NITRATION OF PARAFFINS. DETERMINATION OF NITRO GROUP POSITION IN SECONDARY NITROHEPTANE*

W. BIERNACKI and T. URBAŃSKI

Institute of Organic Chemistry, Polish Academy of Sciences, Warszawa, Poland

Abstract—Secondary nitroheptane obtained by vapour-phase nitration of n-heptane with nitrogen dioxide contains all position isomers. This was proved by paper and gas–liquid chromatographic analyses of nitroheptane and its oxidation product—heptanone.

IN OUR work on vapour-phase nitration of n-heptane with nitrogen dioxide, we encountered the problem of determination of the exact nitro group position in secondary nitroheptane.

The problem of the nitro group substitution into the aliphatic chain, as the result of the liquid-phase nitration, has long been a subject of controversy among the authors.

According to some opinions, on liquid-phase nitration of n-alkanes the entering nitro group substitutes the hydrogen atom at the 2-carbon in the chain, thus giving 2-nitroalkane as the main product.[1,2,3,4]

An opposite view was expressed by Asinger.[5,6,7,8] He maintained that the substitution proceeds according to statistical rules; there is no preferred position in the n-aliphatic chain for the nitro group substitution and the reaction product is composed of all possible position isomers.

According to Asinger, the statement that the methylenic group at carbon-2 is preferred for the nitro group substitution, is based on erroneus determination methods of the nitro group position in the molecule. The authors usually

* Paper LXV in the series "Aliphatic Nitro Compounds".

[1] M. Konowalow, *Ber. Dtsch. Chem. Ges.* **26**, R 878 (1893).

[2] S. S. Nametkin, S. S. Nifontova and R. Ya. Sushchik, *Dokl. Akad. Nauk SSSR* **70**, 241 (1950); *Chem. Abstr.* **45**, 6568 (1951).

[3] A. I. Titov and N. V. Shchitov, *Dokl. Akad. Nauk SSSR* **81**, 1085 (1951).

[4] M. Bender, J. Figueras and M. Kilpatric, *J. Org. Chem.* **23**, 410 (1958).

[5] F. Asinger, *Ber. Dtsch. Chem. Ges.* **77**, 73 (1944).

[6] F. Asinger, G. Geiseler and W. D. Wirth, *Chem. Ber.* **90**, 1987 (1957).

[7] F. Asinger, G. Geiseler and H. J. Schultze, *Chem. Ber.* **92**, 347 (1959).

[8] F. Asinger and K. Halcour, *Chem. Ber.* **94**, 83 (1961).

determined the exact position of the nitro group by converting a nitro compound into the ketone. The oxidation rate of a nitro compound to yield the keto compound depends on the position it occupies in the chain.[9] Identification of the ketones by their semicarbazonic derivatives render the problem still more difficult, for the reaction of the keto compounds with semicarbazide proceeds at different rates, depending on the ketonic group position in the molecule.[10] The reaction rates for the two reactions (i.e. oxidation and semicarbazone formation) are exceptionally high for nitro- and ketoalkanes with their functional groups at carbon-2. This would explain why the early authors always found the 2-nitroparaffins as the predominant or even sole products of the n-paraffin nitration

In the course of our experiments on nitration of n-heptane it was necessary to examine the composition of the nitration products. This could shed the light on the controversial problem of the substitution in the course of nitration of straight-chain hydrocarbons.

For determination of the position of the nitro group in the molecule we applied the method developed by Pritzkow and Müller[11] for the determination of the ketonic group position in the ketoalkanes. According to this method the nitro compound is oxidized to keto compound and the latter is treated with perbenzoic acid to yield the corresponding ester. The ester is converted to hydroxamic acid, which is identified by the paper chromatographic method. The same method was used by Asinger.[6]

Furthermore, we analysed heptanone, obtained by oxidation of secondary nitroheptane, by the GLC method. The isomers present were identified by their retention volumes compared with those of the reference heptanone isomers.

We also succeded in gas chromatographic separation of the original secondary nitroheptane obtained from the nitration reaction. Here again, the isomers present in the nitroheptane analysed were identified by measuring their retention volumes and comparing with those of the reference nitroheptane isomers.

EXPERIMENTAL

Nitroheptane. Secondary nitroheptane was obtained by vapour-phase nitration of n-heptane with nitrogen dioxide at 275° with C_7H_{16}/NO_2 mole ratio of 3:1. The reaction product was treated with aqueous 5% sodium bicarbonate solution, washed with water, dried ($MgSO_4$) and distilled to collect the fraction boiling at 87–107°/38 mm.

The reference nitroheptane isomers used for the gas chromatography were obtained by Meyer's classical method[12] from the corresponding heptyl bromides

[9] F. Asinger, G. Geiseler and M. Hoppe, *Chem. Ber.* **90**, 114 (1957).
[10] F. Asinger, G. Geiseler and P. Laue, *Chem. Ber.* **90**, 458 (1957).
[11] W. Pritzkow and K. A. Müller, *Liebigs Ann.* **597**, 167 (1955).
[12] V. Meyer, *Liebigs Ann.* **175**, 88 (1875).

and purified by the method given by Kornblum *et al.*[13] The products obtained, still contaminated with usual admixtures, were unsuitable for quantitative work.

Heptanone. This was obtained by oxidation of nitroheptane. Two procedures of the oxidation were applied.

Oxidation with potassium permanganate (Nametkin method[14]). Nitroheptane (7·25 g, 0·05 mole) was treated in a separating funnel with KOH (5·6 g, 0·1 mole) in methanol (25 ml). To this solution the stoichiometric quantity of $KMnO_4$ (5·4 g) as the aqueous 1·5% solution was added. The mixture was shaken for 2 min. and extracted with benzene (100 ml). Manganese dioxide present was dissolved by treatment with 5% $NaHSO_3$ solution, followed by acidification with HCl (1:5). The aqueous layer was extracted twice with benzene (50 ml). The combined benzene extracts were washed twice with water (100 ml portions), dried ($MgSO_4$) and distilled. The distillation gave the ketone (4 g; *ca.* 70%) with the following physical properties: b.p. 143–146°; n_D^{20} 1·4079; d_4^{20} 0·8146. (Semicarbazone. Found: N, 24·71. Calc. for $C_8H_{17}ON_3$: N, 24·54%).

Oxidation with H_2O_2 *(Grundmann method*[15]). In a three-necked flask provided with a mechanical stirrer, a thermometer and reflux condenser, nitroheptane (7·25 g, 0·05 mole) was treated with KOH (5·6 g, 0·1 mole) in methanol (50 ml). Then, 20% H_2O_2 solution (15 ml) was added with stirring. After an hour, another portion of 20% H_2O_2 solution was added. The reaction was complet in two hr; the organic layer was extracted with petroleum ether, washed with water (two 50 ml portions), dried ($MgSO_4$) and distilled to give the ketone (2 g; *ca.* 35%) with the following physical properties: b.p. 145–147°; n_D^{20} 1·4070; d_4^{20} 0·8198. (Semicarbazone. Found: N, 24·63. Calc. for $C_8H_{17}ON_3$: N, 24·54%).

The reference heptanone isomers, i.e. 2-heptanone, 3-heptanone and 4-heptanone used for gas chromatography, were synthetized according to the method given by Sherill.[16] Purity of these compounds was checked by gas chromatography and by conventional method (m.p. of the semicarbazonic derivatives).

Oxidation of heptanone with perbenzoic acid. Perbenzoic acid solution was prepared in the known way[17] and contained *ca.* 12 g of the acid in 150 ml chloroform. To this solution heptanone (6·5 g) was added and the reaction flask was kept 14 days in the dark. The chloroform solution was alkalized with N KOH, washed twice with 100 ml portions of water, dried ($MgSO_4$) and distilled to collect the fraction boiling from 135° to 152°.

[13] N. Kornblum, N. Lichtin, J. Patton and D. Iffland, *J. Amer. Chem. Soc.* **69**, 307 (1947).
[14] S. S. Nametkin and E. Pozdnyakova, *Zh. Russ. Fiz. Khim. Obshch.* **45**, 1414 (1913); *Chem. Zentr.* **I**, 757 (1914).
[15] Ch. Grundmann, *Ber. Dtsch. Chem. Ges.* **77**, 82 (1944).
[16] M. L. Sherill, *J. Amer. Chem. Soc.* **52**, 1982 (1930).
[17] Géza Braun, *Organic Syntheses*, Coll. Vol. I, p. 431. John Wiley and Sons, Inc., New York (1948).

Preparation of the hydroxamic acids. One ml of the ester mixture obtained from the perbenzoic acid oxidation of heptanone was treated with alcoholic 5% hydroxylamine solution (25 ml), set aside for $^1/_2$ hr at room temperature, refluxed 15 min on a steam bath and allowed to cool to room temperature. The solution was acidified with acetic acid (8 μl). The hydroxamic acid solution thus obtained was used directly for the chromatographic separation.

The reference hydroxamic acids (in solution) were prepared in an analogous manner from the methyl esters of acetic, propionic, n-butyric and n-valeric acids.

Separation of hydroxamic acids by paper chromatography. The method of descending paper chromatography was used. As the mobile phase, the (3:1:3) benzyl alcohol–formic acid–water was used. The hydroxamic acid solution, 1·0–1·5 ml, was applied to Whatman No. 1 paper. The chromatograms were developed in the chamber for 6 hr and dried 18 hr. Chromatographic spots were produced by spraying the paper with alcoholic 5% $FeCl_3$ solution.

Gas chromatography. An Aerograph A-110-C (Wilkens Instrument Research Inc.) gas chromatograph with coiled air-thermostated steel columns, 4 mm I.D., 152 cm or 304 cm long, a thermal-conductivity detector and a Honeywell-Brown recorder with a 1 mV span were used. The recorder chart speed was maintained constant (28 cm/hr). Hydrogen was used as carrier gas. The inlet pressure of the carrier gas was controlled by a mercury manometer. The rate of the gas flow was measured by a soap-film flowmeter.

The samples were introduced by means of a 10 μl syringe, 2–3 μl of the examined solute being injected at a time.

The following column packings were used: diethylene glycol succinate (25% w/w) on C-22 fire brick of 60/80 mesh grain size and Carbowax 20 M (25% w/w) on the same support (see above).

RESULTS AND DISCUSSION

The paper chromatographic analysis of the examined hydroxamic acid solution has shown the presence of the following compounds: acetylhydroxamic acid (R_f 0·40), propionylhydroxamic acid (R_f 0·58), n-butyrylhydroxamic acid (R_f 0·72) and n-valerylhydroxamic acid (R_f 0·84).

This is the proof that the heptanone analysed was composed of all possible isomers, viz. 2-heptanone, 3-heptanone and 4-heptanone. Consequently, the initial secondary nitroheptane, obtained by the vapour-phase nitration, must have been composed of all its isomers—2-nitroheptane, 3-nitroheptane and 4-nitroheptane.

The above result was confirmed by the gas chromatographic analysis of the heptanone sample, identical with that analysed by paper chromatography. The separation chromatogram is shown below (Fig. 1):

The gas chromatographic separation of the secondary nitroheptane samples,

originating from different nitrations (samples I, II and III) are presented below (Fig. 2 and 3):

The above chromatograms show distinctly that the preference of carbon-2 methylenic group for the nitro group substitution in the n-paraffin nitration

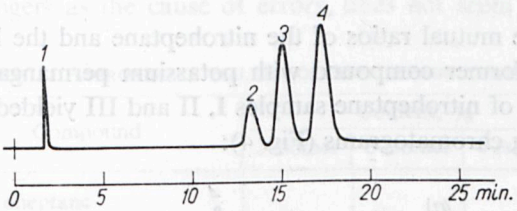

FIG. 1. Separation of heptanone isomers: *1* — air peak, *2* — 4-heptanone, *3* — 3-heptanone, *4* — 2-heptanone.

Separation data: column packing Carbowax 20M (25% w/w) on C–22 fire brick; column temperature 120°; column length 304 cm; hydrogen flow (exit) 30 ml/min.; sample size 3 μl.

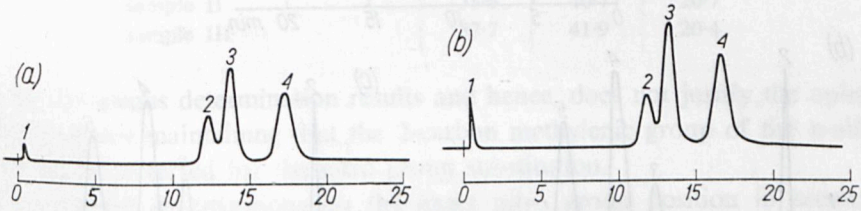

FIG. 2. Separation of s-nitroheptane isomers: (*a*) sample I, (*b*) sample II, *1* — air peak, *2* — 4-nitroheptane, *3* — 3-nitroheptane, *4* — 2-nitroheptane. Separation data: column packing diethylene glycol succinate (25% w/w) on C–22 fire brick; column temperature 112°, column length 152 cm; hydrogen flow (exit) 40 ml/min.; sample size 2 μl.

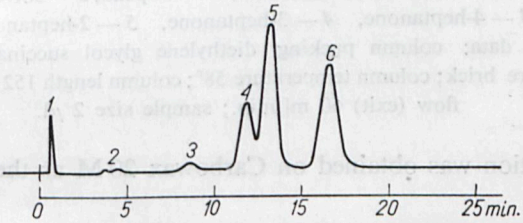

FIG. 3. Separation of s-nitroheptane isomers (sample III): *1* — air peak, *2* and *3* — unidentified peaks, *4* — 4-nitroheptane, *5* — 3-nitroheptane, *6* — 2-nitroheptane. Separation data as in Fig. 2.

reaction, postulated by some authors, does not exist. The presented chromatograms would rather suggest that the substitution of the nitro group in n-alkanes proceeds statistically.

Having no reference heptanone isomers of the purity suitable for quantitative work we could not carry out such determinations of the investigated nitro-

heptane samples. However, we tried to make an approximate evaluation of the mutual ratio in which the nitroheptane and heptanone isomers occured in the samples. Such an estimation was possible owing to the fact that we applied hydrogen as carrier gas and that the compounds were similar in chemical character.[18,19]

To estimate the mutual ratios of the nitroheptane and the heptanone isomers, we oxidized the former compound with potassium permanganate solution. The oxidized portions of nitroheptane samples I, II and III yielded heptanones which gave the following chromatograms (Fig. 4):

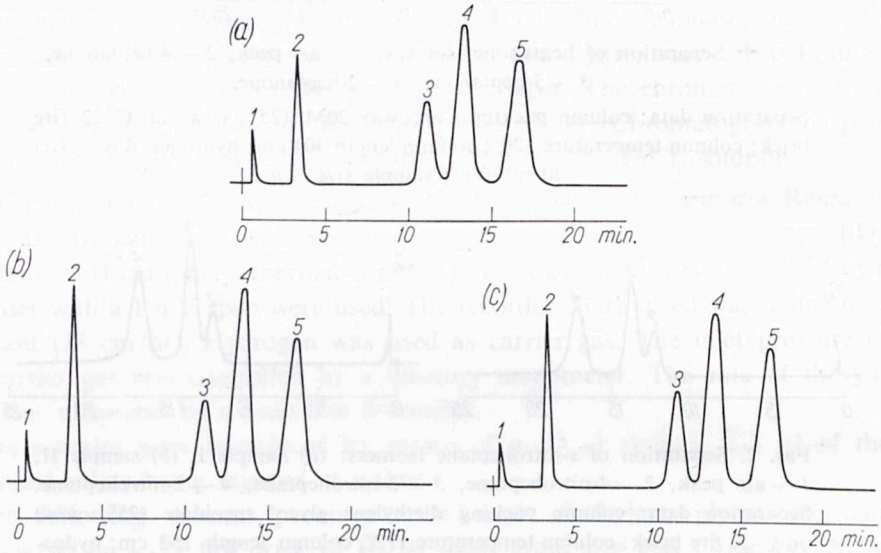

FIG. 4. Separation of heptanone obtained by oxidation of nitroheptane: (*a*) sample I, (*b*) sample II, (*c*) sample III, *1* — air peak, *2* — solvent (benzene), *3* — 4-heptanone, *4* — 3-heptanone, *5* — 2-heptanone.
Separation data: column packing diethylene glycol succinate (25% w/w) on C–22 fire brick; column temperature 58°; column length 152 cm; hydrogen flow (exit) 60 ml/min.; sample size 2 μl.

Similar separation was obtained on Carbowax 20 M as the liquid phase (not shown).

By measuring the peak areas on the chromatograms, the following approximate values of the nitroheptane and heptanone isomers were obtained (Table 1).

As may be seen from the Table or even from a superficial examination of enclosed pairs of chromatograms (Fig. 2a and 4a, 2b and 4b, and 3 and 4c) the mutual ratio in which the nitroheptane isomers exist in the examined samples

[18] A. I. M. Keulemans, *Gas Chromatography*, p. 33, 35. Reinhold Publ. Co., New York (1959).

[19] E. Bayer, *Gas-Chromatographie*, p. 49. Springer Verlag, Berlin (1959).

does not appreciably differ from that of the heptanone isomers present in the oxidation products.

Therefore, the difference in the reaction rate of the oxidation of nitroalkanes to ketoalkanes, depending on the functional group position in the molecule and postulated by Asinger[9] as the cause of errors, does not seem to be responsible

TABLE 1. APPROXIMATE VALUES OF THE ISOMER CONTENT

Compound	Content, %		
	2-isomer	3-isomer	4-isomer
s-Nitroheptane			
Sample I	39·4	42·6	18·0
Sample II	39·0	42·0	19·0
Sample III	37·8	42·6	19·6
Heptanone			
Sample I	38·8	44·6	16·6
Sample II	38·6	40·7	20·7
Sample III	37·7	41·9	20·4

for the erroneous determination results and hence, does not justify the opinions of the authors maintaining that the 2-carbon methylenic group of the n-alkane molecule is preferred for the nitro group substitution.

The present investigations on the exact nitro group position in secondary nitroheptane, obtained by vapour-phase nitration of n-heptane with nitrogen dioxide show that the nitro group substitution takes place at any methylenic carbon of n-alkane and affords all possible isomers. This being in agreement with the views of Asinger.