97. *Infrared Spectra and Structure of Some 1,3-Oxazine Derivatives.*

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Molecular refractivities and infrared absorption spectra have been determined for a number of 3,5-dialkyltetrahydro-5-nitro-1,3-oxazines, as well as for some analogues without nitro-groups (a total of 24 substances).

Values of $[M]_D$ were lower than those calculated, which is explained as due to the influence of the heteroatoms in the ring.

Infrared bands in the regions 1150—1050, 955—925, and 855—800 cm.$^{-1}$ are now assigned to C–O–C acetal bonds, which confirm the acetal character of 1,3-oxazines. Probable assignments have been made for the various carbon–nitrogen bonds.

One of the characteristics of tetrahydro-5-nitro-1,3-oxazines[1] is hydrolysis in an acid medium, with the loss of one molecule of formaldehyde, to derivatives of 3-amino-2-nitropropan-1-ol. This occurs readily under the action of hydrochloric acid in 80% ethanol[2] or of concentrated hydrochloric acid under ultraviolet irradiation.[3] The ease of this reaction suggested that the C–O–C bond in 1,3-oxazines was mainly of hemiacetal character.[4]

To prove finally the cyclic structure of these compounds and to confirm the nature of the C–O–C bond the molecular refractivities and infrared absorption spectra of a few compounds of type (I) have now been investigated. A few absorption spectra of 1,3-oxazine derivatives have been published,[5] but there has been no previous systematic investigation.

The products (I; R = Me or Et) were prepared by condensing nitroethane and 1-nitropropane respectively with formaldehyde and treating the resulting 1,3-diols with formaldehyde and primary amines ranging from ammonia to hexylamine. Particular attention was paid to the purity of the products (I): they were distilled under reduced pressure, cyrstallised as hydrochlorides, recovered as bases and redistilled under reduced pressure.

For comparison, a few 1,3-oxazines without the nitro-group were also investigated, namely, (II)[6] and the 5,6-dihydro-oxazine (III).[7]

Experimental

3,5-Dimethyltetrahydro-5-nitro-1,3-oxazine, prepared from 2-methyl-2-nitropropane-1,3-diol, formaldehyde, and methylamine as described by Senkus[1] (yield 85·4%), had b. p. 85—86°/0·7 mm.

3-*Ethyltetrahydro-5-methyl-5-nitro-1,3-oxazine.* 2-Methyl-2-nitropropane-1,3-diol (0·2 mol., 27 g.) (prepared from nitroethane and formaldehyde) was dissolved in 60% aqueous ethylamine (0·2 mol., 15 g.) and mixed with 30% aqueous formaldehyde (0·2 mol., 20 ml.). The temperature rose by 55° and, after cooling, the whole was kept at room temperature for 48 hr. The colourless oily oxazine was extracted with ether, dried (Na_2SO_4), freed from ether and volatile substances on water-bath, and distilled under reduced pressure (101—103°/3 mm.) as a colourless oil which slowly darkened (28·6 g., 81·8%). This was treated in anhydrous alcohol with

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[1] Hirst, Jones, Minahan, Ochynski, Thomas, and Urbański, *J.*, 1947, 924; U.S.P. 2,447,822; Senkus, *J. Amer. Chem. Soc.*, 1956, **72**, 2968; Urbański, *Nature*, 1951, **168**, 562; Urbański and Lipska, *Roczniki Chem.*, 1952, **26**, 182; Urbański and Gürne, *ibid.*, 1954, **28**, 175; Urbański and Piotrowska, *ibid.*, 1955, **29**, 379; Urbański and Kolesińska, *ibid.*, 1955, **29**, 392; Urbański, Dabrowska, Lesiowska, and Piotrowska, *ibid.*, 1957, **31**, 855.

[2] Eckstein, Sobótka, and Urbański, *Roczniki Chem.*, 1956, **30**, 132.

[3] Gürne and Urbański, *Roczniki Chem.*, 1957, **31**, 855; *ibid.*, 1957, **31**, 869; *J.*, 1959, 1912.

[4] Urbański, *Roczniki Chem.*, 1951, **25**, 257.

[5] Bergmann and Kaluszyner, *Rec. Trav. chim.*, 1959, **78**, 315; O'Sullivan and Sadler, *J.*, 1957, 2916; Urbański, *Roczniki Chem.*, 1958, **32**, 241; Lacey and Ward, *J.*, 1958, 2134; Lynn, *J. Org. Chem.*, 1959, **24**, 711.

[6] Kohn, *Monatsh.*, 1904, **25**, 817; Urbański and Gac-Chylińska, *Roczniki Chem.*, 1956, **30**, 185.

[7] Eckstein, Majewski, and Gluziński, unpublished work.

alcoholic hydrochloric acid at 0°. The precipitated hydrochloride was washed with acetone, suspended in ether, and shaken with sodium hydrogen carbonate solution. The ethereal layer was dried and the free *oxazine* was distilled 84—85°/0·2 mm. (Found: N, 16·4. $C_7H_{14}O_3N_2$ requires N, 16·1%).

The other *oxazines* listed in Table 1 were similarly prepared from 2-methyl- or 2-ethyl-2-nitropropane-1,3-diol.

Refractivities were determined by means of Zeiss–Abbé model G refractometer at 20°. The calculated molecular refractivities are recorded in Table 2.

TABLE 1. 3,5-*Dialkyltetrahydro*-5-*nitro*-1,3-*oxazines*.

3-Subst.	Yield (%)	B. p./mm.	Formula	N (%) Found	N (%) Reqd.
5-*Methyl derivatives*					
Pr^n	64	94°/0·3	$C_8H_{16}O_3N_2$	14·7	14·9
Pr^i [a]	68	98—99°/0·8	—	—	—
Bu^n	59	92—94°/0·2	$C_9H_{18}O_3N_2$	14·2	13·85
n-Pentyl	36	100—101°/0·2	$C_{10}H_{20}O_3N_2$	13·2	12·95
n-Hexyl [b]	60	141—142°/2·2	$C_{11}H_{22}O_3N_2$	11·9	12·2
5-*Ethyl derivatives*					
H [c]	—	108—109°/1	—	—	—
Me	75·5	100—101°/1·2	$C_7H_{14}O_3N_2$	16·4	16·1
Et	87	98—99°/0·7	$C_8H_{16}O_3N_2$	15·2	14·9
Pr^n	70	103—105°/0·6	$C_9H_{18}O_3N_2$	13·7	13·85
Pr^i	79	103—105°/0·1	,,	14·2	13·85
Bu^n [a]	57	111—112°/0·2	—	—	—
n-Pentyl	48	116—117°/0·4	$C_{11}H_{22}O_3N_2$	12·1	12·2
n-Hexyl [b]	47	129—130°/0·25	$C_{12}H_{24}O_3N_2$	11·8	11·5

[a] Cf. Senkus.[1] [b] Sufficient ethanol was added to give a homogeneous solution. [c] Cf. Hirst *et al.*[1]

TABLE 2. *Molecular refractivities of compounds* (I).

R	R′	d_{20}^{20}	n_D^{20}	$[M]_D$ Calc.*	$[M]_D$ Found	$\Delta[M]_D$
Me	Me	1·1698	1·4725	38·89	38·38	0·51
Me	Et	1·1314	1·4700	43·54	42·96	0·58
Me	Pr^n	1·0984	1·4679	48·21	47·62	0·59
Me	Pr^i	1·1081	1·4718	48·22	47·54	0·68
Me	Bu^n	1·0698	1·4671	52·83	52·46	0·37
Me	n-Pentyl	1·0547	1·4666	57·49	56·84	0·65
Me	n-Hexyl	1·0394	1·4669	62·10	61·46	0·64
Et	H	1·2051	1·4816	38·76	37·87	0·89
Et	Me	1·1377	1·4731	43·54	42·94	0·60
Et	Et	1·1030	1·4704	48·19	47·64	0·55
Et	Pr^n	1·0862	1·4702	52·86	51·97	0·89
Et	Pr^i	1·0884	1·4721	52·87	52·04	0·83
Et	Bu^n	1·0579	1·4694	57·48	56·98	0·50
Et	n-Pentyl	1·0419	1·4687	62·14	61·51	0·63
Et	n-Hexyl	1·0285	1·4689	66·75	66·14	0·61

* The refractivity increments used in calculating $[M]_D$ were $-CH_2-$ 4·647; C 2·59; tert.-N 2·74; sec.-NH 3·61; –O– (as in acetals) 1·61; NO_2 aliph. 6·71; Me 5·65; Et 10·30; Pr^n 14·97; Pr 14·98; Bu^n 19·59; n-pentyl 24·25; n-hexyl 28·86.

Infrared absorption spectra were determined by means of a Hilger H-800 double-beam spectrophotometer with 60° prism of sodium chloride. Substances were used as liquids of capillary thickness. The frequencies were checked by means of a polystyrene film. The frequencies are recorded in Tables 3—5.

DISCUSSION

Molecular Refractivities.—Experimental values of the molecular refractivity were found to be lower than the calculated values ($\Delta[M]_D$ 0·4—0·9), as already noted by Bergmann and Kaluszyner[5] for tetrahydro-1,3-oxazine derivatives without the nitro-group. Small (three- and four-membered) and large (seven- and eight-membered) rings are sometimes

TABLE 3. *Infrared frequencies (cm.$^{-1}$) for compounds* (I).

R: Me R′: Me	Me Et	Me Pr^n	Me Pr^i	Me Bu^n	Me n-Pentyl	Me n-Hexyl	Et H	Et Me	Et Et	Et Pr^n	Et Pr^i	Et Bu^n	Et n-Pentyl	Et n-Hexyl	Assignment
							3354m(b)								N–H stretching
2967sh	2965s	2965s	2979s				2976s	2962s	2980s	2954vs	2963s	2942s	2953s		
2936m	2924m	2936s	2937s	2938s	2941vs	2920s	2927s	2929m	2943m	2920s	2927sh	2919s	2927s	2912vs	
			2908m	2918s	2907s										
2872m	2860m	2872s	2878s					2873m	2880m		2874w				
2842m			2844m	2851s	2853s	2845s	2860s	2843m	2863sh	2861s		2851s	2862s	2846s	C–H stretching of CH_3 and CH_2 groups
	2810m	2824s	2821m	2802sh					2826m	2812s	2807w	2816sh			
2776m	2773m	2787s						2785m	2774m				2775m		
	2755m		2756m	2765m	2765m	2769m				2761s		2761m		2766m	
						2735w	2749vw	2736sh			2745w				
2640vw								2704w	2709vw						
2606vw			2613vw		2600vw						2607vw				
1544vs	1543vs	1546vs	1545vs	1541vs	1543vs	1545vs	1540vs	1542vs	1543vs	1543vs	1543vs	1543vs	1542vs	1542vs	NO_2 stretching assym.
1462s	1455m	1458s	1459s	1453s	1453s	1457s	1459s	1462s	1460s	1461s	1460s	1460s	1460s	1460s	CH_2 scissoring
1449s		1442sh					1444sh	1445s	1442s	1440s	1443s	1441s	1443s	1443s	CH_2 scissor. in R = Et
1400m	1402w	1402m	1403m	1399m	1400m	1400m									
	1381m	1381m	1389s				1391m	1390m	1384m	1390s	1386m	1388m		1390m	
			1365s	1376m	1376s	1379m				1378s		1375m	1378m	1373s	
							1357s	1361m	1360m	1359m	1362m	1359m	1359m	1359s	
1354s	1351m	1350s	1352s	1348s	1348s	1349s									NO_2 stretching symm.
			1338m				1341s	1343m	1342m	1342s	1336sh	1341m	1338m	1337s	NO_2 stretching symm.?
	1320sh						1324s	1325s	1325s	1325s	1324m	1326s	1325s	1325s	{NO_2 stretch. symm. or CH_2 wagging?
1302m	1308m	1307s	1307s	1308s	1306s	1308m									CH_2 wagging
1282m		1277m	1281vw	1277m	1277w	1279w	1282w	1280w		1287m	1281vw	1279w	1288w	1281w	
1260m					1260w			1260s		1273m		1257w	1259w		
1249m			1237s	1246w			1241m	1236w		1244m	1231s		1241w	1237m	
1222m	1219m	1217s	1218s	1213s	1210m	1215m	1203w	1212m	1222s	1211s	1210m	1203s	1207s	1208s	C–N?
				1194m											
1150m			1167m			1176m	1160s	1143m			1164w			1171m	
1128m	1135m	1135s	1127s	1132s	1135s	1132m		1131s	1136s	1127s	1123s	1128s	1128s	1129s	
1113s	1105s	1105s	1109s	1103s	1104s	1107s	1118m	1117s	1108s	1104s		1103s	1106s	1106s	
			1096sh			1094s	1099m	1099m			1095sh			1095sh	}C–O–C in ring
1080s	1077s	1079s	1081vs	1080s	1076s	1081s	1064s	1085s	1082s	1080vs	1085s	1086s	1082s		
1053w		1049s	1055m	1045s	1046s	1049m		1057m	1051s	1053s	1057w	1050m	1052s	1053s	
1042m	1046m	1029m	1031m					1045m	1028vw	1030m	1031m	1031w	1028m	1031w	
	1004w	1005m	1005vw	1004w	1004w	1002w	1012s	1025m	1014vw	1015m	1014w	1012vw			
999w	980vw	990m	986w	977w	973vw	982sh		980w	982w	983w	981w				
								964vw	967w	967m	962vw	963w	966vw	966w	
947w	946m	953s	946s	947s	951m	949m	951m	947s	956w	948s	938m	943m	947m	943s	C–O–C in ring
									937m						
912m									911m	912s	909m	910m	914m	914s	
897s	892m	897s	893s	893s	892s	895m	898s	896m	896m			894m	894m		}C–N–C and C–N$<^{C}_{C}$?
							887sh	881m		884s	885w			889s	
	866vw	869m				869sh									
851m	843m	850s	855m	850s	848s	850m	849s	850s	842m	849s	852w	849m	848m	850s	C–O–C in ring
			820w				816sh	817vw	811vw	817w	817w	815vw	818w	818w	
							796s	788w	788w	789m	788vw	787w	788w	788m	
		776w					764m								
		754w	755vw									735vw			
						725w								724w	

TABLE 4. *Infrared frequencies* (*cm.*$^{-1}$) *of compounds* (II).

3347m(b), 2994vs, 2948vs, 2928s, 2893s, 2757w, 2664w, 2613vw, 1459s, 1449s, 1385s, 1369s, 1343m, 1292m, 1260vs, 1212s, 1188s, 1146s, 1115s, 1097s, 1073s, 1043s, 1002vs, 925m, 895m, 818s, 772s, 751s.

TABLE 5. *Infrared frequencies* (*cm.*$^{-1}$) *of compounds* (III).

Ar: Ph	*p*-F·C_6H_4	*o*-Cl·C_6H_4	*m*-Cl·C_6H_4	*p*-Cl·C_6H_4	*p*-Br·C_6H_4	*o*-NO_2·C_6H_4	2,3-$(MeO)_2C_6H_3$	Assignment
3052w	3055w	3047w	3048w	3044w	3044w	3061w	3064w	C–H in arom. ring
3020w								
2928m	2930m	2926s	2917s	2921s	2928m	2928m	2920s	C–H stretch. in CH_2 groups
2878m	2878m		2874m	2873m	2872w	2884m	2877sh	
2848m	2850m	2846m	2844m	2843m	2846m	2851m	2835sh	
		2819m						
1649vs	1645vs	1652vs	1645vs	1644vs	1644vs	1659vs	1655vs	C=N conj. with arom. ring
1602w	1599s	1589m	1590m	1591s	1585s	1604m	1592m	
1580m		1562w	1567s			1572m	1575s	
					1520w	1522vs		
1492m				1482s				
1471w	1468m	1465s	1469s	1470sh	1471m	1466m	1469vs	
1448m	1434w	1431s	1422s	1433m	1434w	1434m	1439s	CH_2 scissoring
							1415s	
				1394s	1390m			
1380w	1376w	1377m	1376w					
1349s	1348s	1346vs	1345vs	1345vs	1343s	1349vs	1344vs	CH_2 wagging
							1306s	
	1280s	1290vs	1284s	1280s	1276s	1286s		
1274s	1270s		1255vs	1264vs	1263s	1269s	1261vs	
		1246s				1252s		
1226w	1216s	1221vw	1222m	1222w	1224w	1221w	1231vs	C–N?
1198vw		1195w	1195vw	1198vw	1198vw	1197vw	1181s	
1174w	1150s			1168m	1170m			
1132s	1128vs	1130vs	1131vs	1130vs	1131vs	1127vs	1130s	C–O–C in ring
1105s	1103s	1105vs	1109s	1100vs	1098s	1107s	1119s	
			1090s	1090vs		1086s	1084vs	
1073m		1071s	1074s		1067s			
	1060m	1057s		1058m		1065m	1057s	
1039w	1033vw	1034s	1039m	1030vw	1030vw	1039w	1033s	
1024m	1014m	1023sh		1014s		1024w		
			998w		1008s		1004s	
			941sh				945w	
933m	929w	927m	923m	929w	928w	927m	923w	C–O–C in ring
			896m					
885vw		881vw	882m			878w	885w	C–N=C in ring?
			862s			860m		
856w	844s	852m		843s	835s	847m	836w	
805w	823s	805m	816m	803m	803m	806m	807m	C–O–C in ring
			795s				793m	
783m	786w					783s		
		764s				757m	762m	
	737m	733s	740s	733s	728m		750s	
		719s	711s			721s	708w	
694s								

characterised[8] by exaltation and depression, respectively. Isocyclic six-membered rings do not seem to produce any deviation of the molecular refractivity, but in our instance this may be the influence of two heteroatoms.

Infrared Absorption Spectra.—N–H *stretching vibrations.* The bands 3354 and 3347 cm.$^{-1}$ for the compounds (I; R = Et, R′ = H) and (II) respectively should be assigned to stretching vibrations of the N–H group. The frequency is lowered by intermolecular hydrogen bonds.

Symmetrical C–H *stretching vibrations.* All the substances (I) examined give numerous bands of strong and medium intensity in the region 2980—2700 cm.$^{-1}$ which should be

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[8] Asmus, " Refraktometrie," in Houben–Weyl's " Methoden der Organischen Chemie," Thieme Stuttgart, 1955, Vol. III, Part 2.

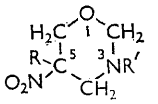
assigned to symmetrical C–H stretching vibrations of methyl and methylene groups. It was difficult to differentiate between various bands by using only a sodium chloride prism; the bands in this region were particularly numerous for compounds of type (I).

Region 1659—1640 *cm.*$^{-1}$. These vibrations are present only for the compounds (III) which differ from (I) and (II) by the absence of O–C–N and the presence of O–C=N bonds. We suggest assigning these frequencies to C=N bonds conjugated with the aromatic ring. The frequencies are similar to C=N vibration frequencies observed by Bergmann *et al.*[9] for aromatic Schiff's bases and by Lynn[5] for derivatives of 2-alkenyl-5,6-dihydro-1,3-oxazines.

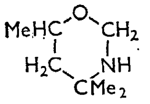
Antisymmetrical NO_2 *stretching vibrations.* Very strong bands at 1546—1540 cm.$^{-1}$ are found in the spectra of compounds (I). Their frequency is shifted towards figures usually assigned to tertiary nitro-paraffins.[10]

Methylene scissoring vibrations. One strong band at 1463—1452 cm.$^{-1}$ is present for all the compounds (I). Another band, at 1445—1440 cm.$^{-1}$, was found in the spectra of the ethyl compounds (I; R = Et) but not in those of the methyl analogues (I; R = Me). This should probably be assigned to CH_2 vibrations of the ethyl group. Two strong bands, at 1459 and 1449 cm.$^{-1}$, are present in the spectrum of the compound (II). The compounds (III) give a band at 1448—1422 cm.$^{-1}$.

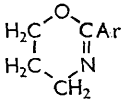
Symmetrical NO_2 *stretching vibrations.* High-intensity bands of frequency 1354—1348 cm.$^{-1}$ are displayed by all the methyl compounds (I; R = Me). They should be assigned to symmetrical NO_2 stretching vibrations. However, the assignment is more complicated for the ethyl compounds (I; R = Et). Two bands near this frequency have been observed: one of medium intensity at 1342—1336 cm.$^{-1}$, and a strong band at 1326—1324 cm.$^{-1}$. It is difficult to decide which of these two should be assigned to NO_2 vibrations. The former is nearer to the frequency observed with the compounds (I; R = Me) but its intensity is then anomalously low; nevertheless in view of the assignment of methylene wagging vibrations (see below) this frequency should be assigned to NO_2 stretching vibrations.



(I)



(II)



(III)

The difficulty of assigning symmetric nitro-group vibrations has been observed earlier by some of the present authors.[11]

Methylene wagging vibrations. All the compounds (I; R = Me) show a frequency 1308—1302 cm.$^{-1}$ which should be assigned to methylene wagging vibrations, although it is unusually low. Again, with the compounds (I; R = Et) the assignment is more complicated and depends on that of symmetrical NO_2 vibrations. If the frequency 1342—1336 cm.$^{-1}$ is due to the latter vibrations, the frequency 1326—1324 cm.$^{-1}$ should be assigned to methylene wagging vibrations of the ethyl groups.

A medium-strength band at 1343 cm.$^{-1}$ in the spectrum of the compound (II) and strong bands at 1349—1343 cm.$^{-1}$ in the spectra of compounds (III) should also be assigned to methylene wagging vibrations.

Band at 1222—1203 *cm.*$^{-1}$. This is present in the spectra of all the compounds (I) examined, and in (II). For compounds (III) the frequency of this band is slightly higher (1231—1216 cm.$^{-1}$). It is probable that it corresponds to C–N vibrations, which are not sufficiently well described in the literature.[12]

[9] Bergmann, Zimkin, and Pinchas, *Rec. Trav. chim.*, 1952, **71**, 168.

[10] Brown, *J. Amer. Chem. Soc.*, 1955, **77**, 6341.

[11] Eckstein, Fluksik, and Sobótka, *Bull. Acad. Polon. Sci., Sér. Sci. chim. géol. géograph.*, 1959, **7**, 803.

[12] Colthup, *J. Opt. Soc. Amer.*, 1950, **40**, 397.

1,3-*Oxazine ring vibrations*. According to the literature [5] the bands of the 1,3-oxazine ring lie in the region of 1150—1050 cm.$^{-1}$. In the spectra of the compounds (I) three strong bands with frequencies 1136—1117, 1113—1099 and 1086—1076 cm.$^{-1}$ were observed. The compound (II) gives strong bands at 1146, 1115, 1097, and 1073 cm.$^{-1}$, and the compounds (III) give bands at 1132—1127, 1119—1098, and 1086—1067 cm.$^{-1}$. In some instances the band is doubled (*e.g.*, for III where Ar = *m*-Cl·C_6H_4). The frequencies agree with the view expressed by Bergmann and his collaborators [5,9,13] who assigned these frequencies to vibrations of the system N–C–O in oxazolidines. Bergmann and Pinchas [14] had earlier found five bands for the bonds C–O–C in acetals and ketals; three of them (1143—1124, 1116—1105, and 1098—1063 cm.$^{-1}$) are found in our spectra. Lagrange and Mastagli,[15] and Barker, Bourne, Pinkard, and Whiffen,[16] are in agreement with Bergmann and Pinchas.

Also some lower-frequency bands of medium intensity, namely 953—937 and 855—842 cm.$^{-1}$ for compounds (I), 925 and 818 cm.$^{-1}$ for (II), 933—927 and 823—803 cm.$^{-1}$ (of variable intensity) for compounds (III), are probably due to cyclic acetal vibrations, in agreement with Barker *et al.*[16]

Band near 890 *cm.*$^{-1}$. In the spectra of the compounds (I) bands of frequency 898—884 cm.$^{-1}$ are present. They correspond to the frequency 895 cm.$^{-1}$ for (II). It is difficult to assign them to any known vibration and we suggest vibrations C–N–C and $\mathrm{C{-}N}\begin{smallmatrix}\diagup\mathrm{C}\\ \diagdown\mathrm{C}\end{smallmatrix}$ in the 1,3-oxazine ring. The frequency is lower for the compounds (III), 885—835 cm.$^{-1}$, owing to a different structure (C=N–C).

The absence of bands corresponding to O–H stretching vibrations in the spectra of the compounds (I) which were prepared from nitro-diols, formaldehyde, and ammonia or amines seems to be final evidence of their cyclic structure. At the same time a new proof has been found that the C–O–C fragment of the 1,3-oxazine ring is of acetal character.

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[13] Bergmann, Zimkin, and Pinchas, *Rec. Trav. chim.*, 1952, **71**, 237.

[14] Bergmann and Pinchas, *Rec. Trav. chim.*, 1952, **71**, 161.

[15] Lagrange and Mastagli, *Compt. rend.*, 1955, **241**, 1947.

[16] Barker, Bourne, Pinkard, and Whiffen, *J.*, 1959, 802, 807.