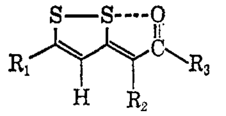
unsymmetrical thiathiophthene derivatives[6] but is significantly longer than the normal range of S–S covalent bond lengths (2.00–2.10 Å)[7] or than the S–S distances found in "dithiofurophthene" derivatives (IIa,b).[2]



IIa, $R_1 = CH_3; R_2 = H; R_3 = CH_3$
b, $R_1, R_2 = C_6H_5; R_3 = H$

The N–O length of 1.31 Å is somewhat longer than the values (1.14–1.24 Å) normally reported in nitroso compounds.[8] The C–N–O angle (113°) is much smaller than that found in *p*-iodonitrosobenzene (125°),[9] or even that for (+)-10-bromo-2-chloro-2-nitrosocamphane (118°),[10] while the C–N distance (1.31 Å) suggests substantial double bond character. The increase in length of S_3–C_3 over S_5–C_5, while not conclusively demonstrated by the analysis, is suggestive of additional bonding involving S_3.

The central eight atoms in I are significantly nonplanar (S_5, S_3, O, N, C_2, C_3, C_4, and C_5 lie 0.016, −0.018, 0.024, 0.054, 0.019, −0.016, −0.027, and −0.034 Å, respectively, from the best plane through the eight atoms); the greatest deviations from planarity occur in the dithiocyclopentene ring. The best planes through the two groups of five atoms (S_3, C_3, C_2, N, and O, and S_5, S_3, C_3, C_4, and C_5) are inclined at an angle of 2° 18′.

The molecular dimensions lead us to postulate significant bonding between S_3 and the oxygen atom of the nitroso group, certainly much more than is found in IIa or IIb. Recent MO calculations by Kapecki and Baldwin[11] imply virtually no covalent bonding between S and O in IIa. Klingsberg[12] has discussed examples where the S—S---O atoms are presumed to be in an approximate linear arrangement and for which various chemical and spectroscopic properties suggest d-orbital participation for the central sulfur atom.[13] Such participation may be an important factor in the bonding in I. The bonding in thiathiophthenes and in I may also be considered as an electron-rich three-center bond, as recently described by Gleiter and Hoffmann.[14] The S–S–O angle (174°) approaches the linear arrangement predicted to be most favorable to such a bond.[14,15]

---

(6) A. Hordvik, E. Sletten, and J. Sletten, *Acta Chem. Scand.*, **20**, 2001 (1966); S. M. Johnson, M. G. Newton, I. C. Paul, R. J. S. Beer, and D. Cartwright, *Chem. Commun.*, 1170 (1967).

(7) A list of S–S covalent distances in various compounds is given by A. Hordvik, *Acta Chem. Scand.*, **20**, 1885 (1966).

(8) H. Ondik and D. Smith, "International Tables for X-ray Crystallography," Vol III, Kynoch Press, Birmingham, England, 1962, p 270.

(9) M. S. Webster, *J. Chem. Soc.*, 2841 (1956).

(10) G. Ferguson, C. J. Fritchie, J. M. Robertson, and G. A. Sim, *ibid.*, 1976 (1961).

(11) J. A. Kapecki and J. E. Baldwin, *J. Am. Chem. Soc.*, in press.

(12) E. Klingsberg, *J. Org. Chem.* **31**, 3489 (1966).

(13) For a pertinent review, see W. G. Salmond, *Quart. Rev.* (London), **22**, 253 (1968).

(14) R. Gleiter and R. Hoffmann, *Tetrahedron*, **24**, 5899 (1968).

(15) Work supported by the National Institutes of Health (GM 12470-05) and the Hoffmann-La Roche Foundation.

(16) Alfred P. Sloan Foundation Fellow.

Paul L. Johnson, Iain C. Paul[16]
W. A. Noyes Chemical Laboratory, University of Illinois
Urbana, Illinois 61801

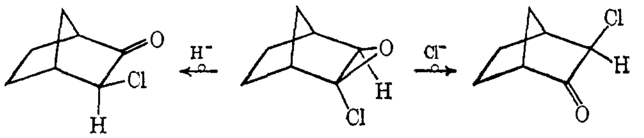
Received November 25, 1968

Molecular Rearrangements. VII.[1] Neat, Thermal Rearrangement of Optically Active 2-Chloronorbornene *exo*-Oxide

Sir:

Our product studies of neat, thermal rearrangements of 2-chloronorbornene *exo*-oxide (**1**) established that the two major products were *exo*-3-chloronorcamphor (**2**, ∼37%) and *exo*-2-chloro-7-ketonorbornane (**3**, ∼35%) and that **2** is not arising by isomerization of *endo*-3-chloronorcamphor, a minor (∼4%) rearrangement product.[1] The formation of the major rearrangement product, **2**, can be rationalized by (1) chlorine as the migrating group, (2) an *endo*-3,2 hydride shift, or (3) multiple (*endo*-6,2, *exo*-5,6, and *endo*-3,5) hydride shifts.[2] Process 3 is equivalent to process 2 without suitable deuterium-labeling studies. Although most previous evidence discounts an *endo*-3,2 hydride shift, the recent observation of such a shift in the related pinacol rearrangement of *endo*-3-phenyl-*exo,cis*-2,3-bornanediol[3] strengthens this as a possibility.

We have now examined this neat, thermal rearrangement with optically active α-chloro epoxide **1** which allows a convenient way to determine if chloride (process 1) or hydride (process 2 or 3) migration occurs. If chloride migrates one enantiomer of **2**, **2a**, will be produced, while if hydride shifts occur the opposite enantiomer, **2b**, will be the product. The results show that >90% of the rearrangement proceeds by chloride migration.



2b **1** **2a**

The synthesis of optically active **1** began with *l*-α-pinene ($[\alpha]^{25}D$ −54.9° (*c* 2.0, ethanol)).[4] Hydroboration yields optically active diisopinocampheylborane which is allowed to asymmetrically hydroborate norbornene.[4] The product is (+)-(1*R*,2*R*)-*exo*-norborneol[5] ($[\alpha]^{27.5}D$ +2.78° (*c* 10.0, $CHCl_3$)) with an optical purity of about 95% based on the average value calculated by Berson and Suzuki.[6] Oxidation with Jones reagent yields (−)-(1*R*)-norcamphor[5] (**4**) ($[\alpha]^{27}D$ −18.18° (*c* 3.07, $CHCl_3$)) which, surprisingly to us, has

---

(1) For paper VI in this series see R. N. McDonald and T. E. Tabor, *J. Org. Chem.*, **33**, 2934 (1968).

(2) For similar multiple hydride shifts in methylnorbornyl cations see J. A. Berson, J. H. Hammons, A. W. McRowe, R. G. Bergman, A. Remanick, and D. Houston, *J. Am. Chem. Soc.*, **89**, 2590 (1967), and previous papers in that series.

(3) A. W. Bushell and P. Wilder, *ibid.*, **89**, 5721 (1967).

(4) Obtained from Columbia Chemicals Co., Inc. This specific rotation is the largest yet reported for this compound; see H. C. Brown, N. R. Ayyangar, and G. Zweifel, *ibid.*, **86**, 397 (1964), and their ref 11.

(5) The absolute configurations of (−)-*exo*-norborneol and (+)-norcamphor have been assigned as 1*S*,2*S* and 1*S*, respectively, both by their relationship to terpenes of known absolute configuration (J. A. Berson, J. S. Walia, A. Remanick, S. Suzuki, P. Reynolds-Warnhoff, and D. Willner, *ibid.*, **83**, 3986 1961)) and by ORD studies (K. Mislow and J. G. Berger, *ibid.*, **84**, 1956 (1962)).

(6) J. A. Berson and S. Suzuki, *ibid.*, **81**, 4088 (1959), report $[\alpha]D$ +2.85–+3.02° for optically pure (+)-*exo*-norbornenol.

lost almost 30% optical purity when compared to the rotation calculated for optically pure norcamphor.[7] Conversion of **4** to the *gem*-dichloride ($[\alpha]^{27}\mathrm{D}$ $-9.44°$ (c 2.1, $CHCl_3$)) by treatment of **4** with a mixture of phosphorus trichloride and phosphorus pentachloride[8] proceeded in good yield with essentially no racemization as shown by its subsequent hydrolysis to **4** with $[\alpha]^{27}\mathrm{D}$ $-17.83°$.[9] Treatment of the *gem*-dichloride with potassium *t*-butoxide in *t*-butyl alcohol[8b] gave (−)-(1*R*)-2-chloronorbornene ($[\alpha]^{26}\mathrm{D}$ $-3.04°$ (c 2.04, $CHCl_3$)) which was epoxidized with *m*-chloroperbenzoic acid to give (+)-(1*R*)-**1** ($[\alpha]^{25.5}\mathrm{D}$ $+2.66°$ (c 6.44, $CHCl_3$)). The elimination and epoxidation reactions are the two steps in the sequence where we have no checks on possible racemization.

To establish the sign and magnitude of rotation for one of the enantiomers of α-chloro ketone **2**, **4** was treated with sulfuryl chloride to give a 79% yield of (−)-(1*R*,3*R*)-**2** (**2a**)[10] ($[\alpha]^{27}\mathrm{D}$ $-$ 60.80° (c 0.82, $CHCl_3$)). To demonstrate that no racemization had occurred in this step, **2a** was dechlorinated[11] to give a 94% yield of **4**, $[\alpha]^{27}\mathrm{D}$ $-17.82°$.[9]

The neat, thermal rearrangements of (+)-(1R)-**1** were carried out in a distillation flask under a platinum spinning-band column at 5 mm and a bath temperature of 80°.[1] The pure major components, **2a** and (+)-**3**, were separated by gas chromatography under conditions where all of the products are stable with the exception of 7-ketonorbornene (about 2% of the product[1]), which decomposes to carbon monoxide and cyclohexadiene. The specific rotations of **2a** from three such runs[12] were −46.3, −49.5, and −53.4°. Assuming no loss in optical purity for the conversion of ketone **4** to (+)-(1*R*)-**1**, comparison of the specific rotations of **2a** obtained from rearrangement of (+)-(1*R*)-**1** and from the chlorination of **4** leads one to conclude that 88, 91, and 94% of the rearrangement proceeds by chlorine migration to **2a**. It must be emphasized that these are minimum percentages since we have no data on any optical purity loss in the elimination reaction to the vinyl chloride and its epoxidation, although it appears unlikely that optical purity losses would accompany these reactions. We therefore conclude that the neat, thermal rearrangement of **1** involves chlorine migration as essentially the only (certainly the predominant) pathway to **2**, the major rearrangement product.

We believe that two results of the investigation of the neat, thermal rearrangement of **1** support a carbonium ion mechanism: (1) the major products are **2** and its Wagner–Meerwein rearranged isomer, **3**, and (2) the high degree of stereospecificity in the formation of these products compared to *endo*-3-chloronorcamphor,[13,14] a minor rearrangement product. We propose that the 3-ketonorbornyl (**5**)[15] and the 7-ketonorbornyl (**6**) cations (or their nonclassical counterpart) are involved.[16] The absence of an equilibrium or hybrid involving **5** and **6** has been reported in the acetolysis of *exo*- and *endo*-**7** ketonorbornyl tosylates,[17] but we cannot as yet rule out such an equilibrium or resonance hybrid in the present work.[18]

The possibility of the formation of an enol hypo-

---

[7] J. A. Berson and A. Remanick, *J. Am. Chem. Soc.*, **86**, 1749 (1964).

[8] (a) R. L. Bixler and C. Niemann, *J. Org. Chem.*, **23**, 742 (1958); (b) N. A. LeBel, P. D. Beirne, E. R. Karger, J. C. Powers, and P. M. Subramanian, *J. Am. Chem. Soc.*, **85**, 3199 (1963).

[9] The discrepancies in the values for **4** are within the errors of the determinations.

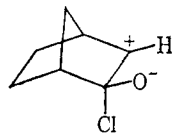
[10] We wish to thank Professor Carl Djerassi for the determination of the CD curve of this α-chloro ketone in alcohol ($[\theta]_{345}$ $-21°$ and $[\theta]_{300}$ $-168°$), establishing its configuration as 1*R*,3*R*.

[11] R. N. McDonald and C. E. Reineke, *J. Org. Chem.*, **32**, 1888 (1967).

[12] The times required to effect nearly complete rearrangement in these three runs differed somewhat.

[13] This stereospecificity is similar to the exclusive formation of *trans*-2-chloro-4-methylcyclohexanone from the neat, thermal rearrangement of the mixture of 1-chloro-*cis*- and -*trans*-4-methylcyclohexene oxides (R. N. McDonald and T. E. Tabor, *J. Am. Chem. Soc.*, **89**, 6573 (1967)).

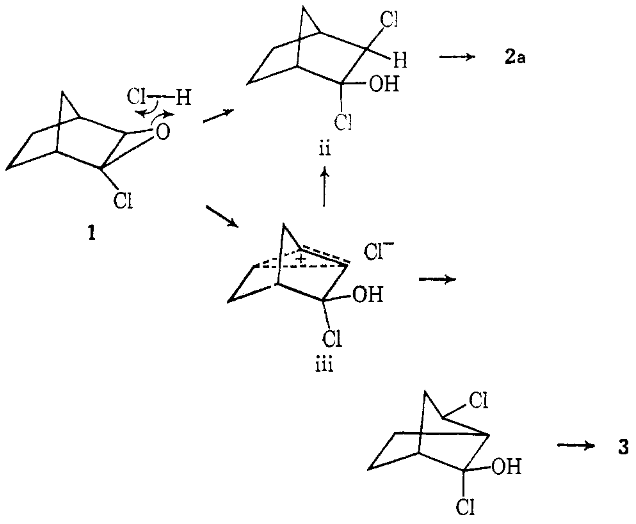
[14] *endo*-3-Chloronorcamphor may be formed by collapse of the 3-ketonorbornyl cation–chloride ion pair or by a totally different process, such as a 3,2-*endo* chloride shift in a possible intermediate i.



i

[15] Dr. Wayne Danen recently ran HMO calculations with a "damped" ω technique for an α-ketocarbonium ion and determined a total π energy of 4.336β and a C═C π bond order of 0.5390. Although admittedly crude, we believe that they are indicative of stabilization of the carbonium ion center by the attached carbonyl group.

[16] A referee has suggested that we may be observing an HCl-catalyzed rearrangement involving ii and/or iii as intermediates. We have tested this proposal by carrying out the neat, thermal rearrangements of **1** with a continuous but very slow bleed of anhydrous HCl or HBr gas entering under the liquid surface. The rate of rearrangement is accelerated and the ratio of chloro ketones **2** and **3** is increased somewhat with both acids. However, *less than 1% of bromo ketones*, analogous to **2** and **3**, *could be observed in the products when HBr was introduced into the rearrangement.* This evidence not only denies the above alternate pathways of rearrangement, but, we believe, points to this as an intramolecular rearrangement of chloride.



[17] P. G. Gassman and J. L. Marshall, *J. Am. Chem. Soc.*, **88**, 2822 (1966).

[18] Although both **2** and its *endo* epimer[14] are formed in a ratio of 37.4:4.3, we find no evidence for the formation of *endo*-2-chloro-7-ketonorbornane (iv),[1] a major product expected by analogy to the *exo*-7-ketonorbornyl tosylate solvolysis result.[17] Also, neither iv nor *endo*-7-ketonorbornyl acetate (v) was observed in the "acetolysis" of **1**;[1] several unknown products were obtained, but none of these was indicated by its spectrum to be iv or v. Chloro ketone iv is as yet an unknown compound, and its stability to the rearrangement, work-up, and analysis conditions may be slightly suspect since keto acetate v has been shown to be labile to heat, acid, and base.[17]

chlorite by a 1,2 shift of chlorine from C_2 to oxygen also exists. As has been argued previously,[13] we believe that such an intermediate might then decompose to the α-ketocarbonium ion–chloride tight ion pair with Wagner–Meerwein rearrangement competing with C_3–chloride bond formation leading to the major products, **2** and **3**. Intermediacy of the enol hypochlorite offers a convenient way to move the chlorine from the *endo* face to the *exo* face of the norbornyl system.

It is also noteworthy that the CD curve of (+)-**3** is not that expected for the 1*R*,2*R* configuration by application of the octant rule; the CD curve in ethanol exhibits a single maxima, $[\theta]_{295}$ +280°. It is difficult to envision how the 1*S*,2*S* configuration could be produced in this rearrangement. Professor Djerassi has informed us[19] that our configuration may be correct and that we are "encountering another example of an unusual effect of a β-halogen atom on a carbonyl group." This same type of effect has recently been observed in the β-haloadamantanones when the halogen has an axial relationship to the carbonyl group.[20] The geometric relationships of the halogen and the carbonyl groups in these axial-β-haloadamantanones and **3** are extremely similar; thus the halogens give "antioctant" contributions to the Cotton effect.

Acknowledgment. The authors are grateful to the U. S. Army Research Office (Durham) and the National Science Foundation for support of the research.

---

(19) Private communication.

(20) G. Snatzke and G. Eckhardt, *Tetrahedron*, **24**, 4543 (1968). We wish to thank Dr. Snatzke for informing us of certain of his data and conclusions prior to publication.

(21) NDEA Fellow, 1964–1967; National Science Foundation Cooperative Fellow, 1967–1968; taken from the Ph.D. thesis of R. N. Steppel.

Richard N. McDonald, Richard N. Steppel[21]
Department of Chemistry, Kansas State University
Manhattan, Kansas 66502

Received June 14, 1968

The Triplet Electron Spin Resonance Signal of 1,3-Diradicals from Bicyclic Azo Compounds

Sir:

The spectroscopic characterization of 1,3-diradicals is a topic of considerable current interest since they are postulated intermediates in several reactions, such as the photochemical and thermal isomerization of cyclopropanes,[1a] the photochemical and thermal decomposition of pyrazolines,[1b] the photolysis of cyclopentene ozonide,[1c] and the addition of carbenoid species to olefins.[1d] Furthermore, the chemistry of 1,3-diradicals may depend on whether the ground state is singlet or triplet.[2] We report here the electron spin resonance (esr) spectra (Figure 1) observed when the azo compounds I–III are irradiated at low temperatures. We assign the spectra to triplet 1,3-diradicals of the form IV–VI.

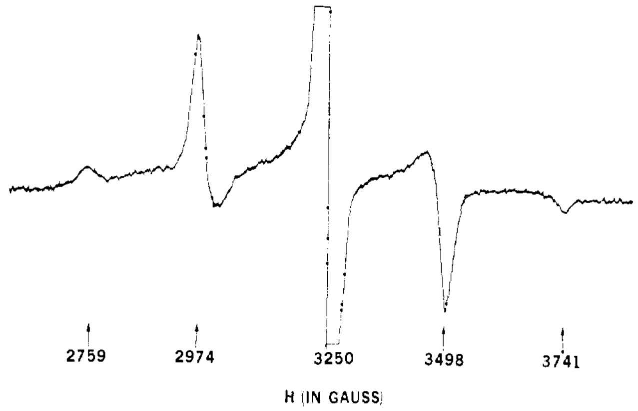
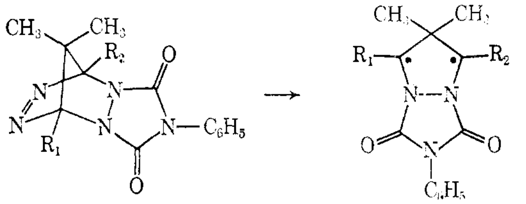


Figure 1. Esr spectrum from irradiation of I.



I, $R_1 = R_2 = C_6H_5$
IIa, $R_1 = C_6H_5$; $R_2 = CH_3$
b, $R_1 = C_6H_5$; $R_2 = CD_3$
III, $R_1 = R_1 = CH_3$

IV, $R_1 = R_2 = C_6H_5$
Va, $R_1 = C_6H_5$; $R_2 = CH_3$
b, $R_1 = C_6H_5$; $R_2 = CD_3$
VI, $R_1 = R_2 = CH_3$

Compounds I–III[3] were prepared by the Diels–Alder reactions of the corresponding isopyrazole with 4-phenyl-1,2,4-triazoline-3,5-dione.[4] When I[5] was irradiated in a quartz tube at 77°K with a 450-W Hanovia medium-pressure mercury arc through a uv filter (Corning 7-54), the pale yellow sample became green and gave the esr spectrum shown in Figure 1. Absorptions at 2759 and 3741 and at 2974 and 3498 G can be assigned, respectively, to the parallel and perpendicular signals of randomly oriented triplet molecules with axially symmetric spin–spin interaction terms. The $\Delta M = \pm 2$ transition for the triplet was observable at 1590 G. The strong absorption near the center of the triplet pattern (~3250 G) is due to other radical specie(s) produced in the irradiation. The spectrum remained unchanged after a period of several hours at 77°K. Upon annealing at 190°K for a few minutes, however, the green color disappeared along with the triplet signal, leaving a canary yellow sample which gave only the central signal in the esr. Further

---

(1) (a) J. P. Chesick, *J. Amer. Chem. Soc.*, **84**, 3250 (1962); M. J. Jorgenson, *ibid.*, **88**, 3463 (1966); P. J. Wagner and G. S. Hammond, *Advan. Photochem.*, **5**, 85 (1968); H. E. O'Neal and S. W. Benson, *J. Phys. Chem.*, **72**, 1866 (1968); (b) R. J. Crawford and A. Mishra, *J. Amer. Chem. Soc.*, **88**, 3963 (1966); W. R. Roth and M. Martin, *Ann.*, **702**, 1 (1967); E. L. Allred and R. L. Smith, *J. Amer. Chem. Soc.*, **89**, 7133 (1967); (c) P. R. Story, W. H. Morrison, III, T. K. Hall, J.-C. Farine, and C. E. Bishop, *Tetrahedron Letters*, 3291 (1968); (d) P. P. Gaspar and G. S. Hammond in "Carbene Chemistry," W. Kirmse, Ed., Academic Press, New York, N. Y., 1964, p 235.

(2) R. Hoffman, *J. Amer. Chem. Soc.*, **90**, 1475 (1968).

(3) Satisfactory combustion analyses were obtained on all new compounds.

(4) A. B. Evnin and D. R. Arnold, *J. Amer. Chem. Soc.*, **90**, 5330 (1968).

(5) The sample was *ca.* 0.1 *M* in dry pyridine and crystallized upon cooling to 77°K. I–III were not appreciably soluble in other suitable solvents (acetonitrile, perfluorolube, perfluoromethylcyclohexane); however, the same signal was obtained in these media.