BULLETIN DE L'ACADÉMIE
POLONAISE DES SCIENCES
Cl. III — Vol. V, No. 3, 1957

CHEMISTRY

On Endo- and Exoisomers of Nitroölefines (1-Cyclohexenyl- and Cyclohexylidenenitromethane). II

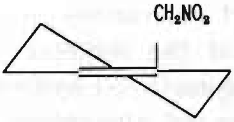
by

Z. ECKSTEIN, T. KRACZKIEWICZ, T. URBAŃSKI
and H. WOJNOWSKA

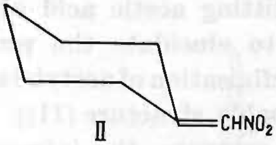
Presented by T. URBAŃSKI on December 10, 1956

In one of our former papers [1] we found that 1-cyclohexenylnitromethane cannot be prepared in a pure form by olefinisation of the acetyl derivative of 1-nitromethyl-1-hydroxycyclohexane. The product so obtained differed from 1-cyclohexenylnitromethane by its physical constants and some chemical reactions.

We originally suggested that one of the products of olefinisation would be an isomer of cyclohexenylnitromethane, i. e., cyclohexylidenenitromethane (II).



I



II

The product (I) is well known in the literature [2]—[5] and its structure can be expressed by the "half-chair" form of Barton [6]. The new product (II) which has now been obtained by us differed from the product (I). Thus, the ultraviolet absorption curve of the compound (I) did not show the maximum typical for the nitrogroup but only a slight bend in the region of 267—300 mμ and the new product (II) gave a sharp maximum at 262 mμ and the bend shifted to 312—350 mμ.

The difference between the absorption curves could be explained by the lack of conjugation of double bonds in the compound (I), where only two separate chromophores exist (*A*). On the contrary, the conjugation (*B*) exists in the compound (II).

Two separate chromophores of the type (*A*) do not suffice to create the maximum of the ultraviolet absorption curve, and this may be due to the steric influence on the nitrogroup of the cyclohexenyl ring. A similar effect has also been observed in the case of 1-cycloheptenylnitromethane [7] and of 1-nitromethyl-1-hydroxycyclohexane [8].

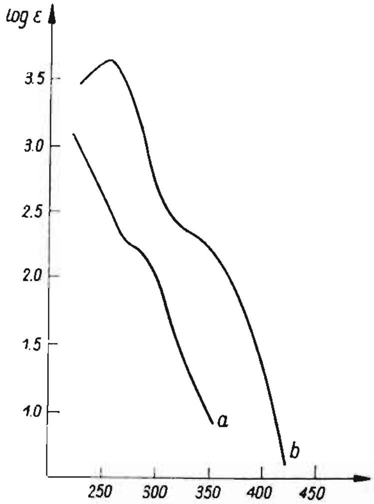
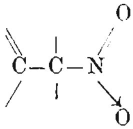
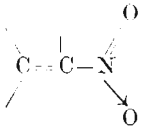


Fig. 1



(*A*)



(*B*)

However, taking into consideration data existing in the literature, the formation of the isomer (II) should be regarded as not very probable. Some of the authors exclude the possibility of formation of the system $R=CHNO_2$, i. e., the existence of the structure with cyclohexylidenenitromethane group [9], [10]. This is based on the assumption of greater stability of the endocyclic (I), than of the exocyclic form (II) in cyclohexane and the tendency to transformation of the product (II) into (I).

The only argument in favour of the stability of the structure (II) would be the fact, that the active hydrogen attached to carbon with a nitrogroup always takes part in all known reactions of forming nitroölefines by splitting acetic acid off acetyl derivatives [3], [11]—[23].

In order to elucidate the problem of the structure of compound obtained by olefinisation of acetylated 1-nitromethyl-1-hydroxycyclohexane (with the probable structure (II)), its infra-red absorption spectrum was examined. To compare, the infra-red absorption of (I) was also investigated (Fig. 2, Table I).

The absorption curve of (I) is very similar to that of 1-cycloheptenylnitromethane according to experiments described in one of the former publications [7]. It shows the presence of characteristic vibrations of the double bond in cycloaliphatic rings ($\nu = 1666$ cm.$^{-1}$) and a marked shifting of deformation vibrations of CH_2 towards lower frequencies (1429 cm.$^{-1}$). Very prominent are both frequencies of the aliphatic nitrogroup (1555 and 1370 cm.$^{-1}$). Thus the structure of the compound (I) as 1-cyclohexenylnitromethane should be considered as being confirmed, although no clear maximum for NO_2 group can be found in the electronic spectrum (Fig. 1, Curve a).

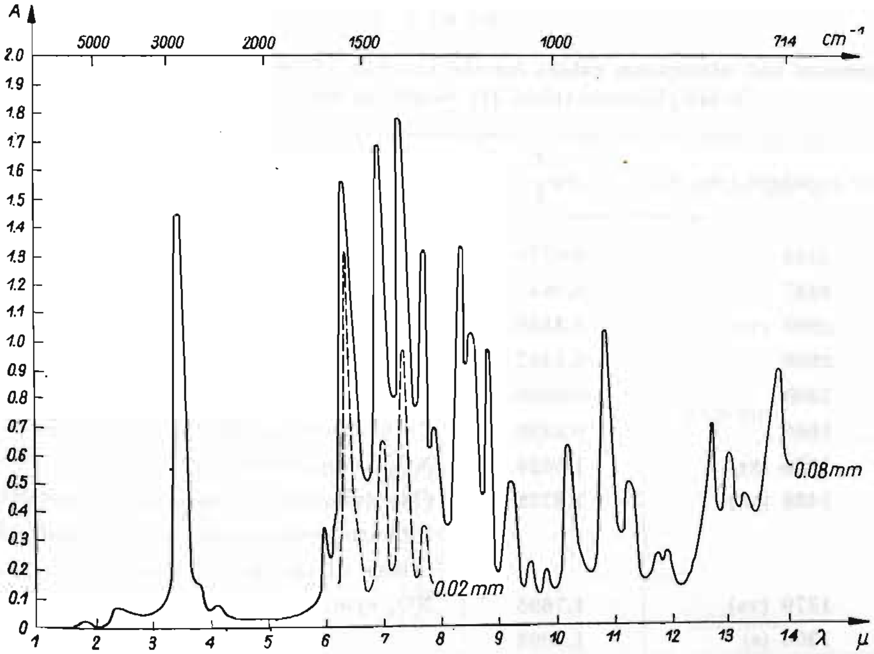


Fig. 2

The spectrum of the olefin (II) prepared from the acetylated 1-nitromethyl-1-hydroxycyclohexane is given in Fig. 3 and Table II.

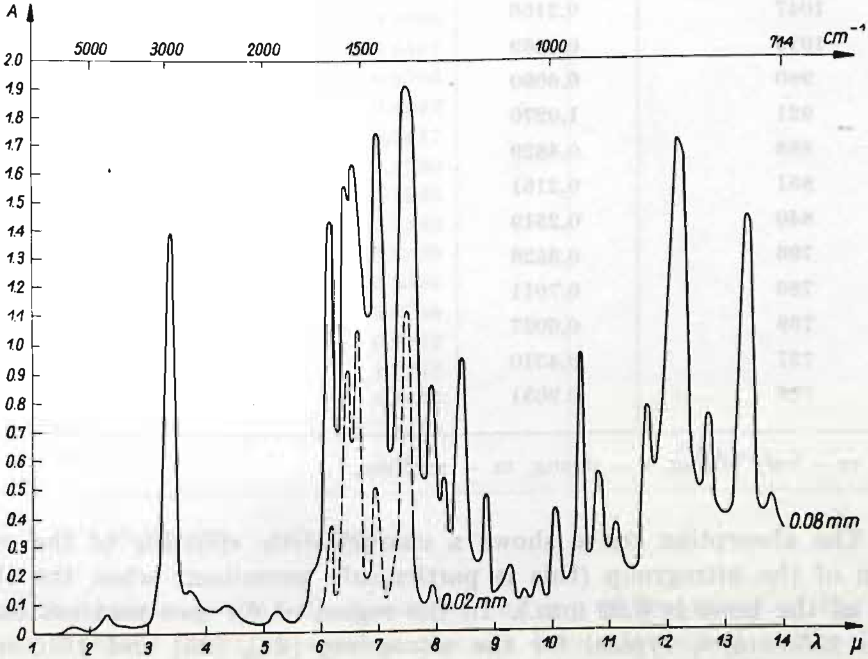


Fig. 3

TABLE I

Frequencies and absorption values for the maxima of the infra-red spectra of 1-cyclohexenylnitromethane (I) (width of the slot 0.08 mm.)

Wave numbers (cm.$^{-1}$)	$\log \frac{I^{\circ}}{I}$	Assignement
5555	0.0170	
4347	0.0641	
2898 (vs)	1.4559	
2666	0.1485	
2409	0.0820	
1666	0.3430	C=C in cycloaliphatic compounds
1555 (vs)	1.5528	NO_2 asym. stretching
1439 (vs)	1.6778	CH_2 deformation frequency in cycloaliphatic compounds, shifted under influence of the double bond C=C
1370 (vs)	1.7695	NO_2 sym. stretching
1306 (s)	1.3098	
1265	0.6904	
1197 (s)	1.3187	
1176 (m)	1.0132	
1136	0.9586	
1092	0.4922	
1047	0.2166	
1015	0.1869	
980	0.6090	
921	1.0270	
888	0.4829	
851	0.2161	
840	0.2519	
796	0.3526	
786	0.7011	
769	0.6037	
757	0.4510	
724	0.9031	

vs — very strong, s — strong, m — medium.

The absorption curve shows a characteristic splitting of the maximum of the nitrogroup (this is particularly prominent when the thickness of the layer is 0.02 mm.). In the region of 6 μ two maxima can be seen: 1550 cm.$^{-1}$, typical for the nitrogroup [24], [25] and 1515 cm.$^{-1}$, which would correspond to the nitrogroup conjugated with the double

TABLE II

Frequencies and absorption values for the maxima of infra-red spectra of the mixture of nitroölefines (I) and (II)

Wave numbers (cm.$^{-1}$)	$\log\frac{I^\circ}{I}$	Width of the slot
5555	0.0119	
4347	0.0755	
2898 (vs)	1.4089	
2702	0.1428	
2300	0.1035	
1923	0.0712	0.08 mm.
1639	0.3747	
1550	0.9137	
1515	1.0864	
1449	0.5031	
1342	1.1249	
1265	0.1611	0.02 mm.
1694 (vw)	0.2103	
1626 (vs)	1.4319	
1576 (vs)	1.5528	
1526 (vs)	1.6383	
1439 (vs)	1.7448	
1351 (vs)	1.9586	
1265	0.8696	
1234	0.5497	
1190	0.9706	
1136	0.4842	
1081	0.2417	
1047 (vw)	0.1390	
1025	0.1965	
995	0.4283	
952	0.9829	
921	0.5591	
900	0.3799	
859	0.7932	
819	1.7212	
787	0.7569	
748	1.4559	
724	0.4737	0.08 mm.

vs — very strong, vw — very weak.

bond of methylene group (*B*). A similar shifting of frequency of the nitrogroup towards lower values has already been mentioned in the literature [10], [26].

It is known that the quantitative determination of isomeric nitroölefines in their mixture can be done by means of the infra-red absorption spectrum. Shechter and Shepherd [10] examined the mixture of 2-methyl-3-nitropropene and 2-methyl-1-nitropropene. They both possessed compounds in pure form and this simplified the quantitative analysis.

In our instance, only the isomer (I) was in the pure form, and the product obtained from the acetylated 1-nitromethyl-1-hydroxycyclohexane was a mixture of two isomers, (I) and (II). Therefore, it was impossible to use the ordinary methods of spectral analysis of mixture of two components.

The method described by Wright [27] allows to eliminate the influence of the presence of another substance on the band of the examined compound.

The curve (Fig. 4) shows the infra-red absorption of the mixture of isomers in solution in cyclohexane (2 ml. of the mixture were dissolved in 25 ml. of cyclohexane) in the range between 6.3 and 6.7 μ. Two bands have been obtained: the first with a wave length of 6.45 μ (frequency 1550 cm.$^{-1}$) corresponds to vibrations of the nitrogroup in the isomer (I), and the second, 6.575 μ (frequency 1519 cm.$^{-1}$), would be assigned to the nitrogroup conjugated with a double bond in the isomer (II). The influence on the 6.45 μ band of isomer (II) was eliminated by plotting the straight line tangent to the spectrum curve at the points corresponding to the wave lengths 6.375 and 6.475 μ. The absorption value was determined from the difference $A = A_a - A_b$. The content of the com-

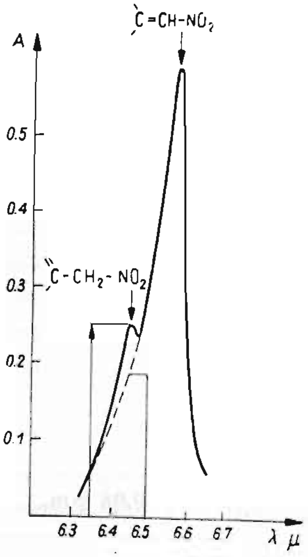


Fig. 4

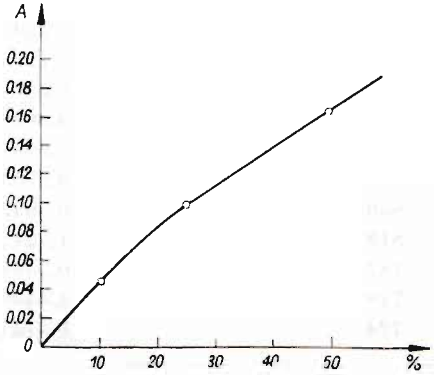


Fig. 5

ponent (I) in the mixture of (I) and (II) was determined from the value A by means of the standard curve (Fig. 5).

The values of $\log I/I_0$ were plotted against the concentrations of solutions of the compound (I). The basic 100% concentration was admitted when 2 ml. of the substance were present in 25 ml. of the solution in cyclohexane. The lower concentrations – 50, 25 and 10% – were obtained by the corresponding dilution of the basic solution.

TABLE III

Data for the standard curve

Content of isomer (I) vol %	A_a	A_b	$A = A_a - A_b$	$\overline{A}$
50.0	0.4732	0.2040	0.1692	
	0.4930	0.3320	0.1610	0.1651
25.0	0.2576	0.1540	0.1036	
	0.2602	0.2570	0.1032	0.1034
10.0	0.1126	0.0716	0.0410	
	0.1508	0.0958	0.0550	0.0480

TABLE IV

Analysis of the mixtures of (I) and (II)

Examined sample	A_a	A_b	$A = A_a - A_b$	$\overline{A}$	Content of the isomer (I) vol %
AO$_{\mathrm{I}}$	0.5087	0.4600	0.0487		
	0.3010	0.2540	0.0470	0.0478	10
AO$_{\mathrm{II}}$	0.2519	0.2100	0.0419		
	0.2669	0.2250	0.0419	0.0419	9
AO$_{\mathrm{II}}$ + 50%	0.3936	0.2846	0.1090		
in 50:50 ratio	0.4256	0.3100	0.1156	0.1123	29.5

The values of absorption of these solutions are tabulated (Table III). The values of absorption of two samples of (II), marked AO$_{\mathrm{I}}$ and AO$_{\mathrm{II}}$, are also tabulated below (Table IV). To check the result obtained for the sample AO$_{\mathrm{II}}$, the solution of the sample was mixed with the 50% solution of the isomer (I) in the ratio 50:50. The content of the isomer (I) in the solution thus obtained was next determined by the method described above. The value was in agreement with the expected figure.

INSTITUTE OF ORGANIC CHEMISTRY, POLISH ACADEMY OF SCIENCES
INSTITUTE OF GENERAL CHEMISTRY, WARSAW

REFERENCES

[1] Z. Eckstein, T. Urbański, H. Wojnowska, *On endo- and exoisomers of nitroölefins (1-cyclohexenyl- and cyclohexylidenitromethane). I.* Bull. Acad. Polon. Sci. Cl. III **5** (1957), 219.

[2] H. B. Frazer, G. A. R. Kon, J. Chem. Soc., **137** (1934), 604.

[3] G. A. Buckley, J. L. Charlis, J. Chem. Soc. (1947), 1372.

[4] D. V. Nightingale, F. B. Erickson, N. C. Knight, J. Org. Chem., **15** (1950), 782.

[5] H. J. Dauben, H. J. Ringold, R. H. Wade, A. G. Anderson, J. Am. Chem. Soc., **73** (1951), 2359.

[6] D. H. R. Barton, R. C. Cookson, W. Klyne, C. W. Shoppe, Chem. and Ind., (1954), 21.

[7] Z. Eckstein, A. Sacha, T. Urbański, *Properties and preparation of 1-cycloheptenylnitromethane,* Bull. Acad. Polon. Sci., Cl. III, **5** (1957), 213.

[8] W. Sobótka, Z. Eckstein, T. Urbański, *On ultraviolet absorption spectra of some β-halogen derivatives of β-nitroalcohols,* Bull. Acad. Polon. Sci., Cl. III, **5** (1957), (in press).

[9] H. C. Brown, J. H. Brewster, H. Shechter, J. Am. Chem. Soc., **76** (1954), 467.

[10] H. Shechter, J. W. Shepherd, J. Am. Chem. Soc., **76** (1954), 3619.

[11] E. Schmidt, G. Rutz, Ber., **61** (1928), 2142.

[12] B. M. Vanderbilt, H. B. Hass, Ind. Eng. Chem., **32** (1940), 34.

[13] H. Cerf de Mauny, Bull. Soc. Chim. (5), **7** (1940), 133.

[14] US pat., 2257980; Chem. Abs., **36** (1942), 494.

[15] D. V. Nightingale, J. R. Janes, J. Am. Chem. Soc., **66** (1944), 352.

[16] A. T. Blomquist, T. H. Shelley, J. Am. Chem. Soc., **70** (1948), 147.

[17] M. H. Gold, J. Am. Chem. Soc., **68** (1946), 2544.

[18] A. Lambert, C. W. Scaife, A. E. Wilder-Smith, J. Chem. Soc., (1947), 1474.

[19] C. T. Bahner, H. T. Kite, J. Am. Chem. Soc., **71** (1949), 3597.

[20] W. E. Parham, J. L. Bleasdale, J. Am. Chem. Soc., **72** (1950), 3843.

[21] Brit. pat., 593109; Chem. Abs., **44** (1950), 653.

[22] F. Brower, H. Burkett, J. Am. Chem. Soc., **75** (1953), 1082.

[23] H. Shechter, F. Conrad, J. Am. Chem. Soc., **76** (1954), 2716.

[24] N. Kornblum, H. E. Ungnade, R. A. Smiley, J. Org. Chem., **21** (1956), 377.

[25] T. Urbański, *On hydrogen bonds in some nitroalcohols. II.* Bull. Acad. Polon. Sci., Cl. III, **4** (1956), 381.

[26] C. E. Anagnostopoulos, L. F. Fieser, J. Am. Chem. Soc., **76** (1954), 532.

[27] N. Wright, Ind. Eng. Chem., Anal. Ed., **13** (1941), 1.