Spectral Data for Aliphatic Epoxides

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Mass spectra, infrared spectra, and index of refraction were determined for 16 straight chain aliphatic epoxides (7–12 carbon length) that were synthesized and purified. Mass spectral data followed the characteristic fragmentation pattern for epoxides with prominent peaks at M-43, M-57, M-71, and M-85. Infrared spectral data showed the characteristic absorption pattern for 1,2-epoxy derivatives at 11.0 and 12.0 μ; the pattern shifted toward a lower wavelength as the epoxide moved closer to the center of the molecule.

Sixteen straight chain aliphatic epoxides (7–12 carbon chain length) were synthesized and purified. The mass spectra, infrared spectra, and index of refraction were determined. Data for the compounds reported have not previously been published in their entirety.

Experimental

The epoxides used in the study were prepared by utilizing *m*-chloroperbenzoic acid in methylene chloride as the oxidizing agent and were purified by collecting in a cold trap from a gas chromatograph with an SE-30 column. The infrared spectral data were obtained with a Perkin-Elmer Model 337 grating infrared spectrometer with a NaCl plate. Mass spectral data were obtained with a Bendix TOF mass spectrometer connected to a Bendix chromatography manifold inlet system, which was connected to a Warner-Chilcott gas chromatograph with an SE-30 column. A Bausch and Lomb Abbe 3L refractometer was used to obtain the index of refraction.

Presentation of Data

Index of refraction. Table I presents the index of refraction of the compounds prepared and the data for those published in the literature.

Mass spectra. The low-resolution mass spectra of the epoxides are shown in Table II. Interpretation of mass spectral data of epoxides of terminal and nonterminal alkenes was covered extensively by Brown et al. (*1*), who found that cleavage of the molecule gave characteristic fragmentation pathways: the prominent peaks characterized at M-29, M-43, M-57, and M-73. His high-resolution mass measurement of 1,2-epoxy derivatives shows *m/e* 71 comprised exclusively of C_4H_7O. The prominent peaks reported in this paper for epoxy derivations with the higher molecular weight follow the fragmentation pattern of Brown et al. The derivatives of decane, undecane, and dodecane have prominent peaks at M-43, M-57, M-71, and M-85, and there is some carbon–hydrogen loss at M-15 and M-29, though the relative intensity is weak. A general discussion of fragmentation patterns of aliphatic epoxides utilizing high-resolution mass spectrometry is given by Budzikiewicz et al. (*2*). A possible assignment of fragmentation ions for the mass units is given in the following discussion.

The molecular ion of *cis*-2,3 and *trans*-2,3-epoxy heptanes is *m/e* 114; this represents 5–7% of the base peak, *m/e* 45 (C_2H_5O), M-69 (C_5H_9).

The molecular ion of the octane derivatives is *m/e* 128; this represents 2–10% of their base peaks. The base peak of 1,2-epoxy octane is *m/e* 71 (C_4H_7O/C_5H_{11}), M-57 (C_4H_9/C_3H_5O). The base peaks of *cis*-2,3, *trans*-2,3, and *trans*-3,4-epoxy octanes are *m/e* 56 (C_3H_4O/C_4H_8), *m/e* 56, and *m/e* 57 (C_3H_5O/C_4H_9), respectively; they represent M-72 (C_5H_{12}/C_4H_8O), M-72, and M-71 (C_5H_{11}/C_4H_7O).

The molecular ion of the nonane derivatives is *m/e* 142; this represents 3–6% of their base peaks. The base peak of 1,2-epoxy nonane is *m/e* 71 (C_4H_7O/C_5H_{11}), M-71. The base peaks of *trans*-2,3, *trans*-3,4, and *trans*-4,5-epoxy nonanes are *m/e* 43 (C_2H_3O/C_3H_7), *m/e* 41 (C_3H_5), and *m/e* 57 (C_4H_9/C_3H_5O); they represent M-99 ($C_7H_{15}/C_6H_{11}O$), M-101 ($C_6H_{13}O$), and M-85 (C_5H_9O/C_6H_{13}).

The molecular ion for the decane derivatives is *m/e* 156; this represents 3–6% of the base peaks. The base peak of 1,2-epoxy decane is *m/e* 41 (C_3H_5), M-115 ($C_7H_{15}O$); however, the strong fragmentation ion at *m/e* 71 is consistent with the other 1,2-epoxy derivatives (even though it is not the base peak) and follows the fragmentation pattern discovered by Brown et al. (*1*). The base peaks of *trans*-2,3, *trans*-4,5, and *trans*-5,6-epoxy decanes are *m/e* 43 (C_2H_3O/C_3H_7), *m/e* 55 (C_4H_7), and *m/e* 57 (C_3H_5O/C_4H_9); they represent M-113 ($C_8H_{17}/C_7H_{13}O$), M-101 ($C_6H_{13}O$), and M-99 ($C_7H_{15}/C_6H_{11}O$).

The molecular ion of 1,2-epoxy undecane is *m/e* 170; this represents 2% of the base peak of *m/e* 43 (C_2H_3O/C_3H_7) and *m/e* 71 (C_4H_7O/C_5H_{11}), M-127 ($C_9H_{19}/C_8H_{15}O$), and M-99 ($C_7H_{15}/C_6H_{11}O$). The mass measurement given for the two base peaks is consistent with the fragmentation pattern seen for 1,2-epoxides, but both register a 100% intensity.

The molecular ion of 1,2-epoxy dodecane is *m/e* 184; this represents 4% of the base peak of *m/e* 43 (C_2H_3O), M-141 ($C_{10}H_{21}$).

The spectra of these aliphatic epoxides have diagnostic

Table I. Index of Refraction

Compound	Temp, °C	n^xD found	n^{20}D reported
c-2,3-Epoxy heptane	22	1.4103	. . .
t-2,3-Epoxy heptane	22	1.4044	. . .
1,2-Epoxy octane	24	1.4180	1.4193 (*3, 5, 10*), 1.4023 (*8*)
c-2,3-Epoxy octane	22	1.4168	. . .
t-2,3-Epoxy octane	22.5	1.4112	. . .
t-3,4-Epoxy octane	22.5	1.4119	. . .
t-4,5-Epoxy octane	24	1.4100	. . .
1,2-Epoxy nonane	22	1.4235	. . .
t-2,3-Epoxy nonane	22	1.4173	. . .
t-3,4-Epoxy nonane	22	1.4165	. . .
t-4,5-Epoxy nonane	22	1.4161	. . .
1,2-Epoxy decane	24	1.4275	1.4295 (7)
t-2,3-Epoxy decane	24	1.4212	. . .
t-4,5-Epoxy decane	24	1.4201	. . .
t-5,6-Epoxy decane	24	1.4202	1.4224 (6)
1,2-Epoxy undecane	22.5	1.4321	. . .
1,2-Epoxy dodecane	22.5	1.4350	1.4356 (*3, 10*), 1.4359 (*8*)

Table II. Mass Spectra of Epoxides of Aliphatic Alkenes

	Epoxy heptane		Epoxy octane				Epoxy nonane				Epoxy decane				Epoxy undecane	Epoxy dodecane
m/e	*c*-2,3	*t*-2,3	1,2	*c*-2,3	*t*-2,3	*t*-3,4	1,2	*t*-2,3	*t*-3,4	*t*-4,5	1,2	*t*-2,3	*t*-4,5	*t*-5,6	1,2	1,2
25	...	...	...	...	1	...	...	...	...	...	...	...	...	...	...	...
26	5	7	4	13	25	4	9	...	...	...	7	8	2	2	3	6
27	46	65	65	86	95	47	87	...	...	...	82	82	50	48	40	70
28	25	56	30	83	85	40	78	...	...	...	73	52	37	22	26	64
29	51	64	86	90	94	66	95	...	...	...	91	89	63	63	62	93
30	3	2	5	6	9	4	6	...	...	...	5	3	2	2	2	5
31	4	6	24	9	16	20	39	...	...	...	36	7	8	7	12	20
32	2	5	4	10	8	3	4	...	...	...	9	4	3	1	2	8
37	...	...	...	...	1	...	...	...	2	1	...	...	...	...	...	...
38	2	2	2	3	7	2	2	...	3	2	2	...	1	1	...	...
39	25	40	43	68	84	34	76	53	41	35	60	47	26	28	23	44
40	8	7	8	17	26	8	16	9	8	7	12	10	4	6	5	11
41	54	79	94	94	91	92	99	87	100	85	100	91	81	80	89	98
42	87	96	72	91	87	84	84	73	54	62	78	86	41	69	37	66
43	80	90	83	98	88	61	97	100	77	82	99	100	87	75	100	100
44	20	29	28	53	73	25	50	22	15	62	59	31	24	31	18	43
45	100	100	17	97	91	12	32	73	8	9	33	92	7	14	13	29
46	2	3	...	7	10	...	...	2	...	1	1	4	...	...	...	1
47	...	1	...	2	4	...	1	...	...	...	1	1	...	...	...	2
50	1	1	1	2	5	1	2	...	2	2	1	...	...	...	...	...
51	2	2	2	6	9	2	5	5	4	4	3	2	1	1	...	2
52	2	2	2	2	6	2	2	2	2	2	3	1	1	1	...	1
53	4	9	9	15	30	9	17	15	15	11	20	15	8	8	8	16
54	5	6	21	21	43	5	48	25	12	8	73	29	9	6	24	48
55	64	86	86	92	91	62	91	90	75	85	94	87	100	71	75	92
56	12	13	77	100	100	7	92	90	72	38	91	95	86	13	57	79
57	66	74	46	85	86	100	84	80	75	100	82	85	94	100	53	89
58	16	16	81	56	68	30	91	77	22	20	84	43	12	19	51	81
59	4	7	12	20	31	66	21	13	46	2	28	16	1	4	13	19
60	...	...	...	...	1	3	...	...	3	...	1	...	...	...	...	...
63	...	...	1	...	4	1	...	...	...	1	...	...	...	...	...	...
64	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...
65	...	1	1	3	4	2	3	3	4	2	3	2	...	1	2	2
66	...	...	2	3	4	1	11	3	2	2	11	5	1	...	4	10
67	4	6	20	24	51	10	56	24	25	14	59	30	17	15	28	71
68	10	13	43	16	35	12	82	50	28	16	76	78	10	12	49	79
69	72	11	41	72	82	26	80	66	32	45	76	89	23	89	46	76
70	12	17	38	15	26	16	57	64	17	19	72	83	5	35	39	55
71	41	55	100	74	85	15	100	52	22	24	98	74	22	38	100	94
72	22	25	16	45	66	6	26	20	37	39	22	36	30	6	11	21
73	1	3	1	5	8	2	3	2	4	16	3	5	40	4	2	13
74	...	...	...	...	...	...	...	...	...	1	...	...	2	...	...	...
77	1	1	1	2	4	1	2	3[a]	4[a]	2[a]	2	2	2	2	2	4
78	...	...	...	...	2	...	...	...	...	...	...	...	...	...	...	...
79	...	1	1	3	6	2	3	...	...	1	2	13	2	2	2	5

80	...	...	...	...	2	...	3	6	7	4	3	1	...	...	2	5
81	6	10	30	23	30	18	65	2	2	2	65	25	14	20	25	56
82	...	2	14	76	86	1	70	27	26	17	80	34	36	9	47	82
83	...	1	6	63	81	2	38	10	26	9	55	67	33	7	31	59
84	...	...	22	40	68	1	34	19	22	7	24	47	15	4	17	36
85	70	86	32	80	87	35	38	12	15	6	34	77	11	8	16	36
86	6	5	4	10	18	13	6	38	18	16	5	5	6	33	2	6
87	...	...	1	...	2	2	2	4	8	19	...	1	1	11	...	...
88	...	...	...	...	...	...	1	...	...	3	...	...	...	1	...	...
91	...	...	...	...	...	2	...	...	1	1	...	...	...	...	...	...
92	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...
93	...	...	...	...	...	...	1	...	...	1	...	...	...	...	...	2
94	...	...	...	...	...	...	1	...	...	...	4	...	...	...	2	3
95	...	...	5	4	10	2	34	11	19	12	57	10	12	6	21	40
96	1	3	17	2	2	...	16	25	4	2	55	7	4	3	25	54
97	...	1	5	2	2	...	23	28	7	5	18	7	1	2	14	30
98	2	3	4	...	1	...	26	14	3	3	22	2	...	1	7	15
99	15	19	10	23	36	42	24	7	12	44	9	6	12	75	3	5
100	...	...	6	2	4	3	4	4	3	6	2	2	3	8	2	2
109	...	...	1	...	...	...	2	2	2	1	13	3	3	...	9	18
110	...	...	4	5	9	4	16	...	...	...	14	38	...	...	14	18
111	...	...	...	...	2	...	3	...	...	1	2	29	...	...	3	10
112	...	...	2	4	6	2	4	...	...	1	21	17	...	...	8	4
113	...	...	...	14	28	2	7	6	19	16	17	10	35	22	3	4
114	5	7	...	1	2	...	8	...	2	2	1	2	4	2	...	2
124			...	...	...	...	8	10	12	5	12	...	...	...	5	11
125			...	...	...	...	...	2	...	1	2	...	...	...	...	3
126			...	...	...	...	1	12	8	6	3	...	...	...	8	9
127			...	...	1	...	2	6	...	1	5	7	1	9	4	6
128			2	10	9	5	...	...	...	...	7	1	1	1	...	3
129			...	...	1	...	...	...	...	...	...	...	...	...	...	...
138							...	...	...	...	7	4	5	2	2	8
139							...	...	...	...	...	...	...	1	...	2
140							...	...	...	...	...	2	1	1	2	12
141							1	...	...	...	...	7	...	...	...	3
142							3	4	4	6	...	1	...	...	2	...
143							...	...	...	1	...	...	...	...	...	...
152											...	...	...	...	3	4
153											...	...	...	...	...	...
154											...	...	...	...	...	2
155											...	...	...	...	...	...
156											3	4	2	6	...	5
166															...	9
167															...	...
168															...	...
169															...	...
170															2	...
184																4

[a] *m/e* 77.5.

peaks in the 31, 45, 59, 73, etc., series and can be used in low-resolution mass spectrometry to differentiate from the 43, 57, 71, etc., series of hydrocarbon peaks.

Infrared spectra. The fundamental frequencies for related epoxides in the frequency range 2.5-8.0 μ were the same for all compounds. Henbest et al. (*4*) report specific C—H stretching bands in the range of 3050-2990 cm^{-1} for the epoxide function. We should have been able to determine these bands with the instrument used but were unable to detect them.

The 1,2-epoxides substantiate data published by Shreve et al. (9) for the characteristic absorption pattern at 11.0 and 12.0 μ for the oxirane derivative of terminally unsaturated compounds. This pattern is eliminated as the epoxide moves closer to the center of the molecule. A single diagnostic peak is shown for all the 2,3-epoxides at 11.7 μ, for all the 3,4-epoxides at 11.3 μ, and for all the 4,5-epoxides between 11 and 11.2 μ.

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Synthesis of a Triazaphosphahomoadamantane[1]

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The compound, 1,3,5-triaza-7-phosphatricyclo[3.3.2.$1^{3,7}$]-undecane, a triazaphosphahomoadamantane, was prepared in 68% yield from the reaction of ethylenediamine, ammonia, and tris(hydroxymethyl)phosphine in excess formaldehyde. The oxide was prepared by conventional means.

The chemistry of tetrakis(hydroxymethyl)phosphonium chloride (Thpc) has been the subject of much interest in recent years because it is used commercially in the production of flame retardant cellulosic textiles (*1*). Textile workers have neutralized Thpc and referred to the solution as "THPOH," realizing that it is a mixture of products, principally tris(hydroxymethyl)phosphine (THP) and formaldehyde (*2*). "THPOH" reacts rapidly with ammonia and diamines to form water-insoluble precipitates; this reaction is the basis for a well-known flame retardant finish (*4*).

Other workers found that copper salts inhibit the reaction of "THPOH" with aqueous ammonium hydroxide at room temperature by formation of a complex (*5*). Excess formaldehyde also prevents this reaction between THPOH and ammonium hydroxide and allows another product to be formed (*3*). This product is 1,3,5-triaza-7-phosphaadamantane (PAA).

To prepare the next member of this series, a phosphahomoadamantane, both ammonia and ethylenediamine must be used. However, copper salts did not inhibit the reaction between "THPOH" and the diamines to form a water-insoluble precipitate. We wish now to report that formaldehyde can inhibit this reaction between "THPOH" and ethylenediamine. To prepare PAA and to prevent formation of the water-insoluble precipitate, a 4:1 excess of formaldehyde to THP ("THPOH") was needed, and a larger excess (10:1) increased the yield of PAA from 40 to 70% (*4*). However, not even an 8:1 excess of formaldehyde to THP ("THPOH") inhibited the reaction of THP with ethylenediamine to form a water-insoluble precipitate. A 16:1 excess of formaldehyde to THP (THPOH) did prevent premature precipitation, and workup yielded a white crystalline compound.

This solid was 1,3,5-triaza-7-phosphatricyclo-[3.3.2.$1^{3,7}$]-undecane (I) by elemental analysis. The infrared spectrum of I showed bands between 6.8 and 9.2 μ, similar to those exhibited by PAA. The NMR spectrum was complex and exhibited a series of peaks between δ 4.8 and δ 3.0. Dreiding models showed that the addition of a methylene group between two nitrogens in the PAA structure to form the phosphahomoadamantane produced nonequivalence among the protons. This nonequivalence would be expected to give rise to a complex NMR spectrum.

The oxide, prepared as an additional proof of structure, also gave an excellent elemental analysis. The ir spectrum showed the strong band at 8.55 μ characteristic of the P═O stretch. The NMR spectrum is complex and exhibited a multiplet of peaks from δ 4.43 to δ 3.0.

Attempts to prepare a methyl iodide derivative resulted in either orange decomposition products or solids which showed by NMR spectroscopy that methyl group incorporation had not been achieved. This failure to produce a methyl iodide derivative may be due to the instability of the phosphahomoadamantane. Both compounds are soluble in polar solvents, but heating them in solution produced decomposition as evidenced by elemental analyses of the recrystallized materials.

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