SUPPORTING INFORMATION

Endo Entry to the Nortricyclyl-Norbornenyl Cation System: Stereochemistry in the Fragmentation of *endo*-5-Norbornenyl-2-oxychlorocarbene

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Supplemental Information for computations

p. S2 Ground state *endo*-5-norbornenyl-2-oxychlorocarbene: **8**

p. S3 Fragmentation Transition State for retention: **8'(TS)**

p. S4 Fragmentation Transition State for inversion: **8(TS)**

p. S5 Fragmentation Transition State for elimination to form norbornadiene

S2

Ground state *endo*-5-norbornenyl-2-oxychlorocarbene: **8**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.275599	.493237	1.028623
2	6	0	.074274	-.052012	.490092
3	6	0	-.332984	-1.045221	-.627521
4	6	0	-1.898758	-.992309	-.556522
5	6	0	-2.096492	-.820799	.970370
6	6	0	-2.303043	.392685	-1.040389
7	8	0	.875351	1.091445	-.027959
8	6	0	2.114875	1.185728	-.288180
9	17	0	3.008504	-.463124	.008399
10	1	0	.687970	-.508369	1.265635
11	1	0	.058691	-.746868	-1.602515
12	1	0	.052003	-2.044777	-.403103
13	1	0	-2.393726	-1.840135	-1.034446
14	1	0	-1.669100	-1.639418	1.562903
15	1	0	-3.140096	-.666262	1.257167
16	6	0	-1.928305	1.275493	-.105083
17	1	0	-1.194309	.999283	1.992441
18	1	0	-2.710208	.609852	-2.022596
19	1	0	-1.962405	2.357443	-.162938

Zero-point correction=	.152249 (Hartree/Particle)
Thermal correction to Energy=	.160743
Thermal correction to Enthalpy=	.161687
Thermal correction to Gibbs Free Energy=	.117776
Sum of electronic and zero-point Energies=	-845.413050
Sum of electronic and thermal Energies=	-845.404556
Sum of electronic and thermal Enthalpies=	-845.403611
Sum of electronic and thermal Free Energies=	-845.447523

Mulliken atomic charges:

1	C	-.171188	8	C	.086329	15	H	.158413
2	C	.100897	9	Cl	-.184985	16	C	-.096140
3	C	-.281920	10	H	.193101	17	H	.142504
4	C	-.156068	11	H	.173053	18	H	.140118
5	C	-.274432	12	H	.166853	19	H	.146455
6	C	-.102263	13	H	.135132			
7	O	-.315822	14	H	.139964			

S3

Fragmentation Transition State for retention: **8'(TS)** Imaginary Frequency = -174.9616 cm^{-1}

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-.596219	-1.067401	.044839
2	6	0	-.273365	-.017674	-.940977
3	6	0	-1.478790	.828708	-1.160253
4	6	0	-2.461138	.235506	-.093098
5	6	0	-2.122214	-1.266475	-.251253
6	6	0	-1.823491	.507164	1.267593
7	8	0	1.158070	1.657359	-.031869
8	6	0	2.281375	1.518188	.255798
9	17	0	2.744907	-.880342	-.054693
10	1	0	.638687	-.018252	-1.527331
11	1	0	-1.268914	1.898332	-1.069003
12	1	0	-1.828897	.662162	-2.193494
13	1	0	-3.502544	.533468	-.219649
14	1	0	-2.334228	-1.665049	-1.250660
15	1	0	-2.578104	-1.906793	.508740
16	6	0	-.706190	-.226011	1.344456
17	1	0	.103216	-1.899999	.081516
18	1	0	-2.177904	1.236930	1.986711
19	1	0	.100914	-.205891	2.065283

Zero-point correction=	.147373 (Hartree/Particle)
Thermal correction to Energy=	.157033
Thermal correction to Enthalpy=	.157977
Thermal correction to Gibbs Free Energy=	.110993
Sum of electronic and zero-point Energies=	-845.386191
Sum of electronic and thermal Energies=	-845.376531
Sum of electronic and thermal Enthalpies=	-845.375586
Sum of electronic and thermal Free Energies=	-845.422571

Mulliken atomic charges:

1	C	-.175017	8	C	.180949	15	H	.179768
2	C	.073248	9	Cl	-.582096	16	C	-.102921
3	C	-.310233	10	H	.256584	17	H	.210024
4	C	-.179343	11	H	.221611	18	H	.162611
5	C	-.277197	12	H	.193534	19	H	.199808
6	C	-.081218	13	H	.154010			
7	O	-.280530	14	H	.156407			

S4

Fragmentation Transition State for inversion: **8(TS)** Imaginary Frequency = -105.0675 cm^{-1}

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.559875	.243440	-1.132928
2	6	0	.193833	-.212692	-.778347
3	6	0	.256345	-1.013990	.447349
4	6	0	1.765695	-.895456	.829271
5	6	0	2.391769	-.970613	-.589378
6	6	0	2.004592	.579610	1.139444
7	8	0	-1.148833	1.737409	-.105664
8	6	0	-2.249541	1.655425	.255406
9	17	0	-2.917486	-.856224	.009928
10	1	0	-.717075	-.139738	-1.363194
11	1	0	-.507324	-.705106	1.175715
12	1	0	-.080686	-2.033330	.178061
13	1	0	2.114279	-1.616784	1.568419
14	1	0	2.188436	-1.914136	-1.109140
15	1	0	3.462326	-.749656	-.620237
16	6	0	1.852310	1.264368	.000248
17	1	0	1.715723	.592032	-2.152782
18	1	0	2.169422	.988831	2.129641
19	1	0	1.793552	2.333871	-.156337

Zero-point correction=	.146596 (Hartree/Particle)
Thermal correction to Energy=	.156447
Thermal correction to Enthalpy=	.157391
Thermal correction to Gibbs Free Energy=	.109201
Sum of electronic and zero-point Energies=	-845.387123
Sum of electronic and thermal Energies=	-845.377272
Sum of electronic and thermal Enthalpies=	-845.376328
Sum of electronic and thermal Free Energies=	-845.424518

Mulliken atomic charges:

1	C	-.200408	8	C	.193932	15	H	.176584
2	C	.080533	9	Cl	-.619868	16	C	-.104084
3	C	-.309547	10	H	.260238	17	H	.172680
4	C	-.184756	11	H	.254102	18	H	.167961
5	C	-.271333	12	H	.225237	19	H	.179604
6	C	-.073889	13	H	.159907			
7	O	-.271520	14	H	.164627			

S5

Transition state for elimination to form norbornadiene: Imaginary Frequency = -240.8561 cm^{-1}

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.747699	.914489	.199368
2	6	0	.711420	.886875	-.898872
3	6	0	.384825	-.514914	-1.207038
4	6	0	1.361444	-1.279655	-.242890
5	6	0	2.580489	-.320329	-.297255
6	6	0	.862384	-1.006624	1.167344
7	8	0	-.934708	1.724726	-.054702
8	6	0	-2.042269	1.466654	.263250
9	17	0	-2.610286	-.856087	-.009207
10	1	0	.619000	1.683223	-1.628601
11	1	0	-.689120	-.737935	-.995541
12	1	0	.547792	-.718497	-2.274099
13	1	0	1.526383	-2.323329	-.511813
14	1	0	3.002893	-.204486	-1.303019
15	1	0	3.376698	-.556960	.414718
16	6	0	1.087229	.285259	1.433183
17	1	0	2.260002	1.866354	.337658
18	1	0	.306562	-1.711376	1.773377
19	1	0	.742983	.868143	2.278917

Zero-point correction=	.147883 (Hartree/Particle)
Thermal correction to Energy=	.157027
Thermal correction to Enthalpy=	.157972
Thermal correction to Gibbs Free Energy=	.112618
Sum of electronic and zero-point Energies=	-845.387395
Sum of electronic and thermal Energies=	-845.378251
Sum of electronic and thermal Enthalpies=	-845.377307
Sum of electronic and thermal Free Energies=	-845.422660

Mulliken atomic charges:

						13	H	.153995
1	C	-.174916	7	O	-.271450	14	H	.149109
2	C	.059924	8	C	.198731	15	H	.172673
3	C	-.319945	9	Cl	-.493579	16	C	-.108180
4	C	-.167124	10	H	.212518	17	H	.157303
5	C	-.277950	11	H	.254943	18	H	.176578
6	C	-.066176	12	H	.180348	19	H	.163198