

## COMMUNICATIONS TO THE EDITOR

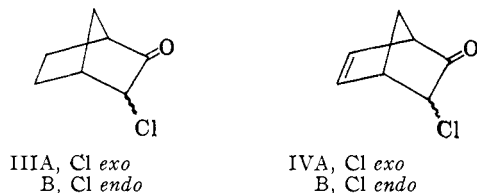
The Steric Course of Nitrosyl Halide Additions to Norbornene and Norbornadiene<sup>1</sup>

Sir:

The addition of nitrosyl chloride to olefins has been of considerable importance in the development of terpene chemistry.<sup>2,3</sup> To enable more rational use of these reactions, we have studied their stereochemistry. The olefins chosen for study were norbornene (I) and norbornadiene (II), and the results obtained cast some light on the addition mechanism.

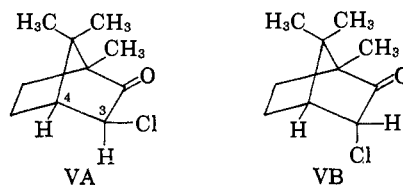


It is well established<sup>4-6</sup> that nitrosyl chloride adds to both I and II without rearrangement. One indication of this is given by the fact that the resultant adducts yield unrearranged  $\alpha$ -chloroketones (III and IV) upon levulinic acid hydrolysis.<sup>7</sup>



The failure of these olefins to rearrange is significant in view of the generally quoted stepwise, ionic addition mechanism ( $\text{NO}^+$ ,  $\text{Cl}^-$ ),<sup>8</sup> especially since norbornadiene is usually prone to rearrangement in reactions with electrophiles.<sup>9</sup>

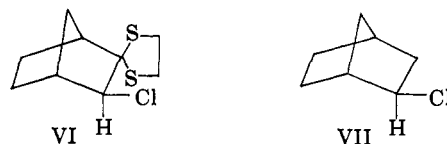
The chloroketone (III) appears homogeneous on the basis of vapor phase and thin layer chromatography; the decision as to whether it possesses an *exo* or *endo* chlorine (IIIA or IIIB) might be expected to be simple on the basis of n.m.r. evidence. Thus, the closely analogous  $\alpha$ -chlorocamphors show the  $\text{C}_3$  proton as a singlet in the *exo* chloro compound (VA) and as a doublet ( $J = 5$  c.p.s.) in its epimer (VB).<sup>10</sup> These spectra are in accord with expectations based on the Karplus correlation of spin-spin coupling constants with dihedral angles; the relevant angles ( $\text{H}-\text{C}_3-\text{C}_4-\text{H}$ ) are seen from models to be *ca.*  $80^\circ$  for VA, corresponding to



$J \cong 0$ , and *ca.*  $40^\circ$  for VB, corresponding to  $J \cong 4.5$  c.p.s.<sup>11</sup>

The chloroketone (III) obtained from the nitroso chloride of I showed a doublet ( $J \cong 4$  c.p.s.) at  $6.2 \tau$ , suggestive of an *endo* chlorine and *exo* proton at  $\text{C}_3$ . However, base treatment equilibrates this ketone with its epimer,<sup>12</sup> isolable in pure state by preparative gas chromatography, the  $\text{C}_3$  proton of which also appears as a doublet ( $J \cong 5$  c.p.s.;  $5.7 \tau$ ), clearly indicating that these spectra represent a problem in themselves.<sup>13</sup>

Chemical evidence indicates that the initial chloroketone (III) is, in fact, the 3-*exo*-chloro compound (IIIA). Thus, it gives a crystalline dithioketal<sup>12</sup> (VI) which could be desulfurized to *exo*-2-chloronorbornane (VII),<sup>14</sup> free of *endo* isomer. Further, chlorination of



the sodium enolate of norcamphor in a kinetically controlled reaction gave a chloroketone identical with that obtained from the nitroso dimer. Given that attack of chlorine from the *exo* face of the norcamphor enolate ion would be expected on the basis of many analogies,<sup>15</sup> this stereochemical assignment appears convincing.

Analogous results were obtained in the norbornadiene series. Hydrogenation of the ketone IV, obtained by hydrolysis of the nitrosyl chloride adduct of II, gives *exo*-3-chloronorcamphor (IIIA), so that this ketone must be IVA. This product can be equilibrated with its epimer IVB<sup>12,16</sup>; the n.m.r. spectra of these compounds are similar to those described for the saturated analogs.

Finally, treatment of I with isoamyl nitrite and hydrobromic acid<sup>8</sup> gives a good yield of a dimeric nitroso bromide.<sup>12</sup> Hydrolysis gives *exo*-3-bromonorcamphor,<sup>17</sup> in which the same type of n.m.r. "anomaly" appears<sup>18</sup> ( $\text{C}_3$  proton at  $6.3 \tau$ ,  $J = 3$  c.p.s.).

Summarizing, these three additions lead to unrearranged *exo* halo ketones in which the halogen configuration has been kinetically determined. Presumably, the adducts themselves have the same stereochemis-

(1) Presented in part at the A.A.S. Symposium on Organic Chemistry, Dec. 27, 1962, Philadelphia, Penna., and at the Eighteenth National Organic Chemistry Symposium of the American Chemical Society, Columbus, Ohio, June 16-20, 1963. Partial support of this work by the Alfred P. Sloan Foundation and the National Science Foundation is acknowledged with pleasure.

(2) W. A. Tilden, *J. Chem. Soc.*, **28**, 514 (1875); see also ref. 3.

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

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

(5) J. B. Miller, *ibid.*, **26**, 4905 (1961).

(6) Unpublished results obtained with Dr. Paul G. Gassman have led us independently to this conclusion.

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

(8) (a) E. Müller, "Houben-Weyl: Methoden der Organischen Chemie," 5/3, 4th Ed., Georg Thieme Verlag, Stuttgart, 1962, pp. 934-941; (b) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, pp. 669-670; (c) R. C. Fuson, "Reactions of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1962, pp. 167-168.

(9) For a recent leading reference, see J. Meinwald, S. S. Labana, and M. S. Chadha, *J. Am. Chem. Soc.*, **85**, 582 (1963).

(10) W. D. Kumler, J. N. Shoolery, and F. V. Brutcher, Jr., *ibid.*, **80**, 2533 (1958).

(11) M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959); M. Karplus and D. H. Anderson, *ibid.*, **30**, 6 (1959); see also H. Conroy, *Advan. Org. Chem.*, **2**, 308 (1960).

(12) Satisfactory elementary analyses were obtained for all new compounds mentioned.

(13) An explanation of this unanticipated observation is presented in the accompanying communication: J. Meinwald and Y. C. Meinwald, *J. Am. Chem. Soc.*, **85**, 2514 (1963).

(14) J. D. Roberts, C. Urbaneck, and R. Armstrong, *ibid.*, **71**, 3049 (1949). We are grateful to Drs. C. F. Wilcox, Jr., and J. G. Zajacek for providing us with an authentic sample of this compound.

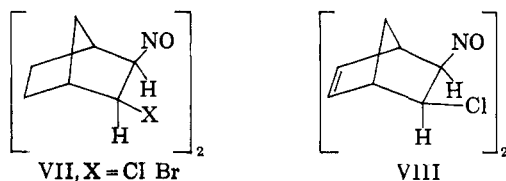
(15) E. J. Corey, R. Hartmann, and P. A. Vatakencherry, *ibid.*, **84**, 2611 (1962), and references cited therein.

(16) This observation was first made by Mr. S. S. Labana.

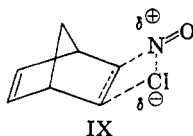
(17) H. Krieger, *Suomen Kemistilehti*, **B31**, 112, 175, 820, 340, 348 (1958).

(18) We wish to thank Dr. E. W. Garbisch, Jr., for copies of 40 Mc. n.m.r. spectra of authentic samples of *exo* and *endo* 3-bromonorcamphor, which helped in the identification of our product.

try. Further, it seems reasonable to assume an *exo* configuration for the nitroso group in these adducts, since mechanisms involving attack by  $\text{NO}^+$ ,  $\text{NO}\cdot$ , or  $\text{NOX}$  molecules would all be expected to deliver the nitroso group from the less hindered side of the olefins.<sup>15</sup> Thus, the previously described adducts may be assigned the *cis-exo* stereochemistry shown in VII and VIII.



These results suggest a new view of nitrosyl halide additions. Lack of structural rearrangement and apparent *cis* addition, as well as lack of incorporation of nucleophilic solvent (ethanol or acetic acid) into the products, all speak against the ionic addition mechanism.<sup>8</sup> A free radical mechanism initiated by  $\text{NO}\cdot$  addition is unlikely, since nitric oxide is unreactive toward norbornadiene.<sup>19</sup> This suggests a four-center mechanism, with little carbonium ion character developing in the transition state. In the case of norbornadiene, the transition state may be pictured as shown in IX.



It is interesting that the reaction of dinitrogen pentoxide with olefins, which gives 1,2-nitronitrates, has also been shown to be a *cis* addition; a cyclic transition state analogous to IX has been suggested.<sup>20</sup> Similarly, the *cis* course of the addition of acetyl nitrate to olefins, giving 1,2-nitroacetates, has been established.<sup>21</sup> The *cis* polar addition of hydrogen bromide to acenaphthalene<sup>22</sup> has been reported, and most recently, *cis* addition of water and methanol to *endo*-trimethylenenorbornene has been detected.<sup>23</sup> It appears that the nitrosyl halide additions discussed in this paper belong to a rapidly growing group of previously unrecognized *cis* addition reactions.

(19) Private communication from Dr. L. P. Kuhn.

(20) T. E. Stevens and W. D. Emmons, *J. Am. Chem. Soc.*, **79**, 6008 (1957); T. E. Stevens, *J. Org. Chem.*, **24**, 1136 (1959).

(21) G. Drefahl, H. Crahmer, and W. Thomas, *Chem. Ber.*, **91**, 282 (1958); G. Drefahl and H. Crahmer, *ibid.*, **91**, 745, 750 (1958); F. G. Bordwell and E. W. Garbisch, Jr., *J. Org. Chem.*, **27**, 2322 (1962).

(22) M. J. S. Dewar and R. C. Fahey, *J. Am. Chem. Soc.*, **84**, 2012 (1962).

(23) S. J. Cristol, L. K. Gaston, and D. W. Johnson, *Tetrahedron Letters*, 185 (1963); S. J. Cristol, W. K. Seifert, D. W. Johnson, and J. B. Jurale, *J. Am. Chem. Soc.*, **84**, 3918 (1962).

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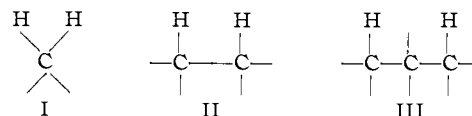
### Long-Range Spin-Spin Couplings in the Nuclear Magnetic Resonance Spectra of Some Bicyclo [2.2.1]heptanes<sup>1</sup>

Sir:

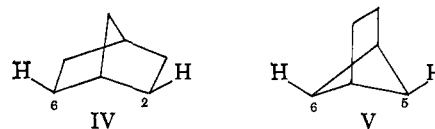
The idea that spin-spin splitting in n.m.r. spectroscopy is dependent upon indirect coupling of neighboring nuclei *via* the electrons in a molecule is generally accepted.<sup>2</sup> Theoretical and experimental progress

(1) Presented in part at the Eighteenth National Organic Chemistry Symposium of the American Chemical Society, Columbus, Ohio, June 16-20, 1963. Partial support of this work by the Alfred P. Sloan Foundation is acknowledged with pleasure.

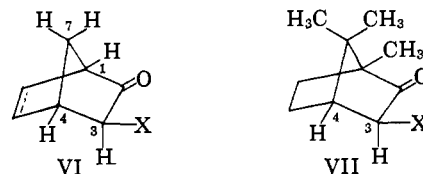
has been made in understanding how spin-spin coupling constants vary with molecular geometry when either two or three bonds (part formulas I and II) separate a pair of interacting protons. Thus, the dependence of  $J$  (coupling constant) on the H-C-H angle



in I<sup>3</sup> and on the H-C-C-H dihedral angle in II<sup>4</sup> is known. It is generally stated that coupling between protons which are separated by more than three bonds in saturated systems is negligible (<1 c.p.s.).<sup>5</sup> However, several counter examples to this rule have been well authenticated in recent years,<sup>6-8</sup> and in order to extend the usefulness of n.m.r. spectroscopy as a structural and stereochemical tool, it would be of interest to know what circumstances lead to important (>1 c.p.s.) "long-range" couplings. In the absence of any theoretical treatment of this problem, experimental data concerning long-range couplings in systems of known geometry becomes of interest. Interactions ( $J \cong 1$  c.p.s.) between the *exo*-2 and *exo*-6 protons in bicyclo[2.2.1]heptanes (IV)<sup>7</sup> and between the *endo*-5 and *endo*-6 protons ( $J \cong 7$  c.p.s.) in bicyclo[2.1.1]hexanes (V)<sup>6,8</sup> provide examples of coupling through four single bonds and have proved valuable in analyzing spectra of these systems.



We have found recently that the spectra of a number of *exo*-3 substituted norcamphors and dehydronorcamphors (VI)<sup>9</sup> show a split *endo*-3 proton ( $J \cong 3-4$  c.p.s.) in the n.m.r., in spite of the fact that the analogous camphors (VII) show the *endo*-3 proton as a singlet.<sup>10</sup>



Two hypotheses may be entertained to explain this surprising contrast. It might be that the geometry of the camphor skeleton is sufficiently different from that of norcamphor (as a result of nonbonded interactions introduced by the methyl groups) to give two significantly different H-C<sub>4</sub>-C<sub>3</sub>-H dihedral angles. This possibility appears unlikely, however, in view of

(2) Leading references: J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959; J. D. Roberts, "An Introduction to the Analysis of Spin-Spin Splitting in High-Resolution Nuclear Magnetic Resonance Spectra," W. A. Benjamin, Inc., New York, N. Y., 1961.

(3) H. S. Gutowsky, M. Karplus, and D. M. Grant, *J. Chem. Phys.*, **31**, 1278 (1959).

(4) M. Karplus, *ibid.*, **30**, 11 (1959); see also H. Conroy in R. A. Raphael, E. C. Taylor, and H. Wynberg, *Advan. Org. Chem.*, **2**, 308 (1960).

(5) J. D. Roberts, "Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, Chapter 3; L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, New York, N. Y., 1959, Chapter 6.

(6) J. Meinwald and A. Lewis, *J. Am. Chem. Soc.*, **83**, 2769 (1961), and references cited therein.

(7) F. A. L. Anet, *Can. J. Chem.*, **39**, 789 (1961).

(8) K. B. Wiberg, B. R. Lowry, and B. J. Nist, *J. Am. Chem. Soc.*, **84**, 1594 (1962).

(9) J. Meinwald, Y. C. Meinwald, and T. N. Baker, III, *ibid.*, **85**, 2513 (1963).

(10) W. D. Kumler, J. N. Shoolery, and F. V. Brucher, Jr., *ibid.*, **80**, 2533 (1958).