

Gas chromatography of alkyl *N*-phenylcarbamates

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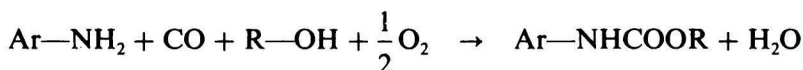
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Methyl, ethyl, up to heptyl *N*-phenylcarbamates were synthesized and their retention indices were measured by gas chromatography at three column temperatures. The relationship between retention indices and number of carbon atoms in the alkyl of carbamate is linear except for the first member of the homologous series. In gas chromatographic investigations we have to take into consideration that alkyl *N*-phenylcarbamates and especially *tert*-butyl *N*-phenylcarbamate are thermolabile substances.

Синтезированы метил-, этил-, вплоть до гептил-*N*-фенилкарбаматы и определены их индексы удерживания с помощью газовой хроматографии при трех различных температурах колон. Наблюдалась линейная зависимость между индексом удерживания и числом углеродных атомов в алкиле карбамата для всех, за исключением первых, членов гомологического ряда. При газовой хроматографическом изучении приходилось принимать во внимание, что алкил-*N*-фенилкарбаматы, в особенности *трет*-бутил-*N*-фенилкарбамат, являются термолабильными веществами.

Alkyl *N*-phenylcarbamates are prepared by carbonylation of nitro aromates or amino aromates with carbon monoxide in the presence of aliphatic alcohols and catalyst of carbonylation. This carbonylation takes place in an autoclave at the pressure of 100—200 kPa and at the temperature of 140—200 °C. The reaction may be described by the following two equations



Besides the main product and starting substances the reaction mixture also contains some substances which simultaneously originate in side reactions. The separation methods and especially gas chromatography and high-efficiency

liquid chromatography are convenient for analysis of such a mixture and, in particular, for the quantitative determination of the formed alkyl *N*-phenylcarbamate.

The gas chromatography has been used for determining the content of methyl and ethyl *N*-phenylcarbamates in the products of carbonylation of nitrobenzene [1—7]. SE-30 or XE-60 served as stationary phases. Different aryl isocyanates may be subjected to reaction with ethanol and subsequently determined in the form of ethyl arylcarbamates. In this case, PS-255 was used as stationary phase [8]. The product of carbonylation of nitrobenzene with methanol was analyzed by using high-efficiency liquid chromatography [9].

In this study we investigated the possibility of using gas chromatography for determination of some alkyl *N*-phenylcarbamates containing longer alkyls. For this purpose, we synthesized the necessary alkyl *N*-phenylcarbamates.

Experimental

The chromatographic analysis was performed with a gas chromatograph CHROM-4 (Laboratorní přístroje, Prague) as well as with a chromatograph HP-5880 A (Hewlett—Packard, USA). A flame ionization detector was used with both instruments. Working conditions for CHROM-4: Column length of 2.5 m, column diameter of 3 mm, stationary phase 5 % SE-30 on Chromaton N AW DMCS, granularity 0.16—0.20 mm, column temperature 160 °C, carrier gas — nitrogen of 24 cm³ min⁻¹ flow. Working conditions for chromatograph HP 5880 A: Capillary column of 30 m length and 0.53 mm diameter, stationary phase HP-5, film thickness 0.35 μm, column temperature either 125 °C or programmed temperature rising from 50 °C to 250 °C with the rate of 5 °C min⁻¹. A chromatogram of alkyl *N*-phenylcarbamates obtained on this stationary phase has been presented in paper [10]. 1 mm³ of the solution of alkyl *N*-phenylcarbamate in acetone or isopropyl alcohol was injected into the column.

The investigated alkyl *N*-phenylcarbamates were prepared by the reaction of phenyl isocyanate (Merck, Darmstadt) with aliphatic alcohol. We used anal. grade or pure methyl, ethyl, ..., and heptyl alcohols for the preparation. The reaction with lower alcohols is vigorous and fairly exothermal and only with higher alcohols (C₄-alcohols and higher) it proceeds more calmly. As the nonconsumed phenyl isocyanate is difficult to remove from the reaction mixture, we used 10 % molar excess of alcohol.

The crude products were recrystallized from hot *n*-heptane (LOBA Chemie, Austria). After cooling white needle-like crystals of alkyl *N*-phenylcarbamates separated from the solution. The melting temperatures of the prepared products were consistent with literature data [11].

In this way, *tert*-butyl *N*-phenylcarbamate (m.p. = 134.5 °C) was prepared as well. Since the reaction of tertiary alcohols with phenyl isocyanate may proceed in different way [12], the prepared carbamate was characterized by IR and ¹H NMR spectra. IR spectrum, $\tilde{\nu}/\text{cm}^{-1}$: 1690—1740 (the first amide band), 1530—1550 (the second amide

band), 3300 ($\nu(\text{NH})$), 1210—1255 and 925—930 (tertiary butyl group). ^1H NMR spectrum, δ/ppm : 8.30 (NH group), 7.75 (aromatic ring), 1.43 (methyl groups of tertiary butanol).

Results and discussion

In order to work up analysis of the technical product of carbonylation by using mixtures of standards, we tested SP-1000 and SE-30 as stationary phases as well as a capillary column containing the HP-5 stationary phase. The retention times of carbamates on the SP-1000 stationary phase were rather long and the selectivity was lower than on the SE-30 stationary phase. On SP-1000 ethyl *N*-phenylcarbamate and isopropyl *N*-phenylcarbamate were overlapping each other and alkyl *N*-phenylcarbamate and propyl *N*-phenylcarbamate were insufficiently separated. For this reason, we used the SE-30 stationary phase or the capillary column in further measurements. A chromatogram of methyl, ethyl, ... up to pentyl *N*-phenylcarbamate obtained on the SE-30 stationary phase is represented in Fig. 1. A chromatogram of the product of carbonylation of nitrobenzene in the presence of methanol is given in Fig. 2.

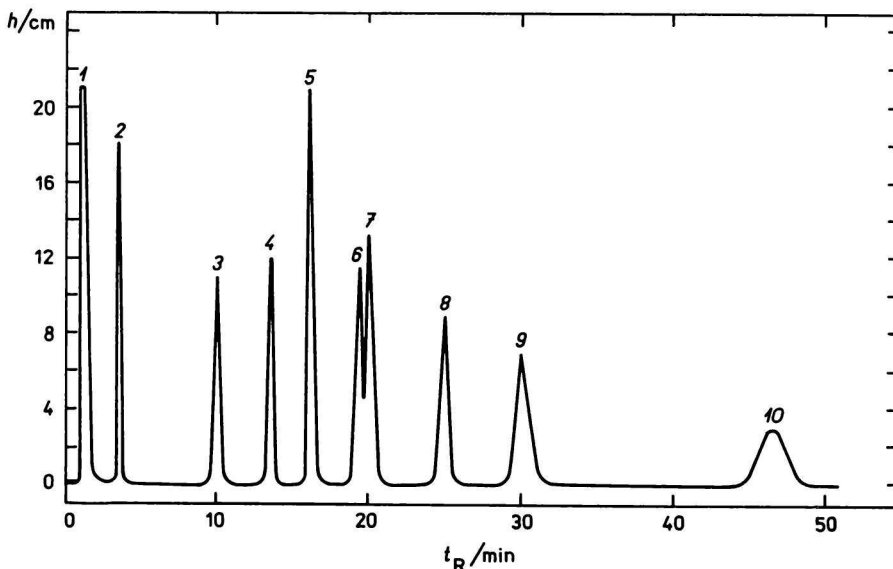


Fig. 1. Chromatogram of alkyl *N*-phenylcarbamates. Column temperature 164°C, nitrogen flow 28.5 cm³ min⁻¹. 1. Solvent; 2. phenyl isocyanate; 3. methyl *N*-phenylcarbamate; 4. ethyl *N*-phenylcarbamate; 5. isopropyl *N*-phenylcarbamate; 6. alkyl *N*-phenylcarbamate; 7. propyl *N*-phenylcarbamate; 8. isobutyl *N*-phenylcarbamate; 9. butyl *N*-phenylcarbamate; 10. n-pentyl *N*-phenylcarbamate.

We measured the retention indices of the prepared alkyl *N*-phenylcarbamates at three column temperatures. The obtained values are listed in Table 1. The dependence of retention indices on alkyl length (Fig. 3) is linear for all three temperatures.

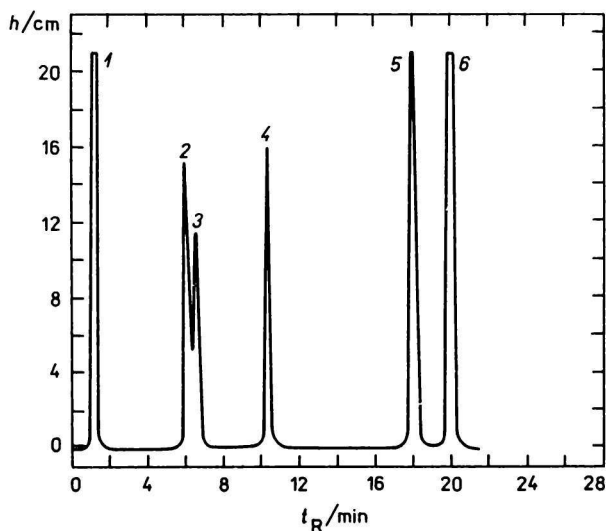


Fig. 2. Chromatogram of the product of carbonylation of nitrobenzene in methanol. The programmed column temperature increasing from 100 °C to 200 °C with the rate of 5 °C min⁻¹. 1. Methanol; 2. phenyl isocyanate; 3. aniline; 4. nitrobenzene; 5. naphthalene (internal standard); 6. methyl *N*-phenylcarbamate.

Table 1

Retention indices of alkyl *N*-phenylcarbamates

Alkyl	<i>I</i>		
	164 °C	182 °C	200 °C
Methyl	1312.6	1329.6	1340.5
Ethyl	1380.6	1400.7	1417.5
Isopropyl	1422.6	1444.8	1453.2
Allyl	1433.6	1497.5	1508.6
Propyl	1483.3	1502.9	1514.3
<i>tert</i> -Butyl	1450.4	—	—
<i>sec</i> -Butyl	1510.2	1540.2	1559.0
Isobutyl	1542.0	1557.0	1572.5
Butyl	1579.3	1603.2	1619.2
Pentyl	1664.5	1698.7	1720.8
Heptyl	—	1886.7	1921.9

GAS CHROMATOGRAPHY OF CARBAMATES

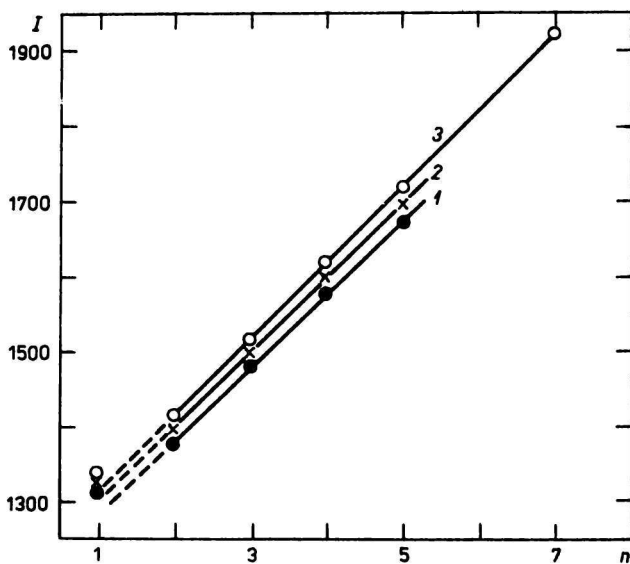


Fig. 3. Dependence of retention index on length of the alkyl (C_n) present in alkyl *N*-phenylcarbamate.
1. 164°C; 2. 182°C; 3. 200°C.

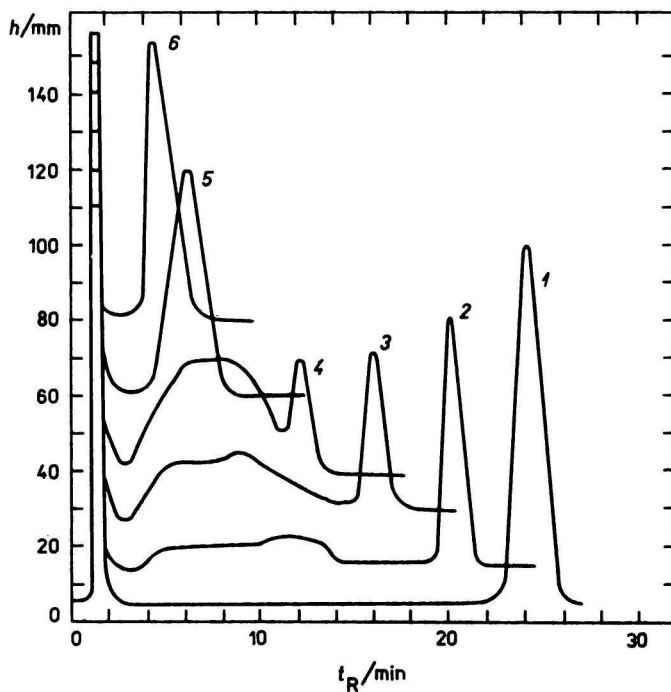


Fig. 4. Influence of column temperature on chromatographic analysis of *tert*-butyl *N*-phenylcarbamate. Column temperature: 1. 154°C; 2. 160°C; 3. 170°C; 4. 180°C; 5. 190°C; 6. 200°C.

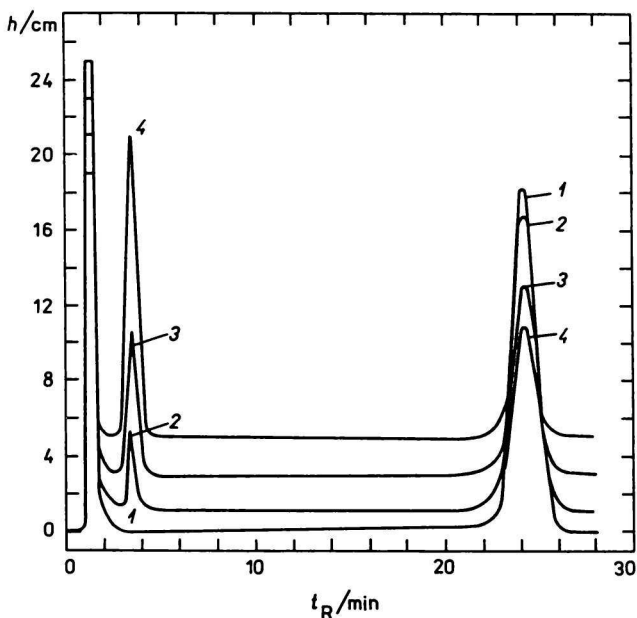


Fig. 5. Influence of dosing device temperature on chromatographic analysis of *tert*-butyl *N*-phenylcarbamate. Dosing device temperature: 1. 175 °C; 2. 205 °C; 3. 215 °C; 4. 255 °C.

As alkyl *N*-phenylcarbamates decomposed at higher temperatures [12] to give phenyl isocyanate and the corresponding alcohol, we investigated the influence of temperature of separating column and injection block on the degree of decomposition of the prepared carbamates. We have found that *tert*-butyl *N*-phenylcarbamate is the least stable. It ensues from Fig. 4 that the decomposition of this substance begins at the column temperature of about 160 °C, which manifests itself by a raise of basic line before elution of carbamate. This wave increases with temperature and the peak of the carbamate itself decreases. This peak entirely vanishes at 200 °C and instead of it a new peak with a short retention time arises. It is likely that gradual dehydration and further reactions of the formed products [12] take place in the column.

The temperature of dosing device also influences the decomposition of carbamate. The peak with short elution time (probably corresponding to phenyl isocyanate) increases with temperature while the peak corresponding to carbamate decreases (Fig. 5).

In conclusion we may state that gas chromatography is a method suited to quantitative determination of methyl, ethyl, ... up to heptyl *N*-phenylcarbamate in the product of carbonylation of mononitro aromates. In analyzing higher alkyl *N*-phenylcarbamates it is more convenient to use a programmed increase

in column temperature. The quantitative determination of *tert*-butyl *N*-phenyl-carbamate is feasible only at a column temperature below 150°C when the decomposition of this compound is still insignificant.

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