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Stability of Diazocarbonyl Compounds under the Conditions of Gas Chromatography and Chromatography-Mass Spectrometry Analysis

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Abstract—The gas chromatographic analysis of alkyldiazoacetates N₂CHCO₂R (R = CH₃ – C₄H₉), α -aliphatic diazoketones RCOCHN₂ (R = C₃H₇, C₅H₁₁, and C₉H₁₉), and aryl-substituted diazoketones Ph (CH₂)_nCOCHN₂ (*n* = 0–2) is shown to be possible when their retention temperatures are below the boiling points of compounds of this series at atmospheric pressure without decomposition (about 140°C). At higher temperatures occurs partial or complete decomposition of α -diazoketones in chromatographic columns to form ketenes. Among the impurities in the reaction mixtures at the diazotization of corresponding alkyl glycinates were identified for the first time the nitrate esters of glycolic acid O₂NOCH₂CO₂R, as well as the dimeric products. All diazocarbonyl compounds and the impurities were characterized by mass spectra. For the first time their gas chromatographic retention indices were determined.

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Among the significant limitations of implementation of gas chromatography for the separation, identification, and quantification of organic compounds is the instability of the latter in the course of analysis. The possible conversion of analytes at the preparation of samples, for example, their hydrolysis with water vapor or oxidation with the air oxygen [1] can be eliminated by a modification of dosing devices and procedures. It is harder to detect the interaction of the components of the analyzed mixtures with each other (for example, the hydrolysis of propylene carbonate by the water traces at the sample input temperature [2]) or their thermal decomposition during analysis. A possible way to overcome the last restriction lies in estimation of the temperature limits of structural stability of the analytes and the relevant change of conditions for their separation, including reduction of temperature in all the units of a gas chromatographic system. For example, 4-acyl-1,3,4-oxadiazolines without substituents in position 2 are stable at the injector temperature up to $\sim 150^{\circ}$ C, but at higher temperatures they are transformed into the corresponding monoacyl hydrazones through decarbonylation [3].

Unfortunately, the criteria of the stability of organic compounds at the chromatographic analysis that

determine the possibility of analysis of the thermally unstable compounds are absent from the literature [4]. In one of the recent symposia on capillary chromatography (Italy, 2010) this issue was considered as relevant for improving capillary columns in the report of the Restek company [5]. In general, the modern design of chromatographic equipment allows its use for the analysis of unstable compounds like organic peroxides [6]. However, gas chromatographic analysis is practically not applied yet to many thermally unstable compounds, e.g., hypohalides, azides, hydroxylamines, isonitriles, hydroperoxides etc., including the diazocarbonyl compounds considered in this paper. One of the latest recommendations for the determination of trace amounts of ethyl diazoacetate considers the use of high-performance liquid chromatography (HPLC) as a method that does not require heating of samples [7].

For the same reason, the main analytical method in the case of diazo compounds has become the massspectrometry, because the transfer of the samples into the gas phase at pressures less than 0.1–1.0 mm Hg requires relatively low temperature. The database of the National Institute of Standards and Technology (NIST, USA) [8] includes the mass spectra of several tens of diazo compounds of different classes. The mass spectrum of diazomethane in comparison with the mass spectrum of the isomeric diazirine was analyzed in detail as early as 1963 [9]. The spectra of the simplest alkyl diazoacetates, including methyl diazoacetoacetate, dimethyl diazomalonate, and 3-diazopentane-2,4-dione were considered in detail in [10], cyclic 2-diazo-1,3-diketones, in [11]. The mass spectra of many compounds of this class, like several α diazoketones [12], 3-diazo-1,4-diphenyl-4-hydroxybutan-2-one [13] and others, were not discussed specifically, but included to the experimental sections of the respective works on the organic synthesis. The absence of thermal limitations at the registration of mass spectra of diazo compound allowed the extension of this method over the complex multifunctional compounds of this class [14-17].

The most informative chromatographic characteristic of organic compounds for their identification are retention indices (RI), which are inter-laboratory reproducible. However, such indices have not been determined even for the simplest aliphatic diazo compounds. Before the beginning of this work the RI evaluation using standard polydimethyl siloxane stationary phases was known only for ethyl diazoacetate (843 ± 6). It was estimated on the ground of the normal boiling temperature of this compound ($140-141^{\circ}C$, according to other sources $143^{\circ}C$) and molar refraction index using algorithm [18]. Estimation of the *RI* by additive scheme [19] considered in the database [8] unfortunately turned out to be impossible for diazo compounds.

This paper deals with chromatographic and gas chromatography-mass spectrometric characterization, especially with the stability under the conditions of analysis, of diazocarbonyl compounds of two types: alkyl diazoacetates **Ia–Ig** and diazomethylketones **IIa– IIe**. As a rule, the samples for the study have not been preliminarily purified, therefore we identified the admixtures in the samples of diazo compounds. As the admixtures, we detected alkyl chloroacetates **III**, nitrites **IV** and nitrates **V** of glycolic acid alkyl esters, "dimeric" products **VI**, and 1-chloroalkan-2-ones **VII**. In the process of the chromatographic analysis we also registered the formation of ketenes **VIII** as a result of decomposition of the diazo compounds.



Preliminary discussion on the subject was reported in [20, 21], where the experimentally determined gas chromatographic *RI* for the diazo compounds were first published.

As a criterion of the possibility of gas-chromatographic analysis of thermally unstable compounds it is advisable to take the maximum values of the boiling points (bp) of homologs of this class under the atmospheric pressure. When the retention temperatures exceed these temperatures the gas-chromatographic analysis is impossible. An example comprises aliphatic azides RN₃ with the bp 20–21°C (R = CH₃), 48–50°C (C₂H₅), 77.5–78°C (C₃H₇), 106.5°C (C₄H₉) and 130– 135°C (C₅H₁₁). For the azides with alkyl fragments larger than C₅H₁₁ the bp at atmospheric pressure are unknown. Thus, the gas chromatographic analysis of alkylazides is possible at temperatures at least up to 130–135°C, which is sufficient for the simplest representatives of this class [22, 23]. In a series like alkyl hypochlorites ROC1 the bp values at the atmospheric pressure are known only for $R = C_3H_7$ (62.9°C) and *t*-C₄H₉ (77–78°C). Consequently, the limit of thermal stability of the compounds of this class is about 80°C, which is clearly insufficient for their gas chromatographic analysis. But even in this series the *RI* values of ethyl (502) and *tert*-butyl hypochlorites (605) have been experimentally determined.

Among the aliphatic diazocarbonyl compounds one of the most commonly used and most thoroughly characterized by physical and chemical constants is

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ethyl diazoacetate [bp 140–143°C; $n_{\rm D}^{20}$ 1.460 (1), d_4^{20} 1.082(10); μ 2.03 D] (we failed to find bp values at the atmospheric pressure for other alkyldiazoacetates). Consequently, the gas chromatographic analysis of diazocarbonyl compounds without their decomposition is limited by the column temperature of approximately 140°C.

In a general case, at the gas-chromatographic analysis of thermally unstable compounds at least three pathways of their decomposition should be taken into consideration.

(1) Thermal or catalytic decomposition prior to the analysis, that is, directly in the reaction mixtures during the isolation of target products, or at the storage of the samples. It is believed that the main direction of alkyl diazoacetates transformations is the formation of diesters of (E)- and (Z)-but-2-enedioic acids [24]. However, the results of gas chromatography-mass spectrometric analysis of the C₁–C₄ esters (see below) has neither revealed the presence of the fumarate and maleate (their RI are known). Nevertheless, in the samples of such esters were found impurities with unknown mass spectra, which could not be interpreted using the database [8]. A similar conclusion about the presence of unidentified impurities in the samples of ethyl diazoacetate was published in [7]. The conclusion that these products were formed not during, but before the chromatographic analysis, is based on the fact that the ratio of peak areas of different components remains practically constant despite varying the analysis temperature.

(2) Thermal decomposition or isomerization of the components of the analyzed samples in the chromatograph injector at the dosing. Such processes could theoretically be detected by varying the temperature of the injector, but in the optimal case, it is desirable to suppress them completely. However, if a high degree of conversion occurs over a wide temperature range, their identification can be a rather difficult task. Examples of such instability are the isomerization of (Z)-4-diazopent-2-enedioate dimethyl into the corresponding pyrazole and the decomposition of dimethyl (E)-4-diazo-3-(trifluoromethyl)pent-2-enedioate with the removal of the nitrogen molecule and the formation of dimethyl cyclopropenedicarboxylate [20, 21]. For this reason, the gas chromatographic analysis of diazocarbonyl compounds was carried out at the injector temperature not higher than 100°C. The value of 77°C, used in [7], is too small, and may

lead to diffuse chromatographic peaks of individual components.

(3) Thermal decomposition of the analytes directly in the chromatographic column. Depending on the nature of the process, in this case either complete absence of signals in the chromatograms occurs, or, if the original compounds and decomposition products are sufficiently volatile, their peaks are recorded, but the relative intensities vary widely, and between them appear additional extensive diffuse peaks. Their appearance is due to the occurrence of reactions in different parts of the chromatographic column at components moving through it, and the degradation products cannot be concentrated in the narrow chromatographic zones.

Both the second and third cases of the thermal instability were revealed in the analysis of diazocarbonyl compounds.

Alkyldiazoacetates Ia-Ig. Table 1 characterizes seven simple alkyldiazoacetates N₂CHCO₂R (I) with R = Me (Ia), Et (Ib), Pr (Ic), *i*-Pr (Id), Bu (Ie), *i*-Bu (If) and t-Bu (Ig). The data include retention temperatures (mode A), the retention indices for the phase HP-5 with 5% of phenyl groups, evaluation of their RI on the dimethylsiloxane stationary phases not containing phenyl groups, as well as standard (70 eV) mass spectra. The full mass spectra are also given. The mass spectra of the compounds Ia [8] and Ib [8, 10] have been pulished earlier.

In the selected conditions of chromatographic separation of the alkyl diazoacetates C1-C4 the retention temperature (T_R) is as low as 54–87°C, which is significantly less than the limit of their estimated thermal stability (~140°C). Hence, for all the esters the thermal decomposition in the analysis can be neglected. However, for the higher homologues of this series the retention temperature will naturally be higher. Relation (1) (experimental part) allows us to estimate the maximum size of the alkyl radical R corresponding to the $T_{\rm R}$ comparable with the limit of thermal stability of the corresponding compound. For butyl diazoacetate Ie the RI is 1058, hence, the estimated RI for the ester with $R = C_8 H_{17}$ is ~(1058 + 400) = 1458, which corresponds to the retention time ~20.3 min, and the value of $T_{\rm R}$ ~142°C. For the analysis of such ester it is necessary to use a shorter chromatographic column and a "soft" option of temperature programming.

Comp. no.	R	М	$T_{\rm R}$, °C	RI ^a	Mass-spectrum, $m/z \ge 40$ ($I_{rel} \ge 2\%$)
Ia	Me	100	54	784±5 ^a 757±8	101 (4), 100 (100) [<i>M</i>], 72 (2) [<i>M</i> – N ₂], 70 (2), 69 (78) [N ₂ CHCO], 59 (4), 44 (3), 43 (23), 42 (10), 41 (51) [CHCO], 40 (3)
Ib	Et	114	62	867±2 ^a 840±4 834±6 [8]	115 (5), 114 (82) [<i>M</i>], 86 (9) [<i>M</i> – N ₂], 70 (3), 69 (100) [N ₂ CHCO], 68 (2), 58 (15), 57 (9), 45 (8), 44 (3), 43 (11), 42 (19), 41 (39) [CHCO], 40(2) ^b
Ic	Pr	128	73	959±2 ^a 931±4	128 (14) $[M]$, 100 (2) $[M - N_2]$, 99 (2), 87 (24) $[N_2CHC(OH)_2]$, 86 (5), 70 (2), 69 (58) $[N_2CHCO]$, 59 (4), 58 (6), 57 (3), 56 (3), 55 (5), 54 (2), 44 (4), 43 (100) $[C_3H_7]$, 42 (18), 41 (80) $[CHCO]$, 40 (3)
Id	<i>i</i> -Pr	128	66	902±1 ^a 875±4	128 (19) [<i>M</i>], 87 (3), 86 (3), 69 (47) [N ₂ CHCO], 59 (5), 55 (2), 45 (2), 44 (4), 43 (100) [C ₃ H ₇], 42 (11), 41 (44) [CHCO], 40 (2)
Ie	Bu	142	87	1058±1 ^a 1031±4	142 (3) [<i>M</i>], 114 (4) [<i>M</i> – N ₂], 113 (2), 101 (6), 99 (3), 87 (26) [N ₂ CHC(OH) ₂], 86 (4), 73 (3), 72 (2), 71 (2), 70 (2), 69 (47) [N ₂ CHCO], 68 (2), 59 (2), 58 (5), 57 (51) [C ₄ H ₉], 56 (34), 55 (22), 54 (2), 53 (2), 44 (4), 43 (12), 42 (16), 41 (100) [CHCO], 40 (3)
If	<i>i-</i> Bu	142	81	1015±1 ^a 988±4	142 (3) [<i>M</i>], 99 (5), 88 (2), 87 (58) [N ₂ CHC(OH) ₂], 86 (2), 73 (2), 71 (2), 70 (4), 69 (100) [N ₂ CHCO], 59 (5), 57 (62) [C ₄ H ₉], 56 (40), 55 (10), 53 (2), 44 (2), 43 (25), 42 (13), 41 (95) [CHCO], 40 (3)
Ig	<i>t</i> -Bu	142	71	940±2 ^a 913±4	142 (0.3) [<i>M</i>], 70 (5), 69 (68) [N ₂ CHCO], 68 (2), 67 (5), 57 (4), 54 (3), 53 (10), 51 (3), 43 (5), 42 (5), 41 (100) [CHCO], 40 (3)

Table 1. Retention temperatures (T_R), retention indices (*RI*), and standard mass spectra (70 eV) of alkyldiazoacetates N₂CHCO₂R (**I**)

^a The retention indices determined in the A mode on a column with the phase HP-5, the second value corresponds to the *RI* estimate on the polmethylsiloxane phases not containing phenyl groups. The average difference $\langle \Delta RI \rangle = 27\pm4$. ^b At the registration of mass-spectrum of ethyl diazoacetate , in the region of $m/z \ge 25$ the maximum signal $(m/z)^{100}$ is at 29 units (Et)

Raising the temperature of analysis of the alkyldiazoacetates leads to a complete absence in the chromatograms of the peaks of both the esters and the possible products of their decomposition. However, the peaks were detected of the degradation products of the column stationary phase due to its interaction with the products of decomposition of the analytes.

Mass spectra of the diazo esters are fully consistent with the known patterns of their fragmentation [8, 10]. In all cases the peaks of molecular ions were recorded that are visible even in the case of $R = t-C_4H_9$, due to the presence of the conjugated system CO–CH=N⁺=N⁻ in the molecules. The characteristic fragment ions are $[M - 28] = [M - N_2]^{++}, [M - RO]^+ = [N_2CHCO]^+ (m/z$ 69), $[M - N_2-RO]^+ = [CHCO]^+ (m/z \ 41)$ and, if $R \ge$ C₃H₇, then $[N_2CHC(OH)_2]^+ (m/z \ 87$, the result of the so-called "double" hydrogen rearrangement).

Identification of impurities in alkyl diazoacetates. At the temperature below 140°C there are no indications of the decomposition of diazocarbonyl compounds in the course of chromatographic analysis, hence, all the detected components with the mass spectra and *RI* listed in Table 2 have formed during the

synthesis. In all alkyl diazoacetates there are the admixtures of the corresponding alkyl chloroacetates IIIa, IIIc-IIIf with shorter retention time (mean value of ΔRI is -25 ± 3). Among the components with high retention times the compounds should be noted with the characteristic mass spectra that are not recognizable using the database [8], that is, not belonging to the class represented in the database. The mass spectra contain, along with the expected peaks of alkyl fragments $[R]^+$, rather intense peaks with m/z 46 and 76, typical of alkyl esters of nitric acid and belonging to the ions [NO₂]⁺, and [CH₂ONO₂]⁺, respectively. As far as their RI also vary in line with the RI values of alkyl diazoacetates (average ΔRI is 112±8, Table 2), they can be unambiguously identified the alkyl esters of glycolic acid nitrate as O₂NOCH₂CO₂R (Va, Vb, Vd, Vf), in a quite notable amount. For example, the sample If contained the isobutyl ester of glycolic acid nitrate in an amount comparable with the isobutyl diazoacetate (Fig. 1).

Formation of such esters is possible due to the presence of uncontrolled amounts of nitrate in the sodium nitrite $(XN_2^+ + NO_3^- \rightarrow XONO_2 + N_2)$, as well

Comp. no.	R	М	<i>RI</i> (A mode)	Mass-spectrum, $m/z \ge 40$ ($I_{rel} \ge 2\%$)				
	Alkyl chloroacetates ClCH ₂ CO ₂ R (III)							
IIIa	Me	108	763±2	110 (3), 108 (9) [<i>M</i>], 79 (9), 78 (2), 77 (27) [<i>M</i> – CH ₃ O], 76 (3), 66 (5), 64 (17), 60 (2), 59 (100) [CO ₂ CH ₃], 51 (15), 50 (2), 49 (45) [CH ₂ Cl], 48 (4), 47 (2), 45 (3), 42 (11)				
IIIb	Et	122	839±2	122 (2) [<i>M</i>], 109 (2), 107 (6), 97 (2), 96 (7), 95 (7), 94 (22) [$M - C_2H_4$], 79 (33), 78 (4), 77 (100) [$M - C_2H_5$ O], 76 (4), 73 (5), 60 (4), 51 (17), 50 (3), 49 (51) [CH ₂ Cl], 48 (5), 47 (2), 45 (15), 44 (2), 43 (17), 42 (51), 41 (14)				
IIIc	Pr	136	933±1	136 (0) [<i>M</i>], 109 (3), 107 (9), 97 (7), 95 (23) [$M - C_3H_5$], 79 (17), 78 (2), 77 (53) [$M - C_3H_7O$], 76 (2), 76 (2), 60 (2), 59 (4), 57 (8), 51 (7), 49 (21) [CH_2Cl], 43 (100) [C_3H_7], 42 (42), 41 (39), 40 (2)				
IIId	<i>i</i> -Pr	136	880±1 ^a 850±4	136 (0) [<i>M</i>], 123 (7), 121 (23), 97 (2), 95 (5), 85 (2), 79 (20), 78 (2), 77 (62), 59 (8), 51 (5), 49 (16) [CH ₂ Cl], 45 (7), 44 (4), 43 (100), 42 (15), 41 (26)				
IIIe	Bu	150	1032±2	150 (0) [<i>M</i>], 109 (2), 107 (5), 95 (6), 79 (13), 78 (2), 77 (38) [$M - C_4H_9O$], 76 (2), 73 (2), 71 (2), 60 (2), 58 (3), 57 (74), 56 (100), 55 (14), 51 (6), 49 (17) [CH ₂ Cl], 43 (11), 42 (13), 41 (65), 40 (2)				
IIIf	<i>i</i> -Bu	150	988±1ª 964±11	150 (0) [<i>M</i>], 110 (4), 109 (5), 108 (13), 107 (8), 79 (17), 78 (2), 77 (54), 76 (3), 72 (3), 71 (6), 59 (4), 58 (3), 57 (56), 56 (100), 55 (7), 51 (6), 49 (16) [CH ₂ Cl], 44 (2), 43 (40), 42 (20), 41 (49), 40 (2)				
	Ethyl nirosooxyacetate ONOCH ₂ CO ₂ Et (IVb) and alkyl nitrooxyacetates (V)							
IVb	Et	133	904±2	133 (0) [<i>M</i>], 105 (6), 104 (6), 88 (2), 87 (57) [<i>M</i> – NO ₂], 76 (4), 73 (2), 61 (7), 60 (100) [ONOCH ₂], 59 (26), 58 (2), 57 (2), 45 (19), 44 (2), 43 (9), 42 (2), 41 (2)				
Va	Me	135	908±2	135 (0) [<i>M</i>], 77 (4), 76 (38) [O ₂ NOCH ₂], 60 (3), 59 (92) [CO ₂ CH ₃], 46 (100) [NO ₂], 45 (23), 44 (6), 43 (2), 42 (4)				
Vb	Et	149	977±2	149 (0) [<i>M</i>], 106 (2), 90 (4), 76 (51) [O ₂ NOCH ₂], 61 (2), 60 (2), 59 (2), 57 (4), 46 (100) [NO ₂], 45 (15), 44 (8), 43 (10), 42 (6)				
Vd	<i>i</i> -Pr	163	1010±2	163 (0) [<i>M</i>], 148 (2), 104 (2), 90 (25), 76 (13) [O ₂ NOCH ₂], 59 (2), 46 (56) [NO ₂], 45 (7), 44 (5), 43 (100) [C ₃ H ₇], 42 (5), 41 (24)				
Vf	<i>i-</i> Bu	177	1120±2	177 (0) [<i>M</i>], 116 (1), 104 (2), 76 (32) [O ₂ NOCH ₂], 61 (7), 59 (3), 58 (6), 57 (100) [C ₄ H ₉], 56 (51), 55 (7), 46 (53) [NO ₂], 44 (5), 43 (50), 42 (11), 41 (74), 40 (2)				
Dimeric compounds $X(CH_2CO_2R)_2$ (VI)								
VIc	Pr	245	1696±3	172 (2), 159 (14), 141 (2), 130 (11), 100 (2), 97 (2), 84 (2), 73 (2), 70 (2), 59 (4), 57 (2), 55 (3), 54 (12), 53 (5), 44 (15), 43 (100), 42 (37), 41 (33), 40 (2)				
VId	<i>i</i> -Pr	245	1586±4	172 (4), 157 (3), 155 (2), 130 (16), 100 (2), 69 (2), 59 (3), 53 (3), 45 (7), 44 (5), 43 (100), 42 (3), 41 (16)				
VIe	Bu	271	1869±5	186 (1), 159 (14), 130 (6), 98 (2), 73 (4), 70 (2), 58 (4), 57 (100), 56 (71), 55 (16), 54 (10), 53 (5), 52 (2), 45 (2), 44 (15), 43 (24), 42 (7), 41 (75), 40 (3)				
VIg	<i>t</i> -Bu	271	1573±4	130 (4), 58 (4), 57 (100), 56 (6), 55 (3), 53 (3), 439 (7), 42 (2), 41 (29)				

Table 2. Retenion indices RI and standard mass-spectra (70 eV) of impurities in the reaction mixtures at the synthesis of alkyl diazoacetates N₂CHCO₂R

^a The retention indices determined in the A mode on a column with the phase HP-5, the second value corresponds to the *RI* estimate on the polyvinylsiloxane phases not containing phenyl groups. The average difference $<\Delta RI > = 27\pm4$.

as more complex processes involving the intermediately forming diazonium cations. It was found for example that reaction of diazo compounds $YCHN_2$ with N_2O_5 results not only in nitro compounds $YC(NO_2)N_2$, but also in the formation of the corresponding nitrates YCH_2ONO_2 [25]. If the main impurities in alkyl diazoacetates obtained from the corresponding amine hydrochloride and sodium nitrite are the esters of nitric acid, it is natural to expect the presence in some amount of the esters of nitrous acid XONO. However, such ester **IVb** was found only in the sample **Ib**, whose mass



Fig. 1. The chromatogram of the reaction mixture containing isobutyl diazoacetate If (A mode). The peak with the retention time 7.41 min corresonds to isobutyl chloroacetate, 8.19 min, to isobutyl diazoacetate, 11.18 min, to isobutul ester of glycolic acid nitrate $O_2NOCH_2CH_2CH(CH_3)_2$.

spectrum contains the peaks characteristic of alkyl nitrite ion $[CH_2ONO]^+$ with m/z 60.

In the samples of alkyl diazoacetates **Ic–Ie**, **Ig** besides the above considered impurities more complex components **VIc–VIe**, **VIg** were detected in varied amounts, which are not esters of (*E*)- or (*Z*)-but-2-enedioic acids. Their mass spectra and *RI* are given in Table 2. Their mass spectra do not contain the peaks of molecular ions, but include the peaks of the ions with the m/z 130, and the maximum peaks confirm the presence of alkyl fragments R.

The RI values of compounds IV allows to assume the presence in the molecule of two structural fragments CH₂CO₂R, that is, they have the general formula $X(CH_2CO_2R)_2$. This follows from the fact that commonly in going from propyl to butyl esters (R = Prand Bu, respectively) the RI values of alkyl diazoacetates I, chloroacetates III, and nitroglycolates increase approximately by 100 index units, while for the component under consideration, by about 200 index units (Table 2). A more detailed analysis of RI, given a similarity of the mass spectra, suggests that they belong to the same series (X = const). To reveal the nature of the X fragment the additive scheme of RI evaluation can be used, based on a hypothetical "assembling" structures of complex molecules from simpler ones. In this case a structural analogy of diesters X(CH₂CO₂R)₂ and the known diesters of butandioic acid ROCOCH₂CH₂CO₂R is of interest:

$$ROCOCH_2XCH \pm_2CO_2R = ROCOCH_2CH_2CO_2R + MeXMe - C_2H_6.$$

This scheme can be transformed to estimate the RI of compound XMe₂ (for ethane, RI = 200):

$$XMe_2 = X(CH_2CO_2R)_2 - ROCOCH_2CH_2CO_2R + C_2H_6.$$

Then, according to the data for the impurities in various alkyldiazoacetats, we get the average RI value 537 ± 4 for XMe₂.

R	$X(CH_2CO_2R)_2$	ROCOCH ₂ CH ₂ CO ₂ R	MeXMe
Pr	1696±3	1356±12	540
<i>i</i> -Pr	1586±4	1248±8	538
Bu	1869±5	1531±4	538
t-Bu	1573±4	1242±4	531

Based on literature data and additive ratios, we calculated *RI* for the following compounds with the formula XMe₂: X = O (327±8), N=N (396±4), N(O)=N (615±19), >N–NO (708±5) and NH–N=N (529±11). Thus, the best correspondence with the experimental value of *RI* was observed for 1,3-dimethyltriazene MeNHN=NMe. An estimate of the *RI* for it is made on the basis of bp (50.8°C) and the molar refraction using the algorithm [18].

The structural fragment $-CO-CH=N^+=N^-$ of diazocarbonyl compounds is polar, therefore their *RI*, determined on a polydimethylsiloxane phases containing 5% of phenyl groups and without the latter are noticeably different. The average value of difference of the indices is 27±4, so the Table 1 comprises two sets of data.

 α -Diazoketones. Table 3 shows the mass spectra and retention indices of aliphatic q-diazoketones RCOCHN₂, R = Pr (IIa), *i*-Pr (IIb), n-C₅H₁₁ (IIc), *i*- C_5H_{11} (IId) and *n*- C_9H_{19} (IIe), and three phenylsubstituted diazoketones $Ph(CH_2)_nCOCHN_2$ with n = 0(IIf), 1 (IIg) and 2 (IIh). The retention temperatures of aliphatic diazoketones (IIa-IIf) in D mode are in the range of 59-137°C. However, even the last of these values (for $R = n-C_9H_{19}$) does not exceed the limit of thermal stability of diazocarbonyl compounds (~140°C), since there are no indications of the decomposition of diazoketones in the course of chromatographic separation. If the temperature rise is programmed with a higher rate (Mode C: 70°C, 10°C min⁻¹), the diazoketones are decomposed in the chromatographic column completely (aliphatic) or partially (aromatic). In all cases, the products are substituted ketenes VIII, formed through the Wolf rearrangement [26]. The first recorded mass spectra of ketenes are shown in Table 3,

Compound	М	$T_{\rm R}$, °C (mode)	RI	Mass-spectrum, $m/z \ge 39 \ (I_{\rm rel} \ge 2\%)$
		II		Diazoketones II
1-Diazopentan-2-one, IIa	112	59 (D)	957±2 ^a 930±4	113 (2), 112 (22) [<i>M</i>], 85 (3), 84 (79) [<i>M</i> – N ₂], 71 (24), 70 (2), 69 (46) [<i>M</i> – C ₃ H ₇ =N ₂ CHCO], 57 (2), 56 (15), 55 (100), 54 (2), 53 (6), 51 (2), 50 (2), 44 (3), 43 (75), 42 (26), 41 (66) [CHCO], 40 (6), 39 (32)
1-Diazo-3- methylbutan-2-one, IIb	112	54 (D)	918±2 ^a 889±4	113 (2), 112 (40) [<i>M</i>], 84 (28) [M – N ₂], 83 (8), 71 (7), 70 (4), 69 (66) [M – C ₃ H ₇], 68 (2), 56 (12), 55 (16), 53 (5), 51 (3), 50 (2), 44 (2), 43 (81), 42 (24), 41 (100) [M – C ₃ H ₇ – N ₂ =CHCO], 40 (6), 39 (41)
1-Diazoheptan-2-one, IIc	140	84 (D)	1157±2 ^a 1130±4	140 (0.6) [<i>M</i>], 112 (11) [<i>M</i> - N ₂], 99 (3), 97 (5), 94 (3), 85 (2), 84 (47) [<i>M</i> - C ₄ H ₈], 83 (16), 79 (3), 71 (11), 70 (9), 69 (36) [<i>M</i> - C ₅ H ₁₁ =N ₂ CHCO], 67 (5), 58 (4), 57 (4), 56 (23), 55 (100), 54 (2), 53 (4), 44 (2), 43 (55), 42 (26), 41 (51) [<i>M</i> - C ₅ H ₁₁ - N ₂ =CHCO], 40 (4), 39 (20)
1-Diazo-5- methyldecan-2-one, IId	140	75 (D)	1083±2ª 1056±4	140 (0.1) $[M]$, 112 (47) $[M - N_2]$, 84 (14), 83 (100) $[M - C_4H_9]$, 81 (5), 71 (27), 70 (10), 69 (15), 65 (6), 59 (2), 55 (97), 54 (6), 53 (13), 51 (7), 43 (49), 42 (23), 41 (44) $[M - C_5H_{11} - N_2=CHCO]$, 40 (9), 39 (29)
1-Diazoundecan-2- one, He	196	137 (D)	1564±3 ^a 1537±5	196 (0.1) [<i>M</i>], 139 (2), 125 (3), 112 (9), 111 (9), 99 (4), 98 (58), 97 (40), 96 (3), 95 (7), 94 (2), 93 (3), 85 (5), 84 (48) [$M - C_8H_{16}$], 83 (61), 82 (18), 81 (10), 80 (2), 79 (5), 71 (11), 70 (28), 69 (32) [$M - C_9H_{19}$ =N ₂ CHCO], 68 (13), 67 (13), 59 (2), 58 (6), 57 (17), 56 (24), 55 (100), 54 (12), 53 (5), 44 (2), 43 (53), 42 (17), 41 (55) [$M - C_9H_{19} - N_2$ =CHCO], 40 (3), 39 (14)
Diazoacetophenone, IIf	146	84 (B) 170 (C) 112 (D)	1359±1 ^a 1304±1	147 (4), 146 (43) [<i>M</i>], 119 (2), 118 (21) [<i>M</i> - N ₂], 106 (4), 105 (53) [C ₆ H ₅ CO], 91 (7), 90 (100) [<i>M</i> - N ₂ - CO], 89 (74) [<i>M</i> - N ₂ - CHO], 78 (3), 77 (47) [C ₆ H ₅], 76 (2), 75 (3), 74 (4), 73 (2), 64 (11), 63 (25), 62 (8), 61 (3), 59 (3), 52 (2), 51 (25), 50 (13), 49 (2), 45 (6), 43 (2), 41 (2), 40 (3), 39 (13)
1-Diazo-3- phenylpropan-2-one, IIg	160	90 (B) - (>175) (C) 118 (D)	1407±1 ^a 1350±1	160 (<0.1) $[M]$, 133 (3), 132 (31) $[M - N_2]$, 105 (10), 104 (100) $[M - N_2 - CO]$, 103 (43) $[M - N_2 - CHO]$, 102 (6), 92 (9), 91 (99) $[C_6H_5CH_2]$, 90 (2), 89 (7), 79 (2), 78 (36), 77 (29), 76 (4), 75 (3), 74 (4), 69 (19), 66 (3), 65 (28), 64 (2), 63 (12), 62 (4), 55 (6), 52 (8), 51 (30), 50 (11), 41 (6), 39 (19)
1-Diazo-4- phenylbutan-2-one, IIh	174	102 (B) - (>181) (C) 145 (D) ^c	1516±1 ^a 1453±1	174 (0.4) [<i>M</i>], 147 (4), 146 (32) [<i>M</i> – N ₂], 145 (13), 131 (9), 129 (3), 128 (4), 127 (12), 119 (6), 118 (64) [<i>M</i> – N ₂ – CO], 117 (46) [<i>M</i> – N ₂ – CHO], 116 (7), 115 (20), 105 (17), 104 (73) [C ₆ H ₅ CHCH ₂], 103 (19), 102 (3), 92 (8), 91 (100) [C ₆ H ₅ CH ₂], 90 (11), 89 (9), 79 (8), 78 (19), 77 (22), 76 (3), 75 (2), 74 (2), 69 (6), 66 (2), 65 (38), 64 (3), 63 (11), 62 (3), 57 (5), 56 (2), 55 (77), 53 (2), 52 (5), 51 (21), 50 (7), 41 (7), 40 (2), 39 (21)
		! I	1-Ch	loroalkane-2-ones VII
1-Chloropentan-2- one, VIIa	120	(D)	878 ± 3^{a} 851 ± 5	120 (2) $[M]$, 79 (2), 77 (5), 72 (3), 71 (54) $[M - CH_2Cl]$, 51 (2), 49 (7) $[CH_2Cl]$, 44 (3), 43 (100) $[C_3H_7]$, 42 (9), 41 (32), 39 (8)
1-Chloroheptan-2- one, VIIc	148	(D)	1077±1 ^a 1050±4	148 (1) $[M]$, 100 (4), 99 (48) $[M - CH_2CI]$, 94 (4), 93 (2), 92 (11) $[M - C_4H_8]$, 81 (2), 79 (2), 77 (5), 72 (4), 71 (66) $[C_5H_{11}]$, 65 (2), 60 (2), 58 (2), 57 (4), 56 (4), 55 (9), 51 (2), 49 (6) $[CH_2CI]$, 44 (4), 43 (100) $[C_3H_7]$, 42 (8), 41 (18), 39 (8)
1-Chloroundecan-2- one, VIIe	204	(D)	1483±2 ^a 1456±4	204 (1) [<i>M</i>], 174 (2), 156 (9), 155 (64) [<i>M</i> – CH ₂ CI], 153 (2), 150 (2), 138 (2), 137 (5), 129 (2), 124 (2), 110 (2), 105 (3), 100 (2), 99 (2), 98 (2), 97 (4), 96 (2), 95 (30), 94 (5), 93 (6), 92 (13) [<i>M</i> – C ₈ H ₁₆], 85 (35), 84 (5), 83 (7), 82 (2), 81 (26), 79 (4), 77 (5), 72 (5), 71 (68), 70 (10), 69 (18), 68 (6), 67 (13), 59 (5), 58 (18), 57 (53), 56 (4), 55 (25), 54 (2), 53 (3), 49 (5), 44 (11), 43 (100) [C ₃ H ₇], 42 (12), 41 (47), 39 (8)
2-Chloro- acetophenone, VIIf	154	(B), (C), (D)	1274±2 ^a 1222±1	154 (1) [<i>M</i>], 106 (6), 105 (100) [<i>M</i> – CH ₂ Cl], 91 (4), 78 (4), 77 (54), 75 (2), 74 (3), 65 (3), 63 (2), 52 (2), 51 (28), 50 (12), 49 (3)

Table 3. Retention temperatures (T_R) , retention indices (RI), and standard mass spectra (70 eV) of diazomethyl ketones RCOCHN₂(II) as well as the impurities in the reaction mixtures

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Table 3. (Contd.)

Compound	M	$T_{\rm R}$, °C (mode)	RI	Mass-spectrum, $m/z \ge 39 \ (I_{\rm rel} \ge 2\%)$	
			1-Cl	hloroalkane-2-ones VII	
3-Phenyl-1- chloropropan-2-one, VIIg	168	(B), (C), (D)	1314±2 ^a 1260±1	170 (3), 168 (9) $[M]$, 131 (2), 119 (12) $[M - CH_2Cl]$, 92 (7), 91 (100) $[C_6H_5CH_2]$, 77 (4), 65 (14), 63 (5), 52 (2), 51 (7), 50 (3), 49 (3), 46 (2), 44 (4), 41 (2)	
4-Phenyl-1- chlorobutan-2-one, VIIh	182	(B), (C), (D)	1432±2 ^a 1377±1	184 (6), 183 (2), 182 (18) $[M]$, 147 (2), 146 (4), 134 (4), 133 (47) $[M - CH_2CI]$, 129 (5), 127 (2), 125 (3), 115 (2), 106 (9), 105 (98) $[M - CH_2CI - CO]$, 104 (12), 103 (11), 102 (2), 92 (7), 91 (100) $[C_6H_5CH_2]$, 89 (2), 79 (14), 78 (8), 77 (21), 66 (2), 65 (12), 63 (3), 55 (5), 52 (2), 51 (13), 50 (3), 48 (4), 43 (3), 41 (2), 39 (6)	
1-Phenyl-3- chlorobutan-2-one, VIIi	182	(B), (C)	1370±1 ^a 1314±4	184 (4), 183 (2), 182 (13) [<i>M</i>], 148 (4), 147 (48) [<i>M</i> – Cl], 146 (2), 133 (8), 131 (4), 129 (5), 128 (2), 126 (2), 119 (2), 118 (3), 117 (15), 116 (9), 115 (22), 106 (5), 105 (33), 104 (5), 103 (9), 102 (2), 92 (7), 91 (100) [C ₆ H ₃ CH ₂], 89 (4), 79 (4), 78 (3), 77 (7), 75 (2), 73 (2), 65 (16), 64 (2), 63 (5), 55 (2), 53 (2), 52 (2), 51 (8), 50 (3), 49 (2), 43 (2), 41 (2), 39 (9), 38 (2)	
Ketenes VIII ^b					
Pent-1-en-1-one, VIIIa	84	(C)	-	84 (21) [<i>M</i>], 56 (7), 55 (100) [$M - C_2H_5$], 53 (3), 51 (2), 50 (3), 42 (3), 41 (13)	
Hept-1-en-1-one, VIIIb	112	(C), (D)	_	112 (8) [<i>M</i>], 94 (3), 84 (5), 83 (5), 70 (4), 69 (11), 68 (18), 67 (3), 57 (3), 56 (19), 55 (100) [$M - C_4H_9$], 53 (2), 43 (7), 42 (14), 41 (33)	
3-Phenylprop-1-en- 1-one, VIIIg	132	(C)	_	133 (13), 132 (100) [<i>M</i>], 131 (85) [<i>M</i> – H], 105 (10), 104 (53) [<i>M</i> – CO], 103 (90) [<i>M</i> – CHO], 102 (11), 98 (2), 92 (2), 91 (27), 89 (5), 81 (5), 79 (4), 78 (46), 77 (38), 76 (11), 75 (5), 74 (7), 66 (2), 65 (10), 63 (12), 62 (5), 61 (5), 57 (3), 56 (2), 55 (21), 52 (22), 51 (63), 50 (30), 49 (3), 44 (18), 41 (9)	
4-Phenylbut-2-en-1- one, VIIIh	146	(C)	-	147 (3), 146 (26) [<i>M</i>], 118 (10), 115 (5), 92 (3), 91 (36) $[C_6H_5CH_2]$, 89 (2), 77 (2), 65 (11), 63 (4), 57 (3), 56 (3), 55 (100) $[M - C_6H_5CH_2]$, 51 (7), 50 (3), 41 (2)	

^a Retention indices, determined in modes A, C, D on the columns for the phase with 5% of phenyl groups, second value *RI* is for the dimethylsiloxane stationary phases not containing phenyl groups (mode B); average value $<\Delta RI>: 27\pm4$ (aliphatic compounds), 56±4 (phenyl-substituted compounds). ^b Substituted ketenes formed at relative high temperatures as the decomposition products of diazocompounds in chromatographic column and registered as diffuse peaks, the calculation of retention indices is impossible. ^c Partial decomposition is observed at $T_R = 145$ °C (see a fragment of the chromatogram, Fig. 2).

but their *RI* cannot be determined, because these products are formed during the separation and provide a broad diffuse peaks.

Retention temperature (T_R) of phenyl-substituted diazoketones **IIe–IIh** are 84–102°C in B mode and 112–145°C in D mode, so that in the B mode the thermal decomposition is not observed. In the case of 4-phenyl-1-diazobutan-2-one **IIIh** at $T_R = 145$ °C indications appear of the partial decomposition, as illustrates the chromatogram fragment shown in Fig. 2. This fact once again confirms the correctness of the assessment of thermal stability of the diazocarbonyl compounds in gas chromatograpic analysis (~140°C). As to the "hardest" C mode with T_R of aryldiazoketones 170–180°C, only the simplest of them (diazoacetophenone PhCOCHN₂ **IIe**, which has a system of conjugated

bonds) is stable, while the other two decompose completely. In this case in none of the modes even traces of phenylketene could be detected.

The expected impurities in all of diazoketones, like in the diazoesters, are 1-chloro-substituted alkane-2ones **VIIa–VIIh** formed in the synthesis of diazoketones, which were detected only in the sereies of **IIe–IIh**. For instance, in a sample of 1-diazo-3phenylpropan-2-one there is a component with a molecular mass of 182 and *RI* 1370 (Mode C), containing one chlorine atom in the molecule (the relative intensity of the peaks at m/z 182 and 184 is ~3:1) and a fragment of PhCH₂ (maximum signal with m/z 91), which is the formal homolog of "normal" 3-phenyl-1chloropropan-2-one. As a result of a joint interpretation of mass spectrometric and chromatographic information, among several alleged versions of its structure could be selected only one, the 1-phenyl-3-chlorobutane-2-one. Estimates of its *RI* by different independent ways are close to the experimental value.

The retention index of 1-phenyl-3-chlorobutane-2one **VIIk** can be estimated on the basis of reference values of *RI* of 1-phenylbutan-2-one (1228±11) and the increment of the of H \rightarrow Cl substitution in the α position to the carbonyl group (117±8) [27]:

$$C_6H_5CH_2COCH_2CH_3 \rightarrow C_6H_5CH_2COCH(Cl)CH_3,$$

(1228±11) + (117±8) = (1345±14).

The second way of estimating the *RI* is based on the transformation of the methyl group in the structure of 3-chlorobutane-2-one in the group $C_6H_5CH_2$ ($\Delta RI = 643\pm13$ [28]):

CH₃COCH(Cl)CH₃ → C₆H₅CH₂COCH(Cl)CH₃, (704±3) [27] + (643±13) = (1347±13).

Adding to these two values the result of applying the algorithm of *RI* prediction based on an assessment of its boiling point (255.3±20°C, ACD software) and molar refraction [18], which gives a value of 1345±15, we obtain the overall average value 1346±14 satisfactorily corresponding to the experimental value of *RI* 1370±1 (Table 2). In addition, differences in the mass spectra of ion series [29] of 1-phenyl-3chlorobutan-2-one and isomeric 4-phenyl-1-chlorobutan-2-one (an impurity in 4-phenyl-1-diazobutan-2one) are quite acceptable (D = 31) to recognize these compounds as belonging to the same homologous series of chloro-substituted nonconjugated arylalkanones. The origin of the appearance of this component in the reaction mixture remains unknown.

As in the case of alkyl diazoacetates, Table 3 shows for each compound two *RI* values, for nonpolar polydimethylsiloxane phase and the phase containing 5% of phenyl groups. For the diazoketones the average difference $\langle \Delta RI \rangle$ can be taken the same as for alkyl diazoacetates (27±4), but for the aryl-substituted ketones it is larger (56±4).

In the mass spectra of aliphatic diazoketones there are strong peaks of molecular ions. Characteristic fragmentation ions are $[M-28] = [M-N_2]^{+*}, [M-R]^{+} = [N_2CHCO]^+$ $(m/z 69), [M - N_2 - R]^+ = [CHCO]^+$ (m/z 41) and, if $R \ge C_5H_{11}$, then $[M - C_nH_{2n}]^{+*}$ (McLafferty rearrangement). Characteristic feature of the nonconjugated phenyl-substituted diazoketones is low intensity of the peaks of molecular ions (< 0.1–0.4%) and a high intensity of the ions $[C_6H_5CH_2]^+$



Retention time, min

Fig. 2. A fragment of the chromatogram of 1-diazo-4phenylbutan-2-one (D mode, $T_{\rm R}$ 145°C): retention time 46.3 min corresponds to 1-chloro-4-phenylbutan-2-one, the main peak (51.5–52.3 min) to 1-diazo-4-phenylbutan-2one, 58.7 relates to a nonidentified component. The tail before the main peak is due to the partial decomposition of the diazo compound in the column with the formation of 4phenylbut-1-en-1-one (its mass spectrum is listed in Table 3).

 $(m/z \ 91)$. The common pathway in the fragmentation, regardless of the presence or absence of the system of conjugation, is a sequence $M^{\star} \rightarrow [M - N_2]^{\star} \rightarrow [M - N_2 - CO]^{\star}$ and $[M - N_2 - CHO]^{\star}$.

EXPERIMENTAL

Alkyl diazoacetates (I) were synthesized according to general procedure [30]. To an aqueous solution of alkyl (C_1 – C_4) aminoacetate hydrochloride (20–40 mmol) was added 10–15 ml of methylene chloride and the mixture was cooled to –5°C. In an argon atmosphere at stirring was added aqueous solution of NaNO₂ (~1.2 molar excess). The mixture was then cooled to approx. –10°C, 5% solution of sulfuric acid was added dropwise to it, and the stirring was continued for another 10–15 min. The organic layer was separated, washed three times with saturated solution of sodium bicarbonate and water, and dried over anhydrous Na₂SO₄.

Diazomethyl ketones (II) were synthesized according to general procedure [31] from acyl chlorides, synthesized in turn from the corresponding carboxylic acids and thionyl chloride [32]. Ether solution of an acid chloride (0.3–0.7 mmol) was added dropwise with stirring to ether solution of diazomethane (molar excess 20 to 30%), and the mixture was cooled in ice bath. The stirring was continued for another 20–30 min, and then the diazomethane excess was removed by a flow of argon.

The 1-diazopentan-2-one (IIa) and 1-diazoheptan-2-one (IIc) preparations contained a little (2-3%) of isomeric 1-diazo-3-methylbutan-2-one (IIb) and 1-diazo-3-methylhexan-2-one (IId), respectively, with respective lower RI values. The chromatographic analysis (B mode) of the source carboxylic acids in the form of butyl esters obtained from the corresponding acid chlorides with 1-butanol (chemically pure for chromatography grade) showed the presence of 2-3%of the impurities of isomeric acids. The butyl butyrate sample (RI 987±2, reference value 976±9) contained a component with RI 945 ± 2 (corresponds to the reference value for butyl isobutyrate, 936±7). In the sample of butyl caproate (1178±2, 1166±7) butyl isocaproate (1149±2, 1138±7) was detected. Mass spectra of these isomers are practically identical.

Solutions of diazo compounds in methylene chloride or diethyl ether were analyzed without an additional treatment, but after approximately 100 times dilution with the same solvent. To characterize the stability of diazo compounds in the conditions of gas chromatographic separation, their analysis was performed on different instruments, different columns and at different temperatures:

A. Using a gas chromatography–mass spectrometer Shimadzu QP 2010 with a silica WCOT column, phase HP-5 MS (polydimethylsiloxane, 5% of phenyl groups), length 25 m, internal diameter 0.20 mm (thickness of stationary phase film 0.33 mm) in the mode of temperature programming from 45°C (initial isothermal section 1 min) to 280°C (isotherm 2 min) at a rate 5°C min⁻¹. The linear velocity of carrier gas (helium) 40 cm s⁻¹, injector temperature 100°C, split ratio 1:200.

B. On the Agilent 5975 gas chromatograph with mass spectrometric detector Agilent 7000 using a WCOT quartz column with the polydimethylsiloxane stationary phase HP Ultra-1, length 17 m, internal diameter 0.20 mm (thickness of stationary phase film 0.11 mm) using temperature programming from 40°C to 200°C (isotherm 2 min) at a rate of 2 deg min⁻¹. The linear velocity of carrier gas (helium) 48 cm s⁻¹, the evaporator temperature 100°C, split ratio 1:200.

C. On a Shimadzu QP 5000 chromatograph–mass spectrometer using WCOT quartz column with a phase HP-5 MSI (polydimethylsiloxane, 5% of phenyl groups), length 25 m, internal diameter 0.20 mm (film thickness of stationary phase 0.25 μ m) in the mode of temperature programming from 70°C to 280°C at a rate 10°C min⁻¹. The carrier gas (helium) linear velocity 40 cm s⁻¹, the evaporator temperature 100°C, split ratio 1:180.

D. On a Shimadzu QP 2010 plus gas chromatograph–mass spectrometer using WCOT quartz column with a phase HP-5 MSI (polydimethylsiloxane, 5% phenyl groups), length 30 m, internal diameter 0.25 mm (film thickness of stationary phase 0.25 μ m) in the mode of temperature programming from 40°C to 200°C at a rate 2°C min⁻¹. The carrier gas (helium) linear rate 51 cm s⁻¹, the evaporator temperature 100°C, split ratio 1:200.

The samples (1 μ l of solution) were dosed with appropriate split ratio, evaporator temperature did not exceed 100°C. Since the analysis was performed with temperature programming, the retention temperature (T_R) of different diazo compounds determined by the relation (1) were different in the A–D modes:

$$T_{\rm R} \approx T_0 + r (t_{\rm R} - t_{T0}),$$
 (1)

where T_0 is initial temperature of the analysis, °C, *r* is the rate of temperature rise, °C min⁻¹, t_R retention time, min, t_{T0} is duration of the initial isothermal section, min.

To calculate the retention indices, in parallel with each sample in the same conditions the retention times of the reference *n*-alkanes C_8-C_{20} were measured. Calculations were performed using the QBasic software [33]. The values of normal boiling points of organic compounds necessary for the evaluation of the retention indices were determined along the algorithm [18] using the ACD software (version 1994–1996).

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