262. *Infrared Absorption Spectra of Aliphatic Nitro-alcohols. Part I. Spectra of Monohydric Nitro-alcohols and their Chloro- and Bromo-derivatives.*

By Z. Eckstein, P. Gluziński, W. Sobótka, and T. Urbański.

Infrared absorption spectra of aliphatic nitro-alcohols and their chloro- and bromo-derivatives have been measured. The length of the carbon chain does not appreciably influence the frequency of NO_2 bands.

Replacement of hydrogen atoms attached to $C_{(1)}$ by one or two chlorine atoms increases (by 14—21 and 30 cm.$^{-1}$ respectively) the frequency of asymmetric NO_2 vibrations and lowers the frequency of symmetric vibrations (17—32 and 50 cm.$^{-1}$ respectively). A similar effect is produced by bromine but the increase of the frequency of asymmetric vibrations is much smaller (5—16 cm.$^{-1}$).

A band at 1424—1416 cm.$^{-1}$ in the spectra of compounds with a primary nitro-group is probably due to scissors vibrations of C–H in $CH_2{\cdot}NO_2$. Assignments are also made for some other bands.

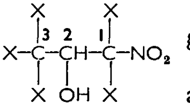
Little has been published so far on infrared absorption spectra of aliphatic nitro-compounds. Nevertheless a conclusion can be drawn that both asymmetric and symmetric vibrations of the nitro-group are subject to shift under the influence of some functional groups attached to the alkyl chain. For instance, Haszeldine[1] found that chlorine, in a few chloronitro-alkanes, has a strong influence on the frequencies of the nitro-group. Brown,[2] and Luther and Günzler,[3] came to a similar conclusion. Urbański and his colleagues[4] examined ultraviolet absorption spectra of halogen derivatives of nitro-alcohols and stated that the intensities of the absorption maxima characterising nitro-group are considerably reduced by halogen atoms.

In the present paper we examined the effects, on the infrared frequencies of the nitro-group of aliphatic β-nitro-alcohols, of the chain length of an alkyl group attached to $C_{(3)}$ (formula A), and of chlorine or bromine in various positions.

The nitro-alcohols, all obtained by known methods, are listed in Table 1. The infrared absorption bands are reported in Table 2.

Nitro-group Stretching Vibrations.—The asymmetric frequencies of the nitro-group are not influenced by the length of the carbon chain (C_2—C_{11}) to which the nitro-group is attached. The length of the carbon chain has a slight influence on the symmetric vibrations: thus the first member (I) has a lower frequency than the others and there is a tendency for lowering of the frequency as the series is ascended.

The presence of chlorine and bromine produces a very strong influence on the character and frequency of the nitro- and hydroxyl absorption. The position of halogen with respect to the nitro-group is most important.



$X_3\overset{3}{C}\text{–}\overset{2}{C}H(OH)\text{–}\overset{1}{C}X_2\text{–}NO_2$

(A)

The asymmetric and the symmetric stretching vibrations of the nitro-group of our compounds (A) are listed in Table 3.

Asymmetric vibrations bands are in all cases very strong: for primary and the secondary nitro-compounds they are at 1554—1550 and 1545 cm.$^{-1}$ respectively [the only deviation is for 1-nitromethylcyclohexanol (XXXI) which gives the frequency 1545 cm.$^{-1}$ although it is the primary nitro-compound].

Introduction of chlorine atom at position 1 strongly increases (by 14—21 cm.$^{-1}$) the frequency of the asymmetric vibrations. The influence of a bromine atom is less prominent (5—16 cm.$^{-1}$). Replacement of both active hydrogen atoms was examined for compounds

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[1] Haszeldine, *J.*, 1953, 2526.

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

[3] Luther and Günzler, *Z. Naturforsch.*, 1955, **10**b, 445.

[4] Sobótka, Urbański, and Eckstein, *Bull. Acad. Polon. Sci.*, *Cl. III*, 1955, **3**, 441; Urbański, Sobótka, and Eckstein, *ibid.*, 1957, **5**, 209; Sobótka, Eckstein, and Urbański, *ibid.*, 1957, **5**, 653.

(IV—VI): the shift of the asymmetric frequency is 30, 25, and 15 cm.$^{-1}$ respectively, chlorine having a notably greater effect than bromine. The weaker influence of bromine is probably due to its lower electronegativity and seems to confirm the hypothesis [4,5] about the different influence of substitution by chlorine and bromine on the electronic spectrum of aliphatic nitro-alcohols.

No marked change of asymmetric frequency occurs when the position 3 is substituted by chlorine in derivatives of 1-nitropropan-2-ol (X—XIV), 1-methyl-1-nitropropan-2-ol (XVI—XVIII), or 1-nitropentan-2-ol (XXV). The shift (1—3 cm.$^{-1}$) was near the experimental error.

TABLE 1. *Physical properties of substances* HO·CHR·CXX′·NO$_2$.

No.	R	X	X′	B. p. °C	mm.	d_{20}^{20}	n_D^{20}	$[M]_D$ calc.	$[M]_D$ exper.
I	H	H	H	92—94	6	1·2975	1·4403	18·55	18·51
II	H	H	Cl	90	4—5	1·4934	1·4699	23·77	23·44
III	H	H	Br	101—102	5	1·9201	1·5020	26·67	26·13
IV	H	Cl	Cl	65—66	1·0	1·5824	1·4743	28·58	28·43
V	H	Cl	Br	70—71	0·8	1·9014	1·5044	31·48	31·85
VI	H	Br	Br	87	1·2	2·2521	1·5441	34·38	34·88
VII	Me	H	H	72·5—73	0·5	1·1906	1·4383	23·29	23·16
VIII	Me	H	Cl	71	0·6	1·3645	1·4603	28·06	27·93
IX	Me	H	Br	90—90·5	1·7	1·7485	1·4930	30·93	30·57
X	CH$_2$Cl	H	H	101—103	6	1·4234	1·4838	28·01	28·03
XI	CHCl$_2$	H	H	105	5	1·5691	1·5026	32·82	32·75
XII	CCl$_3$	H	H [a]	—	—	—	—	—	—
XIII	CCl$_3$	H	Cl	103—104	0·7	1·7081	1·5146	42·67	42·84
XIV	CCl$_3$	H	Br	104—106	0·8	1·9834	1·5361	45·56	45·17
XV	Me	H	Me	70—73	0·5	1·1353	1·4431	27·80	27·81
XVI	CH$_2$Cl	H	Me	102—103	3	1·3393	1·4781	32·63	32·45
XVII	CHCl$_2$	H	Me	113	2	1·4843	1·4971	37·45	37·00
XVIII	CCl$_3$	H	Me	109—110	2	1·5493	1·5032	42·26	42·40
XIX	Et	H	H	82·5	1·2	1·1353	1·4435	28·00	27·90
XX	Et	H	Cl	89	2	1·2793	1·4600	32·77	32·85
XXI	Et	H	Br	94—95	1	1·5941	1·4860	35·67	35·65
XXII	Pr^n	H	H	80—81	0·6	1·0908	1·4439	32·71	32·39
XXIII	Pr^n	H	Cl	87	1	1·2286	1·4575	37·48	37·18
XXIV	Pr^n	H	Br [b]	98—100	1	1·5222 *	1·4823 *	40·38	39·73 *
XXV	CH$_3$·CHCl·CCl$_2$	H	H	145	0·5	1·5111	1·5122	46·90	46·85
XXVI	Bu^n	H	H	103	2·5	1·0576	1·4482	37·11	37·26
XXVII	Bu^i	H	H	90	1·1	1·0587	1·4474	37·23	37·14
XVIII	Bu^i	H	Cl	79	0·5	1·1852	1·4586	41·85	41·83
XXIX	Bu^i	H	Br	107—108	1·2	1·4386	1·4837	44·79	44·93
XXX	n-C$_5$H$_{11}$	H	H	113	1·5	1·0306	1·4495	41·76	41·99
XXXI	C$_6$H$_{10}$(OH)·CH$_2$·NO$_2$			93	0·4	1·1616	1·4881	40·02	39·47
XXXII	C$_6$H$_{10}$(OH)·CHCl·NO$_2$			96·5	0·4	1·2907	1·5000	44·80	44·09
XXXIII	C$_6$H$_{10}$(OH)·CHBr·NO$_2$			118	1·0	1·5476	1·5208	47·70	46·80
XXIV	n-C$_6$H$_{13}$	H	H	115—118	1·5	1·0095	1·4499	46·41	46·63
XXXV	C$_6$H$_{11}$	H	H	123	1·0	1·1194	1·4880	44·64	44·52
XXXVI	C$_6$H$_{11}$	H	Cl	118	1·2	1·2365	1·4952	49·41	48·83
XXXVII	C$_6$H$_{11}$	H	Br	132	1·5	1·4764	1·5160	52·32	51·55
XXXVIII	n-C$_7$H$_{15}$	H	H	128	1·5	0·9966	1·4526	51·06	51·20
XXXIX	n-C$_8$H$_{17}$	H	H	126—128	1·0	0·9931	1·4550	55·70	55·53
XL	n-C$_9$H$_{19}$	H	H	142	1·5	0·9674	1·4549	60·35	60·9

Examined as a supercooled liquid. [a] M. p. 45°. [b] M. p. 35°.

Assignment of bands of symmetric vibrations of NO$_2$ was much more difficult: a number of bands have both frequencies and intensities similar to that expected and this is particularly true for our chloro-derivatives; a similar difficulty we described in our earlier papers.[6,7] We base our assignment on comparison of the spectra of nitro-alcohols and halogenonitro-alcohols with those of nitroalkanes and halogenonitroalkanes having chains

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[5] Urbański, Eckstein, and Sobótka, *Roczniki Chem.*, 1955, **29**, 399; Eckstein, *ibid.*, 1956, **30**, 1151.

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

[7] Eckstein, Gluziński, Hofman, and Urbański, *J.*, 1961, 489.

of same length and structure of carbon chain: for these, as we shall detail elsewhere,[8] the frequencies symmetric NO_2 vibrations are the same within experimental error (~3 cm.$^{-1}$). For instance, the spectrum of 1-chloro-1-nitropropane-2-ol (VIII) has strong bands at **1384** and **1367** cm.$^{-1}$; the spectrum of 1-chloro-1-nitropropane has a strong band **1364** cm.$^{-1}$, indicating the second of the above values as corresponding to symmetric NO_2 vibrations.

TABLE 2. *Some frequencies in the infrared absorption spectra.*

No.	Band frequencies (cm.$^{-1}$)
I	3551—3415m(b), 1554vs, 1421m, 1375s
II	3552—3405m(b), 3011m, 1571vs, 1353s
III	3539—3390m(b), 3023w, 1566vs, 1353m
IV	3533—3406s(b), 1584vs, 1325s, 899s, 847s
V	3532—3397m(b), 1579vs, 1324s
VI	3554—3430m(b), 1569vs, 1323s
VII	3538—3418s(b), 1552vs, 1423s, 1386s
VIII	3541—3427s(b), 1570vs, 1384s, 1367s, 1335w
IX	3535—3425m(b), 1566vs, 1365s
X	3537—3440m(b), 3026vw, 1553vs, 1423m, 1384s
XI	3534m(b), 3006vw, 1555vs, 1418m, 1379s, 790s
XII *	3525s(b), 3028w, 1558vs, 1419s, 1377s, 807vs
XIII	3518s(b), 3006w, 1579vs, 1355s, 822s, 803s
XIV	3509m(b), 3006w, 1566vs, 1353s, 825s
XV	3539—3452m(b), 1545vs, 1389s, 1361m
XVI	3531—3433m(b), 3004m, 1549vs, 1391m, 1362m
XVII	3526s(b), 3003m, 1549vs, 1391s, 1362s, 783s
XVIII	3526m(b), 3004vw, 1549vs, 1390m, 1357s, 824s, 797s
XIX	3543—3428s(b), 1553vs, 1421s, 1385s
XX	3538—3443s(b), 1572vs, 1368s, 1350s, 1331s
XXI	3545—3453s(b), 1565vs, 1366s
XXII	3549—3444s(b), 1553vs, 1424s, 1385s
XXIII	3530—3414m(b), 1570vs, 1370m, 1355m
XXIV *	3541—3447m(b), 1563vs, 1356s
XXV	3529m(b), 3039vw, 1556vs, 1417m, 1382s, 812s
XXVI	3535—3456m(b), 1551vs, 1418m, 1381s
XXVII	3538—3436s(b), 1552vs, 1422s, 1385s
XXVIII	3544—3442m(b), 1566vs, 1368s, 1353s
XXIX	3534—3435m(b), 1557vs, 1353s
XXX	3541—3449m(b), 1550vs, 1417m, 1381s
XXXI	3524—3448m(b), 1545vs, 1422sh, 1382s
XXXII	3538—3483m(b), 1562vs, 1353s
XXXIII	3537—3449m(b), 1556vs, 1350s
XXXIV	3541—3454m(b), 1550vs, 1417m, 1381s
XXXV	3522—3416m(b), 1550vs, 1419m, 1384s
XXXVI	3545—3476m(b), 1571vs, 1366m
XXXVII	3551—3457m(b), 1566vs, 1356m
XXXVIII	3534—3443m(b), 1551vs, 1416m, 1378s
XXXIX	3537—3438m(b), 1551vs, 1417m, 1377s
XL	3541—3451m(b), 1550vs, 1418m, 1379s

* Measurements of supercooled liquid.

We could not confirm the frequency **1340** cm.$^{-1}$ assigned by Haszeldine[1] for 1-chloro-1-nitropropane as we found only a weak band **1335** cm.$^{-1}$ in this compound which could not be assigned to the frequency in question. Similarly, 1-chloro-1-nitropentan-2-ol (XXIII) has bands at **1370** and **1355** cm.$^{-1}$, and the second was chosen as it is identical with the frequency of symmetric NO_2 vibrations of 1-chloro-1-nitropentane (**1355** cm.$^{-1}$).

Comparison of the spectrum of a nitro-alcohol with that of the corresponding nitroparaffin does not always give a simple solution. 1-Chloro-1-nitrobutan-2-ol (XX) gives bands of almost identical intensity (strong) at **1368**, **1350**, and **1331** cm.$^{-1}$. The 1-chloro-1-nitrobutane gives a strong band at **1355** with a shoulder **1367** cm.$^{-1}$. Eventually we assigned the band **1368** cm.$^{-1}$ to symmetric NO_2 vibrations.

Broadly speaking, no general method of identification of bands of symmetric NO_2 vibrations exists, and the assignment is not always certain. The assignments made are

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[8] Urbański, Eckstein, Sobótka, and Gluziński, unpublished work.

recorded in Table 3. The shift due to chlorine and bromine atom in the position 1 is in the direction of lower frequency, *i.e.*, in the opposite direction to that for asymmetric vibrations. The lowering is relatively strong and amounts to 17—32 cm.$^{-1}$. No difference between the action of chlorine and bromine was noticed, except for the derivatives of cyclohexylnitroethanol (XXXVI and XXXVII respectively) where the bromo-compound had a frequency lower by 10 cm.$^{-1}$.

TABLE 3. *Comparison of frequencies of the nitro-group in nitro-alcohols and their halogen* (Cl *and* Br) *derivatives.*

No.	Compound *	$\nu(NO_2)$ (cm.$^{-1}$) asymm.	symm.	No.	Compound *	$\nu(NO_2)$ (cm.$^{-1}$) asymm.	symm.
I	$HO\cdot CH_2\cdot CH_2\cdot NO_2$	1554	1375	II	$HO\cdot CH_2\cdot CHCl\cdot NO_2$	1571	1353
				III	$HO\cdot CH_2\cdot CHBr\cdot NO_2$	1566	1353
				IV	$HO\cdot CH_2\cdot CCl_2\cdot NO_2$	1584	1325
				V	$HO\cdot CH_2\cdot CBrCl\cdot NO_2$	1579	1324
				VI	$HO\cdot CH_2\cdot CBr_2\cdot NO_2$	1569	1323
VII	$CH_3\cdot CH(OH)\cdot CH_2\cdot NO_2$	1552	1386	VIII	$CH_3\cdot CH(OH)\cdot CHCl\cdot NO_2$	1570	1367
				IX	$CH_3\cdot CH(OH)\cdot CHBr\cdot NO_2$	1566	1365
				X	$CH_2Cl\cdot CH(OH)\cdot CH_2\cdot NO_2$	1553	1384
				XI	$CHCl_2\cdot CH(OH)\cdot CH_2\cdot NO_2$	1555	1379
				XII †	$CCl_3\cdot CH(OH)\cdot CH_2\cdot NO_2$	1558	1377
				XIII	$CCl_3\cdot CH(OH)\cdot CHCl\cdot NO_2$	1579	1355
				XIV	$CCl_3\cdot CH(OH)\cdot CHBr\cdot NO_2$	1566	1358
XV	$CH_3\cdot CH(OH)\cdot CHMe\cdot NO_2$	1545	1361	XVI	$CH_2Cl\cdot CH(OH)\cdot CHMe\cdot NO_2$	1549	1364
				XVII	$CHCl_2\cdot CH(OH)\cdot CHMe\cdot NO_2$	1549	1362
				XVIII	$CCl_3\cdot CH(OH)\cdot CHMe\cdot NO_2$	1549	1357
XIX	$CH_3\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot NO_2$	1553	1385	XX	$CH_2\cdot CH_2\cdot CH(OH)\cdot CHCl\cdot NO_2$	1572	1368
				XXI	$CH_3\cdot CH_2\cdot CH(OH)\cdot CHBr\cdot NO_2$	1565	1366
XXII	$CH_3\cdot CH_2\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot NO_2$	1553	1385	XXIII	$CH_3\cdot CH_2\cdot CH_2\cdot CH(OH)\cdot CHCl\cdot NO_2$	1570	1355
				XXIV †	$CH_3\cdot CH_2\cdot CH_2\cdot CH(OH)\cdot CHBr\cdot NO_2$	1563	1356
				XXV	$CH_3\cdot CHCl\cdot CCl_2\cdot CH(OH)\cdot CH_2\cdot NO_2$	1556	1382
XXVII	$Me_2CH\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot NO_2$	1552	1385	XXVIII	$Me_2CH\cdot CH_2\cdot CH(OH)\cdot CHCl\cdot NO_2$	1566	1353
				XXIX	$Me_2CH\cdot CH_2\cdot CH(OH)\cdot CHBr\cdot NO_2$	1557	1353
XXXI	$C_6H_{10}(OH)\cdot CH_2\cdot NO_2$	1545	1382	XXXII	$C_6H_{10}(OH)\cdot CHCl\cdot NO_2$	1562	1353
				XXXIII	$C_6H_{10}(OH)\cdot CHBr\cdot NO_2$	1556	1350
XXXV	$C_6H_{11}\cdot CH(OH)\cdot CH_2\cdot NO_2$	1550	1384	XXXVI	$C_6H_{11}\cdot CH(OH)\cdot CHCl\cdot NO_2$	1571	1366
				XXXVII	$C_6H_{11}\cdot CH(OH)\cdot CHBr\cdot NO_2$	1566	1356

* C_6H_{10} denotes cyclohexylidene. † Measurements of a supercooled liquid.

Two halogen atoms (IV—VI) produce a greater shift (50—52 cm.$^{-1}$), the same for chlorine as for bromine.

When chlorine atoms were introduced at position 3 only an insignificant shifting of symmetric vibrations (—3 to —9 cm.$^{-1}$) was observed. Replacement at position 1 and 3 (XIII, XIV) had a considerably greater effect.

The observed shifts of the bands of the nitro-group are in agreement with the findings by Haszeldine [1] and Brown [2] for the chlorine and bromine derivatives of nitroparaffins.

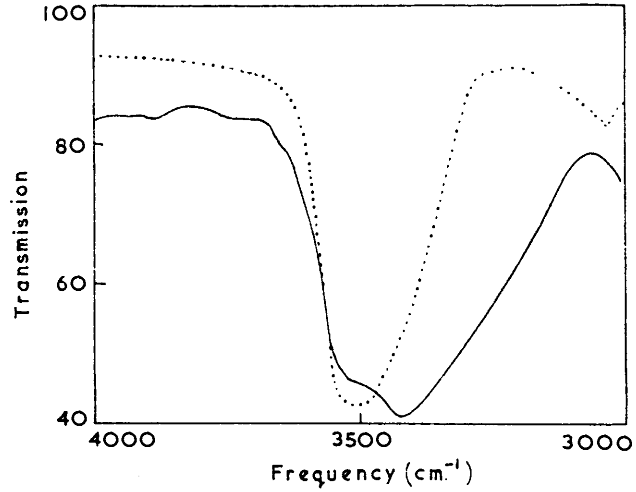
It seems to us that the shifts of the NO_2 frequencies can be explained (at least partly) by the fact that replacement at position 1 changes the nature of the nitro-compound. It is known that both bands of NO_2 vibrations for aliphatic secondary nitro-compounds are at lower frequencies than are those of aliphatic primary nitro-compounds. One halogen atom at position 1 produces a secondary nitro-compound and the final result is composed of two superposed partial effects, (1) that of the halogen, and (2) that of the nature of the nitro-group. For asymmetric NO_2 vibrations the effect (1) produces a shift to higher and effect (2) to lower frequencies; a higher frequency results which denotes the greater power of effect (1). For symmetric NO_2 vibrations both effects are in the same direction and a relatively large lowering of the frequency results.

Hydroxyl Group.—All our nitro-alcohols give an absorption band between 3554 and 3390 cm.$^{-1}$ characterising the O–H stretching vibration. This band is broad and of middle intensity, indicating intermolecular hydrogen bonds. Two maxima (3554—3509 and 3483—3390 cm.$^{-1}$; full line in Figure) are observed. When two or three atoms of chlorine are attached at position 3 the second maximum disappears and the band becomes narrower (dotted line): this may signify that one type of hydrogen bond disappears for these compounds.

It should also be pointed out that the acidity of the hydroxyl groups is greater for the 3-trichloro-derivatives. This can be deduced by analogy with trichloroethanol: it may have a bearing on the ability to form hydrogen bonds.

Band at 3039—3003 *cm.*$^{-1}$.—A weak band at 3039—3003 cm.$^{-1}$ was noticed for all the halogenonitro-alcohols containing one or more halogen atoms at position 3. This band is not present for unsubstituted nitro-alcohols and present only for some substituted products, such as 2-chloro- and 2-bromo-2-nitroethanol (II and III). Plyler and Benedict [9] found a similar band in the spectra of alkyl chlorides. It may be due to some C–H vibrations.

O–H *stretching vibrations of* 1-*nitropropan*-2-*ol* (*full line*) *and* 1,1-*dichloro*-3-*nitropropan*-2-*ol* (*dotted line*).



Band at 1424—1416 *cm.*$^{-1}$.—This band was found in all our nitro-alcohols containing primary nitro-groups. It is of high or medium intensity. Similar bands were reported by Brown.[2] They are probably produced by the scissors vibrations of the C–H bonds in the $CH_2{\cdot}NO_2$ group. Urbański [10] reported bands of frequencies 4167 and 3704 cm.$^{-1}$ for similar nitro-alcohols and these are probably overtones of the band in question.

Band at 1391—1389 *cm.*$^{-1}$.—A strong band of this frequency was found in the spectra of all the nitro-alcohols with a system $CH_3{\cdot}C{\cdot}NO_2$ (XV—XVIII), also by Brown,[2] according to whom it is due to deformation vibrations of C–H bonds in the methyl group attached to $C{\cdot}NO_2$.

Bands at 825—783 *cm.*$^{-1}$.—Strong and very strong bands 825—783 cm.$^{-1}$ are present in the spectra of all the nitro-alcohols containing two and three chlorine atoms at position 3 (XII—XIV, XVII—XVIII, XXV). They are probably formed by the vibrations of the groups CCl_2 and CCl_3. However the literature [11] reports lower frequencies (780—710 cm.$^{-1}$).

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[9] Plyler and Benedict, *J. Res. Nat. Bur. Standards*, 1951, **47**, 202.

[10] Urbański, *Bull. Acad. Polon. Sci., Cl. III*, 1956, **4**, 87; 1956, **4**, 381; *Roczniki Chem.*, 1957, **31**, 37.

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

Also strong bands at 899 and 847 cm.$^{-1}$ in the spectrum of 2,2-dichloro-2-nitroethanol (IV) may be assigned to CCl_2 and their shift to higher frequency may be due to the presence of the NO_2 group attached to the same carbon atom.

EXPERIMENTAL

The compounds were purified by repeated distillation under reduced pressure.

Refractive index at 20° ± 0·05° was determined by means of an Abbé refractometer, model G (Zeiss), standarised for the sodium *D* line.

Density was determined in a pycnometer at 20°.

Infrared absorption spectra were determined in a double-beam spectrophotometer (Hilger model H-800) with optics of rock salt and automatic recording. The substances were used in liquid form (liquids or supercooled liquids) in capillary thickness. The wavelengths were controlled by means of a polystyrene film. The maximum experimental error was 3 cm.$^{-1}$.

1-*Chloro*-3-*nitropropan*-2-*ol* (X).—Chloroacetaldehyde (23·6 g., 0·3 mol.), in the form of an 80% aqueous solution of its hydrate (33 g.), was mixed with nitromethane (23 g., 0·38 mol.). Potassium carbonate (0·7 g.) in water (7 ml.) was added dropwise. The whole was warmed for 15 min. at 80°, then cooled to 35°. Dioxan (17 ml.) was added and whole left for 48 hr., then shaken with water and extracted with ether. The ether extract was shaken with a small quantity of concentrated hydrochloric acid, washed with water, dried, ($MgSO_4$), and evaporated. Two distillations under reduced pressure gave the *product*, b. p. 101—103°/6 mm. (5 g., 12%) (Found: N, 10·1. $C_3H_6ClNO_3$ requires N, 10·0%).

1,1,1,3-*Tetrachloro*-3-*nitropropan*-2-*ol* (XIII).—1,1,1-Trichloro-3-nitropropan-2-ol (XII) (83·2 g., 0·4 mole) was dissolved in methanol (40 ml.) and cooled to −5°. Sodium methoxide solution (from sodium, 9·2 g.; 0·4 g.-atom) (100 ml.) was added dropwise. The mixture was left at −10° for 24 hr. The precipitated sodium derivative of (XII) was collected and washed with ether (yield, 70·0 g., 76·5%).

This sodium derivative (35 g., 0·153 mole) was suspended in dry chloroform (65 ml.), and dry chlorine was introduced at −5°. Samples of the precipitate were taken from the reacting medium and ignited. The reaction was ended when the precipitate was composed of sodium chloride only. The chloroform solution was then filtered, washed with aqueous sodium hydrogen carbonate and water, and dried (Na_2SO_4). The solvent and the *product* (XIII) were distilled under reduced pressure. The fraction of b. p. 103—104°/0·7 mm. was collected (23·7 g., 64·0%) (Found: N, 6·0. $C_3H_3Cl_4NO_3$ requires N, 5·8%).

3-*Bromo*-1,1,1-*trichloro*-3-*nitropropan*-2-*ol* (XIV).—The sodium derivative (28 g., 0·122 mole) of the nitro-alcohol (XII) was suspended in anhydrous chloroform (60 ml.) and cooled to −5°. Bromine (17·5 g., 0·11 mole) in chloroform (10 ml.) was added dropwise until the mixture acquired a pale yellow colour. The sodium bromide was filtered off, and the solution washed with saturated aqueous sodium hydrogen carbonate and water. The solvent and the *product* (XIV) were distilled under reduced pressure. The fraction of b. p. 104—106°/0·8 mm. was collected (yield, 26·0 g., 74·4%) (Found: N, 4·85. $C_3H_3BrCl_3NO_3$ requires N, 4·9%).

1,1-*Dichloro*-3-*methyl*-3-*nitropropan*-2-*ol* (XVII).—Freshly distilled dichloroacetaldehyde (22·5 g., 0·2 mole) (prepared from dichloroacetal) was distilled with water (3·6 ml., 0·2 mole) and a drop of concentrated sulphuric acid, affording crystalline dichloroacetaldehyde hydrate (23 g., 0·175 mole), which was mixed with nitroethane (16·5 g., 0·22 mole) and warmed to 50° with stirring. Potassium hydrogen carbonate (0·4 g.) was added, the temperature rising spontaneously to 63°. After the reaction subsided the whole was warmed to 70° and left to cool with continuous mixing. The aqueous layer was collected and the organic layer washed three times with water. The combined aqueous solutions were extracted with ether, and the extract was washed several times with aqueous sodium hydrogen sulphite, then with saturated solution of sodium chloride, and dried ($MgSO_4$). Ether and the *product* (XVII) were distilled under reduced pressure. The fraction of b. p. 110—116°/2 mm. was collected and redistilled at 113°/2 mm. (yield, 9·3 g., 28·2%) (Found: N, 7·2. $C_4H_7Cl_2NO_3$ requires N, 7·45%).

CHEMICAL ORGANIC LABORATORIES, POLISH ACADEMY OF SCIENCES,
WARSAW, POLAND.

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