolubility. Contrary to one report[2] we find that the absorption of IV at 1572 cm.$^{-1}$ (6.36 μ) is too weak to be diagnostic as is typical for olefins of the $RCH=CHR$ type. However, IV does show typically strong olefinic hydrogen out-of-plane bending absorption at 740 cm.$^{-1}$ which serves to further distinguish it from I. It is of interest to note that in our experience large losses are encountered on recrystallizing I and IV and dimeric nitrosyl chloride adducts in general. These compounds dissolve slowly in hot solvents accompanied by the gradual appearance of a blue color (nitroso monomer) which disappears on cooling. The large losses encountered are presumed due to conversion of the monomer to the oxime although attempts to obtain this conversion by refluxing in solvents in the absence of a base gave erratic results under apparently identical conditions. It should also be noted that although I is not a primary irritant it can cause severe dermatitis in those who become sensitized to it.

The chloro oxime was obtained analytically pure but had a wide melting point range suggesting a mixture of *syn-anti* forms. The chloro ketone was reduced to a mixture of norborneols which on oxidation gave norcamphor identical with an authentic sample. Although the presumed mechanism of nitrosyl chloride addition supposes only one position

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(1) C. K. Ingold, *Structure and Mechanism in Organic Chemistry*, Cornell University Press, Ithaca, N. Y., 1953, p. 669.

(2) G. T. Youngblood, C. D. Trivette, Jr., and P. Wilder, Jr., *J. Org. Chem.*, **23**, 684 (1958).

(3) G. T. Youngblood, Ph.D. dissertation, Duke University, 1956.

(4) J. D. Roberts, E. R. Trumbull, Jr., Winifred Bennett, and Rose Armstrong, *J. Am. Chem. Soc.*, **72**, 3116 (1950).

(5) W. E. Parham, W. T. Hunter, Roberta Hanson, and T. Lahr, *J. Am. Chem. Soc.*, **74**, 5646 (1952).

for the chlorine substituent (see Equation 1) this supposition was confirmed by chlorination of norcamphor.

EXPERIMENTAL

5-Chloro-6-nitrosonorbornene-2 dimer (IV). A mixture of 40 g. (0.435 mole) of norbornadiene, 50.8 g. (0.43 mole) of *i*-amyl nitrite, and 400 ml. of ethanol was held at −10° while 36 ml. of concd. hydrochloric acid was added dropwise. The solution was kept in a refrigerator overnight and then filtered. The solid obtained was washed thoroughly with methanol and dried over potassium hydroxide to yield 47.5 g. (69% yield) of a white solid, m.p. 130° dec. Recrystallization from chloroform/methanol gave two crops of crystals, m.p. 159° dec. and 161.5° dec., having identical infrared spectra.

In a second preparation a mixture of 70 g. (0.76 mole) of norbornadiene and 700 ml. of ethanol was held at −20° while nitrosyl chloride was introduced above the surface of the solution until a deep green-blue color resulted. Warming to 0° gave a white solid which was filtered, washed with methanol, and dried over potassium hydroxide to yield 97 g. (81% yield) of solid, m.p. 128° dec. Recrystallization from approximately 4 l. of 1,2-dichloroethane gave 67.8 g. of white crystals, m.p. 151.5° dec. Recrystallization from boiling acetic acid gave 41.3 g. of dark crystals, m.p. 151° dec. Recrystallization again from 1,2-dichloroethane gave 28.3 g. of white crystals, m.p. 151° dec. A third recrystallization from 1,2-dichloroethane followed by drying over phosphorus pentoxide at room temperature for 2 days gave a white solid, m.p. 156.2–158.2° dec. (reported[2] m.p. 164°).

2-Chloro-3-nitrosonorbornane dimer (I). (a) *From 5-chloro-6-nitrosonorbornene-2 dimer* (IV).[6] Four grams of 5-chloro-6-nitrosonorbornene-2 dimer in 200 ml. of dioxane was hydrogenated for 1.5 hr. at an initial pressure of 40.5 p.s.i. using 4% palladium-on-charcoal as a catalyst. The reaction mixture was filtered and then diluted with 1.5 l. of water. The precipitated white solid was filtered, washed with water and methanol, and dried over potassium hydroxide to yield 2.4 g. of product, m.p. 149–151° dec. Recrystallization from 1,2-dichloroethane gave a solid having m.p. 155.8–157° dec. (reported[7] m.p. 157–158°), mixed melting point with starting material 152–155.6° dec.

(b) *From norbornene.* A solution of 50 g. of norbornene in approximately 250 ml. of liquid sulfur dioxide was maintained at −60° while nitrosyl chloride was bubbled through the solution. When the solution acquired the color of nitrosyl chloride it was filtered. The solid was washed twice with methanol and then repeatedly with water until free of sulfur dioxide odor. After drying 52.5 g. (62% yield) of a white powder was obtained which after recrystallization from dioxane gave crystals, m.p. 153–154° dec. (reported m.p.[7] 157–158°).

The use of liquid sulfur dioxide in this type of reaction has been previously reported.[8] The use of chloroform, ethanol and acetic acid as solvents gave products identical with the above and in about the same yield.

3-Chloronorcamphor oxime. Attempts to isomerize 2-chloro-3-nitrosonorbornane dimer to the title compound by treatment of a chloroform solution with hydrogen chloride with, and without, irradiation[9] were unsuccessful. Similarly unsuccessful was heating in acetic acid and dioxane. The following successful method is that of Bordenca and Allison.[10]

A mixture of 100 g. of 2-chloro-3-nitrosonorbornane dimer, 40 g. of urea, and 500 ml. of *i*-propyl alcohol was refluxed for 3 hr. During reflux the mixture became homogeneous and slightly yellow but there was no appearance of a blue color. Evaporation under reduced pressure gave 300 ml. of a viscous liquid containing some solids. The liquid was diluted with 600 ml. of water and the mixture was extracted four times with 100-ml. portions of chloroform. The combined chloroform extracts were washed four times with 100-ml. portions of water and then dried with sodium sulfate. Removal of the solvent under reduced pressure gave 102 g. (102% yield) of a yellow solid, m.p. 62–67°. Sublimation under oil pump vacuum at 50° gave a white solid having m.p. 60.5–71° which on crystalling from the melt had m.p. 65–73.5° and then m.p. 64.5–67° on crystallizing from the melt a second time. When heated to 90° and allowed to crystallize from the melt the solid had m.p. 62–67°. Attempts to recrystallize from solvents were unsuccessful. A sample was then fractionally sublimed at 50° and 0.3 mm. Five sublimate fractions were taken and a residue was deliberately left. The melting point of these fractions ranged between 50° and 79° and all had virtually identical infrared spectra. That fraction having the largest melting point range, 58–78.5°, was selected for analysis to test the hypothesis that the variable melting point was due to a mixture of *syn-anti* forms.

Anal. Calcd. for $C_7H_{10}ClNO$: C, 52.68; H, 6.32; Cl, 22.22; N, 8.78; mol. wt., 159.5. Found: C, 52.79, 52.73; H, 6.56, 6.58; Cl, 22.06, 22.03; N, 8.89, 8.71; mol. wt., 157, 160 (Signer).

The benzoate was prepared in 33% yield by reaction with benzoyl chloride and pyridine. Recrystallization from ethanol gave an analytical sample, m.p. 110.0–111.3°.

Anal. Calcd. for $C_{14}H_{14}ClNO_2$: C, 63.76; H, 5.35; Cl, 13.45; N, 5.31. Found: C, 64.05, 63.89; H, 5.42, 5.47; Cl, 13.53, 13.48; N, 5.40, 5.62.

3-Chloronorcamphor. (a) *Preparation from the oxime.* Following the procedure of DePuy and Ponder[11] a mixture of 50 g. (0.313 mole) of 3-chloronorcamphor oxime, 292 ml. (328.5 g., 2.83 moles) of freshly distilled levulinic acid, and 32 ml. of *N* hydrochloric acid was heated with stirring on a steam bath for 3 hr. After standing at room temperature for 14 hr. the dark solution was poured into 1.5 l. of water. The solution was extracted four times with 200-ml. portions of chloroform. The combined chloroform extracts were washed twice with 1.5-l. portions of water and then four times with 300-ml. portions of 5% sodium bicarbonate solution. The chloroform extract was then dried with sodium sulfate and the solvent removed under aspirator vacuum to yield an amber-colored liquid. This liquid was then rapidly distilled through a short column to give 27.6 g. (61% yield) of distillate, b.p. 98–108° (12 mm.), and 13.42 g. of a black gummy residue. Redistillation gave an analytical sample having b.p. 100.5° (10 mm.); n_{D}^{25} 1.4961; $d = 1.220$; molecular refractivity 34.62 (found), 35.05 (calculated); ϵ_{max} 31.7, 33.6, 32.8 at 308 mμ (0.0103, 0.0206, 0.0411*M* in dioxane); ϵ_{max} 32.2 at 308 mμ (0.0149*M* in ethyl acetate).

Anal. Calcd. for C_7H_9ClO: C, 58.14; H, 6.27; Cl, 24.52; mol. wt., 145. Found: C, 58.12, 58.40; H, 6.43, 6.23; Cl, 24.43, 24.45; mol. wt., 134, 134 (in exaltone).

(b) *Preparation from norcamphor.* A solution of 55 g. (0.50 mole) of norcamphor in 100 ml. of acetic acid was kept at room temperature or below while chlorine was bubbled through the solution. After 2.5 hr. the solution had gained 42.1 g. which after correction for the solubility of chlorine in acetic acid gave a gain of 34.4 g. (theory 35.5 g.). Nitrogen was bubbled through the solution until the chlorine color was discharged. The mixture was then distilled through a wide-bore, short-pass system at 10 mm. until the pot temperature reached 80°. Distillation was then continued through a 6-in. Vigreux column at 14 mm. It was necessary to dismantle the apparatus several times to wash the norcamphor out of the system. When norcamphor no longer distilled out the following fractions were obtained: (1) b.p. 101.5–105.5°, n_{D}^{26} 1.4875, 0.80 g.; (2) b.p. 105.5–107.3°, n_{D}^{26} 1.4962, 17.68 g.; (3) b.p. 107.3–109.0°, n_{D}^{26} 1.4965

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(6) The unpublished procedure of Dr. H. E. Knipmeyer.

(7) G. Komppa and S. Beckmann, *Ann.*, **512**, 172 (1934).

(8) R. K. Allison, U. S. Patent **2,485,180.**

(9) E. Mueller, Canadian Patent **578,069.**

(10) C. Bordenca, R. K. Allison, and P. H. Dirstine, *Ind. Eng. Chem.*, **43**, 1196 (1951).

(11) C. H. DePuy and B. W. Ponder, *J. Am. Chem. Soc.*, **81**, 4629 (1959).

$d = 1.22$, 13.16 g.; (4) b.p. 109.0°, n_D^{26} 1.4969, 1.62 g.; total yield 45%.

The physical properties of fraction 3 are in agreement with those reported above for 3-chloronorcamphor and the infrared spectra were identical.

(c) *Conversion to norcamphor*. To a solution of 5.24 g. (0.0362 mole) of 3-chloronorcamphor in 360 ml. of isopropyl alcohol was added 1.65 g. (0.050 mole) of sodium in small pieces. After 20 min. when reaction had subsided the mixture was refluxed for 10 min. An additional 16.7 g. (0.7 mole) of sodium was then added as rapidly as possible after which refluxing was continued for 4.75 hr. After cooling to room temperature the resulting solid was dissolved in 250 ml. of water. The solution was made acidic to Congo Red and extracted with three 200-ml. portions of ether. The combined ether extracts were washed with 750 ml. of water. The water wash was then extracted with 200 ml. of ether. The combined ether extracts were then washed twice with 200 ml. portions of 5% sodium bicarbonate solution. After drying with sodium sulfate, removal of the solvent under reduced pressure, and drying on a porous plate there was obtained 1.40 g. of a yellow solid which gave a negative Beilstein halogen test. Crystallization from petroleum ether (b.p. 30–60°) gave a white solid, m.p. 109–122°, whose infrared spectrum and melting point indicated a mixture of *exo*- and *endo*-norborneol.

Following the procedure of Hall[12] 0.98 g. of the above solid was added in small portions over a period of 15 min. to a mixture of 2.35 g. of potassium dichromate, 12 ml. of water, and 1.09 ml. of concd. sulfuric acid. The maximum temperature reached was 42°. After stirring for 3 hr. the mixture was extracted with five 10-ml. portions of ether. The combined ether extracts were washed with two 20-ml. portions of water and two 10-ml. portions of 5% sodium bicarbonate solution. After drying with sodium sulfate and removal of the solvent under reduced pressure there was obtained a yellow sticky solid. Sublimation at 60° under oil pump vacuum gave a white solid, m.p. 92–95.3° (reported[12] m.p. 92–93° for norcamphor), whose infrared spectrum was identical with that of an authentic sample of norcamphor.

NMR spectra. The spectra were obtained at room temperature using a Varian Associates high resolution NMR spectrometer system with a V4311 RF unit operating at 56.4 Mc. The chemical shifts are reported as τ units[13] and areas were measured with a planimeter. We are indebted to Dr. T. H. Regan for obtaining and interpreting these spectra.

The spectrum of norbornadiene (5% in carbon tetrachloride) shows absorption at 8.07 (bridge hydrogens), 6.49 (bridgehead hydrogens), and an unsymmetrical triplet at 3.23 (olefinic hydrogens).

The spectrum of norbornene (5% in carbon tetrachloride) shows an unsymmetrical triplet at 4.12 (olefinic hydrogens) and a broad band with unresolved multiplicity at 7.20 (bridgehead hydrogens). Complex absorption in the region 8.30–9.04 was not interpreted.

The spectrum of 5-chloro-6-nitrosonorbornene-2 dimer (saturated in deuterochloroform) shows an unsymmetrical triplet at 3.83 (olefinic hydrogens). The remaining assignments are tentative because of low solubility and thus a low signal to noise ratio. The bridgehead hydrogens absorb at 6.72 and 6.99; absorption at 4.91, 5.07, 5.66, and 5.80 is a typical AB spectral pattern one pair of which is attributable to the hydrogen on C-5 and the other pair to the hydrogen on C-6. A second AB pattern at 7.70 and 8.01 is attributable to the bridge hydrogens.

The spectrum of 2-chloro-3-nitrosonorbornane dimer (saturated in deuterochloroform) shows absorption at 7.20 and 7.50 (bridgehead hydrogens) and a typical AB pattern at 5.05, 5.18, 5.62, and 5.76, one pair of which is assigned to the hydrogen on C-2 and the other pair to the hydrogen on C-3. Complex absorption in the region 7.73–8.55 was not interpreted.

The spectrum of 3-chloronorcamphor (20% in carbon tetrachloride) shows a doublet at 6.40 assigned to the hydrogen on C-3. Broad unresolved absorption at 7.34 with twice the area of the peak at 6.40 is assigned to the two bridgehead hydrogens. Complex absorption in the region 7.78–8.56 was not interpreted.

The spectrum of 3-chloronorcamphor oxime (5% in deuterochloroform) has absorption at 0.60 (oximino hydrogen). A peak at 5.60 is assigned to the hydrogen on C-3 and is split into a doublet by coupling with the adjacent bridgehead hydrogen. This peak is assigned to either the *syn* or *anti* form of the oxime and a second doublet peak at 5.76 is similarly assigned to the presence of the other isomer.[14] The total area of the 5.60 and 5.76 peaks is equal to the area of the 0.60 peak, indicating that they together represent one hydrogen. A peak at 7.39 has an area proportional to one hydrogen and is assigned to the bridgehead hydrogen adjacent to the chlorine. Two peaks at 6.47 and 7.04 have a total area equivalent to one hydrogen and are assigned to the bridgehead hydrogen alpha to the oximino group in the *syn* and *anti* forms. Consistent with these assignments, the ratio of the area of the 5.76 and 5.60 peaks is equal to the ratio of the areas of the 6.47 and 7.04 peaks. Complex absorption in the region 7.82–8.53 was not interpreted.

The chemical shifts in cycles per second (c.p.s.) at 40 mc. with reference to water have been reported for five norbornene derivatives.[15] Using 5.20 as the chemical shift of external water with reference to tetramethylsilane[16] and the formula, $\tau = 10 - (5.20 + \text{c.p.s. } H_2O/40)$, the reported ranges are: 2.70–3.75 (olefinic hydrogen), 5.82–6.90 (bridgehead hydrogen), 5.30–5.60 (hydrogen on a bridge carbon bearing a halogen).

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[12] H. K. Hall, Jr., *J. Am. Chem. Soc.*, **82**, 1209 (1960).

[13] G. V. D. Tiers, *J. Phys. Chem.*, **62**, 1151 (1958).

[14] E. Lustig, *J. Phys. Chem.*, **65**, 491 (1961).

[15] L. Kaplan, H. Kwart, and P. von R. Schleyer, *J. Am. Chem. Soc.*, **82**, 2341 (1960).

[16] R. A. Y. Jones, A. R. Katritzky, and J. M. Lagowski, *Chem. & Ind. (London)*, 870 (1960).