[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY, ITHACA, N. Y.]

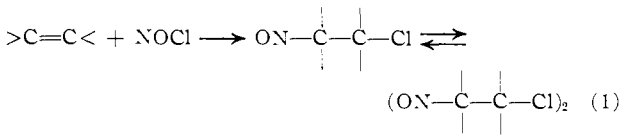
The Addition of Nitrosyl Halides to Olefins. Dependence of Steric Course on Olefin Structure[1,2]

BY JERROLD MEINWALD, YVONNE C. MEINWALD, AND T. NELSON BAKER, III

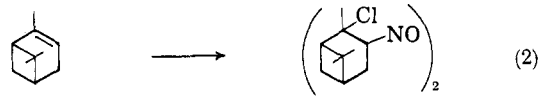
RECEIVED MAY 9, 1964

The addition of nitrosyl chloride and nitrosyl bromide to norbornene, *anti*-7-methoxynorbornene, and norbornadiene follows a *cis* stereochemical course and is unaccompanied by molecular rearrangement. Norbornene-*endo*-5-carboxylic acid yields chiefly a mixture of dimeric nitrosochlorides without participation of the *endo*-carboxyl group. In contrast to the norbornene adducts, the blue nitrosochloride of Δ^9-octalin is shown to be *trans*. These results are compared with those of oxymercuration and other addition reactions. A long-range coupling between the *endo*-3 and *anti*-7 protons (2–4 c.p.s.) is observed in the n.m.r. spectra of a number of substituted norbornanes.

The reaction of olefins with nitrosyl chloride to give nitrosochlorides, which dimerize if unhindered (eq. 1), has been known since 1875,[3] and has played an important role in early studies of terpenes.[4] The use of an alkyl nitrite and hydrochloric or hydrobromic acid, generating the nitrosyl halide *in situ*, provides a convenient, alternate technique for carrying out these additions.[5] With unsymmetrically substituted olefins, addition of the nitroso group to the less substituted carbon atom is generally observed, as shown in eq. 2 for the case of α-pinene.[6]

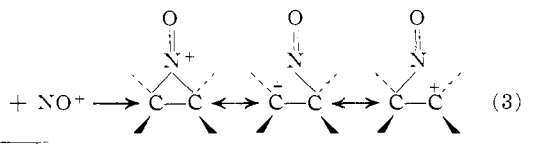


(1)

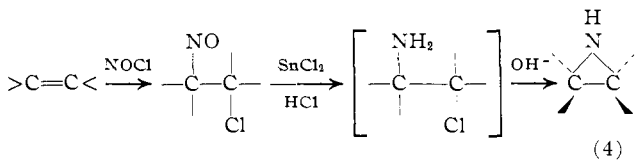


(2)

Based on these considerations, a mechanism involving NO^+ and Cl^- has been generally assumed.[7] For example, Kaplan, Kwart, and Schleyer have suggested that nitrosyl chloride ionizes to give the nitrosonium ion (NO^+) which adds to an olefin to give a highly stabilized onium ion intermediate (eq. 3), which should open to give a *trans*-nitrosochloride. A novel preparation of aziridines from tetrasubstituted olefins,[8] consisting of nitrosyl chloride addition followed by stannous chloride reduction (to give a chloramine) and base cyclization (eq. 4), is consistent with this proposal. Although for a cyclic olefin such as 1,2-dimethylcyclohexene the cyclization requires a *trans*-chloroamine, the conditions utilized for the production of this intermediate make the stereochemistry of the initial nitrosochloride ambiguous. Probably for this reason, no conclusion was drawn from this work about the stereochemistry of the nitrosyl chloride addition.[9]



(3)



(4)

Since a knowledge of the stereochemistry of nitrosyl halide additions should increase the synthetic utility of these reactions as well as help in elucidating their mechanisms, we have studied this problem explicitly for a variety of olefins.[2]

Additions to Norbornenes.—The first report of the synthesis of norbornene by Komppa and Beckmann also describes the formation of its crystalline, dimeric nitrosochloride.[10] These workers did not establish the structure of this adduct, but more recently Miller demonstrated that it has an unrearranged carbon skeleton.[11] Thus, the adduct could be converted into 3-chloronorcamphor *via* preliminary conversion to a mixture of stereoisomeric oximes. The stereochemical homogeneity of the chloroketone, however, was not established, and no attempt was made in this work to answer the stereochemical question raised above.

We have found that norbornene nitrosochloride (I) can be converted directly into a chloroketone (IIa) in good yield by warming with levulinic acid and hydrochloric acid.[12] Vapor phase chromatography of IIa showed it to be homogeneous. Both infrared spectral evidence (carbonyl maximum at 5.69 μ (CS_2), compared with 5.75 μ for norcamphor and 5.62 μ for 7-ketonorbornane[13]) and ultraviolet spectral evidence[14] (λ_{max}^{EtOH} 299 mμ, ϵ 36; norcamphor λ_{max}^{EtOH} 288 mμ, ϵ 29) serve to

(1) Partial support of this work by the Alfred P. Sloan Foundation and the National Science Foundation is acknowledged with pleasure.

(2) (a) Presented in part at the A.A.A.S. Symposium on Organic Chemistry, Dec. 27, 1962, Philadelphia, Pa., and at the Eighteenth National Organic Chemistry Symposium of the American Chemical Society, June 16–20, 1963, Columbus, Ohio. (b) For preliminary communications see J. Meinwald, Y. C. Meinwald, and T. N. Baker, III, *J. Am. Chem. Soc.*, **85**, 2513 (1963); J. Meinwald and Y. C. Meinwald, *ibid.*, **85**, 2514 (1963).

(3) W. A. Tilden, *J. Chem. Soc.*, **28**, 514 (1875).

(4) (a) O. Wallach, "Terpene und Campher," 2nd Ed., Veit and Co., Leipzig, 1914, pp. 69–75; (b) L. J. Beckham, W. A. Fessler, and M. A. Kise, *Chem. Rev.*, **48**, 319 (1951).

(5) O. Wallach, *Ann.*, **252**, 106 (1889); *Ber.*, **28**, 1308 (1895).

(6) (a) G. L. Simonson, "The Terpenes," Vol. 2, 2nd Ed., Cambridge University Press, New York, N. Y., 1949, pp. 178–190; (b) W. A. Tilden, *J. Chem. Soc.*, **28**, 514 (1875); **31**, 554 (1877).

(7) (a) L. Kaplan, H. Kwart, and P. von R. Schleyer, *J. Am. Chem. Soc.*, **82**, 234 (1960); (b) E. Müller, "Houben-Weyl: Methoden der Organischen Chemie," 5/3, 4th ed., Georg Thieme Verlag, Stuttgart, 1962, pp. 934–941; (c) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, pp. 669, 670; (d) R. C. Fuson, "Reactions of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1962, pp. 167, 168.

(8) G. L. Closs and S. J. Brois, *J. Am. Chem. Soc.*, **82**, 6068 (1960).

(9) Evidence that nitrosyl chloride reacts with Δ^5-steroids to give 5α-chloro-6β-nitro steroids has been presented by K. Tanabe and R. Hayashi, *Chem. Pharm. Bull.* (Tokyo), **10**, 1177 (1962). If this reaction proceeds *via* a nitrosochloride, it provides an example of *trans* addition.

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

(11) (a) J. B. Miller, *J. Org. Chem.*, **26**, 4905 (1961); (b) G. T. Youngblood, C. D. Trivette, Jr., and P. Wilder, Jr., *ibid.*, **23**, 684 (1958).

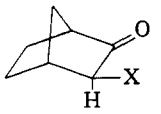
(12) C. H. DePuy and B. W. Ponder, *J. Am. Chem. Soc.*, **81**, 4629 (1959).

(13) (a) P. D. Bartlett and B. E. Tate, *ibid.*, **78**, 2473 (1956); (b) C. J. Norton, Ph.D. Thesis, Harvard University, 1955.

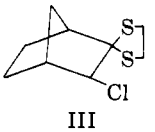
(14) R. C. Cookson, *J. Chem. Soc.*, 282 (1954).

confirm Miller's conclusion that this compound is a 3-chloronorcamphor, but they give no indication of the configuration of the chlorine. We have established the configuration shown in formula IIa for this compound.

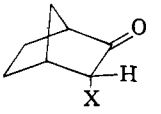
Treatment of IIa with ethane-1,2-dithiol and boron trifluoride etherate gave a crystalline dithioketal (III).



IIa, X = Cl
b, X = Br



III



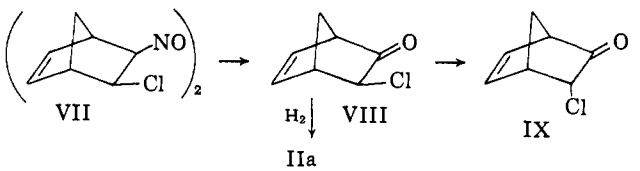
IVa, X = Cl
b, X = Br

Desulfurization of III with W-2 Raney nickel gave the known *exo*-2-chloronorbornane[15] as the only chlorine-containing product, indicating an *exo* configuration for the chlorine in IIa. Furthermore, the sodium enolate of norcamphor reacted with chlorine to give a good yield of IIa of 98% purity. This product results from kinetic control, since treatment with aqueous potassium carbonate converts it into a roughly equimolar equilibrium mixture of IIa and its *endo* epimer IVa. It was possible to isolate IVa as a crystalline compound by preparative v.p.c. Since it is established that kinetically controlled reactions of norbornanes involve *exo* attack,[16] these experiments prove IIa to be *exo*-3-chloronorcamphor.

Whereas the epimeric 3-chloronorcamphors were previously unknown, the 3-bromonorcamphors have been described recently by Krieger.[17] Treatment of norbornene with isoamyl nitrite and hydrobromic acid yielded a dimeric nitrosobromide (V). Levulinic acid hydrolysis gave pure *exo*-3-bromonorcamphor (IIb) in 84% yield, demonstrating the similarity of nitrosyl bromide and nitrosyl chloride additions. The *endo*-3-bromonorcamphor (VIb) could be obtained by base equilibration of IIb, and was isolated pure by chromatography.

From these results, the stereochemistry of the nitrosohalide adducts themselves (I and V) would seem to be *cis-exo*, since initial attack by NO^+, NOCl, or even NO would all be expected to place the nitroso group in an *exo* position.[16] This conclusion appears contrary to earlier speculation based on an "onium" ion intermediate, however, and the corresponding reactions of norbornadiene and 2-norbornene-*endo*-5-carboxylic acid (VI) were studied in order to see whether any carbonium ion character could be discerned in these additions.

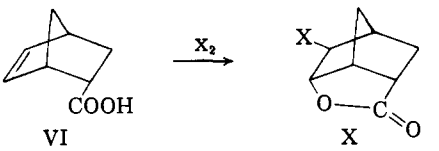
The dimeric adduct VII from norbornadiene and nitrosyl chloride[11a,b] was readily shown to be analogous to that from norbornene, since it could be hydrolyzed to an unsaturated *exo*-chloroketone VIII, which gave *exo*-3-chloronorcamphor (IIa) upon catalytic hydrogenation. Once more it can be shown that no epimerization of the chloro group accompanies these transformations, since treatment with aqueous base converts VIII into an equimolar mixture of VIII and its *endo* isomer IX.



VII → VIII (H_2) → IIa; VIII → IX

The behavior of norbornadiene is more striking than that of norbornene because of the especially great tendency for this diene to undergo rearrangement or cyclization in electrophilic reactions.[18]

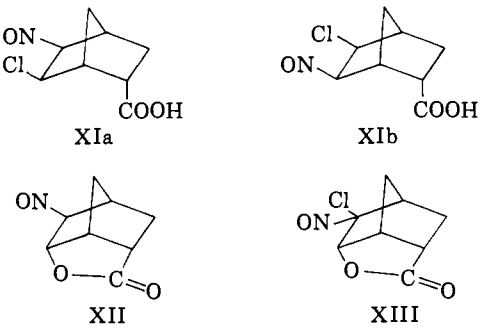
2-Norbornene-*endo*-5-carboxylic acid (VI) is well known to give lactonic products in electrophilic reactions. Thus, treatment of VI with iodine or bromine



VI → (X_2) → X

results in formation of halolactones X.[19]

When VI was treated with isoamyl nitrite and hydrochloric acid or directly with nitrosyl chloride, a solid, acidic dimer XI was obtained analytically pure, but with a wide melting range. In addition, part of the acid appeared as a glass and never crystallized. This behavior suggests that a mixture of nitrosochlorides, XIa and XIb, was formed. Nevertheless, about 90% of the product proved to be acidic, and none of the nitrosolactone XII to be expected from carboxyl participation could be found. When a large excess of nitrosyl chloride was employed, a small amount of a dimeric lactonic product could be isolated. It is possible that this product, which is never an important one, results from the chlorination[4b] of unisolated nitrosolactone XII, and that it has structure XIII. In this case, it may represent evidence in favor of a small amount of carbonium ion character in these reactions. The fact that the major product is the simple adduct, however, means that this character must be minimal.



XIa XIb XII XIII

In examining the n.m.r. spectra of the haloketones IIa, IIb, IVa, IVb, VIII, and IX, as well as those of a number of related compounds, a puzzling feature which at first confused our configurational assignments was consistently observed. This was the splitting of the C_3-proton into a doublet (see Table I for a summary of the data) *independent of its configuration*. This was surprising, since Kumler, Schoolery, and Brutcher had shown that while the *exo*-C_3-proton in *endo*-3-chlorocamphor (XIVa) is split into a doublet by the adjacent

(15) (a) L. Schmerling, *J. Am. Chem. Soc.*, **68**, 195 (1946); (b) J. D. Roberts, L. Urbanek, and R. Armstrong, *ibid.*, **71**, 3049 (1949); **72**, 3329 (1950).

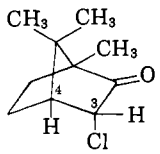
(16) E. J. Corey, R. Hartmann, and P. A. Vatakencherry, *ibid.*, **84**, 2611 (1962), and references cited therein.

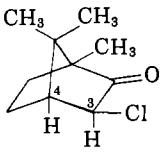
(17) H. Krieger, *Suomen Kemi.*, **B31**, 112, 175, 820, 340, 348 (1958).

(18) (a) L. Schmerling, J. R. Luvisi, and R. W. Welch, *J. Am. Chem. Soc.*, **78**, 2819 (1956); (b) S. Winstein, *ibid*, **83**, 1516 (1961); (c) T. E. Traylor and A. W. Baker, *ibid.*, **85**, 2746 (1963).

(19) (a) J. D. Roberts, E. R. Trumbull, Jr., W. Bennett, and R. Armstrong, *ibid.*, **72**, 3116 (1950); (b) C. D. Ver Nooy and C. S. Rondesvedt, Jr., *ibid.*, **77**, 3583 (1955).

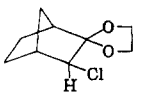
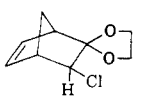
bridgehead proton (C_4), the *endo*-C_3 proton in the epimeric *exo*-3-chlorocamphor (XIVb) remains unsplit.[20]


XIVa


XIVb

This observation, which is in accord with expectations based on the Karplus correlation of vicinal coupling constants with dihedral angles,[21] would appear to provide a very simple means of assigning configurations, and has been used for this purpose in the recent literature. The failure of the norbornanes listed in Tables I and II to follow this pattern points out the possible

TABLE I

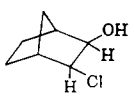
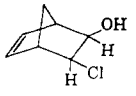
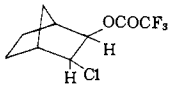
Compound[a]	τ (C_3H)	$J_{3,4}$, c.p.s.	J_3, *anti*-7, c.p.s.
IVa	5.71[b]	5.0	...
IIa	6.23	...	4.0
IX	5.72[b]	4.0	...
VIII	6.07	...	3.0
IVb	5.83[b]	5.0	...
IIb	6.23	...	3.5
XVIb	6.00[b]	4.0	...
XVb	6.20 (*singlet*)	...	...
XVb	6.13 (*singlet*)	...	...
	6.65	...	3.0
III	5.94	...	2.5
	6.60	...	2.5

[a] See text for structural formulas not shown in table. [b] All compounds with an *exo*-3-proton show an additional "long-range" coupling with the *exo*-5-proton ($J_{3,5} \cong 1$ c.p.s.), first noted by Anet.[22d]

danger in the case of a norbornane of using an observed n.m.r. splitting to identify an *exo* proton, and suggests that a "long-range" coupling with a J-value comparable

TABLE II

AB PORTION OF ABX PATTERNS[a]

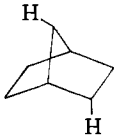
Compound	Centers of doublets, c.p.s.	Separation in doublets, c.p.s. ($J_{2,7}$ and $J_{3,7}$)
	219 225 236 242	2
	224 230 237 243	2
	288 294 242 248	2

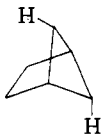
[a] Unpublished results of S. S. Labana. Each compound in this table shows a quartert of doublets at low field corresponding to the AB portion of an ABX pattern, where A = *endo*-2-proton, B = *endo*-3-proton, X = *anti*-7-proton.

(20) W. D. Kumler, J. N. Schoolery, and F. V. Brutcher, Jr., *J. Am. Chem. Soc.*, **80**, 2533 (1958).

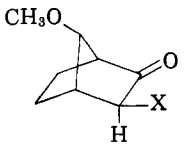
(21) M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959).

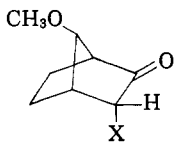
to the vicinal one may occur. The three possible protons which might be responsible for this coupling in a norbornane are the C_1-, *syn*-C_7-, and *anti*-C_7-protons, since these are all absent in bornane derivatives. Of these three, the *anti*-C_7-proton appeared to be the most likely candidate, in view of the similarity of the geometrical relationship between the *endo*-C_3- and the *anti*-C_7-protons in a norbornane (A) and the *endo*-C_5- and *endo*-C_6-protons in a bicyclo[2.1.1]hexane (B), for which a 7 c.p.s. coupling constant is observed.[22a,b]


A


B

This hypothesis was tested by preparing *exo*-3-bromo-*anti*-7-methoxynorbornane (XVa), *exo*-3-chloro-*anti*-7-methoxynorbornane (XVb), and its *endo* isomer XVI, using the nitrosyl halide additions and levulinic


XV


XVI

a, X = Br; b, X = Cl

acid hydrolysis techniques described above. The n.m.r. data for these compounds, summarized toward the end of Table I, show that the replacement of the *anti* proton at C_7 by a methoxyl group causes the *endo*-C_3-proton to appear as a singlet, confirming the hypothesis that the "anomalous" splitting is caused by interaction with the *anti*-C_7-protons. Table II summarizes some essential features of the spectra of some related norbornanes in which the same sort of long-range coupling appears, but with a J of about 2 c.p.s. The spectra in these cases are more complex because of the greater number of protons which interact.

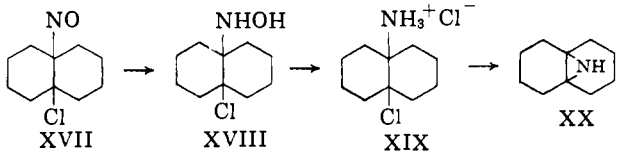
Addition to Δ^9-Octalin.—So far it has been shown that the addition of nitrosyl chloride and bromide to a number of norbornenes gives *cis-exo* adducts even where good opportunities for other reaction paths were provided. It seemed desirable, however, to study at least one nitrosyl chloride addition reaction to a simple, unstrained olefin. The olefin chosen was Δ^9-octalin, which is known to give a blue, crystalline, monomeric nitrosochloride, XVII.[23,24] Since this adduct has the nitroso group on a tertiary carbon atom, it was

(22) (a) J. Meinwald and A. Lewis, *J. Am. Chem. Soc.*, **83**, 2769 (1961); (b) K. B. Wiberg, B. R. Lowry, and B. J. Nist, *ibid.*, **84**, 1594 (1962); (c) A. Rassat, C. W. Jefford, J. M. Lehn, and B. Waegell, *Tetrahedron Letters*, **5**, 233 (1964); (d) F. A. L. Anet, *Can. J. Chem.*, **39**, 789 (1961); (e) Comprehensive discussions of the n.m.r. spectra of norbornanes have recently been provided by E. I. Snyder and B. Franzus, *J. Am. Chem. Soc.*, **86**, 1166 (1964), and by P. Laszlo and P. von R. Schleyer, *ibid.*, **86**, 1171 (1964).

(23) (a) W. Hückel and M. Blohm, *Ann.*, **502**, 114 (1933); (b) W. G. Dauben, E. C. Martin, and G. Fonken, *J. Org. Chem.*, **23**, 1205 (1958); (c) A. S. Hussey, J. Sauvage, and R. H. Baker, *ibid.*, **26**, 256 (1961).

(24) The nitrosochloride XVIII was prepared as previously described, and its n.m.r. spectrum was examined to see whether it would provide any preliminary indication of its stereochemistry. The spectrum of this material showed a remarkable amount of detail for a decalin, with well-resolved peaks extending from 6.5 to 9.5 τ. It is apparent that a number of the decalin protons experience unusually large chemical shifts, presumably owing to the magnetic anisotropy of the nitrosyl group. We hope to be able to explore the implication of this observation in more detail in a subsequent study.

hoped that the configuration at both the nitrogen- and the chlorine-bearing carbon atoms could be demonstrated directly. The scheme chosen was to reduce the nitrosochloride XVIII to the corresponding chloramine, with retention of configuration at both tertiary carbon atoms, and to see whether base treatment gives an aziridine (*trans* precursor) or an unsaturated amine (*cis* precursor).



The reduction of XVII was successfully accomplished by stepwise catalytic hydrogenation. Prereduced Adams catalyst in ethyl acetate converts XVII to 9-hydroxylamino-10-chlorodecalin (XVIII),[23a] and subsequent reduction of XVIII in ethanolic aqueous hydrochloric acid with freshly prereduced Adams catalyst gave a smooth conversion to the desired chloroamine hydrochlorido XIX. Treatment of XIX with aqueous potassium hydroxide afforded the pure aziridine XX in good yield, establishing a *trans* configuration for the initial adduct XVII. The structure of XX was proved on the basis of its elementary analysis, infrared spectrum, and n.m.r. spectrum.

Attempts to carry out the same conversion (XVII → XIX) in one step with Adams catalyst in acetic acid and hydrochloric acid, or using sodium dithionate, were unsuccessful. Lithium aluminum hydride reduction also failed to take the desired course, giving 10-hydroxylamino-$\Delta^{1,9}$-octalin[23a] as the only readily characterizable product. Stannous chloride reduction gave a large amount of neutral product. If the crude reaction mixture was treated directly with base without attempting to isolate intermediates using the method of Closs,[8] the desired aziridine XX was obtained in modest yield, contaminated with 10-hydroxylamino-$\Delta^{1,9}$-octalin. The fixed *trans* diaxial conformation of the nitroso and chloro groups in XVII is probably responsible for the ready formation of side products in this sequence.

Discussion

We can see from the above results that the steric course of nitrosyl halide addition to olefins depends on the olefin structure. Thus, Δ^9-octalin gives a *trans* adduct, in accord with the generally assumed ionic reaction mechanism, and it is probable that most other unstrained olefins behave similarly.[9] On the other hand, norbornene and norbornadiene form unrearranged, *cis* adducts, suggesting that if these reactions are ionic ones, very little electron demand is made on these olefins in the transition state. Most electrophilic additions to norbornanes involve a combination of *trans* addition and skeletal rearrangement[18]; however, there is a close similarity between the pattern of reactivity uncovered in this work and that shown in the oxymercurization reaction. *Unstrained* olefins undergo *trans* addition *via* an electrophilic mechanisms, but norbornene has been shown to give a *cis*-oxymercuration product.[18c] Traylor has considered several explanations for this result; the one that finds the closest analogy to nitrosyl halide addition relies on a postulated steric resistance to *trans* opening of the intermediate "mercurinium" ion derived from norbornene. The similarity between these two reactions is not complete, however, since norbornadiene gives a *tricyclic* oxymercuration product,[18c] whereas nitrosyl chloride addition does not call the second double bond into play. One must conclude that there is greater carbonium character in the transition state for oxymercuration than there is for nitrosyl halide addition. The observation that norbornene-*endo*-5-carboxylic acid forms a *lactonic* mercuration product,[25] but an *acidic* nitrosochloride supports this conclusion. Finally, the lack of solvent intervention when nitrosochlorides are made in alcohol or acetic acid points in the same direction.

Although it is possible that norbornenes (and, by implication, similarly strained olefins) react by a 4-center mechanism to give *cis* adducts, this mechanism could not explain the *trans* addition to Δ^9-octalin. One possibility is, therefore, that two independent mechanisms are utilized for these two different types of substrate. Alternatively, a single mechanism can be postulated to accommodate both cases. As a first step, the olefin would react with the nitrosyl halide to give an onium ion, as discussed above, with the cyclic contributing structure being the most important. For an intermediate in which *trans* displacement of on of the C–N bonds is sterically acceptable, the cyclic intermediate is opened by attack of halide ion to give a *trans* adduct. For a more constrained substrate, in which such a *trans* displacement would require a difficult twisting about a C–C bond in a relatively inflexible system, it may be postulated that attack of halide ion from a *cis* position is more favorable, and a *cis* adduct results.

A decision between these possibilities does not seem possible on the basis of the data now available. It is hoped, however, that the demonstration of a relationship between the structure of an olefin and the stereochemistry of its derived nitrosyl halide adduct may prove useful.

Experimental

The Addition of Nitrosyl Chloride to Norbornene.—Norbornene (12.0 g., 0.127 mole) was dissolved in 150 ml. of chloroform and the resultant solution was cooled to −60° with a Dry Ice–acetone bath. Nitrosyl chloride (Matheson Co.) was bubbled slowly into the rapidly stirred solution until the blue color of the nitrosochloride monomer was replaced by a yellow-brown color characteristic of excess nitrosyl chloride. At this time, 360 ml. of hexane, previously cooled to −70°, was added rapidly and stirring was continued for 30 min. The yellow-brown slurry was filtered and, after washing with hexane, 13.5 g. (65%) of nitrosochloride dimer I was obtained. The crude product showed m.p. 145–150°. After one recrystallization in chloroform–hexane it showed m.p. 155.5–156.5°. The crude product had a characteristic infrared spectrum which differed from that of the crystallized product. The latter, however, had properties in good agreement with those reported by Miller[11a] and Beckmann.[10]

exo-**3-Chloronorcamphor (II).** (a)—The nitrosochloride dimer I (23.3 g., 0.073 mole) was stirred at 75° with 475 g. of levulinic acid and 35 ml. of 2 *N* hydrochloric acid until the solution became clear. The reaction mixture was cooled to room temperature and diluted with 1500 ml. of water. The resultant solution was extracted with ether. The ethereal extract was washed with water and saturated sodium bicarbonate solution, and dried over anhydrous magnesium sulfate. After removal of solvent at reduced

(25) (a) H. H. Henbest and B. Nicholls, *J. Chem. Soc.*, 227 (1959); (b) M. Malaiyandi and G. F. Wright, *Can. J. Chem.*, **41**, 1493 (1963); (c) T. G. Traylor and A. Factor, Abstracts, 147th National Meeting of the American Chemical Society, Philadelphia, Pa., April 6–10, 1964, p. 36N.

pressure, the product was distilled at 87–89° (4.5 mm.). The yield was 16.6–17.9 g. (79–85%); v.p.c. at 183° (15% Carbowax on firebrick column) showed one single peak at 10.2 min. A small sample was chromatographed on Merck acid-washed alumina using 10% methylene chloride–90% 30–60° petroleum ether as eluting solvent, and redistilled to give an analytical sample, b.p. 88–89° (4.5 mm.), $n^{28.5}$D 1.4941, infrared 5.69 μ, ultraviolet λ_{max}^{EtOH} 299 mμ (ϵ 36.4), $\lambda_{max}^{isooctane}$ 305 mμ (ϵ 40).

Anal. Calcd. for C_7H_9ClO: C, 58.14; H, 6.27; Cl, 24.52. Found: C, 58.41; H, 6.57; Cl, 24.30.

A 2,4-dinitrophenylhydrazone was prepared and recrystallized from ethanol; m.p. 149.5–151°.

Anal. Calcd. for $C_{13}H_{13}ClN_4O_4$: C, 48.08; H, 4.03; Cl, 10.92; N, 17.26. Found: C, 48.15; H, 4.15; Cl, 10.70; N, 17.01.

(b) Base-Catalyzed Chlorination of Norcamphor.—To a stirred solution of norcamphor (2.2 g., 0.02 mole) in 10 ml. of anhydrous ether under a nitrogen atmosphere was added 45.0 ml. (0.0225 mole) of 0.5 *M* triphenylmethylsodium in ether (Metallomer Laboratories) over a period of 10 min. The mixture was stirred for another 30 min. It was then heated to reflux and a stream of chlorine (passed through anhydrous sodium bicarbonate and dried over sulfuric acid followed by silica gel) was bubbled into the refluxing reaction mixture. The reaction mixture immediately decolorized and turned yellow as excess chlorine was added. The mixture was cooled to room temperature and was stirred for an additional 30 min. After pouring into water, the reaction mixture was extracted with ether. The ethereal extract was washed with saturated sodium bicarbonate solution and water. After drying and removal of ether, 4.5 g. of residue was obtained. Distillation gave 1.95 g. (68%) of IIa, b.p. 64–66° (1 mm.), n^{26}D 1.4955. The infrared spectrum was identical with that of IIa prepared above; v.p.c. analysis showed the presence of less than 1% of the *endo* isomer IVa.

***endo*-3-Chloronorcamphor (IVa).**—A mixture of 2.1 g. of IIa, 4.0 g. of potassium carbonate, and 30 ml. of water was refluxed under a nitrogen atmosphere for 1.5 hr. At the end of this period, the reaction mixture was cooled and extracted with ether. The ether layer was washed with water and dried over magnesium sulfate; v.p.c. analysis (183°, Carbowax column) showed two well resolved peaks identified as IIa (retention time 10.3 min.) and IVa (retention time 14.0 min.) in the ratio of 45 to 55%. Preparative v.p.c. at 185° allowed separation of the mixture and afforded both the previously described *exo* isomer IIa and the *endo* isomer IVa, m.p. 53–56°; IVa was further purified by sublimation at 30° (0.08 mm.) to give an analytical sample, m.p. 57–58.5°, ultraviolet λ_{max}^{EtOH} 300 mμ (ϵ 48), infrared (CS_2) 5.69 μ.

Anal. Calcd. for C_7H_9OCl: C, 58.14; H, 6.27; Cl, 24.52. Found: C, 57.84; H, 6.24; Cl, 23.34.

A 2,4-dinitrophenylhydrazone was prepared and recrystallized from ethanol; m.p. 159–159.5°.

Anal. Calcd. for $C_{13}H_{13}ClNO_4O$: C, 48.08; H, 4.03; Cl, 10.92; N, 17.26. Found: C, 48.24; H, 4.20; Cl, 10.62; N, 17.29.

***exo*-3-Chloronorcamphor Ethylene Dithioketal (III).**—To a solution of 0.5 g. (3.5 mmoles) of IIa in 0.6 g. (4.5 mmoles) of ethane-1,2-dithiol was added a few drops of boron trifluoride etherate (Eastman, White Label) with thorough mixing.[26] The mixture was left standing at room temperature for 6 hr. The excess dithiol was removed at 55–65° under reduced pressure. The viscous residue was crystallized from 30–60° petroleum ether at −50° to give 0.39 g. (51%) of dithioketal III, m.p. 41.5–45°. The analytical sample, m.p. 44–45.5°, was recrystallized from petroleum ether.

Anal. Calcd. for $C_9H_{13}S_2Cl$: C, 48.96; H, 5.93; S, 29.05; Cl, 16.06. Found: C, 48.97; H, 6.00; S, 29.07; Cl, 15.65.

Desulfurization of III.—To a suspension of 3 g. of W-2 Raney nickel[27] in 10 ml. of cyclohexane was added 360 mg. (1.5 mmoles) of III. The mixture was shaken until solution of dithioketal was complete, and it was then heated to reflux for 4 hr.; v.p.c. analysis of the supernatant liquid (15% Carbowax on firebrick, 130°) showed the presence of three components with retention times of 4.5, 7.8, and 11.5 min., with the fastest peak as the major product. Separation of the components of preparative v.p.c. afforded 28 mg. (13%) of 2-*exo*-chlorononbornane, n^{24}D 1.4830. The infrared spectrum of this material was identical with that of authentic 2-*exo*chlorononbornane, b.p. 54–55° (16 mm.), n^{24}D 1.4831, prepared by the method of Schmerling.[15a] The second component was proved to be norcamphor by comparison of its infrared spectrum with that of authentic norcamphor. The third component was not obtained in sufficient amount for further investigation.

The Addition of Nitrosyl Chloride to Norbornadiene.—The nitrosochloride dimer VI was prepared in 55–75% yield according to the method of Wilder.[11b] The crude product had m.p. 150–156° dec. After recrystallization from chloroform–hexane, VI showed m.p. 164.5–165°.

***exo*-3-Chlorodehydronorcamphor (VIII)** was prepared according to the procedure described above for IIa. It required 3 days for the solution to become clear. The yield of VIII was 65–70%, b.p. 78–80° (7 mm.); v.p.c. analysis (183°, Carbowax) showed a single peak (retention time 9.8 min.). An analytical sample was further purified by chromatography and redistilled at 83–84° (8.5 mm.). It showed n^{23}D 1.5111, infrared 5.72 μ, ultraviolet λ_{max}^{EtOH} 312 mμ (ϵ 252), $\lambda_{max}^{isooctane}$ 317 mμ (ϵ 167).

Anal. Calcd. for C_7H_7ClO: C, 58.95; H, 4.95; Cl, 24.58. Found: C, 58.89; H, 5.25; Cl, 24.28.

The 2,4-dinitrophenylhydrazone showed m.p. 158.5–160°, λ_{max}^{EtOH} 359 mμ (ϵ 22,600).

Anal. Calcd. for $C_{13}H_{11}ClN_4O_4$: C, 48.38; H, 3.44; N, 17.36; Cl, 10.99. Found: C, 48.43; H, 3.59; N, 17.39; Cl, 11.06.

Hydrogenation of VIII.—A solution of VIII (480 mg. 3.36 mmoles) in 15 ml. of ethyl acetate was hydrogenated over prereduced platinum dioxide at room temperature. Hydrogen uptake came to 83.4 ml. in 4 hr. (99% of theory). After removal of the catalyst and solvent, the residue was distilled at 90–92° (9 mm.) to give 416 mg. (86%) of IIa, n^{23}D 1.4956. The infrared spectrum of this product was superimposable on that of the material prepared by levulinic acid hydrolysis of I. A mixture melting point of the corresponding 2,4-dinitrophenylhydrazones showed no depression.

***endo*-3-Chlorodehydronorcamphor (IX).**—The equilibration of VIII in aqueous potassium carbonate solution was carried out as described above for the equilibration of IIa. From 2.1 g. of VIII, 1.7 g. (81% recovery) of the equilibrium mixture containing 55% of the *exo* isomer VIII (v.p.c. 183°, Carbowax, retention time 9.8 min.) and 45% of the *endo* isomer IX (v.p.c. 183°, Carbowax, retention time 11.8 min.) was obtained. Pure IX was obtained by preparative v.p.c. at 185°. The analytical sample showed n^{27}D 1.5102, infrared 5.72 μ, ultraviolet λ_{max}^{EtOH} 312 mμ (ϵ 226).

Anal. Calcd. for C_7H_7OCl: C, 58.95; H, 4.95; Cl, 24.58. Found: C, 59.07; H, 5.10; Cl, 24.82.

The 2,4-dinitrophenylhydrazone was recrystallized from ethanol, m.p. 179.5–180°.

Anal. Calcd. for $C_{13}H_{11}N_4O_4Cl$: C, 48.38; H, 3.44; N, 17.36; Cl, 10.99. Found: C, 48.19; H, 3.54; N, 17.38; Cl, 10.84.

The Equilibration of *endo*-3-Chlorodehydronorcamphor (IX) in Aqueous Potassium Carbonate Solution.—A 25-mg. sample of IX was refluxed in aqueous potassium carbonate solution as described above; v.p.c. analysis of the product showed the presence of a mixture containing 56% of the *exo* isomer VIII and 44% of the *endo* isomer IX.

Hydrogenation of IX.—A 162-mg. (1.35 mmoles) sample of IX was hydrogenated as described above for the *exo* isomer VIII. The product IVa was obtained in 64% yield, m.p. 50–54°. The infrared spectrum was identical with that of IVa obtained previously.

***exo*-3-Chlorodehydronorcamphor Ethylene Ketal.**—To a solution of 5.0 g. (0.035 mole) of VIII in 125 ml. of benzene was added 6.25 g. (0.10 mole) of ethylene glycol and 0.30 g. of *p*-toluenesulfonic acid monohydrate. The reaction mixture was stirred and refluxed for 12 hr. with azeotropic removal of benzene–water. The remaining benzene was removed by distillation, and the residue was taken up in ether, washed with saturated sodium bicarbonate solution, and water. After drying and removal of ether, the ethylene ketal was distilled at 80–81° (2.2 mm.) to give a product showing n^{25}D 1.5090. The yield was 5.7 g. (87%).

Anal. Calcd. for $C_9H_{11}O_2Cl$: C, 57.91; H, 5.94; Cl, 19.00. Found: C, 57.99; H, 6.06; Cl, 19.26.

***exo*-3-Chloronorcamphor Ethylene Ketal.**—A 0.515-g. sample of 3-*exo*-chlorodehydronorcamphor ethylene ketal was hydrogenated in ethyl acetate over prereduced platinum dioxide to give 0.44 g. (85%) of the saturated ethylene ketal, b.p. 83–86° (3–3.2 mm.), n^{27}D 1.4975.

Anal. Calcd. for $C_9H_{13}O_2Cl$: C, 57.30; H, 6.94; Cl, 18.80. Found: C, 57.38; H, 7.24; Cl, 18.57.

(26) L. F. Fieser, *J. Am. Chem. Soc.*, **76**, 1945 (1954).

(27) R. Mozingo, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 181.

The Addition of Nitrosyl Bromide to Norbornene.—Norbornene (4.7 g., 0.08 mole) and isoamyl nitrite (7.02 g., 0.06 mole) were dissolved in 10 ml. of ethanol and cooled to about 0° in an ice–salt bath. A solution of 10 g. of 48% hydrobromic acid (0.59 mole) in 12 ml. of ethanol was added dropwise with stirring over a 30-min. period. Stirring at ice bath temperature was continued for another 10–20 min. after the addition was completed. The nitrosobromide dimer V was collected by filtration and washed with ethanol. The yield was 8.1 g. (80%), m.p. 134–136°. An analytical sample, m.p. 138–139°, was obtained by recrystallization from chloroform.

Anal. Calcd. for $(C_7H_{10}NOBr)_2$: C, 41.20; H, 4.94; N, 6.86; Br, 39.16. Found: C, 41.01; H, 4.85; N, 6.82; Br, 39.28.

***exo*-3-Bromonorcamphor (IIb).**—The levulinic acid hydrolysis of V was carried out essentially as described above in the hydrolysis of I. The amount of levulinic acid used was reduced to three times the weight of the dimer, and hydrobromic acid was used instead of hydrochloric acid.[28] The ketone IIb was obtained in 84% yield, b.p. 66–67° (0.55 mm.), m.p. 30–32°; v.p.c. (Carbowax, 170°) showed one single fraction (retention time 12 min.). The infrared spectrum of this ketone, with its carbonyl band at 5.70 μ, was identical with that reported by Krieger.[17]

***endo*-3-Bromonorcamphor (IVb).**—The *exo*-bromoketone IIb was equilibrated to a mixture of 56–60% of IIb and 44–40% of IVb in aqueous potassium carbonate, as described above. The mixture was separated by chromatography on silica gel (BDH) using 20% ether in petroleum ether as eluting agent. The combined fractions of the *endo* isomer (Carbowax, column, 170°, retention time 15.5 min.), after distillation, showed it contained less than 2% of the *exo* compound. Its infrared spectrum, with its carbonyl band at 5.68 μ, was identical with that published by Krieger.[17]

A 0.5-g. sample of the mixture of epimers (60% *exo* and 40% *endo*) was treated with 1.5 g. of levulinic acid and 0.5 ml. of 1 *N* HBr at 70° under a nitrogen atmosphere for 24 hr. The recovered material proved in vapor phase chromatography to contain 56% IIb and 44% IVb.

***anti*-7-Methoxynorbornene.**—A solution of 11.7 g. (0.106 mole) of *anti*-7-norbornenol, prepared by the method of Story,[29] in 30 ml. of dry benzene was addded dropwise to a suspension of 7 g. of sodium hydride (Metal Hydrides, Inc.) in 100 ml. of dry benzene under a nitrogen atmosphere with stirring. The mixture was stirred at room temperature for 6 hr. and 28.4 g. (0.2 mole) of methyl iodide was added. The reaction mixture was heated to 75°, and stirring was continued for 3 hr. At the end of that period, the reaction mixture was cooled and 25 ml. of water was introduced slowly. The organic layer was separated, washed with water, and dried with magnesium sulfate. After careful removal of solvent, the residue was distilled at 91-92° (160 mm.) to give 9.9 g. (80% yield) of the methyl ether.

Anal. Calcd. for $C_8H_{12}O$: C, 77.37; H, 9.74. Found: C, 78.07; H, 9.46.

Addition of Nitrosyl Chloride to *anti*-7-Methoxynorbornene.—A dimeric nitrosochloride adduct was prepared in 40% yield using the method described for the addition of nitrosyl chloride to norbornadiene. The crude product showed m.p. 162–163° dec. Recrystallization from chloroform gave an analytical sample, m.p. 167–168°.

Anal. Calcd. for $C_8H_{12}ClNO_2$: C, 50.66; H, 6.38; N, 7.39; Cl, 18.70. Found: C, 50.36; H, 6.38; N, 7.20; Cl, 18.51.

Addition of Nitrosyl Bromide to *anti*-7-Methoxynorbornene.—The addition was carried out in 48% yield as described in the nitrosyl bromide addition to norbornene. The crude product, m.p. 142–143°, was recrystallized from chloroform–ethanol. The recrystallized material showed m.p. 152–153°.

Anal. Calcd. for $C_8H_{12}BrNO_2$: C, 41.04; H, 5.17; N, 5.98; Br, 34.14. Found: C, 40.64; H, 5.32; N, 5.99; Br, 34.56.

***anti*-7-Methoxy-*exo*-3-Chloronorcamphor XVb.**—The crude dimeric nitrochloride adduct (1 g.) was treated with 3 g. of levulinic acid and 1.8 g. of 1 *N* hydrochloric acid at 90–95° for 24 hr. with stirring. After the same work-up as described above, the crude product (0.9 g.) appeared as a light brown oil. This material was purified by chromatography on a 30-g. silica gel (BDH) column, eluting with 20% ether in petroleum ether, followed by distillation at 100° (14 mm., bath temperature), to give 0.527 g. of pure XVb; v.p.c. (Carbowax column, 160°) showed a single peak with a retention time of 15.5 min.

Anal. Calcd. for $C_8H_{11}ClO_2$: C, 55.02; H, 6.35; Cl, 20.30. Found: C, 55.04; H, 6.55; Cl, 20.08.

***anti*-7-Methoxy-*endo*-3-chloronorcamphor (XVI).**—The *exo*-chloroketone XVb was equilibrated to a mixture of XVb and XVI as described above; v.p.c. analysis of the mixture (Carbowax column, 170°) showed it to contain 57% of XVb (retention time 12 min.) and 43% of XVI (retention time 20 min.). Pure XVI was obtained by chromatography of the mixture on silica gel, and was distilled at 94° (4.5 mm., bath temp.).

Anal. Calcd. for $C_8H_{11}ClO_2$: C, 55.02; H, 6.35; Cl, 20.30. Found: C, 55.19; H, 6.36; Cl, 19.86.

***anti*-7-Methoxy-*exo*-3-bromonorcamphor (XVa)** was prepared as described above for XVb, using 1 *N* hydrobromic acid instead of hydrochloric acid. The pure *exo*-bromoketone was distilled at 78° (0.6 mm.).

Anal. Calcd. for $C_8H_{11}BrO_2$: C, 43.85; H, 5.06; Br, 36.48. Found: C, 43.55; H, 5.07; Br, 36.42.

Addition of Nitrosyl Chloride to Norbornene-*endo*-5-carboxylic Acid. (a)—A mixture of 2 g. of norbornene-*endo*-5-carboxylic acid and 2.5 g. of isoamyl nitrite in 8 ml. of 95% ethanol was cooled in an ice–salt bath. A solution of 2.8 ml. of concentrated hydrochloric acid in 5 ml. of 95% ethanol was added with stirring in 15 min. Stirring was continued at ice bath temperature for 1.5 hr. The reaction mixture was poured into 50 ml. of 10% sodium carbonate solution and diluted with 50 ml. of water. The basic aqueous solution was washed with ether thoroughly. Upon evaporation of the ether layer, the infrared spectrum of the neutral product showed the presence of isoamyl alcohol, but no carbonyl absorption. The basic aqueous layer was acidified with hydrochloric acid and extracted with four 20-ml. portions of ether. The ethereal extract was washed with water, dried, and evaporated to dryness to give 2.3 g. of semisolid residue. Upon trituration with ethanol, a solid precipitate, m.p. 155–168°, was obtained. The solid was recrystallized from acetone giving an analytical sample, m.p. 182–183° dec.

Anal. Calcd. for $C_8H_{10}ClNO_3$: C, 47.18; H, 4.95; N, 6.88; Cl, 17.41. Found: C, 47.38; H, 5.09; N, 6.71; Cl, 17.04.

(b)—To a solution of 2.8 g. (0.02 mole) of norbornene-*endo*-5-carboxylic acid in 30 ml. of chloroform, cooled in a Dry Ice–acetone bath to $\sim -60°$, was added a cooled solution of 1.4 g. of nitrosyl chloride in 5 ml. of chloroform in 0.5 hr. with stirring. The reaction mixture was allowed to warm up to about $-20°$, and was stirred for an additional 15 min. The excess nitrosyl chloride was removed under reduced pressure, and the reaction mixture was extracted with 10% sodium carbonate solution. Upon acidification of the basic layer, the semisolid was extracted with ether. After concentration of the ether layer, a crop of crystalline, acidic dimer (0.8 g.), m.p. 175–178°, was obtained. Recrystallization from acetone raised the m.p. to 182–183°. This material is identical with that obtained in the previous experiment. From the ether mother liquor, a second crop of solid (1.6 g.), m.p. 158–170°, was obtained. After recrystallization, an acid, m.p. 173–174°, was obtained. The residue appeared as 1.2 g. of viscous glass. The total weight of acidic dimer was 3.6 g. (90%).

Anal. Calcd. for $C_8H_{10}ClO_3N$: C, 47.18; H, 4.95. Found: C, 47.01; H, 5.02.

9-Nitroso-10-chlorodecalin (XVII).—Δ^9-Octalin was prepared by the dehydration of decahydronaphthol-2 according to the procedure of Baker, Sauvage, and Hussey.[23c] The blue nitrosyl chloride adduct was purified by recrystallization from acetone, followed by sublimation at 55° (0.1 mm.). The pure adduct showed m.p. 90–91°.

Lithium Aluminum Hydride Reduction of XVII.—A solution of 1 g. (0.005 mole) of XVII in 100 ml. of anhydrous ether was added dropwise to a suspension of 0.3 g. of lithium aluminum hydride in 5 ml. of anhydrous ether with stirring and cooling over a 15-min. period. The reaction mixture was stirred for 15 min. more and worked up by decomposing the excess lithium aluminum hydride with water. The solid inorganic salts were removed by filtration and washed with ether. The combined ether solution was washed once with saturated sodium chloride solution, dried, and evaporated to give 0.8 g. of a mixture of crystals and oil. After addition of pentane, 0.37 g. of 10-hydroxylamino-$\Delta^{1,9}$-octalin, m.p. 133–136° dec., was obtained (lit.[23a] m.p. 138-143° dec.) n.m.r.: 4.39 τ for olefinic proton, 4.61 τ for amino proton and hydroxyl proton.

(28) The use of hydrochloric acid in this step causes some halogen exchange and gives a product contaminated with *exo*-3-chloronorcamphor.

(29) P. R. Story, *J. Org. Chem.*, **26**, 287 (1961).

Anal. Calcd. for $C_{10}H_{17}NO$: C, 71.81; H, 10.35; N, 8.38. Found: C, 71.77; H, 10.35; N, 8.38.

From the mother liquor, the residue appeared as a mixture of basic products which was not further characterized. If the reaction was allowed to stand overnight before working up, the only isolable product was still 10-hydroxylamino-$\Delta^{1,9}$-octalin.

Reduction of XVII with Stannous Chloride.—The nitrosochloride adduct XVII (1 g., 0.005 mole) was added to a mixture of 4.5 g. of stannous chloride dihydrate in 6 ml. of concentrated hydrochloric acid with vigorous stirring. The reaction mixture was warmed on a water bath at 55–60°. The blue color disappeared after 30 min. The water bath was removed and stirring continued for another hour. The reaction mixture was diluted with water and washed with petroleum ether three times to remove any neutral products. The acidic solution was neutralized carefully with 10% sodium bicarbonate solution and extracted with ether. The ether layer was washed with saturated sodium chloride solution and dried over magnesium sulfate. Upon removal of solvent, the residue partially solidified. Recrystallization from hexane gave 0.2 g. of 9-hydroxylamino-10-chlorodecalin (XVIII), m.p. 116–117.5° (lit.[23a] 116–120°); n.m.r. 4.38 τ for amino proton and hydroxyl proton).

Anal. Calcd. for $C_{10}H_{18}ClNO$: C, 58.96; H, 8.90; N, 6.87; Cl, 17.41. Found: C, 58.66; H, 8.89; N, 6.66; Cl, 17.23.

The hydroxylamine hydrochloride was prepared by treatment of this product with ethereal hydrogen chloride; m.p. 169–170° dec. (lit.[23a] 172–174°).

The hexane mother liquor yielded no other pure components.

Reduction of XVII with Stannous Chloride Followed by Treatment with Base.—Compound XVII (2.0 g., 0.01 mole) was reduced with stannous chloride and concentrated hydrochloric acid as described above. After the same work-up, 1 g. of crude basic product was obtained. The basic mixture was treated with a solution of 6 g. of sodium hydroxide in 50 ml. of water and steam distilled. The distillate was collected in an ice bath until it was no longer cloudy. The distillate was extracted with ether and the ether layer dried with magnesium sulfate. After careful removal of the ether, 0.6 g. of an oil containing some crystals was obtained. Upon trituration with pentane, 0.1 g. of 10-hydroxylamino-$\Delta^{1,9}$-octalin, m.p. 133–136° dec., was obtained. The pentane mother liquor was evaporated to dryness, and the oily residue (0.43 g.) was distilled at 60–70° (1.5–2 mm.). Although thin layer chromatography on silica gel of the distilled sample showed two spots with one predominating, the infrared and n.m.r. spectra of this sample are essentially identical with those of the pure ethylenimine XX prepared and characterized by the method described below.

9-Amino-10-chlorodecalin Hydrochloride (XIX).—9-Nitroso-10-chlorodecalin (1 g.) was hydrogenated in ethyl acetate using prereduced platinum dioxide catalyst. The hydrogenation was completed in 2 hr. and stopped after 1 molar equivalent of hydrogen was absorbed. After removal of the catalyst and solvent, the solid residue was recrystallized from hexane to give 0.8–0.9 g. of crystals of XVIII, m.p. 116–118° dec.

A solution of XVIII (187 mg.) in 5 ml. of dilute hydrochloric acid and 5 ml. of ethanol was hydrogenated with prereduced platinum dioxide in dilute hydrochloric acid. The reduction was over in 3 hr. The catalyst was removed by filtration and the filtrate concentrated by warming on a steam bath under a stream of dry nitrogen. The amine hydrochloride (188 mg.) crystallized as plates, m.p. 233–235° dec. A small sample was recrystallized from water for analysis, yielding colorless crystals, m.p. 235–237° dec.

Anal. Calcd. for $C_{10}H_{19}NCl_2$: C, 53.58; H, 8.54; N, 6.25; Cl, 31.63. Found: C, 53.51; H, 8.59; N, 6.11; Cl, 31.52.

11-Azatricyclo[4.4.1.0^{1,6}]undecane (XX).—A mixture of 1.05 g. of 9-amino-10-chlorodecalin hydrochloride (XIX) and 8 g. of sodium hydroxide in 80 ml. of water was heated to boiling, and the distillate collected in an ice–water bath, until it was no longer cloudy. The aziridine steam distilled with the water and was extracted into ether. The ether extract was dried and evaporated. The residual oil was distilled at 75–90° (1.5 mm., bath temp.) to give 0.545 g. (78%) of XX indicated by thin layer chromatography on silica gel to be a single component. The infrared spectrum showed weak absorption at 3.10 μ. The n.m.r. spectrum showed two unresolved multiplets centered at 8.58 and 8.28 τ. No absorption in the olefinic region was observed.

Anal. Calcd. for $C_{10}H_{17}N$: C, 79.41; H, 11.33; N, 9.26. Found: C, 79.14; H, 11.32; N, 9.12.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, TEXAS CHRISTIAN UNIVERSITY, FORT WORTH 29, TEXAS]

Stereochemistry of the Reaction of Benzal Chloride with Olefins

BY JOE E. HODGKINS, JAMES D. WOODYARD, AND DANNY L. STEPHENSON

RECEIVED FEBRUARY 19, 1964

Benzal chloride and potassium *t*-butoxide react in cyclohexene to form both 7-chloro-7-phenylnorcaranes. These compounds can be reduced by various reagents with either inversion or retention of configuration to give both 7-phenylnorcaranes. *endo*- and *exo*-7-phenylnorcarane have been separated and characterized. Benzal chloride and potassium *t*-butoxide form the expected cyclopropane derivatives with 1-heptene, 2,4-dimethyl-2-pentene, and *cis*- and *trans*-4-methyl-2-pentene. A study of the products from the latter olefins showed the reaction to be stereospecific and somewhat stereoselective.

In 1954, Doering and Hoffmann[1] obtained 7,7-dichloronorcarane (7,7-dichlorobicyclo[4.1.0]heptane) from the reaction of potassium *t*-butoxide, chloroform, and cyclohexene. This was the first structural evidence of the postulated dichlorocarbene intermediate proposed by Hine[2] for the alkaline hydrolysis of chloroform. This "divalent carbon reaction" has been extended to include the base-catalyzed reactions of a number of other halogen-substituted compounds in the presence of olefins.[3a-f] In the more specific case of phenyl-substituted chloromethanes, Closs and Closs[4] have shown that benzyl chloride and *n*-butyllithium react with cyclohexene to form a mixture of 7-phenylnorcaranes, which was characterized, but the two isomers were not separated. McElvain and Weyna[5a,b] have isolated 1,1-dimethyl-2,2-diethoxy-3-phenyl-3-chlorocyclopropane from the reaction of sodium *t*-butoxide and benzal chloride in dimethylketene diethyl acetal. Recently, Moss[6] studied the reaction of benzal chloride with some olefins and developed an improved reaction employing methyllithium as the base. It was our purpose to study the stereochemistry and behavior of the reaction of benzal chloride and potassium *t*-butoxide with several olefins.

(1) W. von E. Doering and A. K. Hoffmann, *J. Am. Chem. Soc.*, **76**, 6162 (1954).

(2) J. Hine, *ibid.*, **72**, 2438 (1950).

(3) (a) P. S. Skell and A. Y. Garner, *ibid.*, **78**, 5430 (1956); (b) G. L. Closs and L. E. Closs, *ibid.*, **81**, 2579 (1959); (c) W. von E. Doering and W. A. Henderson, *ibid.*, **80**, 5274 (1958); (d) W. E. Parham, E. C. Loew, and E. E. Schweizer, *J. Org. Chem.*, **24**, 1900 (1959); (e) L. Friedman and J. G. Berger, *J. Am. Chem. Soc.*, **83**, 5758 (1960); (f) P. S. Skell and A. P. Krapcho, *ibid.*, **83**, 754 (1961).

(4) G. L. Closs and L. E. Closs, *Tetrahedron Letters*, **No. 24**, 26 (1960).

(5) (a) S. M. McElvain and P. L. Weyna, *J. Am. Chem. Soc.*, **81**, 2579 (1959); (b) R. Breslow, R. Haynie, and J. Mirra, *ibid.*, **81**, 247 (1959).

(6) R. A. Moss, *J. Org. Chem.*, **27**, 2683 (1962).