Table I. Selected Bond Lengths (Å) and Bond Angles (Deg)

Bond	Distance	Bond	Distance
Pt(2)–Pt(1)	2.870 (3)	C(45)–S(4)	1.73 (5)
Pt(1)–S(5)	2.336 (7)	C(45)–S(5)	1.64 (4)
Pt(1)–S(6)	2.309 (7)	C(17)–S(1)	1.66 (6)
Pt(1)–S(7)	2.277 (10)	C(17)–S(7)	1.72 (5)
Pt(1)–S(8)	2.322 (8)	C(17)–C(11)	1.50 (6)
Pt(2)–S(1)	2.318 (10)	C(45)–C(41)	1.48 (4)
Pt(2)–S(2)	2.314 (10)	C(68)–C(62)	1.38 (4)
Pt(2)–S(3)	2.323 (7)	C(23)–C(21)	1.42 (6)
Pt(2)–S(4)	2.283 (6)		
C(23)–S(2)	1.69 (3)	Bonds	Angle
C(23)–S(3)	1.68 (4)	S(6)–Pt(1)–S(8)	73.9 (5)
C(68)–S(6)	1.71 (4)	S(5)–Pt(1)–S(8)	100.8 (4)
C(68)–S(8)	1.72 (4)	S(6)–Pt(1)–S(7)	92.8 (5)
		S(5)–Pt(1)–S(7)	92.0 (5)
Some Nonbonded distances		S(3)–Pt(2)–S(2)	73.2 (4)
S(4)–S(7)	3.48 (3)	S(3)–Pt(2)–S(1)	100.8 (5)
S(4)–S(5)	3.00 (3)	S(2)–Pt(2)–S(4)	96.5 (5)
S(2)–S(8)	3.73 (4)	S(1)–Pt(2)–S(4)	89.5 (5)
		S(4)–C(45)–S(5)	125.5 (26)
		S(6)–C(68)–S(8)	108.3 (23)

Angle between S(1)–S(2)–S(3)–S(4) and S(5)–S(6)–S(7)–S(8) planes, 12.4°

Rms deviation (Å) of platinum atoms from planes[a] Pt(1), +0.10 Pt(2), −0.05

[a] Standard deviation of atoms in plane <0.005 Å. Cell dimensions $a = 15.564$ (6), $b = 15.480$ (6), $c = 12.555$ (3) Å; $\alpha = 90.58$ (1)°, $\beta = 116.80$ (1)°, $\gamma = 122.55$ (1).

Å. In these "one-dimensional metal chain" compounds[15] Rundle[16] and others[17] have suggested the existence of metal–metal bonding formed by overlap of d_{z^2} and p_z orbitals on the metal atoms. This overlap[18] apparently leads to various anisotropic physical properties such as electron conduction along the metal–metal chain.[19]

σ overlap does not specify the relative rotational orientation of one metal–ligand plane with respect to another. Thus it appears significant that in compounds thought to contain a Pt(II)–Pt(II) bond, one idealized metal–ligand square is rotated from the next nearest ML_4 square toward a staggered $L_4M{-}ML_4$ structure. In no case is the M_2L_8 geometry close to the eclipsed structures of $Re_2Cl_8^{2-}$, $Cu_2(O_2CCH_3)_4 \cdot 2H_2O$, or several other species[20] some of which contain multiple metal–metal bonding.

Assuming a σ overlap between the metal atom centers, a staggered configuration minimizes the interaction between the filled nonbonding d_{xy} orbitals (in planar d^8 complexes) on adjacent metal atom centers. Alternatively, overlap of the filled nonbonding d_{xy} orbital on one center with the empty $d_{x^2-y^2}$ orbital on the next center is maximized when one ML_4 square is rotated 45° relative to the next one. This d–d orbital interaction leads to net δ bond formation. The very large S–C–S angle in the bridging dithiocumate ligands compared with the terminal ligands seems to exclude consideration of steric interactions between sulfur atoms as the primary cause of the antiprismatic structure.[21]

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(15) C. H. Wei and L. F. Dahl, *Inorg. Chem.*, **9**, 1878 (1970).

(16) R. E. Rundle, *J. Phys. Chem.*, **61**, 45 (1957).

(17) K. Krogmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 35 (1969).

(18) J. R. Miller, *Advan. Inorg. Chem. Radiochem.*, **4**, 133 (1962).

(19) See ref 15 for a recent discussion of the bonding.

(20) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," Interscience, New York, N. Y., 1966; F. A. Cotton, *Accounts Chem. Res.*, **2**, 240 (1969).

(21) The support of the National Science Foundation, GP-11701, is gratefully acknowledged. This structure was reported in part at the 161st National Meeting of the American Chemical Society, Los Angeles, Calif., March 1971, Abstracts, INOR 129.

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Preparation and Solvolysis of Optically Active 1,2-Dimethyl-*exo*-2-norbornyl Chloride. Direct Evidence for a Classical Bicyclo[2.2.1]hept-2-yl Carbonium Ion[1]

Sir:

We wish to report that low-temperature hydrochlorination of optically active 1-methyl-2-methylenenorbornane (I) gives active 1,2-dimethyl-*exo*-2-norbornyl chloride (II-Cl) and methanolysis of the latter gives active products. Thus, neither hydrochlorination nor solvolysis passes through a symmetrical intermediate—in this system, as in the parent norbornyl system, the bridged nonclassical ion is symmetrical and the classical ion is asymmetric.

The report[2] that hydrochlorination of deuterium-labeled I does not result in randomization of the methyl groups in the product suggested that active II-Cl could be prepared from active I. Under conditions reported[2] to give minimum (35%) scrambling to the methyl groups (hydrochlorination of neat I at 0°) the reaction does not go to completion and we were unable to separate active chloride from the unreacted olefin.[3] However, optically active II-Cl was obtained in pure form as follows.

Hydrochlorination[2] of a precooled pentane solution of (−)-I[4] at −78° was complete in about 2 min. The reaction flask was immediately chilled with liquid nitrogen and attached to a vacuum line and the pentane and excess HCl were vacuum transferred as the reaction flask was warmed to 0°. Efficient stirring during hydrochlorination and rapid work-up are necessary to avoid extensive racemization. The residual (−)-II-Cl, mp 120–122° dec, was shown to be homogeneous by elemental analysis and solvolysis equivalent. The spectral properties were the same as those of racemic II-Cl and the mass spectrum had parent peaks at 158 and 160. Absence of unreacted (−)-I (which has a much higher rotation) was clear from the nmr spectrum and rotary dispersion curves for the two compounds. The chloride racemizes in chloroform ($k \sim 4 \times 10^{-3}$ min^{-1} at 30°) and accurate rotations could not be determined. The most active samples had $[\alpha]_D$[5] about 3% as large as that of the starting olefin. Samples of (−)-II-Cl were prepared shortly before use and stored at 0°.

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(1) This research was supported by the National Institutes of Health (GM 14134) and the National Science Foundation (GP-21116X).

(2) H. C. Brown and L.-T. Liu, *J. Amer. Chem. Soc.*, **89**, 466 (1967).

(3) Incomplete reaction presumably results from encapsulation of liquid olefin by solid adduct. Evidently unreacted olefin did not interfere with the nmr analysis in the earlier work;[2] in the present work it was essential to obtain pure II-Cl.

(4) H. L. Goering, C. Brown, S. Chang, J. V. Clevenger, and K. Humski, *J. Org. Chem.*, **34**, 624 (1969).

(5) Rotations are for chloroform.

The optical purity of (−)-II-Cl was determined by conversion to (−)-I[6] with either potassium *tert*-butoxide in dimethyl sulfoxide (45°) or 2,6-lutidine in chloroform (30°). Both methods gave the same results which suggests that optical configuration is not lost. In any event, this correlation gives a lower limit of the optical purity of II-Cl. The most active samples of (−)-II-Cl gave (−)-I with ~27% of the original activity. We believe that most, if not all, of the loss occurs during hydrochlorination—the activity of the chloride varies and depends on reaction conditions.

The formation of active II-Cl from active I corroborates the earlier report[2] that hydrochlorination does not pass through a symmetrical intermediate. This was considered evidence that the carbonium ion has a classical, rather than a nonclassical structure.[2] However, the mechanism of hydrochlorination in nonpolar solvents has not been established[7] and it is not clear that carbonium ions are involved.

We now report direct evidence that solvolysis of II-Cl involves the asymmetric classical carbonium ion. Titrimetric (k_t) and polarimetric (k_α) rate constants for methanolysis of II-Cl are given in Table I. Both rates are first order and $k_\alpha > k_t$. Thus, ion-pair return results in racemization of the unsolvolyzed substrate. The chloride is much more reactive than the *p*-nitrobenzoate derivative (II-OPNB) investigated earlier,[8] *e.g.*, at 0° k_t for II-Cl is ~3 × 10^5 times larger than the extrapolated value for II-OPNB. This results from a large difference in activation energies; $E_a = 21.5$ kcal for II-Cl and 29.0 kcal for II-OPNB.

Table I. Polarimetric (k_α) and Titrimetric (k_t) Rate Constants for Methanolysis of II-Cl[a]

Temp, °C	10^3k_t, min^{-1}	10^3k_α, min^{-1}
−7.10	3.00 ± 0.08^b	
0.00	8.51 ± 0.06^b	
0.00	8.62 ± 0.12^c	$19.5 \pm 0.07^{b,c}$
9.90	34.6 ± 0.3^b	

[a] Substrate concentration 0.003 *M* except as noted. [b] Average of two independent experiments. [c] Substrate concentration 0.24 *M*.

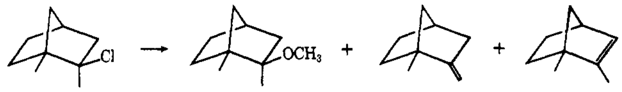
In the product studies summarized in Table II the solvent contained a slight excess of 2,6-lutidine. Under these conditions the products are optically stable. The lutidine does not change k_α and thus presumably has no important effect on the solvolysis.

Methanolysis of II-Cl at 0° gives 93.8% II-OCH$_3$, 4% I, and 2.2% 1,2-dimethyl-2-norbornene (III). Addition of II-Cl to refluxing methanol (65°) gave 81% II-OCH$_3$, 10% I, and 9% III. As expected,[9] the substitution to elimination ratio is much larger for II-Cl (~4.3) than for II-OPNB (~0.12).[8]

As shown in Table II products derived from (−)-II-Cl are optically active. Optical purities of (−)-II-OCH$_3$ and (−)-I were determined directly from their rotations.[6] The values for (−)-II-Cl are average optical purities for complete solvolysis obtained by multiplying initial values by k_t/k_α.[10] The relative optical purities show that the E1 product I is more active (~50% retention) than the SN1 product, II-OCH$_3$ (~14% retention).

Both hydrochlorination of active I and subsequent solvolysis of the adduct result in partial loss of optical configuration. The similar stereochemistry for hydrochlorination and E1 elimination suggests that these reactions pass through the same intermediate; presumably an ion-pair intermediate which racemizes in competition with product formation.

Table II. Rotations[6] and Optical Purities (OP) of Products for the Methanolysis of (−)-II-Cl at 0°[a]



(−)-II-Cl	(−)-II-OCH$_3$	(−)-I	III
	93.8%	4%	2.2%[b]
% OP[c]	[α]^{30}D (% OP), deg	[α]^{30}D (% OP), deg	
4.7	−0.24 (0.69)		
3.1	−0.13 (0.37)	−1.74 (1.6)	
3.1	−0.18 (0.51)		
3.8	−0.19 (0.54)		
3.2	−0.15 (0.43)		

[a] Substrate concentration 0.12 *M;* solvent contained 0.13 *M* 2,6-lutidine. [b] This row shows product composition determined by gc. [c] Average optical purity determined by multiplying initial OP by k_t/k_α (S. Winstein and D. Trifan, *J. Amer. Chem. Soc.*, **74,** 1154 (1952)).

The results in Table II are remarkably similar to those for the methanolysis of II-OPNB at 65° with regard to the activities of the SN1 and E1 products (II-OPNB gives II-OCH$_3$ and I with 8 and 60% retention). Thus, the change in leaving groups, which changes reactivity >10^5 fold, has little effect on the amounts of activity retained in the products. From this it seems that loss of activity does not result from simultaneous assisted and unassisted ionization because the relative rates of independent processes would not be expected to be constant over this reactivity range. For the same reason it seems implausible that the different activities of the E1 and SN1 products are due to a parallel concerted elimination reaction superimposed on the carbonium ion process.[8]

Clearly, I and II-OCH$_3$ are derived from different intermediates. A possible interpretation is that I (and possibly II) is derived from the initially formed intimate ion pair and that II-OCH$_3$ is formed from a solvent-separated ion pair or the dissociated carbonium ion. It is significant that the asymmetry of the product-forming intermediates is independent of the counterion or the temperature at which the intermediates are generated. This indicates that the asymmetry of these intermediates results from an asymmetric cation.

The evidence indicates that ionization is totally unassisted and partial loss of configuration results from racemization of intermediates in competition with product formation. Activation energies of reactions of reactive intermediates are small and thus differences for competing reactions are necessarily very small.

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(6) Absolute configurations and rotations have been established for I and II-OCH$_3$.[4]

(7) (a) R. C. Fahey, *Top. Stereochem.*, **3**, 237 (1968); (b) T. G. Traylor, *Accounts Chem. Res.*, **2**, 1952 (1969); S. J. Cristol and J. M. Sullivan, *J. Amer. Chem. Soc.*, **93**, 1967 (1971).

(8) H. L. Goering and K. Humski, *ibid.*, **90**, 6213 (1968).

(9) S. G. Smith and J. W. Goon, *J. Org. Chem.*, **34**, 3127 (1969).

(10) See Winstein and Trifan, Table II, footnote *c*.

Presumably this is why the amount of racemization is insensitive to temperature.

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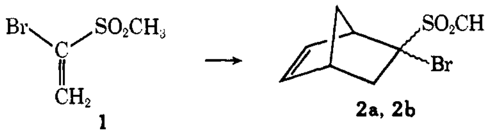
Bromovinyl Sulfone Chemistry. Synthesis and Rearrangement of the 5-Bromo-5-methylsulfonylbicyclo[2.2.1]hept-2-enes

Sir:

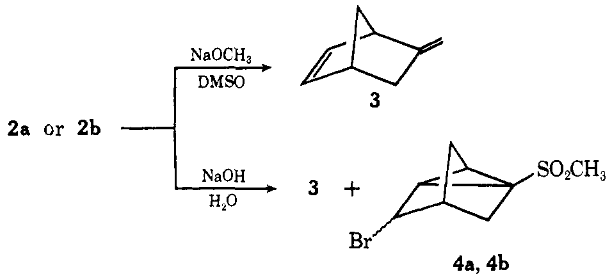
The Ramberg–Bäcklund rearrangement of α-halo sulfones is a particularly attractive method for the introduction of double bonds within a molecular framework.[1] The usual synthetic sequence consists of sulfide preparation, α-halogenation, oxidation of sulfur to the sulfone, and subsequent base-induced rearrangement of the α-halo sulfone. We would like to communicate an alternative, short sequence that involves preparation of the requisite α-halo sulfone *via* a cycloaddition reaction of methyl α-bromovinyl sulfone (**1**). In addition, we would like to present evidence of homolytic cleavage of the carbon–bromine bond of α-bromo sulfones under traditional conditions of the Ramberg–Bäcklund rearrangement.

Methyl α-bromovinyl sulfone (**1**), bp 63–64° (0.4 mm),[2] was prepared in 80% overall yield by bromination–dehydrobromination of methyl vinyl sulfone.[3] The Diels–Alder reaction of **1** with cyclopentadiene afforded a mixture of α-bromo sulfones **2a**, **2b**[2] in 85% yield. Bromo sulfone **2a**, mp 101.5–102.5°,[2] could be purified by fractional recrystallization of the crude mixture of isomers from chloroform–hexane: $\nu_{max}^{CCl_4}$ 1144 and 1323 cm^{-1}; $\lambda_{max}^{CCl_4}$ (near ir) 1.655 μ (ϵ 0.640); $\delta_{TMS}^{CDCl_3}$ 1.45–2.93 (m, 4, methylene), 3.10 (m, 1, bridgehead), 3.22 (s, 3, SO$_2$CH_3), 3.55 (m, 1, bridgehead), 6.20 (four-line pattern, 1, vinyl), 6.45 (four-line pattern, 1, vinyl). Isomer **2b**, mp 103.5–104.5°,[2] was obtained in pure form by column chromatography of the mixture of isomers on silica gel: $\nu_{max}^{CCl_4}$ 1146 and 1326 cm^{-1}; $\lambda_{max}^{CCl_4}$ (near ir) 1.655 μ (ϵ 0.550); $\delta_{TMS}^{CDCl_3}$ 1.70–2.55 (m, 4, methylene), 3.11 (m, 1, bridgehead), 3.13 (s, 3, SO$_2$CH_3), 3.47 (m, 1, bridgehead), 6.11 (four-line pattern, 1, vinyl), 6.31 (four-line pattern, 1, vinyl).



1 **2a, 2b**

While treatment of **2a** or **2b** with sodium methoxide in dry DMSO resulted in formation of the expected 5-methylene-2-norbornene (**3**) in >90% yields, treatment of either isomer with refluxing 2 *N* sodium hydroxide solution unexpectedly afforded a mixture of rearranged bromo sulfones **4a** and **4b**,[4] in addition to olefin **3**.

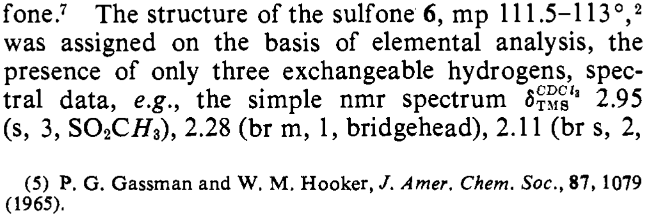


3

4a, 4b

Chromatography of the sulfone mixture (**4a**, **4b**) on silica gel with increasing percentages of ether–petroleum ether as eluent gave pure **4a**: mp 96–97°;[2] $\nu_{max}^{CCl_4}$ 1128, 1148, 1181, and 1323 cm^{-1}; $\lambda_{max}^{CCl_4}$ (near ir) 1.655 μ (ϵ 1.085); $\delta_{TMS}^{CDCl_3}$ 1.60–2.56 (7, methylene and bridgehead), 3.03 (s, 3, SO$_2$CH_3), 4.01 (m, 1, CHBr). Further elution afforded pure **4b**: mp 102.5–103.5°;[2] $\nu_{max}^{CCl_4}$ 1127, 1150, and 1323 cm^{-1}; $\lambda_{max}^{CCl_4}$ (near ir) 1.655 μ (ϵ 0.849); $\delta_{max}^{CDCl_3}$ 1.52–2.52 (7, methylene and bridgehead), 2.95 (s, 3, SO$_2$CH_3), 4.02 (m, 1, CHBr). The gross structures and diastereomeric relationship of **4a** and **4b** were deduced from the following data: the similar nmr spectra with no vinyl proton absorptions but with characteristic absorptions for SO$_2$CH_3 and CHBr; the incorporation of only three deuteriums upon exchange with sodium deuteroxide–deuterium oxide; the near-infrared absorptions with extinction coefficients of a magnitude expected for the nortricyclane ring structure;[5] and the identical mass spectral fragmentation patterns of the two isomers.

Some insight into the origin of **4a** and **4b** was gained from the following observations. Isomers **4a** and **4b** are obtained from **2a** or **2b** by the action of free-radical initiators such as benzoyl peroxide or potassium persulfate[6] in the absence of base. Specifically, treatment of solutions of **2a** or **2b** in *tert*-butyl alcohol–water (1:1 by volume) with 10 mol % of potassium persulfate at 100° afforded a mixture of **4a** and **4b** in 80–90% yield (**4a**:**4b** = 57:43). No olefin was detected under these conditions. Replacement of the *tert*-butyl alcohol with isopropyl alcohol resulted in the formation of three additional bromine-free sulfones presumably by hydrogen abstraction from isopropyl alcohol. Two of these new products, **5a** and **5b**,[2] were identical with the Diels–Alder adducts of cyclopentadiene and methyl vinyl sulfone.[7] The structure of the sulfone **6**, mp 111.5–113°,[2] was assigned on the basis of elemental analysis, the presence of only three exchangeable hydrogens, spectral data, *e.g.*, the simple nmr spectrum $\delta_{TMS}^{CDCl_3}$ 2.95 (s, 3, SO$_2$CH_3), 2.28 (br m, 1, bridgehead), 2.11 (br s, 2,



5a

5b **6**

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(1) (a) L. A. Paquette, *Accounts Chem. Res.*, **1**, 209 (1968); (b) F. G. Bordwell, *ibid.*, **3**, 281 (1970).

(2) All new compounds cited herein gave acceptable (±0.3%) combustion analysis values.

(3) G. D. Buckley, J. L. Charlish, and J. D. Rose, *J. Chem. Soc.*, *1514* (1947).

(4) The ratio of **4a**:**4b** is 57:43 from either **2a** or **2b**. The yield of **4a**, **4b** is 37% from **2a** and 59% from **2b**.

(5) P. G. Gassman and W. M. Hooker, *J. Amer. Chem. Soc.*, **87**, 1079 (1965).

(6) (a) P. D. Bartlett and J. D. Cotman, Jr., *ibid.*, **71**, 1419 (1949); (b) I. M. Kolthoff and I. K. Miller, *ibid.*, **73**, 3055 (1951).

(7) (a) H. R. Snyder, H. V. Anderson, and D. P. Hallada, *ibid.*, **73**, 3258 (1951); (b) J. C. Philips and M. Oku, unpublished results.